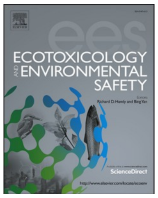
Ecotoxicology and Environmental Safety 278 (2024) 116349

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Characterization of fire investigators' polyaromatic hydrocarbon exposures using silicone wristbands

Umer Bakali [a], Jeramy L.R. Baum [a,b], Paola Louzado-Feliciano [c], Chitvan Killawala [a,d], Katerina M. Santiago [c], Jeffrey L. Pauley [e], Emre Dikici [a,g], Natasha Schaefer Solle [f,h], Erin N. Kobetz [c,f,h], Leonidas G. Bachas [b], Sapna K. Deo [a,f,g], Alberto J. Caban-Martinez [c,f,*], Sylvia Daunert [a,f,g]

[a] Department of Biochemistry and Molecular Biology, Leonard M. Miller School of Medicine, University of Miami, Miami, FL, USA
[b] Department of Chemistry, College of Arts and Sciences, University of Miami, Coral Gables, FL, USA
[c] Department of Public Health Sciences, Leonard M. Miller School of Medicine, University of Miami, Miami, FL, USA
[d] Department of Biomedical Engineering, College of Engineering, University of Miami, Coral Gables, FL, USA
[e] International Association of Arson Investigators, Bowie, MD, USA
[f] Sylvester Comprehensive Cancer Center, University of Miami, Miami, FL, USA
[g] Dr. John T. Macdonald Foundation Biomedical Nanotechnology Institute of the University of Miami (BioNIUM), Miami, FL, USA
[h] Department of Medicine, Leonard M. Miller School of Medicine, University of Miami, Miami, FL, USA

ARTICLE INFO

Edited by Professor Bing Yan

Keywords:
Fire investigator
Firefighter
PAH
Carcinogen
Passive sampling
Wristbands

ABSTRACT

Background: Exposures to polyaromatic hydrocarbons (PAHs) contribute to cancer in the fire service. Fire investigators are involved in evaluations of post-fire scenes. In the US, it is estimated that there are up to 9000 fire investigators, compared to approximately 1.1 million total firefighting personnel. This exploratory study contributes initial evidence of PAH exposures sustained by this understudied group using worn silicone passive samplers.

Objectives: Evaluate PAH exposures sustained by fire investigators at post-fire scenes using worn silicone passive samplers. Assess explanatory factors and health risks of PAH exposure at post-fire scenes.

Methods: As part of a cross-sectional study design, silicone wristbands were distributed to 16 North Carolina fire investigators, including eight public, seven private, and one public and private. Wristbands were worn during 46 post-fire scene investigations. Fire investigators completed pre- and post-surveys providing sociodemographic, occupational, and post-fire scene characteristics. Solvent extracts from wristbands were analyzed via gas chromatography-mass spectrometry (GC-MS). Results were used to estimate vapor-phase PAH concentration in the air at post-fire scenes.

Results: Fire investigations lasted an average of 148 minutes, standard deviation ± 93 minutes. A significant positive correlation ($r=0.455$, $p<.001$) was found between investigation duration and PAH concentrations on wristbands. Significantly greater time-normalized PAH exposures ($p=0.039$) were observed for investigations of newer post-fire scenes compared to older post-fire scenes. Regulatory airborne PAH exposure limits were exceeded in six investigations, based on exposure to estimated vapor-phase PAH concentrations in the air at post-fire scenes.

Discussion: Higher levels of off-gassing and suspended particulates at younger post-fire scenes may explain greater PAH exposure. Weaker correlations are found between wristband PAH concentration and investigation duration at older post-fire scenes, suggesting reduction of off-gassing PAHs over time. Exceedances of regulatory PAH limits indicate a need for protection against vapor-phase contaminants, especially at more recent post-fire scenes.

---

[*] Correspondence to: University of Miami Miller School of Medicine, 1120 NW 14th Street, Soffer Clinical Research Center Rm. 1035, Miami, FL 33136, USA.
E-mail address: ACaban@med.miami.edu (A.J. Caban-Martinez).

https://doi.org/10.1016/j.ecoenv.2024.116349
Received 22 November 2023; Received in revised form 31 March 2024; Accepted 16 April 2024

1. Introduction

In the United States, there are approximately 1.1 million firefighters, including approximately 360,000 career and approximately 723,000 volunteer fire service personnel according to the National Fire Protection Association (NFPA) (Fahy et al., 2021). By comparison, only about 14,600 fire service personnel are classified as fire inspectors and fire investigators according to the US Bureau of Labor Statistics (Bakali et al., 2021). Fire investigators specialize in determining the cause of fires and whether they are the result of criminal intent. It is estimated that of these 14,600, the true number of fire investigators is likely between 7000 and 9000. In June 2022 the International Agency for Research on Cancer (IARC) reclassified the practice of firefighting as Group 1, or known carcinogen to humans, (Demers et al., 2022) after reviewing substantial evidence showing that firefighters are at greater risk for certain cancers than the general population (Demers et al., 2022; IARC, 2010). Despite this, most current research on carcinogenic exposures in the fire service center around structural firefighters. However, previous studies on fire investigators compiled by the International Association of Arson Investigators (IAAI) have noted that fire investigators are distinguished from their structural firefighter counterparts in a number of characteristics, namely that they are generally present at more fire scenes for a longer time and often wear less personal protective equipment (PPE) and less or no respiratory protection at all (Fire Investigator Health and Safety Best Practices, 2022). As a result of their small population, little data is currently available regarding the carcinogenic occupational exposures of fire investigators (Horn et al., 2022).

Polyaromatic hydrocarbons (PAHs) are a family of compounds produced by radical reactions of hydrocarbons with each other, catalyzed by high-heat and low-oxygen conditions (Richter and Howard, 2000). Exposure to PAHs in occupational settings may occur from petrogenic sources, i.e., off-gassing from crude oil, asphalt, or petroleum fuels, (Fernando et al., 2019) as well as pyrogenic sources which involve incomplete combustion of fossil fuels and biomass (Bukowska et al., 2022). Firefighters may be exposed to PAHs through inhalation, ingestion, and/or dermal absorption (Sousa et al., 2022). These compounds are classified by the IARC as known, probable, and possible carcinogens, and 16 PAHs are named by the US EPA in their list of 126 priority pollutants (Priority Pollutant List, 2014). PAHs have been shown to have not only mutagenic properties, but also properties of endocrine disruption, (Khan et al., 2021) neurotoxicity, (Olasehinde and Olaniran, 2022) immunotoxicity, (Yu et al., 2022) hematotoxicity, (Kamal et al., 2015) and reproductive toxicity (Kamal et al., 2015; El-Sikaily et al., 2023). Many of these toxic effects center around the activation of the aryl hydrocarbon receptor (AhR), which is associated with xenobiotic metabolism, leading to the expression of cytochrome peroxidases that transform parent PAHs into their more reactive diol and epoxide metabolite forms, which are capable of forming DNA adducts leading to carcinogenesis (Kamal et al., 2015). The internalization of PAHs during firefighting is associated with the excretion of hydroxylated PAHs in the urine, especially for the lower-molecular weight (LMW) PAHs. These species have estimated half-lives in the body ranging from approximately two to over 14 hours (Rossbach et al., 2020). As a result, repeat fireground exposures within several days may have compounding genotoxic effects (Rossbach et al., 2020).

Fire services classify fire situations by type of fuel; for example, Class A fires are those that burn biomass and objects manufactured from solid organic material such as wood, paper, and grass. Class B fires are those that burn liquid and gaseous hydrocarbon fuels, such as gasoline, propane, and kerosene (O'Connor, 2021). Many residential and commercial fires burn fuels from both classifications, further compounding health and exposure hazards (Hwang et al., 2021). The types of contaminants that are observed at fire scenes depend on the character of the fuel, including its composition and burning temperature. Fire services classify fire situations by the type of fuel being burnt to inform strategy for extinguishing different types of fires. For example, fuels of different classifications can produce different concentrations and species of toxic compounds when burned. Benzo[*a*]pyrene is among the most infamous compounds in this family, classified as a Group 1 known carcinogen (Chemical Agents, 2012). The molecular weight of different PAH species influences their distribution behavior in both the extreme conditions of active fire situations and in normal ambient conditions. LMW PAHs, which are typically defined as those PAHs with three or fewer aromatic rings, are more volatile than higher molecular weight (HMW) PAHs, which possess four or more aromatic rings. Furthermore, LMW PAHs in the environment at ambient temperatures are more likely to be in the gaseous phase, whereas HMW PAHs are more frequently adsorbed to particulate matter, such as ash and soot (Srogi, 2007; Zhang et al., 2019). The variety in distribution behavior between lower and higher molecular weight species of PAHs, their ubiquity in fire situations in which carbon-containing fuels are being burned, and their persistence in post-fire scenes makes them valuable target analytes for studying carcinogenic exposure in firefighters, including fire investigators who are present at post-fire scenes for extended periods of times with less PPE.

To study airborne chemical exposures in environmental and occupational health contexts, various active and passive air sampling techniques have been employed. Active sampling techniques involve the use of a pump to flow surrounding air and its components into a sorbent material, or trap, such as a filter, resin, or polymer (Gill et al., 2020). By comparison, passive sampling techniques do not use pumps, instead relying on passive trapping of compounds from the surrounding air (Qu et al., 2018; Sedlačková et al., 2021). Among passive sampling techniques, the use of silicone wristbands has been increasingly employed in occupational exposure monitoring since initial studies validating them were performed by O'Connell and coworkers in 2014 (Wacławik et al., 2022; Alkon et al., 2022; O'Connell et al., 2014). We and others have previously demonstrated the use of silicone passive samplers for effective sampling of toxic semi-volatile compounds in the occupational setting of firefighters and first responders (Bakali et al., 2021; Baum et al., 2020; Poutasse et al., 2020, 2021; Levasseur et al., 2022). Volatile and semi-volatile organic compounds in the vapor phase sorb to silicone and can thereafter be extracted and analyzed using various analytical methods, including gas chromatography-mass spectrometry (GC-MS). Due to their robust and inexpensive characteristics compared to other passive atmospheric sampling methods, silicone wristbands are effective tools for monitoring the exposure of firefighters and fire investigators.

According to the International Association of Arson Investigators (IAAI), post-fire scenes are described in stages as *hot scenes*, *warm scenes*, or *cold scenes.* These stages are dependent on the state of the scene after the fire has been extinguished and whether *overhaul*, the process of ensuring that any hidden fires within the structure of a fire scene have been extinguished, has been completed. Specifically, *hot scene A* is one in which *overhaul* has not yet commenced following the fire, *hot scene B* is one in which overhaul has occurred and no more than two hours have passed since the fire has been controlled, a *warm scene* is one in which a fire situation has been fully extinguished for at least two hours but not more than 72 hours, and a *cold scene* is one in which the fire has been extinguished for at least 72 hours and no detectable off-gassing is present (Fire Investigator Health and Safety Best Practices, 2022; Horn et al., 2022).

In the present study, we 1) determine the extent of exposure to the 16 EPA priority PAHs sustained by fire investigators during post-fire scene investigations, 2) evaluate features of post-fire scene investigations as potential factors in PAH exposure, and 3) conduct a health risk assessment based on estimates of PAH concentrations in the air of post-fire scenes. We hypothesize: $\mathbf{H_1}$) the amount of time spent by fire investigators at post-fire scenes positively correlates with intensity of the 16 EPA PAH exposure observed on wristbands worn; and $\mathbf{H_2}$) Fire scenes with short periods between fire suppression and fire investigation, i.e., *hot scenes*, will result in greater PAH exposures compared to fire scenes with longer periods between fire suppression and investigation.

2. Materials and methods

2.1. Fire investigator sample recruitment and consent

Public and private fire investigators from North Carolina were engaged via their state professional association, and were subsequently invited to learn about the study using email and study flyers. Eligibility criteria for inclusion in the study included that subjects were fire investigators who could speak, read, and write in English and were 18 years of age or older. Fire investigators of all ethnicities were encouraged to participate. Fire investigators met with the study team online to review the study protocol and procedures. Following the consenting process, fire investigators were mailed bubble wrapped envelopes containing silicone wristbands in glass vials and pre- and post-fire investigation surveys. Pre-questionnaires and post-questionnaires were self-administered prior to and following fire investigators' post-fire scene investigations, respectively. Examples of occupational data collected in these questionnaires include the amount of time spent at the post-fire scene, the scale of the fire situation, their personal decontamination practices post investigation and the number of days that elapsed between the initial fire and the post-fire investigation. This study was approved by the Institutional Review Boards of the University of Miami, Coral Gables, FL. (IRB # 20170339)

A total of 16 fire investigators were consented and contributed samples to the study from January 2020 to September 2022. Fire investigators wore silicone wristbands during 46 individual post-fire scene investigations of varying scale and duration. No two wristband samples were representative of the same post-fire scene, i.e., a post-fire scene was not investigated again on a different day.

2.2. Silicone wristband preparation and distribution

Wristband preparation and cleaning steps have been previously described in greater detail elsewhere (Bakali et al., 2021). Silicone wristbands for distribution to fire investigators were purchased from Netbrands (Guangdong, China). Each silicone wristband weighed approximately 4.36 g with a variation of less than 1% among wristbands. The density of polydimethylsiloxane, from which the silicone wristbands are made, is approximately 0.97 g/mL, yielding an average wristband volume of about 4.5 mL. Wristbands were solvent cleaned prior to distribution to remove any extraneous contamination. Briefly, wristbands were washed in clean jars first by being submerged in 1:1 (by volume) solution of ethyl acetate and hexane, followed by shaking at 120 rpm for one hour in an orbital shaker. The used solvent was discarded and the wristbands were then submerged in 1:1 by volume solution of ethyl acetate and methanol and shaken for one hour at 120 rpm before discarding the used solvent. Wristbands were then placed in a vacuum oven at 70 °C and approximately 20 kPa overnight to drive off residual solvent. After removing cleaned wristbands from the vacuum oven, each prepared wristband was inserted into an individual 40-mL amber glass vial and capped for distribution. All solvents used in the study were HPLC-grade and purchased from MilliporeSigma (St. Louis, MO). All glassware used was certified clean and purchased from ThermoFisher Scientific (Waltham, MA).

After being worn by fire investigators during their post-fire scene investigations, wristbands were taken off and placed back in their individual amber glass vials. Fire investigator participants labeled the wristband vials with their study ID and included responses to their post-investigation questionnaire. Wristbands were then shipped back to the laboratory and refrigerated at 4 °C until ready for extraction and analysis.

2.3. Extraction and gas chromatography – mass spectrometry analysis

Extraction and analysis were performed for the 16 EPA Priority PAHs: naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fln), pyrene (Pyr), benz[*a*]anthracene (B[*a*]A), chrysene (Chry), benzo[*b*]fluoranthene (B[*b*]f), benzo[*k*]fluoranthene (B[*k*]f), benzo[*a*]pyrene (B[*a*]p), indeno[123-cd]pyrene (InP), dibenz[ah]anthracene (Db[ah]A), and benzo[ghi]perylene (B[ghi]P).

The protocol used for extracting PAHs from returned silicone wristbands has been described in previous publications (Bakali et al., 2021; Baum et al., 2020). Briefly, silicone wristbands were extracted using HPLC-grade ethyl acetate to generate 60 mL of extract, which was then evaporated down under a gentle nitrogen stream to a final volume of 4 mL to preconcentrate the extract prior to GC-MS analysis. Nitrogen used was ultra-high purity (99.999%) purchased from Airgas (Radnor, PA). Prepared extracts were then transferred to amber autosampler vials and stored at −80 °C until ready for analysis. Extracts were allowed to return to room temperature before GC-MS analysis was performed.

GC-MS analyses were performed using a Shimadzu 2010 Plus gas chromatograph coupled with a Shimadzu QP2020 single-quadrupole mass spectrometer (Shimadzu Scientific Instruments, Columbia, MD). Calibration and quality control/quality assurance data corresponding to the method used can be found in the Supplementary Material, Table S1. Separation was performed using an Agilent HP-5MS UI column of the dimensions 30 m length, 0.25 mm interior diameter, and 0.25 μm film thickness (Agilent Technologies, Santa Clara, CA). A splitless liquid injection of 2 μL was performed; the injection port temperature was set to 280 °C. Carrier gas used was ultra-high purity helium, purchased from Airgas (Radnor, PA). Oven temperature ramping started at 50 °C, increasing at a rate of 8 °C/min following sample injection to a final temperature of 300 °C. Eluting compounds were ionized via electron impact ionization prior to mass spectrometry.

2.4. Statistical analysis

Data gathered from GC-MS analysis of silicone wristband extracts were reported in nanograms per milliliter. These values were converted by multiplying by the final volume of the solvent extract (4 mL) and then dividing by the average mass of the wristband (4.36 g) to produce PAH concentration values in units of ng/g.

Post-fire scenes were classified as *hot scenes, warm scenes,* or *cold scenes* based on the length of time reported to have elapsed between the initial fire report and the time of the investigation. Specifically, *hot scenes* were defined as scenes investigated on the same day as the initial fire report, *warm scenes* were defined as scenes investigated between one and three days of the initial fire report, and *cold scenes* were defined as scenes investigated later than three days following the initial fire report. Correlations and linear regression analyses were conducted on comparisons of time spent by fire investigators at post-fire scenes and their respective PAH exposures. These analyses were further stratified by whether the wristband was worn at a *hot scene,* or either a *warm or cold scene* to determine the explanatory strength of post-fire scene age on exposure.

For statistical comparison of wristband results between different types of post-fire scenes, PAH concentrations on wristbands were normalized by the reported amount of time spent by fire investigators at the post-fire scene in which it was worn, yielding results in ng/g*h. Due to a lack of sample size for *warm* and *cold scenes*, these data were pooled for statistical comparison to *hot scenes.* A one-tailed t-test was performed to test the hypothesis that *hot scenes* yielded greater exposure than *warm or cold scenes.*

All statistical analyses and figures were conducted and produced using GraphPad Prism software (version 9.4.1, Dotmatics, Boston, MA).

2.5. Estimating PAH concentrations in air for health risk assessment

To conduct a health risk assessment of fire investigators' exposures during their investigations of post-fire scenes, it was necessary to estimate the concentration of vapor-phase PAHs in the air at each scene using the silicone wristbands. An estimate of air concentrations for each PAH can be calculated using the following equation shown in Eq. 1 adapted (O'Connell et al., 2022) where C_a is the estimated atmospheric concentration in μg/m^3, N_{PAH} is the mass of each PAH on the wristband in ng, V_s is the volume of the silicone wristband of approximately 4.5 mL, $K_{PDMS\text{-}air}$ is the partitioning coefficient between the silicone and the air, k_e is the rate constant for the uptake of the individual PAH, and t is the time of exposure in days. PAHs with a log $K_{PDMS\text{-}air}$ greater than approximately 8 were excluded from the calculation since these PAHs are likely particulate-bound, and cannot be accurately estimated using silicone wristbands which can only reliably capture volatiles in the vapor-phase.

$$C_a = \frac{N_{PAH}}{V_s * K_{PDMS-air} * \left(1 - e^{-k_e * t}\right)} \tag{1}$$

The $K_{PDMS\text{-}air}$ for each PAH at 25 °C and 50% relative humidity was retrieved from calculated values in the EPA Comptox 2017 database (Sprunger et al., 2007). Rate constant k_e was calculated from the BP-TEST model recommended in (O'Connell et al., 2022). These estimated PAH air concentrations were used to determine eight-hour time-weighted average (TWA) exposures comparable to the permissible exposure limit (PEL) of 0.2 mg/m^3 in air for PAHs as coal-tar pitch volatiles published by the US Occupational Safety and Health Administration (OSHA), as well as the recommended exposure limit (REL) of 0.1 mg/m^3 published by the US National Institute for Occupational Safety & Health (NIOSH) (Gehle, 2009). It was assumed that no other fire investigations occurred during the eight-hour period other than the one in which the wristband was worn, and that PAH exposure outside of post-fire scenes during this time was negligible.

Additionally, these concentrations of vapor-phase PAHs in air were used to estimate the potential inhaled dose of PAHs by multiplying by inhalation rates listed for light-intensity exercise in the EPA Exposure Factors Handbook (Chapter 6, 2011). Light-intensity exercise was thought to best approximate the activity level of fire investigators at post-fire scenes. The inhalation rate estimate was either 0.012 or 0.013 m^3/min of air depending on the age of the participant.

3. Results

3.1. Fire investigator and post-fire scene characteristics

Of the 16 fire investigators sampled, eight indicated that they were employed in the public sector, seven indicated that they were employed in the private sector, and one indicated that they were employed in both. The age of the fire investigators at the time of recruitment ranged from 25 to 67 years, with an average age of 45.5 years and standard deviation of 10.6 years. Of the fire investigators recruited, 14 were male and two were female. All fire investigators recruited identified as white. Full sociodemographic and work characteristics are displayed in the Supplementary Data, Table S1.

For the 46 individual post-fire scene investigations, the average investigation duration was 2 hours and 28 minutes, with a minimum recorded time of 9 minutes and a maximum of 7 hours. On average, investigations were performed 3.7 days after the fire was reported, with the latest investigation occurring 61 days after the fire. A total of 28 out of 46 post-fire scenes were classified as *hot scenes.* Seven investigations were classified as *warm scenes*, occurring between one and three days following the fire report are classified. Finally, 11 post-fire scene investigations occurring later than three days following the fire report were classified as *cold scenes.*

Visualizations and numeric data illustrating the amount of time spent by fire investigators at post-fire scenes as well as the age of post-fire scenes are shown in the Supplementary Material, Figures S1 and S2, and Table S3.

3.2. Polyaromatic hydrocarbons observed on wristbands worn by fire investigators

Analysis of wristband extracts via GC-MS showed higher overall concentrations of LMW PAHs, i.e., those which are defined as two- and three-ringed PAHs. Six of the 16 PAHs analyzed are LMW PAHs, including Naph, Acy, Ace, Flu, Ant, and Phe. Of the LMW PAHs, the highest concentrations in wristband extracts were observed for Naph, the lightest and most volatile of all PAHs. Although concentrations of naphthalene observed from wristband extracts vary widely, they represent the majority of PAH exposure in most wristband samples obtained from post-fire scenes. On average, LMW PAHs accounted for about 90% of the total exposure to the 16 EPA priority PAHs observed in wristband samples, with naphthalene alone accounting for about 47% of total exposure. By comparison, about 10% of exposure observed was due to HMW PAHs. The most significant HMW PAH exposures came from Fln, Pyr, and B[*a*]P, which accounted for 3%, 2.4%, and 0.8% of total EPA16 PAH exposure, respectively. Fig. 1 displays the concentrations of each of the EPA16 PAHs extracted from the silicone wristbands worn by fire investigators at post-fire scenes.

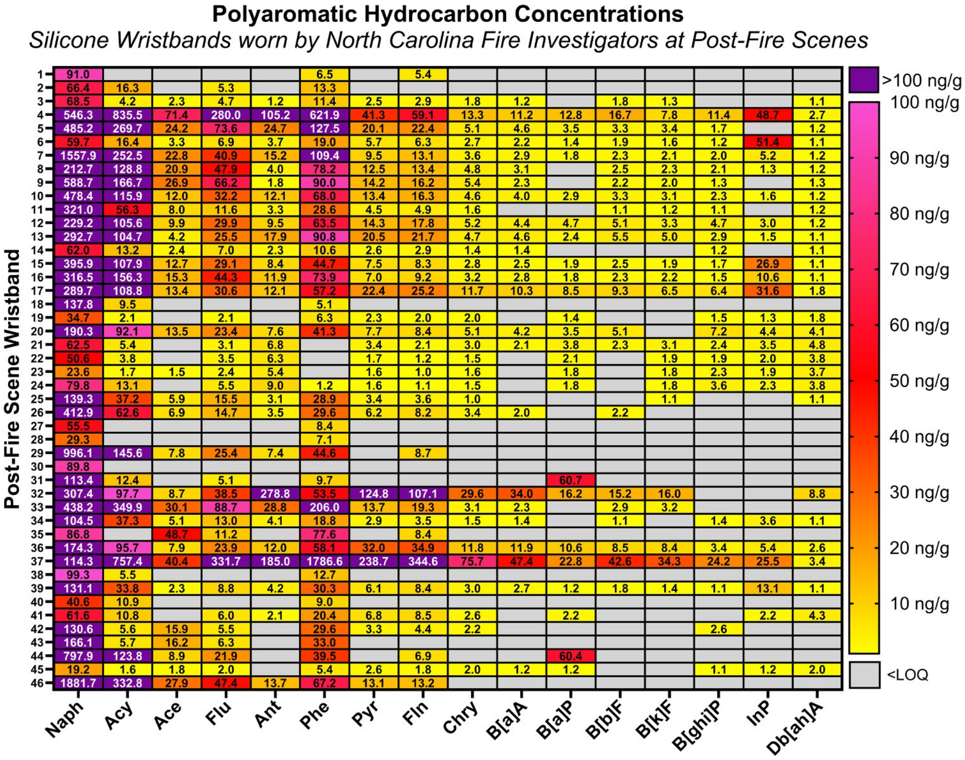
3.3. Correlations between time spent at post-fire scenes and EPA16 PAH exposure

It was hypothesized *a priori* that the amount of time that fire investigators spent at post-fire scenes would positively correlate with intensity of EPA16 PAH exposure observed on wristbands worn. Pearson's *r* was computed to determine the strength of the correlation between these two variables, finding a moderately positive but significant correlation between the two variables ($r=0.455$, $p<0.001$). Additionally, a linear regression was performed to determine the explanatory strength of the amount of time fire investigators spent at post-fire scenes on the level of total PAH exposure that they sustained. One wristband was not included in the correlation because time spent at the scene was not recorded for it. The scatterplot of this comparison is shown in Fig. 2. Numeric data for Fig. 2 is included in the Supplementary material, Table S4.

Correlations between time spent at post-fire scenes and PAHs observed on wristband samples were stratified by the status of the post-fire scene, i.e., whether the post-fire scene was a hot scene or warm/cold scene. Scatterplots of each comparison with their respective regression line are shown in Fig. 3. Moderate, positive correlations were estimated between time spent at *hot scenes* and EPA16, LMW, and HMW PAHs. Notably, *r* and R^2 values for the scatterplot of time spent at *hot scenes* and total exposure to EPA16 PAHs were higher than those observed for the correlation between all scenes and EPA16 PAHs in Fig. 2. To compare trends between *hot scenes*, in which it is expected that PAHs are being actively generated, and *warm* and *cold scenes*, in which it is expected that PAH generation has slowed or halted, data from *warm* and *cold scenes* were pooled together. No correlation was found between time spent at *warm* and *cold scenes* for EPA16 and LMW PAHs, though this is due to several high outliers; removal of these outliers produces moderately strong correlations for these categories, and linear regression produces a larger R^2 value. Outliers were removed by calculating the interquartile range of EPA16 PAH data and removing values above the sum of 1.5 times the interquartile range and the third quartile value; LMW and HMW PAH data points corresponding to these participants with high outlier values were also removed for consistency. Numeric data represented in Fig. 3 are included in the Supplementary Material, Tables S6, S7, and S8.

3.4. Statistical comparisons of PAH exposure intensities at different post-fire scenes

To conduct statistical comparisons of the effect of the age of the post-fire scene on the level of PAH exposure observed, exposures on



Post-Fire Scene Wristband	Naph	Acy	Ace	Flu	Ant	Phe	Pyr	Fln	Chry	B[a]A	B[a]P	B[b]F	B[k]F	B[ghi]P	InP	Db[ah]A
1	91.0					6.5		5.4								
2	66.4	16.3		5.3		13.3										
3	68.5	4.2	2.3	4.7	1.2	11.4	2.5	2.9	1.8	1.2		1.8	1.3			1.1
4	546.3	835.5	71.4	280.0	105.2	621.9	41.3	59.1	13.3	11.2	12.8	16.7	7.8	11.4	48.7	2.7
5	485.2	269.7	24.2	73.6	24.7	127.5	20.1	22.4	5.1	4.6	3.5	3.3	3.4	1.7		1.2
6	59.7	16.4	3.3	6.9	3.7	19.0	5.7	6.3	2.7	2.2	1.4	1.9	1.6	1.2	51.4	1.1
7	1557.9	252.5	22.8	40.9	15.2	109.4	9.5	13.1	3.6	2.9	1.8	2.3	2.1	2.0	5.2	1.2
8	212.7	128.8	20.9	47.9	4.0	78.2	12.5	13.4	4.8	3.1		2.5	2.3	2.1	1.3	1.2
9	588.7	166.7	26.9	66.2	1.8	90.0	14.2	16.2	5.4	2.3		2.2	2.0	1.3		1.3
10	478.4	115.9	12.0	32.2	12.1	68.0	13.4	16.3	4.6	4.0	2.9	3.3	3.1	2.3	1.6	1.2
11	321.0	56.3	8.0	11.6	3.3	28.6	4.5	4.9	1.6			1.1	1.2	1.1		1.2
12	229.2	105.6	9.9	29.9	9.5	63.5	14.3	17.8	5.2	4.4	4.7	5.1	3.3	4.7	3.0	1.2
13	292.7	104.7	4.2	25.5	17.9	90.8	20.5	21.7	4.7	4.6	2.4	5.5	5.0	2.9	1.5	1.1
14	62.0	13.2	2.4	7.0	2.3	10.6	2.6	2.9	1.4	1.4				1.2		1.1
15	395.9	107.9	12.7	29.1	8.4	44.7	7.5	8.3	2.8	2.5	1.9	2.5	1.9	1.7	26.9	1.1
16	316.5	156.3	15.3	44.3	11.9	73.9	7.0	9.2	3.2	2.8	1.8	2.3	2.2	1.5	10.6	1.1
17	289.7	108.8	13.4	30.6	12.1	57.2	22.4	25.2	11.7	10.3	8.5	9.3	6.5	6.4	31.6	1.8
18	137.8	9.5				5.1										
19	34.7	2.1		2.1		6.3	2.3	2.0	2.0		1.4			1.5	1.3	1.8
20	190.3	92.1	13.5	23.4	7.6	41.3	7.7	8.4	5.1	4.2	3.5	5.1		7.2	4.4	4.1
21	62.5	5.4		3.1	6.8		3.4	2.1	3.0	2.1	3.8	2.3	3.1	2.4	3.5	4.8
22	50.6	3.8		3.5	6.3		1.7	1.2	1.5		2.1		1.9	1.9	2.0	3.8
23	23.6	1.7	1.5	2.4	5.4		1.6	1.0	1.6		1.8		1.8	2.3	1.9	3.7
24	79.8	13.1		5.5	9.0	1.2	1.6	1.1	1.5		1.8		1.8	3.6	2.3	3.8
25	139.3	37.2	5.9	15.5	3.1	28.9	3.4	3.6	1.0				1.1			1.1
26	412.9	62.6	6.9	14.7	3.5	29.6	6.2	8.2	3.4	2.0		2.2				
27	55.5					8.4										
28	29.3					7.1										
29	996.1	145.6	7.8	25.4	7.4	44.6		8.7								
30	89.8															
31	113.4	12.4		5.1		9.7					60.7					
32	307.4	97.7	8.7	38.5	278.8	53.5	124.8	107.1	29.6	34.0	16.2	15.2	16.0			8.8
33	438.2	349.9	30.1	88.7	28.8	206.0	13.7	19.3	3.1	2.3		2.9	3.2			
34	104.5	37.3	5.1	13.0	4.1	18.8	2.9	3.5	1.5	1.4		1.1		1.4	3.6	1.1
35	86.8		48.7	11.2		77.6		8.4								
36	174.3	95.7	7.9	23.9	12.0	58.1	32.0	34.9	11.8	11.9	10.6	8.5	8.4	3.4	5.4	2.6
37	114.3	757.4	40.4	331.7	185.0	1786.6	238.7	344.6	75.7	47.4	22.8	42.6	34.3	24.2	25.5	3.4
38	99.3	5.5				12.7										
39	131.1	33.8	2.3	8.8	4.2	30.3	6.1	8.4	3.0	2.7	1.2	1.8	1.4	1.1	13.1	1.1
40	40.6	10.9				9.0										
41	61.6	10.8		6.0	2.1	20.4	6.8	8.5	2.6		2.2				2.2	4.3
42	130.6	5.6	15.9	5.5		29.6	3.3	4.4	2.2					2.6		
43	166.1	5.7	16.2	6.3		33.0										
44	797.9	123.8	8.9	21.9		39.5		6.9			60.4					
45	19.2	1.6	1.8	2.0		5.4	2.6	1.8	2.0	1.2	1.2			1.1	1.2	2.0
46	1881.7	332.8	27.9	47.4	13.7	67.2	13.1	13.2								

Fig. 1. Heatmap associating concentrations of the 16 EPA priority PAHs observed in wristband extracts to post-fire scene investigations. Each row on the heatmap corresponds to a wristband worn by a fire investigator at a post-fire scene, and each column corresponds to a PAH. Concentrations are reported in nanograms of PAH per gram of silicone wristband. Gray cells indicate values that are under the limit of quantitation (LOQ).

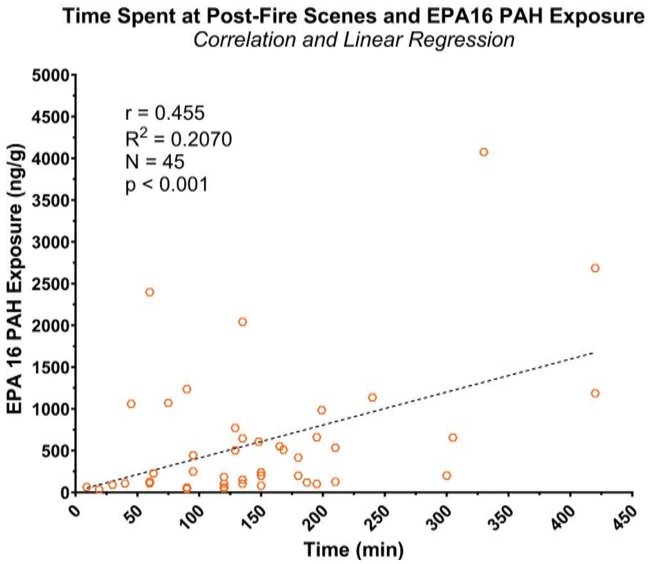


Fig. 2. Scatterplot of comparison between time fire investigators spent at post-fire scenes and level of EPA16 PAH exposure sustained.

wristbands were normalized by the amount of time spent at each post-fire scene, producing values with units of exposure (in ng PAH/g silicone) per hour. It was hypothesized that *hot scenes*, which were expected to exhibit active PAH generation, would have higher levels of PAH exposure than *warm* and *cold scenes*, which were pooled together to allow for greater sample size for the comparison. One sample was removed from analysis in the *hot scene* category because the participant did not record the amount of time they spent at the post-fire scene, preventing normalization of exposure by time worn. A total of $n = 27$ samples from *hot scenes* and $n = 18$ samples from *warm* and *cold scenes* were compared. Comparisons between *hot scene* exposure and *warm* and *cold scene* exposure are illustrated in Fig. 4. Numeric data represented in Fig. 4 are included in the Supplementary Material, Table S9.

3.5. Estimating air concentrations and respirable quantities of vapor-phase PAHs at post-fire scenes

Concentrations of PAHs in the ambient air within post-fire scenes were estimated from concentrations of PAHs extracted from silicone wristbands with log $K_{PDMS\text{-}air}$ values below approximately 8 using Eq. 1. Above this cutoff, PAHs have been shown to be more likely to be particulate-bound with negligible concentrations in the vapor-phase (O'Connell et al., 2022). A heatmap of estimated ambient air concentrations is shown in the Supplementary Information, Figure S3. Most of the vapor-phase PAH concentration was attributable to naphthalene.

Inappropriate or otherwise inadequate personal protective equipment may leave fire investigators susceptible to inhalation of vapor-phase PAHs. Potentially respirable quantities of vapor-phase PAHs were calculated from air concentration estimates by multiplying by inhalation rate estimates for light-intensity activity noted in the EPA Exposure Factors Handbook (Chapter 6, 2011). Quantities are shown in Fig. 5.

Additionally, from estimated air concentrations of vapor-phase PAHs, eight-hour TWA values in μg/m^3 were calculated using the time that fire investigators reported to be at post-fire scenes, shown in Fig. 6. Exceedances of the OSHA 0.2 mg/m^3 PEL for PAH concentrations in air were found for six out of 45 total post-fire scene wristbands analyzed, including five from *hot scenes* (Fig. 6). For the National Institute Occupational Safety and Health (NIOSH) recommended exposure limit (REL) of 0.1 mg/m^3, the number of exceedances rises to 14, including 12 from *hot scenes.*

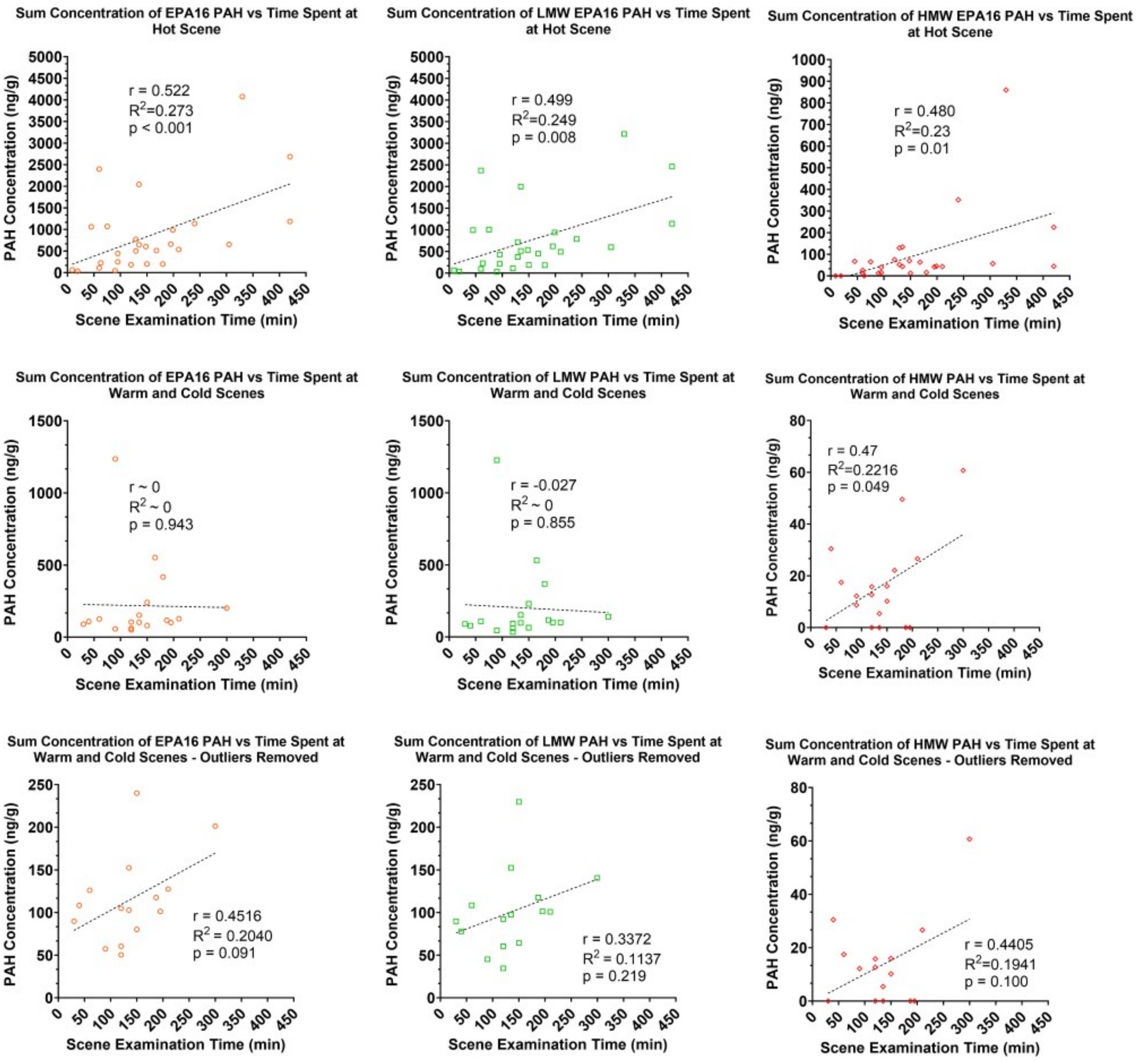


Fig. 3. Scatterplots of correlations and linear regressions conducted between time spent at hot scenes and warm and cold scenes. Post-fire scenes and exposures to all 16 EPA priority PAHs, lower molecular weight PAHs, and higher molecular weight PAHs. The third row of scatterplots displays scatterplots of data from warm and cold scenes with outliers removed.

3.6. Decontamination practices among fire investigators surveyed

Fire investigators are generally less well-protected against chemical exposures during their occupational tasks than their structural firefighter counterparts (Fire Investigator Health and Safety Best Practices, 2022; Horn et al., 2022). To give insight as to the prevalence of decontamination measures taken by fire investigators after returning wristbands following post-fire scene investigations, showering and gear cleaning behaviors were recorded in post-investigation questionnaires. Fire investigators reported taking a shower at least once following post-fire scene investigations for 41 out of 46 investigations examined. Showers were taken an average of 1.73 hours following the end of the investigation. Delays in showering were cited as being due to transit time required to return from the scene. Additionally, fire investigators reported taking steps for decontaminating their gear following 40 of 46 investigations and reported using dish soap and water, laundry detergents, or all-purpose cleaners for decontamination.

4. Discussion

4.1. PAH exposures measured on silicone wristbands

The ambient temperature at post-fire scenes is substantially lower than the temperature of the scene of an active fire. At these ambient temperatures, HMW PAHs are not volatile, and are limited to deposition via particulate-bound interactions (Zhang et al., 2020). Trends observed from wristband extract data shown in the heatmap in Fig. 1 illustrate that LMW PAHs comprise, on average, 90% of the total mass of PAHs found. which reflects the greater proportion of LMW PAHs likely to be present in the gas phase in the air at post-fire scenes. A moderately strong correlation (r=0.455) was estimated between concentrations of PAHs present on wristbands worn by fire investigators and the time they spent at the post-fire scene (Fig. 2). The amount of time spent at post-fire scenes has greater explanatory strength when the scene in question is a *hot scene*. (Fig. 3). By comparison, exposures to PAHs at *warm* and *cold scenes* are poorly explained by the amount of time that fire investigators

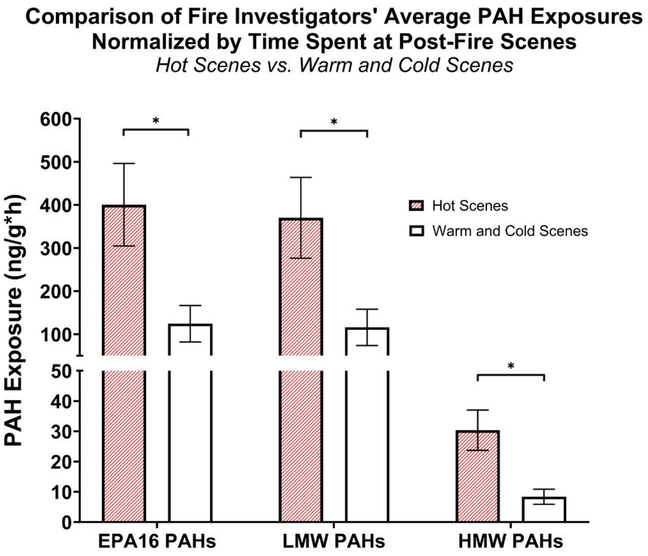


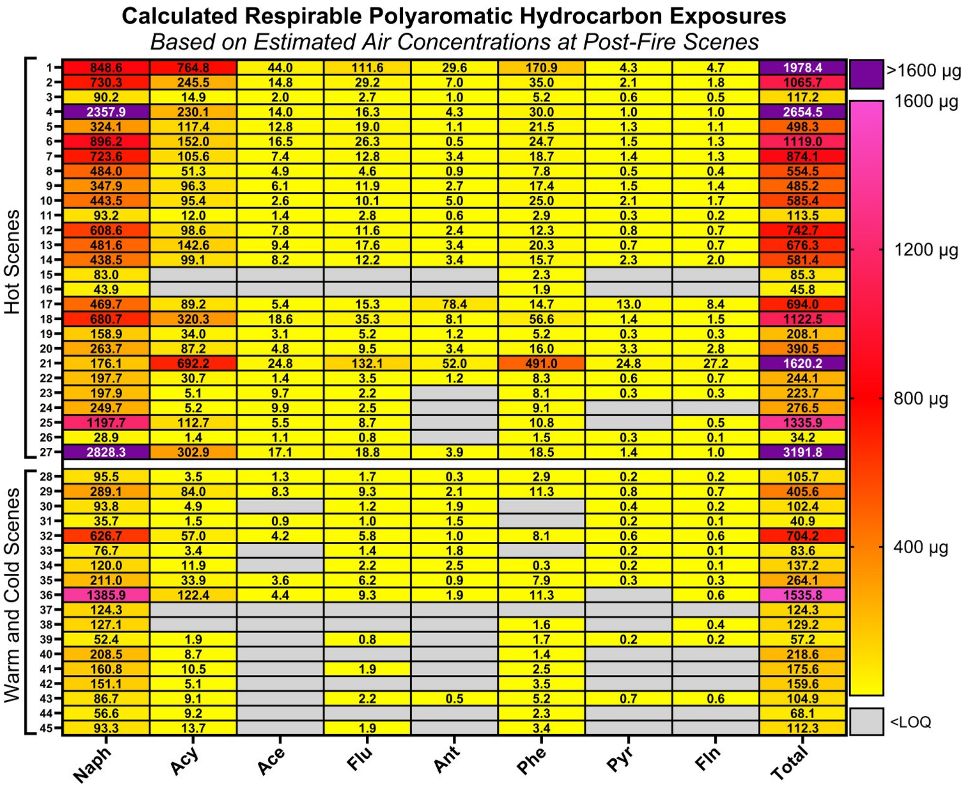
Fig. 4. Statistical comparisons of PAH exposure observed on silicone wristbands worn by fire investigators at post-fire scenes normalized by time spent at the scene. One-tailed t-tests were performed for comparison of time-normalized PAH exposures in hot scenes versus in warm and cold scenes with the hypothesis that hot scenes would exhibit greater levels of exposure. Significant differences were found for all comparisons. For total PAHs, $p = 0.029$; LMW PAHs, $p = 0.04$; HMW PAHs, $p = 0.012$. Error bars are representative of the standard error of the mean.

spend at these scenes, though this is due to the presence of high outlier values influenced by extreme exposures to LMW PAHs, especially naphthalene and acenaphthylene. Compared to LMW PAHs, the explanatory strength of time spent at post-fire scenes on HMW PAH exposure is not as substantially affected by the age of the post-fire scene. However, even when outliers are removed, the explanatory power of time spent at *warm* and *cold scenes* on total PAH exposure is not as large as that of time spent in *hot scenes*. (Fig. 3)

The most likely explanation as to the weaker correlation between PAH concentrations observed on wristbands to time spent at the *warm* and *cold scenes* is that the concentration of off-gassing volatiles and abundance of suspended particulates recede due to environmental aging of the post-fire scene (Zhang et al., 2020; Kim et al., 2009). The resulting reduction in airborne PAHs make fire investigators' exposures to them more dependent on other explanatory factors, including the types of fuel present at the scene and the actions and maneuvers taken by fire investigators while conducting their post-fire scene audit. This explanation is corroborated by the findings of Horn and coworkers, who also report a reduction in the level of off-gassing VOCs and PAHs observed in *warm scenes* and *cold scenes* compared to *hot scenes (*Horn et al., 2022*)*. Further evidence comes from the finding that average levels of all PAHs found on silicone wristbands worn by fire investigators were significantly lower for *warm* and *cold scenes* compared to *hot scenes* (Fig. 4). Although the lower overall exposure to PAHs observed at *warm* and *cold scenes* compared to *hot scenes* is expected, it should be noted that these values still suggest potentially unsafe levels of occupational exposure for fire investigators. This is especially true when considering that fire investigators may be present at post-fire scenes for many hours without adequate personal protection (Fire Investigator Health and Safety Best Practices, 2022; Horn et al., 2022).

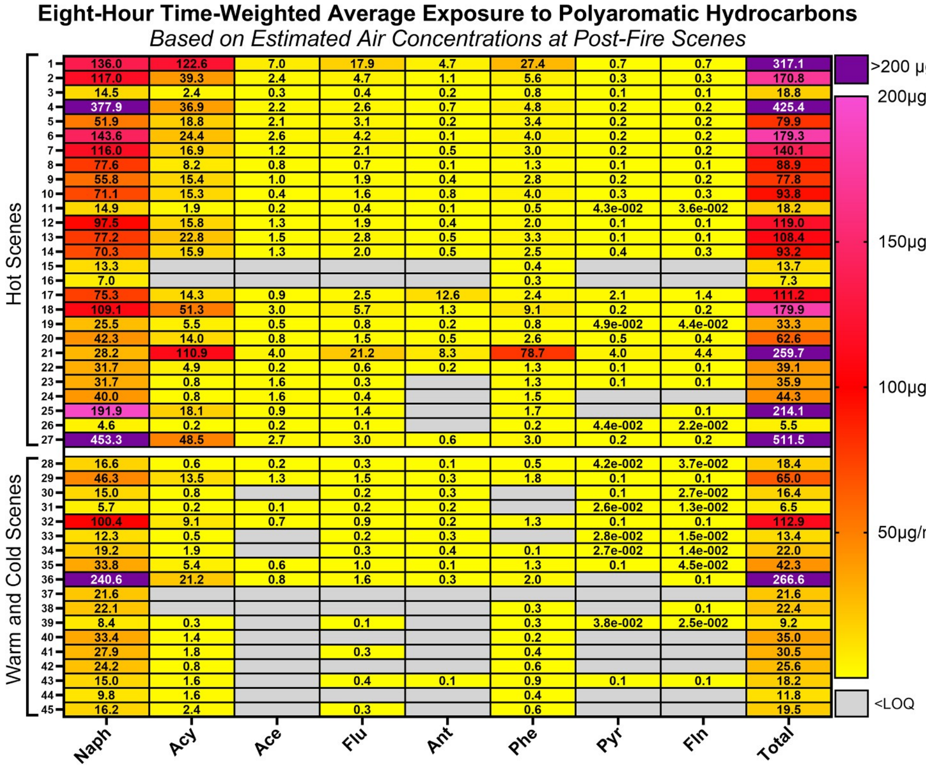
4.2. Assessing health risks to fire investigators

Among fire investigators, inconsistencies in the use and/or availability of PPE for conducting post-fire scene investigations constitutes a health risk (Horn, G.). Improper or inadequate PPE may lead to inadvertent exposure to volatile, semi-volatile, and particulate



		Naph	Acy	Ace	Flu	Ant	Phe	Pyr	Fln	Total
Hot Scenes	1	848.6	764.8	44.0	111.6	29.6	170.9	4.3	4.7	1978.4
	2	730.3	245.5	14.8	29.2	7.0	35.0	2.1	1.8	1065.7
	3	90.2	14.9	2.0	2.7	1.0	5.2	0.6	0.5	117.2
	4	2357.9	230.1	14.0	16.3	4.3	30.0	1.0	1.0	2654.5
	5	324.1	117.4	12.8	19.0	1.1	21.5	1.3	1.1	498.3
	6	896.2	152.0	16.5	26.3	0.5	24.7	1.5	1.3	1119.0
	7	723.6	105.6	7.4	12.8	3.4	18.7	1.4	1.3	874.1
	8	484.0	51.3	4.9	4.6	0.9	7.8	0.5	0.4	554.5
	9	347.9	96.3	6.1	11.9	2.7	17.4	1.5	1.4	485.2
	10	443.5	95.4	2.6	10.1	5.0	25.0	2.1	1.7	585.4
	11	93.2	12.0	1.4	2.8	0.6	2.9	0.3	0.2	113.5
	12	608.6	98.6	7.8	11.6	2.4	12.3	0.8	0.7	742.7
	13	481.6	142.6	9.4	17.6	3.4	20.3	0.7	0.7	676.3
	14	438.5	99.1	8.2	12.2	3.4	15.7	2.3	2.0	581.4
	15	83.0					2.3			85.3
	16	43.9					1.9			45.8
	17	469.7	89.2	5.4	15.3	78.4	14.7	13.0	8.4	694.0
	18	680.7	320.3	18.6	35.3	8.1	56.6	1.4	1.5	1122.5
	19	158.9	34.0	3.1	5.2	1.2	5.2	0.3	0.3	208.1
	20	263.7	87.2	4.8	9.5	3.4	16.0	3.3	2.8	390.5
	21	176.1	692.2	24.8	132.1	52.0	491.0	24.8	27.2	1620.2
	22	197.7	30.7	1.4	3.5	1.2	8.3	0.6	0.7	244.1
	23	197.9	5.1	9.7	2.2		8.1	0.3	0.3	223.7
	24	249.7	5.2	9.9	2.5		9.1			276.5
	25	1197.7	112.7	5.5	8.7		10.8		0.5	1335.9
	26	28.9	1.4	1.1	0.8		1.5	0.3	0.1	34.2
	27	2828.3	302.9	17.1	18.8	3.9	18.5	1.4	1.0	3191.8
Warm and Cold Scenes	28	95.5	3.5	1.3	1.7	0.3	2.9	0.2	0.2	105.7
	29	289.1	84.0	8.3	9.3	2.1	11.3	0.8	0.7	405.6
	30	93.8	4.9		1.2	1.9		0.4	0.2	102.4
	31	35.7	1.5	0.9	1.0	1.5		0.2	0.1	40.9
	32	626.7	57.0	4.2	5.8	1.0	8.1	0.6	0.6	704.2
	33	76.7	3.4		1.4	1.8		0.2	0.1	83.6
	34	120.0	11.9		2.2	2.5	0.3	0.2	0.1	137.2
	35	211.0	33.9	3.6	6.2	0.9	7.9	0.3	0.3	264.1
	36	1385.9	122.4	4.4	9.3	1.9	11.3		0.6	1535.8
	37	124.3								124.3
	38	127.1					1.6		0.4	129.2
	39	52.4	1.9		0.8		1.7	0.2	0.2	57.2
	40	208.5	8.7				1.4			218.6
	41	160.8	10.5		1.9		2.5			175.6
	42	151.1	5.1				3.5			159.6
	43	86.7	9.1		2.2	0.5	5.2	0.7	0.6	104.9
	44	56.6	9.2				2.3			68.1
	45	93.3	13.7		1.9		3.4			112.3

Fig. 5. Heatmap of potentially respirable quantities of vapor-phase PAHs determined by multiplying estimated concentrations of PAHs in air by inhalation rates and time spent at post-fire scenes. The upper limit cutoff in the heatmap of 1600 μg was informed by using the total exposure of an assumed eight-hour work day at the OSHA PEL of 0.2 mg/m^3 of PAHs in air.



	Naph	Acy	Ace	Flu	Ant	Phe	Pyr	Fln	Total
1	136.0	122.6	7.0	17.9	4.7	27.4	0.7	0.7	317.1
2	117.0	39.3	2.4	4.7	1.1	5.6	0.3	0.3	170.8
3	14.5	2.4	0.3	0.4	0.2	0.8	0.1	0.1	18.8
4	377.9	36.9	2.2	2.6	0.7	4.8	0.2	0.2	425.4
5	51.9	18.8	2.1	3.1	0.2	3.4	0.2	0.2	79.9
6	143.6	24.4	2.6	4.2	0.1	4.0	0.2	0.2	179.3
7	116.0	16.9	1.2	2.1	0.5	3.0	0.2	0.2	140.1
8	77.6	8.2	0.8	0.7	0.1	1.3	0.1	0.1	88.9
9	55.8	15.4	1.0	1.9	0.4	2.8	0.2	0.2	77.8
10	71.1	15.3	0.4	1.6	0.8	4.0	0.3	0.3	93.8
11	14.9	1.9	0.2	0.4	0.1	0.5	4.3e-002	3.6e-002	18.2
12	97.5	15.8	1.3	1.9	0.4	2.0	0.1	0.1	119.0
13	77.2	22.8	1.5	2.8	0.5	3.3	0.1	0.1	108.4
14	70.3	15.9	1.3	2.0	0.5	2.5	0.4	0.3	93.2
15	13.3					0.4			13.7
16	7.0					0.3			7.3
17	75.3	14.3	0.9	2.5	12.6	2.4	2.1	1.4	111.2
18	109.1	51.3	3.0	5.7	1.3	9.1	0.2	0.2	179.9
19	25.5	5.5	0.5	0.8	0.2	0.8	4.9e-002	4.4e-002	33.3
20	42.3	14.0	0.8	1.5	0.5	2.6	0.5	0.4	62.6
21	28.2	110.9	4.0	21.2	8.3	78.7	4.0	4.4	259.7
22	31.7	4.9	0.2	0.6	0.2	1.3	0.1	0.1	39.1
23	31.7	0.8	1.6	0.3		1.3	0.1	0.1	35.9
24	40.0	0.8	1.6	0.4		1.5			44.3
25	191.9	18.1	0.9	1.4		1.7		0.1	214.1
26	4.6	0.2	0.2	0.1		0.2	4.4e-002	2.2e-002	5.5
27	453.3	48.5	2.7	3.0	0.6	3.0	0.2	0.2	511.5
28	16.6	0.6	0.2	0.3	0.1	0.5	4.2e-002	3.7e-002	18.4
29	46.3	13.5	1.3	1.5	0.3	1.8	0.1	0.1	65.0
30	15.0	0.8		0.2	0.3		0.1	2.7e-002	16.4
31	5.7	0.2	0.1	0.2	0.2		2.6e-002	1.3e-002	6.5
32	100.4	9.1	0.7	0.9	0.2	1.3	0.1	0.1	112.9
33	12.3	0.5		0.2	0.3		2.8e-002	1.5e-002	13.4
34	19.2	1.9		0.3	0.4	0.1	2.7e-002	1.4e-002	22.0
35	33.8	5.4	0.6	1.0	0.1	1.3	0.1	4.5e-002	42.3
36	240.6	21.2	0.8	1.6	0.3	2.0		0.1	266.6
37	21.6								21.6
38	22.1					0.3		0.1	22.4
39	8.4	0.3		0.1		0.3	3.8e-002	2.5e-002	9.2
40	33.4	1.4				0.2			35.0
41	27.9	1.8		0.3		0.4			30.5
42	24.2	0.8				0.6			25.6
43	15.0	1.6		0.4	0.1	0.9	0.1	0.1	18.2
44	9.8	1.6				0.4			11.8
45	16.2	2.4		0.3		0.6			19.5

Fig. 6. Heatmap of eight-hour time-weighted average PAH exposures using estimated air concentrations of PAHs in the vapor-phase. The upper cutoff value of 200 μg/m^3 of PAHs is representative of the 0.2 mg/m^3 OSHA PEL. Concentrations are stratified by whether they are associated with hot scenes or warm and cold scenes.

contaminants. For example, fire investigators using gear that is not rated for protection against volatile compounds and gases, such as N95 masks or disposable Tyvek® full-body coveralls, may conduct their work tasks under the false assumption that they are protected (Fire Investigator Health and Safety Best Practices, 2022). Even more concerning is the possibility of fire investigators not using PPE altogether, as anecdotes have described fire investigators conducted post-fire scene investigations in casual streetwear, i.e., jeans and a t-shirt (Fire Investigator Health and Safety Best Practices, 2022). As a result, inhalational exposure to PAHs is a notable health risk for fire investigators. The median calculated respirable quantity of vapor-phase PAHs was 581.4 μg for *hot scenes* and 126.7 μg for *warm* and *cold scenes;* most of the respirable PAH exposure was attributable to naphthalene (Fig. 5). The expected respirable doses are lower than what is expected to be harmful according to the toxicological profile of PAHs published by the Agency for Toxic Substances and Disease Registry (ATSDR), which reports intakes ranging from 0.03 mg of pyrene to 0.3 mg of anthracene per kilogram of body weight as "not likely to cause harmful health effects." (Mumtaz and George, 1995) Nevertheless, exceedances of the legally-enforceable OSHA eight-hour TWA PEL of 0.2 mg/m^3 were estimated for six post-fire scene investigations, including five from *hot scenes*, shown in Fig. 6. Using the NIOSH eight-hour TWA REL of 0.1 mg/m^3 for comparison, this number increases to 14 exceedances, including 12 for *hot scenes.* This suggests a considerable inhalational exposure risk for fire investigators who are not donning PPE capable of mitigating exposure to volatile compounds, especially at *hot scenes.* In the present study, 61% of post-fire scene investigations are those of *hot scenes* conducted on the same day the fire was controlled. This further highlights the need for adequate PPE, since *hot scenes* are likely to make up the majority of investigations performed by public fire investigators.

It should be noted that the data shown in Figs. 5 and 6 do not take airborne particulate-bound PAHs into account. While no attempt was made to model concentrations of airborne particulate-bound PAHs, as silicone wristbands cannot reliably capture them, it can be inferred that the total PAH concentration in the air at post-fire scenes is appreciably higher when particulate-bound PAHs are included, probably leading to more exceedances overall.

4.3. *Strengths and limitations*

This exploratory study contributes some of the first evidence of fire investigators' exposures to carcinogens at post-fire scenes using a wearable sampling methodology, and helps to address gaps in understanding for exposure in an understudied occupational group in the fire service. Silicone wristbands present a lightweight, inexpensive, and non-invasive method of capturing fire investigator's exposures in a manner that is unlikely to affect how they carry out their work tasks. Additionally, this study is among the first to apply chemical-air equivalency models to estimate ambient concentrations of PAHs in the vapor-phase using silicone wristbands in an occupational context. From the ambient PAH concentrations determined, a health risk assessment for fire investigators' inhalation of vapor-phase PAHs was performed, finding exceedances for total PAHs at multiple post-fire scenes. These findings are especially relevant for those individuals who may not be wearing adequate respiratory protection at post-fire scenes.

The present study clearly establishes a positive correlation between the amount of time spent by fire investigators at post-fire scenes and PAH exposure sustained, especially at *hot scenes.* However, a future study may benefit from the collection of additional information which may explain generation, deposition, and fire-investigators' contact with PAHs beyond time spent at the scene. For example, this may include data on fuels burnt at the post-fire scene, which may produce different PAH profiles when burnt, as well as the specific type of PPE used by fire investigators during their investigations (Bralewska and Rakowska, 2020; Finardi et al., 2017).

Literature concerning the use of silicone materials for passive sampling shows that they are more reliably used for assessment of compounds in the vapor phase, rather than compounds in the particulate-bound phase (Samon et al., 2022; Hamzai et al., 2022). While authors note that soot has been observed on the wristbands analyzed in this study, which is likely the major source of the HMW PAHs found in the analysis of the wristbands, exposures to particulate-bound PAHs cannot be reliably estimated using silicone wristbands alone.

Chemical-air equivalency models can be used to determine ambient PAH concentrations in the air. However, ambient temperature, humidity, and air flow in the post-fire scene may affect the deposition, aerosolization, and partitioning of PAHs (Dotel et al., 2020; Newman et al., 2011). The models used in the present study were validated for 25 °C and 50% relative humidity, but specific temperature, humidity, and ventilation parameters were not recorded for post-fire scene investigations, and may have been substantially different. Additional models at different temperatures and humidity must be validated to improve the applicability of silicone wristband chemical-air equivalencies to more dynamic occupational contexts. Lastly, due to the self-reported nature of post-survey data by fire investigator participants, a future study may benefit from independent verification of data.

5. Conclusions

This study documented 16 EPA priority PAHs on silicone wristbands that showed a high tendency toward fire investigators' exposure to vapor-phase LMW PAHs during their occupational tasks. LMW PAHs are more volatile than HMW PAHs and are found in the gaseous phase at higher concentrations than HMW PAHs at the temperatures of a post-fire scene that has been controlled. Furthermore, HMW PAHs are more likely to be distributed through the aerosolization of soot and particulate to which they are bound (Zhang et al., 2019; Gill et al., 2020; Zhang et al., 2020) which in turn, makes them less likely to be aerosolized in a fire situation that has been controlled and is not generating large amounts of smoke.

A positive correlation was discovered between the amount of time fire investigators spend at post-fire scenes and the level of PAH exposure they sustain. However, other factors that may influence fire investigators' exposures to both types of PAHs, include the composition of the structure that was burned and the specific tasks and maneuvers performed while at the post-fire scene. Additionally, comparisons between post-fire scenes of different ages show that the strongest correlations were observed for all types of PAH exposure when plotted against time spent at more recently extinguished *hot scenes*. This finding supports that the age of less recently extinguished *warm* and *cold scenes* may encompass other factors that influence PAH deposition, such as weather.

After normalizing for exposure by the amount of time fire investigators spent at the post-fire scenes, statistical comparisons showed that exposure was significantly greater for *hot scenes* than for *warm* and *cold scenes* for all PAH categories, falling in line with expectations that recently controlled fires may still exhibit some active PAH generation and greater PAH off-gassing than less recently controlled fires. These conclusions are in line with a health risk assessment performed in the present study by modeling vapor-phase PAH concentrations in air, which found multiple exceedances of the OSHA eight-hour time-weighted average PEL of 0.2 mg/m^3 (Fig. 6).

To the best of our knowledge, this exploratory study is the first to evaluate fire investigators' occupational exposures to PAHs using passive samplers worn during real-world post-fire scene investigations. The findings presented herein show that fire investigators are exposed to significant concentrations of PAHs during their work tasks, specifically more volatile LMW PAHs present in the air at post-fire scenes. Importantly, this work helps elucidate fire investigators' health risks and recommends the use of more robust and scrupulous use of PPE and decontamination procedures. This is especially true when responding to post-fire scenes of recently controlled fires, when at post-fire scenes for prolonged periods of time, and when responding to multiple post-fire scenes.

CRediT authorship contribution statement

Umer Bakali: Methodology, Formal Analysis, Visualization, Writing – Original Draft, Data Curation, Investigation, Validation. **Jeramy L.R. Baum:** Investigation, Writing – Review & Editing. **Paola Louzado-Feliciano:** Investigation, Methodology, Data Curation. **Chitvan Killawala:** Visualization, Writing – Original Draft. **Katerina M. Santiago:** Investigation, Methodology, Data Curation. **Jeffrey L. Pauley:** Conceptualization, Methodology, Writing – Review & Editing, Investigation, Resources, Project Administration. **Emre Dikici:** Writing – Review & Editing. **Natasha Schaefer Solle:** Writing – Review & Editing, Supervision, Project Administration. **Erin N. Kobetz:** Supervision, Project Administration, Funding Acquisition. **Leonidas G. Bachas:** Supervision, Writing – Review & Editing. **Sapna K. Deo:** Supervision, Writing – Review & Editing. **Alberto J. Caban-Martinez:** Conceptualization, Methodology, Writing – Review & Editing, Visualization, Supervision, Project Administration, Funding Acquisition. **Sylvia Daunert:** Writing – Review & Editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

This work was supported by funding from the State of Florida appropriation #FM708 to the University of Miami (UM) Sylvester Comprehensive Cancer Center for the Firefighter Cancer Initiative and by the University of Miami U-Link Climate Resilience Challenge Grant. This work was supported by funding from the National Institutes of Health, Award #P30CA240139. The authors thank public and private fire investigators from the state of North Carolina for their participation in the study. Umer Bakali is thankful to Dr. Vincent Reynolds for his perspective on the study. Dr. Sylvia Daunert is grateful for support from the Lucille P. Markey Chair in Biochemistry and Molecular Biology of the Miller School of Medicine of the University of Miami.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2024.116349.

References

Alkon, A., Gunier, R.B., Hazard, K., Castorina, R., Hoffman, P.D., Scott, R.P., Anderson, K.A., Bradman, A., 2022. Preschool-age children's pesticide exposures in child care centers and at home in Northern California. J. Pediatr. Health Care *36* (1), 34–45.

Bakali, U., Baum, J.L.R., Killawala, C., Kobetz, E.N., Solle, N.S., Deo, S.K., Caban-Martinez, A.J., Bachas, L.G., Daunert, S., 2021. Mapping carcinogen exposure across urban fire incident response arenas using passive silicone-based samplers. Ecotoxicol. Environ. Saf. *228*, 112929.

Baum, J.L.R., Bakali, U., Killawala, C., Santiago, K.M., Dikici, E., Kobetz, E.N., Solle, N.S., Deo, S., Bachas, L., Daunert, S., 2020. Evaluation of silicone-based wristbands as passive sampling systems using PAHs as an exposure proxy for carcinogen monitoring in firefighters: evidence from the firefighter cancer initiative. Ecotoxicol. Environ. Saf. *205*, 111100.

Bralewska, K., Rakowska, J., 2020. Concentrations of Particulate Matter and PM-Bound Polycyclic Aromatic Hydrocarbons Released during Combustion of Various Types of Materials and Possible Toxicological Potential of the Emissions: The Results of Preliminary Studies. Int. J. Environ. Res. Public Health [Online].

Bukowska, B., Mokra, K., Michałowicz, J., 2022. Benzo[a]pyrene—environmental occurrence, human exposure, and mechanisms of toxicity. Int. J. Mol. Sci. *23* (11), 6348.

Chapter 6 - Inhalation Rates. In Exposure Factors Handbook 2011 Edition (Final Report), U.S. Environmental Protection Agency: Washington, DC, 2011.

Chemical Agents and Related Occupations. International Agency for Research on Cancer: 2012; p. 628. 〈https://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Chemical-Agents-And-Related-Occupations-2012〉.

Demers, P.A., DeMarini, D.M., Fent, K.W., Glass, D.C., Hansen, J., Adetona, O., Andersen, M.H.G., Freeman, L.E.B., Caban-Martinez, A.J., Daniels, R.D., Driscoll, T. R., Goodrich, J.M., Graber, J.M., Kirkham, T.L., Kjaerheim, K., Kriebel, D., Long, A. S., Main, L.C., Oliveira, M., Peters, S., Teras, L.R., Watkins, E.R., Burgess, J.L., Stec, A.A., White, P.A., DeBono, N.L., Benbrahim-Tallaa, L., de Conti, A., El Ghissassi, F., Grosse, Y., Stayner, L.T., Suonio, E., Viegas, S., Wedekind, R., Boucheron, P., Hosseini, B., Kim, J., Zahed, H., Mattock, H., Madia, F., Schubauer-Berigan, M.K., 2022. Carcinogenicity of occupational exposure as a firefighter. Lancet Oncol. *23* (8), 985–986.

Dotel, J., Gong, P., Wang, X., Pokhrel, B., Wang, C., Nawab, J., 2020. Determination of dry deposition velocity of polycyclic aromatic hydrocarbons under the sub-tropical climate and its implication for regional cycling. Environ. Pollut. *261*, 114143.

El-Sikaily, A., Helal, M., Nsonwu-Anyanwu, A.C., Azab, H., Abd ElMoneim, N., Farahat, E.O.S., Saad, A., 2023. Impacts of PAH accumulation on reproductive hormones, indices of oxidative stress and BPDE-albumin adduct in women with recurrent pregnancy loss. Toxicol. Res. *39* (3), 517–531.

Fahy, R., Evarts, B., Stein, G.P., 2021. US Fire Department Profile. *NFPA Res.* [Online] 2019. 〈https://www.nfpa.org/-/media/Files/News-and-Research/Fire-statistics-and-reports/Emergency-responders/osfdprofile.pdf〉.

Fernando, H., Ju, H., Kakumanu, R., Bhopale, K.K., Croisant, S., Elferink, C., Kaphalia, B. S., Ansari, G.A.S., 2019. Distribution of petrogenic polycyclic aromatic hydrocarbons (PAHs) in seafood following Deepwater Horizon oil spill. Mar. Pollut. Bull. *145*, 200–207.

Finardi, S., Radice, P., Cecinato, A., Gariazzo, C., Gherardi, M., Romagnoli, P., 2017. Seasonal variation of PAHs concentration and source attribution through diagnostic ratios analysis. Urban Clim. *22*, 19–34.

Fire Investigator Health and Safety Best Practices. Third Edition; The International Association of Arson Investigators, Inc. Health & Safety Committee: 2022. 〈https://www.firearson.com/Download.aspx?DownloadId=ac98a144-2a36-45bb-b49b-fdb0af6e06b4〉.

Gehle, K., Toxicity of polycyclic aromatic hydrocarbons (PAHs). 2009.

Gill, R., Hurley, S., Brown, R., Tarrant, D., Dhaliwal, J., Sarala, R., Park, J.-S., Patton, S., Petreas, M., 2020. Polybrominated Diphenyl Ether and Organophosphate Flame Retardants in Canadian Fire Station Dust. Chemosphere *253*, 126669.

Hamzai, L., Lopez Galvez, N., Hoh, E., Dodder, N.G., Matt, G.E., Quintana, P.J., 2022. A systematic review of the use of silicone wristbands for environmental exposure assessment, with a focus on polycyclic aromatic hydrocarbons (PAHs). J. Expo. Sci. Environ. Epidemiol. *32* (2), 244–258.

Horn, G. Research Corner: Airborne Contamination During Post-Fire Investigations. 〈https://www.firehouse.com/safety-health/article/21273901/why-fire-investigators-are-at-risk-of-airborne-contaminants〉.

Horn, G.P., Madrzykowski, D., Neumann, D.L., Mayer, A.C., Fent, K.W., 2022. Airborne contamination during post-fire investigations: Hot, warm and cold scenes. J. Occup. Environ. Hyg. *19* (1), 35–49.

Hwang, J., Xu, C., Agnew, R.J., Clifton, S., Malone, T.R., 2021. Health Risks of Structural Firefighters from Exposure to Polycyclic Aromatic Hydrocarbons: A Systematic Review and Meta-Analysis. Int. J. Environ. Res. Public Health *18* (8), 4209.

IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. Painting, Firefighting, and Shiftwork. IARC: Lyon (FR), 2010. 〈https://www.ncbi.nlm.nih.gov/books/NBK326802/〉.

Kamal, A., Cincinelli, A., Martellini, T., Malik, R.N., 2015. A review of PAH exposure from the combustion of biomass fuel and their less surveyed effect on the blood parameters. Environ. Sci. Pollut. Res. *22* (6), 4076–4098.

Khan, A., Ahsan, A., Farooq, M.A., Naveed, M., Li, H., 2021. Role of Polycyclic Aromatic Hydrocarbons as EDCs in Metabolic Disorders. In: Akash, M.S.H., Rehman, K., Hashmi, M.Z. (Eds.), Endocrine Disrupting Chemicals-induced Metabolic Disorders and Treatment Strategies. Springer International Publishing, Cham, pp. 323–341.

Kim, D., Kumfer, B.M., Anastasio, C., Kennedy, I.M., Young, T.M., 2009. Environmental aging of polycyclic aromatic hydrocarbons on soot and its effect on source identification. Chemosphere *76* (8), 1075–1081.

Levasseur, J.L., Hoffman, K., Herkert, N.J., Cooper, E., Hay, D., Stapleton, H.M., 2022. Characterizing firefighter's exposure to over 130 SVOCs using silicone wristbands: A pilot study comparing on-duty and off-duty exposures. Sci. Total Environ. *834*, 155237.

Mumtaz, M., George, J. Toxicological Profile for Polycyclic Aromatic Hydrocarbons; 1995.

Newman, J.S., Su, P., Yee, G.G., 2011. Smoke deposition velocity in industrial fire environments. Fire Saf. Sci. 655–668.

O'Connell, S.G., Anderson, K.A., Epstein, M.I., 2022. Determining chemical air equivalency using silicone personal monitors. J. Expo. Sci. Environ. Epidemiol. *32* (2), 268–279.

O'Connell, S.G., Kincl, L.D., Anderson, K.A., 2014. Silicone Wristbands as Personal Passive Samplers. Environ. Sci. Technol. *48* (6), 3327–3335.

O'Connor, B. Fire Extinguisher Types NFPA Today [Online], 2021. 〈https://www.nfpa.org/News-and-Research/Publications-and-media/Blogs-Landing-Page/NFPA-Today/Blog-Posts/2021/07/16/Fire-Extinguisher-Types〉.

Olasehinde, T.A., Olaniran, A.O., 2022. Neurotoxicity of Polycyclic Aromatic Hydrocarbons: A Systematic Mapping and Review of Neuropathological Mechanisms. Toxics *10* (8).

Poutasse, C., Haddock, C., Poston, W., Jahnke, S., Tidwell, L., Bonner, E., Hoffman, P., Anderson, K., 2021. Firefighter exposures to potential endocrine disrupting chemicals measured by military-style silicone dog tags. Environ. Int. *158*, 106914.

Poutasse, C., Poston, W., Jahnke, S., Haddock, C., Tidwell, L., Hoffman, P., Anderson, K., 2020. Discovery of firefighter chemical exposures using military-style silicone dog tags. Environ. Int. *142*, 105818.

Priority Pollutant List. United States Environmental Protection Agency: 2014.

Qu, C., Doherty, A.L., Xing, X., Sun, W., Albanese, S., Lima, A., Qi, S., De Vivo, B., 2018. Chapter 20 - Polyurethane Foam-Based Passive Air Samplers in Monitoring Persistent Organic Pollutants: Theory and Application. In: De Vivo, B., Belkin, H.E., Lima, A. (Eds.), In *Environmental Geochemistry (Second Edition)*. Elsevier, pp. 521–542.

Richter, H., Howard, J.B., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways. Prog. Energy Combust. Sci. *26* (4), 565–608.

Rossbach, B., Wollschläger, D., Letzel, S., Gottschalk, W., Muttray, A., 2020. Internal exposure of firefighting instructors to polycyclic aromatic hydrocarbons (PAH) during live fire training. Toxicol. Lett. *331*, 102–111.

Samon, S.M., Hammel, S.C., Stapleton, H.M., Anderson, K.A., 2022. Silicone wristbands as personal passive sampling devices: current knowledge, recommendations for use, and future directions. Environ. Int., 107339

Sedlačková, L., Melymuk, L., Vrana, B., 2021. Calibration of silicone for passive sampling of semivolatile organic contaminants in indoor air. Chemosphere *279*, 130536.

Sousa, G., Teixeira, J., Delerue-Matos, C., Sarmento, B., Morais, S., Wang, X., Rodrigues, F., Oliveira, M., 2022. Exposure to PAHs during firefighting activities: a review on skin levels, in vitro/in vivo bioavailability, and health risks. Int. J. Environ. Res. Public Health *19* (19), 12677.

Sprunger, L., Proctor, A., Acree, W.E., Abraham, M.H., 2007. Characterization of the sorption of gaseous and organic solutes onto polydimethyl siloxane solid-phase microextraction surfaces using the Abraham model. J. Chromatogr. A *1175* (2), 162–173.

Srogi, K., 2007. Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ. Chem. Lett. *5* (4), 169–195.

Wacławik, M., Rodzaj, W., Wielgomas, B., 2022. Silicone Wristbands in Exposure Assessment: Analytical Considerations and Comparison with Other Approaches. Int. J. Environ. Res. Public Health *19* (4), 1935.

Yu, Y.-y, Jin, H., Lu, Q., 2022. Effect of polycyclic aromatic hydrocarbons on immunity. J. Transl. Autoimmun. *5*, 100177.

Zhang, J., Liu, W., Xu, Y., Cai, C., Liu, Y., Tao, S., Liu, W., 2019. Distribution characteristics of and personal exposure with polycyclic aromatic hydrocarbons and particulate matter in indoor and outdoor air of rural households in Northern China. Environ. Pollut. *255*, 113176.

Zhang, L., Yang, L., Zhou, Q., Zhang, X., Xing, W., Wei, Y., Hu, M., Zhao, L., Toriba, A., Hayakawa, K., Tang, N., 2020. Size distribution of particulate polycyclic aromatic hydrocarbons in fresh combustion smoke and ambient air: a review. J. Environ. Sci. *88*, 370–384.