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Original Article

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Airborne and Dermal Exposure to Polycyclic Aromatic Hydrocarbons, Volatile Organic Compounds, and Particles among Firefighters and Police Investigators

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Abstract

Aims: The main aim of this study was to assess dermal exposure to polycyclic aromatic hydrocarbons (PAHs) and airway exposure to PAHs, volatile organic compounds (VOCs; benzene and 1,3-butadiene), and particles among firefighters (FFs) and police forensic investigators (PFIs) in Sweden.
Methods: Active (pump with a filter and sorbent tube) and passive (polyurethane foam -cyl and perkin elmer carbopack-tube) personal air sampling and dermal tape stripping (wrist and collar bone) were performed on seven FF team leaders during training fires and nine PFIs investigating the aftermath of live fire events. In addition, passive personal air sampling was performed on eight FF team leaders during live emergency fires. PAHs and VOCs were analysed using high-resolution gas chromatography low-resolution mass spectrometry. The mass concentration of total dust (particles) was determined using standard gravimetric methods.
Results: The air samples showed that the exposure to PAHs, benzene, 1,3-butadiene, and particles was below Swedish occupational exposure limits (OELs). Naphthalene was the predominant PAH in all air samples. Benzene and 1,3-butadiene were more abundant in live emergency fires, which caused higher exposures than the other studied situations. Both gaseous- and particle-associated PAHs were present on skin. The wrists seemed to be less well protected than the collarbone area.
Conclusions: FFs and PFIs are exposed to several hazardous compounds during their work. Air exposures varied considerably between working scenarios. The observed exposures were substantially

higher than urban background levels but well below Swedish OELs. The measured dermal PAH exposures were comparable to previously reported doses for US FFs but lower than the exposures reported for Swedish chimney sweeps.

Keywords: airway exposure; carcinogenic; dermal exposure; firefighter; polycyclic aromatic hydrocarbons

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are released during incomplete combustion or pyrolysis of organic material. These ubiquitous compounds are known for their cytotoxic and mutagenic properties and some of them are classified by the International Agency for Research on Cancer (IARC) as being carcinogenic (benzo(a)pyrene), probably carcinogenic (dibenzo(a,h) anthracene), or possibly carcinogenic (e.g. naphthalene and benzo(a)anthracene) in humans (IARC, 2010a). Some PAHs are classified as endocrine disrupting chemicals (WHO/UNEP, 2012), and 16 of them are listed as priority environmental pollutants by the US Environmental Protection Agency (USEPA) (USEPA, 2005). Volatile organic compounds (VOCs) are another group of compounds that can originate from various ambient and occupational sources. Benzene and 1,3-butadiene have attracted particular attention because of their potential adverse effects on human health. The IARC recently reconfirmed that benzene is carcinogenic, may cause acute myeloid leukaemia, and is likely to cause other leukaemia subtypes and lymphoid neoplasms in humans (IARC, 2012). The IARC also concluded that 1,3-butadiene is carcinogenic and may cause cancer of the haematolymphatic organs (IARC, 2012).

In a typical firefighting scenario, PAHs will be present in both the gaseous and particulate phases, making it important to sample both phases to comprehensively assess the exposure of individuals working in such circumstances. Dermal exposure may also occur by the deposition of particles or gaseous substances on the skin. Firefighters (FFs), police forensic investigators (PFIs), and other personnel working in firefighting-related environments are exposed to many different particles and combustion products from smoke and ash, including carcinogenic substances such as benzo(a)pyrene, benzene, 1,3-butadiene, arsenic, cadmium, and formaldehyde (Austin et al., 2001; IARC, 2008, 2010a,b; Blomqvist et al., 2012). It is also important to remember that the particles themselves are hazardous and are known to influence the risk of cardiovascular disease (Brook et al., 2010; Pope et al., 2016).

Many previous studies have suggested that FFs may have a higher risk of certain types of cancer, which has caused concern among workers in sectors where exposure to smoke from fires is common (LeMasters et al., 2006; Daniels et al., 2014; Pukkala et al., 2014; Glass et al., 2016). During the last 10 years, several studies have addressed the issue of FFs' exposure to PAHs and other hazardous compounds (Fent and Evans, 2011; Baxter et al., 2014; Fent et al., 2014; Kirk and Logan, 2015; Fernando et al., 2016; Oliveira et al., 2017; Fent et al., 2018; Stec et al., 2018; Wingfors et al., 2018). However, these studies vary widely in terms of the work processes that were examined, the material that was burned, and the safety equipment that was used.

Most studies in this area have examined training situations involving controlled structure burns and burning wood. These investigations have shown that the concentrations of exhaled benzene and urinary PAH metabolites increase significantly after exposure (Fent et al., 2014) and that levels of urinary biomarkers of wood smoke exposure change after training exercises (Fernando et al., 2016; Wingfors et al., 2018). Personal monitoring of 16 PAHs using Tenax and polyurethane foam (PUF) in a glass tube yielded measured concentrations ranging from 32 to 355 μg m^{-3} inside 'structural firefighting ensembles' during live fire training (Kirk and Logan, 2015). Personal sampling of 15 quantified PAHs from the position of pump operator/command during training fires ranged from <30 to 220 μg m^{-3} (Fent et al., 2018). Exposures ranging from 150 to 240 μg m^{-3} were observed for 22 PAHs using a similar setup featuring glass fibre filters and PUF plugs (Wingfors et al., 2018). Oliveira et al. (2017) monitored PAH exposure in the breathing zones over the course of complete work shifts at different fire stations, revealing that total PAH concentrations varied widely (46.4–428 ng m^{-3}). The most commonly detected PAH, and the one that is quantitatively dominant in air monitoring samples, is the possibly carcinogenic naphthalene.

Kirk and Logan (2015) also observed the deposition of PAHs on protective equipment at concentrations between 69 and 290 ng cm^{-2}. Baxter et al. (2014) reported dermal sample concentrations of PAHs in the range of 50–160 ng/sample surface (neck and face), as well as workspace contamination with PAHs after overhaul activity. Fent et al. (2014) measured combined levels of six PAHs on skin after exposures in the range of 12–50 μg m^{-2} on several body locations. Wingfors

et al. (2018) reported that the depositions of 14 PAHs increased by 21–99 ng/30 cm^2 skin wipe (neck and jaw) after a training exercise. Stec et al. (2018) reported that levels of 12 PAHs in skin wipe samples (neck, jaw, and hands) taken from firefighters, with suboptimal protection and routines, after training exercises were 10–575 mg m^{-2} higher than the levels observed before training, and also observed workplace contamination with PAHs.

The motivation for our study is that the scientific literature contains little PAH exposure data for FFs working without full airway protection, which is common in some team leading positions. Also, there is no current data on PAH and VOC exposure among Swedish FFs and PFIs that could be used to assess potential health risks.

This study evaluated exposure to 32 different PAHs, two VOCs, and particles (total dust) among FFs and PFIs in various settings during and after fire events. Airway exposure was studied for all of the included occupational groups, whereas dermal exposure was studied for FFs in training situations (FFTs) and PFIs.

Methods

Active and passive sampling methods were used to measure airway exposure to PAHs, VOCs, and total dust in the breathing zones of seven team-leading FFTs and nine PFIs working in the aftermath of live fire events. In addition, the dermal exposure of FFTs and PFIs was measured on the wrist and collarbone by tape stripping after the end of their working shifts. We also measured airway exposure in eight team-leading FFs during emergency (FFE) events by passive air monitoring. The characteristics of the study population are summarized in Table 1.

Firefighter team leaders: training situation

Air (active and passive) and dermal samples were collected from FFT team leaders standing 5–10 m from the entrance of the building used for training sessions. The purpose of the team leaders was to coordinate the training event. They did not start the fire or enter the building during the exercise. The team leader typically wore upper and lower body protective clothing but not full turn out gear, no helmet or neck protection, and no respiratory protection. The building had two storeys, imitating a typical furnished house. The fire was started in one room using different types of wood (mostly pallets), and smoke was allowed to fill the remainder of the house. Air measurements commenced a few minutes before the training session started. The same firehouse was used in all seven training sessions. Sampling was performed during 7 days in May 2014 in the Stockholm region of Sweden.

Police forensic investigators: live events

Active and passive air sampling followed by dermal sampling was performed after five different fires around Stockholm (September–December 2014). The fires occurred in diverse settings including a country cottage, an apartment building, an office, an antique store, and a clothes warehouse. Personal protective equipment varied but typically included a disposable overall, respiratory protection (of various designs and types), and gloves (of varying material). All fires visited were located indoors except for the country cottage. In three cases, PFIs entered the site within 12 h of the fire. However, at the country cottage and clothes warehouse, the PFIs only entered the site 30 h and 5 days, respectively, after the fire. Air measuring equipment was activated as the PFIs approached the forensic analysis site and deactivated when they left.

Table 1. Descriptive factors regarding participants in the three study groups and the respective average airway exposure sampling time. Note that FFTs and PFIs were studied using both active and passive airway sampling.

Factors	FFT	PFI	FFE
Number of participants (*N*)	7	9	8
Gender (m/w)	7/0	5/4	8/0
Current smoking (y/n)	0/7	0/9	0/8
Mean measuring time in minutes (min–max)	110 (74–196)	135 (49–288)	110 (20–240)
Measuring method*	Active and passive	Active and passive	Passive
Number of events	7	5	8
Entered structure	No	Yes	No
Breathing protection used	No	Varying	No
Dermal sampling performed	Yes	Yes	No

*Active sampling for PAH: 37-mm filter in open-faced cassette followed by XAD sorbent tube. Passive sampling for PAH: PUF-cyl placed inside protective net.

Firefighter team leaders: emergency events

Passive air exposure measurements were performed during eight emergency firefighting events in the Stockholm region, Sweden, between October 2014 and July 2015. The settings of these emergencies included houses, flats, and car fires (both in garages and outside). The purpose of the team leaders was to coordinate the effort but not to participate in search, attack, or similar activities. The FFs wore complete turn out gear but team leaders did not wear respiratory protection. Before participation, the FFs received training on how to use the passive sampling equipment and how to log sampling times. The equipment was attached and activated inside the response vehicle while en route to the fire incident (at most 10 min before reaching the fire). For practical reasons, neither active exposure measurements nor dermal sampling was performed.

Air sampling

The methods used for passive and active PAH sampling are described in detail elsewhere (Strandberg et al., 2018b), and are therefore only briefly outlined here.

Active sampling of PAHs and total dust

The sampling apparatus consisted of a pump (AirCheck XR5000; SKC Inc.) with a flow rate set to 2.0 ± 0.1 l min^{-1} and a 37-mm diameter Teflon filter (2 µm; Pall Corp.) in an open-face filter cassette to collect particulate matter (total dust) and associated PAHs. Air passing through the filter then flowed through a sorbent tube (7 × 70 mm, 2-section, 40/80 mg sorbent, with glass wool ends, WWW separators; SKC Inc.) containing XAD-2 to collect the gaseous PAH fraction.

The flow was checked before and after each measurement with a Bios DryCal DC-Lite (Butler, PA, USA). The filters were prepared and weighed according to a previously described procedure (Jørgensen et al., 2013). The filter cassette was attached in the breathing zone on the outside of the protective clothes. After sampling, the filter cassettes were sealed with lids and sealing caps, and stored at –20°C. XAD tubes were sealed with end caps and stored at –20°C.

Passive sampling of PAHs and some VOC

The PUF passive air samplers used in this study were cylindrical (PUF-cyl; length: 10 cm, diameter: 2.2 cm; Klaus Ziemer GmbH, Germany). When used for sampling, the PUF-cyl is placed inside a protective cover net (diameter: 2.2 cm, length: 10 cm) with a mesh size of 1.0 mm (AB Derma, Sweden). PAH samples were prepared, analysed, and quantitatively determined as described previously (Strandberg et al., 2018b). Samplers were mounted on holders using support plates that were attached to the participants' clothes with safety pins. Before use, each PUF-cyl was pre-cleaned via Soxhlet extraction using dichloromethane, dried in a vacuum desiccator for several hours, and stored in multiple layers of aluminium foil inside airtight Ziploc bags to reduce the risk of contamination. Before use, and after the measurements, the samples were wrapped in aluminium foil and stored in a freezer at –20°C. During sampling, the samplers were attached in the participants' breathing zones.

The VOCs benzene and 1,3-butadiene were measured using Perkin Elmer tubes (MA, USA and Markes International Ltd, UK) containing the adsorbent Carbopack X 60/80 (Supelco, Bellefonte, PA, USA). Before sampling, the sealing nut was replaced with a diffusion cap. During sampling, the tube was attached in the breathing zone of the test subject. After sampling, the diffusion cap was removed, the sealing nut was screwed back on, and the tube was stored in a refrigerator at +4°C.

Dermal sampling

To assess dermal PAH exposure, we performed tape stripping on the wrists and collarbones of the participating FFTs and PFIs. It was not possible to perform dermal sampling on the FFE group. The FFTs (N = 7) were repeatedly sampled (giving a total n of 14) and divided into three work task groups: FFTs acting as fire starters (n = 3), FFTs acting as leaders entering the burning house (n = 3), and FFT team leaders outside the house (n = 8). Dermal exposure was assessed by performing repeated measurements on the skin to gather data on exposure during different work tasks with the potential to result in skin contamination. If samples were collected from the right wrist and right collarbone on the first sampling occasion, they would be collected from the left side on the second sampling occasion to avoid disturbing the skin barrier between samplings. In addition, individual participants were only allowed to contribute data on multiple occasions if they were sampled under low-exposure conditions on the first sampling occasion and high-exposure conditions on the second. Individuals acting as FFT team leaders outdoors were considered to be working under low-exposure conditions, whereas those acting as fire starters or entering the burning building were considered to be working under high-exposure conditions.

We also performed dermal sampling on office workers (n = 7) who volunteered to act as controls. The office workers were assumed to have no occupational

exposure to PAH or exposure to burning wood at home. They all worked at the Centre for Occupational and Environmental Medicine, Stockholm, Sweden.

The method of dermal sampling has been described in detail previously (Strandberg et al., 2018a). Briefly, 15 cm^2 areas each on lower wrist and collar bone were sampled using three consecutive tapes (each tape 15 cm^2; Fixomull adhesive tape; BSN medical GmbH & Co, Hamburg, Germany). The tapes were applied to the surface area and a gentle pressure was applied manually by the same operator on all sampling occasions. The tape was then removed from the skin, folded in two, and placed in a Petri dish. The three tapes from each area were pooled into a single sample. The Petri dishes were wrapped in aluminium foil and stored in a freezer at –20°C on delivery to the laboratory.

Chemical analysis

Air samples

The analytical procedures and instrumentation used in the PAH analysis of the PUF-cyl and active (XAD-2 and filter) samples are described in detail in an earlier publication (Jørgensen et al., 2013; Strandberg et al., 2018b), as are the details of the VOC analysis (Strandberg et al., 2014). In brief, after extraction and clean up, the PAHs were separated and detected by high-resolution chromatography/low-resolution mass spectrometry using a 7890 A chromatograph coupled to a 5975C spectrometer (Agilent Technologies, Inc., Santa Clara, CA, USA). The VOC samples were analysed using a Unity Ultra Thermal Desorber (Markes International Ltd.) coupled to a gas chromatograph (Agilent 6890N) and a mass spectrometer (Agilent 5973).

For the VOC analysis, quality control (QC) samples of benzene and 1,3-butadiene at two predetermined loadings (10 and 100 ng) obtained from VSL Dutch Metrology Institute (the Netherlands) were analysed at the same time as the samples. The measured concentrations of the QC samples were consistently within 15% of the certified levels. For the PAH analysis, a certified reference material (SRM 1649a urban dust) was used for QC. Six QC samples containing different masses of the SRM were analysed in parallel with the samples. The measured levels of 13 PAHs in these QC samples were generally within 10% of the corresponding certified values. All QC results were considered acceptable. Six field blanks were collected for each sampler type and processed in parallel with the samples to assess the residual levels of the target compounds. The limit of detection (LOD) for each sampler type was calculated as three times the standard deviation (SD) or background noise of the blanks. The mass concentration of total dust was determined using standard gravimetric methods (Lewne et al., 2017).

The analytes targeted in the PAH analysis were the 32 PAHs listed in Supplementary Table 2, available at *Annals of Occupational Hygiene* online. The summed concentrations of these PAHs are reported as 'sum 32 PAH' values. The summed concentrations of the 16 PAHs classified as priority pollutants by the USEPA (ATSDR, 2005) are reported as 'sum 16 PAH' values, and the summed concentrations of chrysene, benzo(a) pyrene, fluoranthene, pyrene, anthracene, and phenanthrene are reported as 'sum 6 PAH' values.

Dermal samples

Dermal samples were analysed using a newly published method in which extracts are cleaned up by semipermeable membrane (SPM) dialysis (Strandberg et al., 2018a). Briefly, the tape strips were extracted three times in 5 ml dichloromethane using ultrasonication (with fresh solvent for each extraction) for 30 min. The extracts were then combined, the dichloromethane was evaporated under a stream of nitrogen gas, and the residual material was taken up in *n*-hexane. The extracts were then placed in an SPM for clean up by dialysis and further purification by on-column elution using a 9-mm inner diameter chromatography column packed with 2 g of aluminium oxide, 4 g of silica gel, and 1 cm of sodium sulphate. The chemical analysis and limit of quantification (10 × SD of blank samples) determinations were performed as described in the previous section.

Statistical analyses

Descriptive statistics were calculated using SAS for Windows, version 9.4 (SAS Institute, Inc., Cary, NC, USA). For group comparisons, the nonparametric Kruskal–Wallis test was performed followed by Dunn's multiple comparison test ($\alpha = .05$). Group comparisons and figures were made using GraphPad Prism 7.01 (GraphPad Software, Inc., USA).

Results

Airway exposure

Next, we present selected results from the analysis of air samples obtained by active and passive methods (Table 2). For the full data set, please see Supplementary Table 1, available at *Annals of Occupational Hygiene* online . Two sets of active and passive samples (one from an FFT and one from a PFI) were excluded due to malfunctions of the sampling equipment. The geometric mean (GM) total dust exposure for FFTs was 137 µg m^{-3}, whereas

Table 2. Airway exposures determined by active and passive methods for team-leading FFTs, PFIs, and team-leading FFEs. Exposures were measured for the sum of 32 PAHs, the sum of 16 PAHs, all individual PAHs classified by the IARC as carcinogenic, probably carcinogenic or possibly carcinogenic, two VOCs, and total dust. GM: geometric mean; GSD: geometric standard deviation.

Sampling method	*n*	FFT (*N* = 7) GM (GSD)	Range	PFI (*N* = 9) GM (GSD)	Range	FFE (*N* = 8) GM (GSD)	Range
PAH (active; ng m^{-3})							
Total 32 PAH	21	3600 (1.97)	1740–16 000	6500 (6.89)	219–88 400	—	
Total 16 PAH (USEPA)	21	2980 (1.93)	1420–12 100	5490 (7.46)	154–80 000	—	
PAH (passive; ng m^{-3})							
Total 32 PAH	29	2230 (2.16)	608–9700	4490 (7.17)	100–33 900	7560 (4.66)	1650–91 100
Total 16 PAH (USEPA)	29	1920 (2.20)	478–8600	3500 (7.32)	70.8–22 700	5430 (4.81)	1075–61 100
PAH (active; ng m^{-3})							
Naphthalene	21	1810 (1.58)	1010–3680	4580 (8.00)	117–76 900	—	
Benzo(a)pyrene	21	8.67 (3.06)	1.46–51.4	0.432 (2.01)	0.169–1.07	—	
Dibenzo(a.h)anthracene	21	2.03 (2.92)	0.423–11.6	0.0523 (1.57)	0.0396–0.107	—	
Benzo(a)anthracene	21	2.56 (2.23)	1.03–10.1	0.159 (2.41)	0.0369–0.463	—	
Chrysene	1	4.57 (1.90)	2.32–14.4	0.333 (4.76)	0.118–4.06	—	
Benzo(b)fluoranthene	21	10.8 (2.05)	4.48–38.9	0.794 (2.34)	0.252–2.61	—	
Benzo(k)fluoranthene	21	5.31 (2.34)	1.51–16.3	0.411 (2.10)	0.120–1.26	—	
Indeno(1,2,3-c,d)pyrene	21	15.8 (2.66)	3.06–74.4	0.677 (1.77)	0.262–1.46	—	
PAH (passive; ng m^{-3})							
Naphthalene	29	1500 (225)	407–6900	2420 (10.5)	25.8–19 500	4360 (4.66)	863–43 000
Benzo(a)pyrene	29	6.55 (2.97)	1.40–41.7	1.60 (2.86)	0.275–5.42	13.2 (5.05)	0.970–83.1
Dibenzo(a.h)anthracene	29	0.756 (9.03)	0.0369–13.1	0.307 (9.12)	0.0369–6.49	0.827 (16.1)	0.0369–21.3
Benzo(a)anthracene	29	5.70 (3.86)	0.340–46.1	0.819 (2.92)	0.232–5.050	14.7 (4.95)	0.961–159
Chrysene	29	7.92 (4.31)	1.49–92.8	1.84 (1.60)	1.49–6.05	15.2 (8.76)	1.49–270
Benzo(b)fluoranthene	29	4.44 (3.29)	0.423–27.4	0.896 (3.46)	0.170–7.10	14.0 (5.53)	0.554–130
Benzo(k)fluoranthene	29	4.39 (2.94)	1.07–24.3	0.771 (3.63)	0.127–6.05	14.6 (5.47)	0.613–169
Indeno(1,2,3-c,d)pyrene	29	8.33 (2.80)	1.49–40.9	2.18 (3.90)	0.284–25.0	16.4 (5.58)	0.670–126
VOC (passive; µg m^{-3})							
Benzene	31	18.0 (2.14)	5.37–79.0	19.3 (3.39)	1.84–78.3	250 (2.66)	48.9–665
1,3-Butadiene	31	2.69 (2.32)	0.454–9.58	9.68 (3.97)	1.13–100	23.6 (3.78)	3.94–226
Total dust (µg m^{-3})	20	137 (1.82)	47.0–268	176 (1.60)	70.1–314	—	

*Results for one active filter were excluded from the descriptive statistics and group comparisons because of the extremely high PAH concentration (20 000 µg m^{-3}) captured on this filter; the filter worn by a colleague working next to the person wearing the excluded filter collected only 110 µg m^{-3} of PAH.

that for PFIs was 176 µg m^{-3} (no dust exposure measurements were performed for FFEs). The passive measurements indicated that the GMs of the sum 32 PAH exposure for the FFT, PFI, and FFE groups were 2230 ng m^{-3}, 4490 ng m^{-3}, and 7560 ng m^{-3}, respectively.

On a molar basis, >90% of the sum 32 PAHs captured during the sampling campaign were found in the gas phase; <10% was particle associated. Naphthalene was the dominant PAH captured by both active and passive sampling for all groups, accounting for 54 to 67% of the total PAH load based on the analyses of all 32 PAHs in the passive samples. Conversely, benzo(a) pyrene accounted for between 0.2 and 0.3% of the total PAH load for FFTs and FFEs, and <0.1% of the total PAH load for PFIs.

Figure 1 shows the dominant VOCs and PAHs in the collected samples together with the measured concentrations of the sum 16 and sum 32 PAHs. The group with the highest exposure to both PAH and VOC (i.e. benzene and 1,3-butadiene) was FFE, followed by PFIs and then FFT.

Two VOCs were considered in this study: benzene and butadiene. The levels of benzene were twice as high as those of 1,3-butadiene in samples collected from PFIs, 7 times as high in samples collected from the FFT group, and 11 times as high in samples

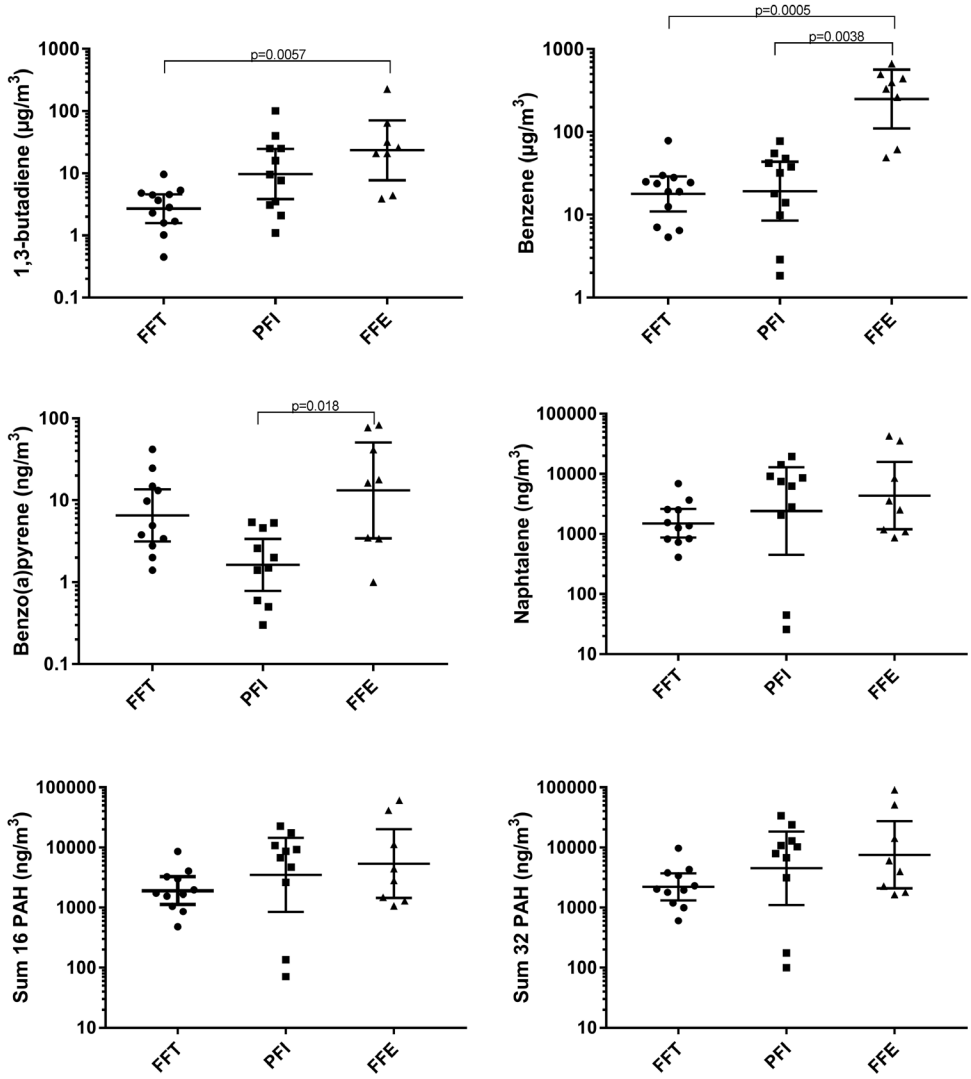

Figure 1. Passive airway exposures (in ng m^{-3}) to 1,3-butadiene, benzene, benzo(a)pyrene, naphthalene, the sum 16 PAHs, and the sum 32 PAHs in team-leading FFTs, PFIs, and team-leading FFEs. Dots represent results for individual samples and bars indicate the geometric mean and 95% confidence interval. Note that the vertical axis uses a logarithmic scale. *P*-values are based on Kruskal–Wallis analysis with Dunn's multiple comparison test using a value of $\alpha = 0.05$.

collected from the FFE group. The benzene exposure of the FFE group was >10 times that for the FFT and PFI groups.

The results obtained by passive monitoring for the three groups showed that FFEs had statistically significantly higher exposures to 1,3-butadiene ($P = 0.006$) and benzene ($P = 0.0005$) than FFTs. FFEs also had higher exposures to benzene than PFIs ($P = 0.0038$). There were no statistically significant differences between the three groups with respect to sum 16 PAH or sum 32 PAH exposure (Fig. 1). However, the FFE group's exposure to the carcinogen benzo(a)pyrene was 10 times that of the PFI group ($P = 0.018$).

Dermal exposure

Supplementary Tables 2 and 3, available at *Annals of Occupational Hygiene* online, present the skin exposures to individual PAHs on the wrist and collarbone (in ng cm^{-2}) for FFs during three work tasks (acting as leaders entering a burning house, acting as fire starters, and acting as team leaders outside the house), for PFIs, and for a control group of office workers. Exposures at

the wrist seemed to be generally higher than those at the collarbone for all exposed occupations, but this rule did not hold for all individual PAHs.

The skin samples showed that exposures to the sum 32 PAHs among working FFs and PFIs ranged from 2 to 16 ng cm^{-2} on the wrist, and 2 to 4.6 ng cm^{-2} in the collarbone area (Supplementary Tables 2 and 3, available at *Annals of Occupational Hygiene* online). The most abundant PAHs on the skin in all groups, on both the wrist and the collarbone, were phenanthrene, fluoranthene, and chrysene. The median measured levels of these compounds were 1–4, 0.2–2, and 0.1–0.5 ng cm^{-2}, respectively. The most abundant individual PAH was acenaphthene, whose median level was 5.2 ng cm^{-2}, but this compound was only detected in skin samples from PFIs.

Figure 2 shows the measured dermal exposures at the wrist for FFs, PFIs, and the control group. Results are shown for three individual PAHs (chrysene, benzo(a) pyrene, and fluoranthene) as well as the sum 32, sum 16, and sum 6 PAH groups. There was significant variation in the levels of individual PAHs. For example, the dermal exposures at the wrist among FFT fire starters were significantly greater than those for the controls in all studied cases. FFT fire starters also had higher dermal exposures to chrysene (P = 0.026) and benzo(a)pyrene (P = 0.042) at the wrist than PFIs. The exposure of FFT fire starters to the sum 32 PAHs was higher than that for the controls (P = 0.056), as was that for the PFIs (P = 0.028).

The dermal exposures of FFs and PFIs in the collarbone area were generally lower than those at the wrist and comparable to the exposures observed for the control group (see Supplementary Table 3, available at *Annals of Occupational Hygiene* online).

Discussion

Airway exposures to PAHs and VOCs were measured for Swedish FFTs and FFEs, and for PFIs working in the aftermath of live fire events. In addition, airway particle exposure and dermal PAH exposure were measured for FFT and PFIs. Both the airways and skin of FFs and PFIs were found to be exposed to PAHs. All the studied work environments were heavily contaminated by PAHs, although the levels were well below

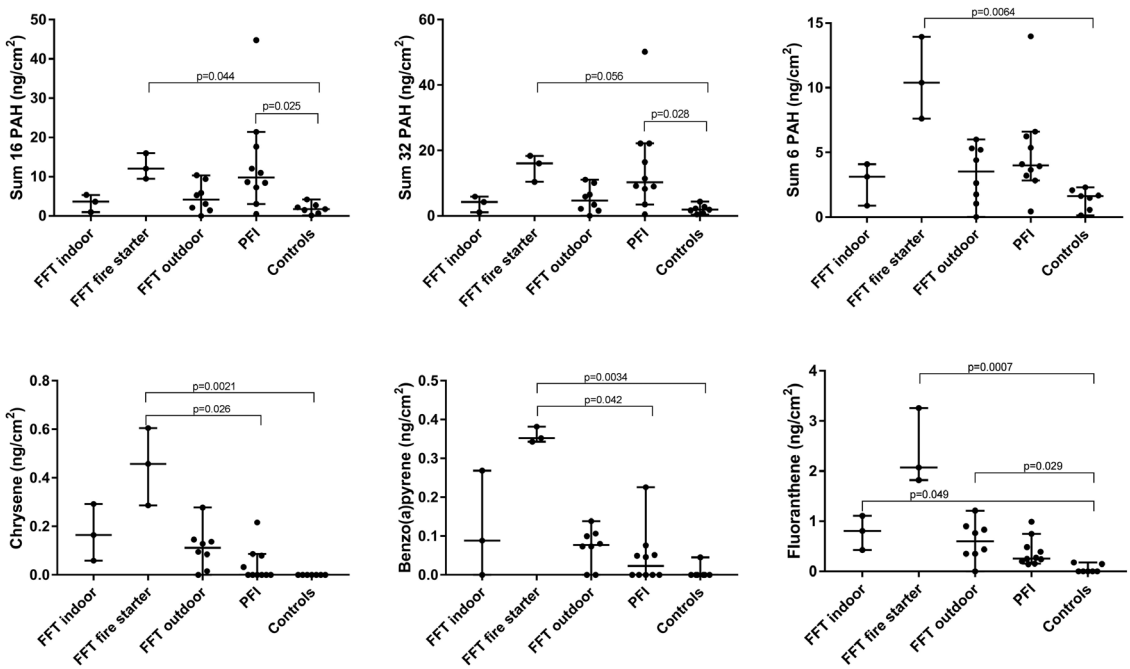

Figure 2. Levels of the most abundant individual PAHs and the sum 32, sum 16, and sum 6 PAHs (ng cm^{-2}) in skin samples collected from the wrists of team-leading FFTs, PFIs, and control persons. The FFTs were divided into three subgroups based on the tasks they were doing on the sampling day (acting as team leaders entering a burning house, acting as fire starters, and acting as team leaders outside the house). Dots represent results for individual samples and bars indicate the geometric mean and 95% confidence interval. *P*-values were derived by Kruskal–Wallis analysis with Dunn's multiple comparison test using a value of $\alpha = 0.05$.

the Swedish occupational exposure limits (OELs). The patterns of airway and dermal exposure differed, with naphthalene being the dominant PAH in air samples whereas acenaphthene and phenanthrene dominated in the dermal samples (although acenaphthene was only detected in samples from PFIs). This may be partly due to the comparatively greater volatility and lower hydrophobicity of naphthalene compared to other PAHs. Benzo(a)pyrene was present in both sample types, but at very low levels on skin. The dermal occupational PAH exposure was generally higher on the wrist than in the collarbone area. However, most PAHs were also detected on the skin of control persons (office workers) at low concentrations, and the exposures observed for FFs and PFIs in the collarbone area were comparable to those observed for the control group, indicating the ubiquitous presence of PAHs in ambient air.

Active sampling with filters and XAD is the recommended method for total dust and PAH evaluations because it can accurately sample both gaseous and particulate fractions. Our results show that the levels of dust exposure for the FFTs and PFIs were well below the Swedish OEL for dust. The sum 32 and sum 16 PAH exposures determined by active air sampling for the PFI group were both 1.8 times higher than the corresponding values for the FTT group. These differences were not statistically significant, but there were statistically significant differences between these groups with respect to naphthalene and benzo(a)pyrene exposure: the PFIs had a higher naphthalene exposure, and the FTTs had a higher benzo(a)pyrene exposure (Supplementary Figure 1, available at *Annals of Occupational Hygiene* online).

In accordance with the active sampling results, passive sampling revealed that the sum 32 and sum 16 PAH exposures of the PFIs were 2.0 and 1.8 times greater, respectively, than the corresponding values for FFTs. Passive sampling can be a valuable complement to active methods, especially in situations such as emergencies where active methods cannot be used. The PUF passive sampler is a particularly promising tool for such sampling campaigns because it reliably accumulates both gaseous- and particle-associated PAHs even after short exposure times of about 1 h (Strandberg et al., 2018). The passive sampling results indicated that the FFE group had even higher sum 32 and sum 16 PAH exposures than the PFI group (1.7 and 1.6 times higher, respectively). It is also notable that the exposure to sum PAHs seemed to differ between emergency events and training scenarios, with exposures during emergencies being 3.4 times higher for sum 32 PAHs and 2.8 times higher for sum 16 PAHs. Further studies will be needed to determine whether these differences are due to differences in the material that is burned, the firefighters' working practices, or the measurement parameters.

Naphthalene was by far the most abundant PAH in air samples, accounting for 50% (FFT) and 70% (PFI) of the concentration of sum 32 PAHs measured by active air sampling and 67% (FFT), 54% (PFI), and 58% (FFE) of those measured by passive air sampling. These results are consistent with a recent publication (Oliveira et al., 2017). Furthermore, active sampling indicating that PFIs were exposed to higher levels of naphthalene and its derivatives in the gaseous phase than FFTs. This unexpected result may reflect the fact that PFIs often work much closer to the sources of PAHs than FFTs. The naphthalene exposures of FFEs were indistinguishable from those for FFTs, which supports the hypothesis that distance to source is a key factor governing naphthalene exposure because the distances between the team leaders and the PAH sources should be similar in both cases. For most of the other studied PAHs, the exposures among FFEs were higher than those among FFT. This may be due to differences in the composition of the combustibles in live and training fires. Alternatively, it may be because emergency responders deploy quickly and reach the fire before optimal combustion occurs.

Passive VOC sampling revealed that benzene exposure was significantly higher among FFEs than for the other groups. This may be because FFEs were sampled during responses to car and house fires, in which the amount and composition of the burning material differ from those in training situations. FFE exposure also occurs during very different phases of fire development than in training exercises or post-fire investigations. Similar results were obtained for 1,3-butadiene: the measured exposures for FFEs were significantly higher than those for FFTs but not significantly higher than those for PFIs. In addition, the highest 1,3-butadiene exposures clearly occurred during car fires (data not shown).

All of the airway exposures observed during this work were well below the relevant Swedish OELs. The highest group geometric mean exposure to naphthalene was 4600 ng m^{-3}, which is <0.01% of the Swedish and European Union OEL. Similarly, the highest group mean exposure for benzo(a)pyrene (13.2 ng m^{-3}) was ~0.7% of the Swedish OEL, and the highest mean exposures to benzene, 1,3-butadiene, and total dust were 250, 24, and 176 µg m^{-3}, respectively (corresponding to 17, 2, and 4% of the respective Swedish OELs). Even the maximum observed concentrations of individual PAHs were well below the relevant OELs; the highest exposure as a proportion of the relevant OEL was 44%, which was

observed for a single participant's exposure to benzene. These results are consistent with the findings reported for the position of command/pump operator for controlled residential fires (Fent et al., 2018).

No OELs for dermal exposure have been defined for PAHs in Sweden. Therefore, it was not possible to say whether the measured exposures should be considered low or high. The recovery from human skin, using the same tape stripping method, has previously been evaluated to 70 and 63% for pyrene and 60 and 54% for benzo(a)pyrene, after 0 and 30 min, respectively (Kammer et al., 2011). Because we could not collect dermal samples from the FFE group, we included a few samples from FFT group members performing tasks similar to those done by the FFE group (namely entering burning houses wearing full turnout gear [FFT indoor] and starting training fires [FFT fire starter]). Although the sample sizes for these two groups were small (n = 3), the results obtained indicate that FFT fire starters had higher dermal exposures to several PAHs. The PFI group also had relatively high dermal exposures. These results suggest that manual handling of items from a fire results in higher dermal PAH levels. Surprisingly, we were unable to quantify naphthalene in any of the dermal samples. This may be because its high volatility and low hydrophobicity compared to other PAHs prevent it from being retained on the skin surface. Alternatively, it could be due to the high limit of quantification and low recovery of this PAH when the tape-stripping method is used (Strandberg et al., 2018b).

Our results cannot be straightforwardly compared to those of earlier exposure studies focusing on FFs. Some earlier studies reported exposure levels greatly exceeding those presented here despite also examining FFTs (Fent et al., 2014; Kirk and Logan, 2015; Fernando et al., 2016; Wingfors et al., 2018). However, those studies were performed in enclosed spaces where the test subjects were wearing full protective breathing apparatus. In keeping with our results relating to dermal sampling from the collarbone area, Wingfors and Nyholm (2018) conclude that FFs' protective clothing is very effective at preventing dermal exposure (Wingfors et al., 2018). Some studies used a combined approach involving both exposure measurements and biomarker monitoring. In a recent study of this type (Keir et al., 2017), naphthalene was the only PAH exhibiting a significant correlation between sum PAH levels measured in personal air samples and urinary metabolite levels. The authors suggested that this could be because naphthalene is the only air-sampled compound included in their study that exists at high enough concentrations to show up as a urinary metabolite. This is consistent with the observation that naphthalene was the dominant PAH in our air samples. Another factor may be that, as a gas, naphthalene is also more likely to penetrate the turnout gear. A recent study with personal air sampling from pump operators/command position matches our team leaders. The slightly higher reported exposure for 15 PAHs may be due to differences in burning material, sampling pack, and shorter sampling time (Fent et al., 2018).

Some studies have also measured both dermal contamination of PAHs and PAH deposition on the protective turnout gear worn by FFs (Baxter et al., 2014; Fent et al., 2014; Kirk and Logan, 2015; Fent et al., 2017; Stec et al., 2018). Care must be taken when comparing their results to our dermal sampling data because of the different sampling methods that were used and differences in their capacity to remove adsorbed compounds from the skin's surface. With this complication borne in mind, our results (sum 6 PAH: 0.1–14 ng cm^{-2}) are on the same order of magnitude as the measurements of Fent et al. (12–50 µg m^{-2} = 1.2–5 ng cm^{-2} for the same PAHs). Our measurements of sum 32 PAH exposure are also in the same range (0.1–50 ng cm^{-2}) as those reported by Fent et al., and our measured dermal exposures of 1.5–750 ng/sample surface are consistent with previous measurements of PAH contamination at the neck (Wingfors et al., 2018) and the neck and face (Baxter et al., 2014), which were in the range of 50–160 ng/sample surface. However, the PAH levels observed by Kirk and Logan (2015) on the protective gear of FFs (70–270 ng cm^{-2}) were higher than the dermal exposures observed in this work. In other studies where air sampling was conducted much closer to the source, 95% of the measured PAHs were reported to be in the particle phase or bound to particles (Fent et al., 2014). Conversely, in this work, personal air sampling was performed on team leaders who work further away from the fire, and >sss90% of the sampled sum 32 PAHs were collected from the gas phase. This could be interpreted as a positive result because most PAHs classified as carcinogenic or possibly carcinogenic exist predominantly in the particle phase.

Our results represent 'snapshots' of the everyday activities of FFs and PFIs during which they are exposed to PAHs. An individual FF or PFI's cumulative PAH exposure over their career will heavily depend on how often that individual participates in high exposure events. This, in turn, will depend on where the individual is based, differing most between densely populated urban areas and less populated rural ones. A study on a cohort of Swedish FFs in Stockholm during 1933–1983 (Tornling et al., 1994b) found that on average, the FFs

attended approximately one emergency fire event per week (Tornling et al., 1994a).

We have previously reported personal air measurements of PAHs and total dust in different types of restaurant kitchens in Sweden (Lewne et al., 2017), showing that PAH exposures were highest in Asian restaurant kitchens. The sum 16 PAH exposure observed in these kitchens was found to be 340 ng m^{-3} based on active sampling over an 8-h shift. In this work, the geometric mean of the sum 16 PAH exposure for FFTs was found to be 2980 ng m^{-3}. The FFs were thus exposed to much higher PAH levels than the cooks in the Asian kitchens during their active exposure time. However, if the actual exposure time of FFE fire events was only around 6 h per week, the two groups would have roughly equal overall weekly PAH exposures. The total dust exposure was higher for the cooks, but it is likely that there are marked differences in the chemical composition of the dust and particles that these two groups are exposed to (Lewne et al., 2017).

Studies reporting personal exposure measurements from live fire events (i.e. not training situations) are rare in the scientific literature, making it difficult to compare our results to other studies. Even more rare are studies in which investigators were on site to manage sampling equipment as the FFs worked, and to collect follow-up samples with little to no delay. To the authors' knowledge, this is the first exposure study to gather data on both airway and dermal exposure among PFIs, although there have been studies on FFs in similar situations, that is during investigations after overhauls (Fent et al., 2013).

We chose to measure exposures among FF team leaders, who do not use respiratory protection for practical reasons (primarily, to facilitate communication with surrounding personnel). The exposure measurements, therefore, reflect the FFs' actual exposure while working, unlike other studies that examined FFs wearing full respiratory protective equipment.

As noted earlier, we are only aware of one other publication reporting personal air sampling exposure measurements in situations involving subjects not wearing respiratory protection. However, our study was subject to some practical constraints, such as the short and variable time available for measurement, and the impossibility of performing active air sampling or dermal sampling during live emergency firefighting situations. We believe that the similarity of the results obtained by active and passive sampling at least partially compensates for these limitations and shows that passive methods can be used in situations where active sampling is not feasible.

Conclusion

The results presented here show that the airways of PFIs and FF team leaders working in training and emergency situations that prevent the consistent use of full protective equipment are exposed to diverse PAHs, VOCs, and particles. Under the conditions prevailing during our measurements, the levels of these particles and compounds were substantially higher than their urban background levels. However, the exposures measured in this work were well below established Swedish OELs. In addition, the measured dermal PAH exposures of the FFs participating in this study were consistent with those reported previously, indicating that further preventive actions to protect the skin may be warranted. Although the airway and dermal exposures observed in this work were low compared to the relevant OELs, this does not mean that the corresponding exposures are harmless. Moreover, if conditions change, exposure could increase substantially. It should also be noted that our results represent only 'snapshots' of the daily activities of FFs and PFIs and that further studies will be needed to provide a comprehensive assessment of the exposure risks among these groups.

All of the study participants read and signed informed consent forms approved by the ethical review board at Karolinska Institutet, Stockholm, Sweden.

Supplementary Data

Supplementary data are available at *Annals of Work Exposures and Health* online.

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Conflicts of interest

The authors have no conflicts of interest to declare.

References

ATSDR. (2005) Toxicology profile for polyaromatic hydrocarbons. In *Book toxicology profile for polyaromatic hydrocarbons*. Boca Raton City, FL: CRC Press.

Austin CC, Wang D, Ecobichon DJ *et al*. (2001) Characterization of volatile organic compounds in smoke at municipal structural fires. *J Toxicol Environ Health A*; **63**: 437–58.

Baxter CS, Hoffman JD, Knipp MJ *et al*. (2014) Exposure of firefighters to particulates and polycyclic aromatic hydrocarbons. *J Occup Environ Hyg*; **11**: D85–91.

Blomqvist P, Simonson-McNamee M, Andersson P *et al*. (2012) Polycyclic Aromatic Hydrocarbons (PAHs) quantified in large-scale fire experiments. *Fire Technology*; **48**: 513–28.

Brook RD, Rajagopalan S, Pope CA III *et al*.; American Heart Association Council on Epidemiology and Prevention, Council on the Kidney in Cardiovascular Disease, and Council on Nutrition, Physical Activity and Metabolism. (2010) Particulate matter air pollution and cardiovascular disease: an update to the scientific statement from the American Heart Association. *Circulation*; **121**: 2331–78.

Daniels RD, Kubale TL, Yiin JH *et al*. (2014) Mortality and cancer incidence in a pooled cohort of US firefighters from San Francisco, Chicago and Philadelphia (1950–2009). *Occup Environ Med*; **71**: 388–97.

Fent KW, Alexander B, Roberts J *et al*. (2017) Contamination of firefighter personal protective equipment and skin and the effectiveness of decontamination procedures. *J Occup Environ Hyg*; **14**: 801–14.

Fent KW, Eisenberg J, Evans D. (2013) *Evaluation of dermal exposure to polycyclic aromatic hydrocarbons in fire fighters. Book evaluation of dermal exposure to polycyclic aromatic hydrocarbons in fire fighters*. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.

Fent KW, Eisenberg J, Snawder J *et al*. (2014) Systemic exposure to PAHs and benzene in firefighters suppressing controlled structure fires. *Ann Occup Hyg*; **58**: 830–45.

Fent KW, Evans DE. (2011) Assessing the risk to firefighters from chemical vapors and gases during vehicle fire suppression. *J Environ Monit*; **13**: 536–43.

Fent KW, Evans DE, Babik K *et al*. (2018) Airborne contaminants during controlled residential fires. *J Occup Environ Hyg*; **15**: 399–412.

Fernando S, Shaw L, Shaw D *et al*. (2016) Evaluation of firefighter exposure to wood smoke during training exercises at burn houses. *Environ Sci Technol*; **50**: 1536–43.

Glass DC, Pircher S, Del Monaco A *et al*. (2016) Mortality and cancer incidence in a cohort of male paid Australian firefighters. *Occup Environ Med*; **73**: 761–71.

IARC. (2008) 1,3-butadiene, ethylene oxide and vinyl halides (vinyl fluoride, vinyl chloride and vinyl bromide). *IARC Monogr Eval Carcinog Risks Hum*; **97**: 3–471.

IARC. (2010a) Painting, firefighting, and shiftwork. *IARC Work Group Eval Carcinog Risks Hum*; **98**: 9–764.

IARC. (2010b) Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. *IARC Monogr Eval Carcinog Risks Hum*; **92**: 1–853.

IARC. (2012) Chemical agents and related occupations. A review of human carcinogens. *IARC Monogr Eval Carcinog Risks Hum*; **100**: 9–567.

Jørgensen RB, Strandberg B, Sjaastad AK *et al*. (2013) Simulated restaurant cook exposure to emissions of PAHs, mutagenic aldehydes, and particles from frying Bacon. *J Occup Environ Hyg*; **10**: 122–31.

Kammer R, Tinnerberg H, Eriksson K. (2011) Evaluation of a tape-stripping technique for measuring dermal exposure to pyrene and benzo(a)pyrene. *J Environ Monit*; **13**: 2165–71.

Keir JLA, Akhtar US, Matschke DMJ *et al*. (2017) Elevated exposures to polycyclic aromatic hydrocarbons and other organic mutagens in Ottawa firefighters participating in emergency, on-shift fire suppression. *Environ Sci Technol*; **51**: 12745–55.

Kirk KM, Logan MB. (2015) Firefighting instructors' exposures to polycyclic aromatic hydrocarbons during live fire training scenarios. *J Occup Environ Hyg*; **12**: 227–34.

LeMasters GK, Genaidy AM, Succop P *et al*. (2006) Cancer risk among firefighters: a review and meta-analysis of 32 studies. *J Occup Environ Med*; **48**: 1189–202.

Lewne M, Johannesson S, Strandberg B *et al*. (2017) Exposure to particles, polycyclic aromatic hydrocarbons, and nitrogen dioxide in Swedish restaurant kitchen workers. *Ann Work Expo Health*; **61**: 152–63.

Oliveira M, Slezakova K, Alves MJ *et al*. (2017) Polycyclic aromatic hydrocarbons at fire stations: firefighters' exposure monitoring and biomonitoring, and assessment of the contribution to total internal dose. *J Hazard Mater*; **323**: 184–94.

Pope CA III, Bhatnagar A, McCracken JP *et al*. (2016) Exposure to fine particulate air pollution is associated with endothelial injury and systemic inflammation. *Circ Res*; **119**: 1204–14.

Pukkala E, Martinsen JI, Weiderpass E *et al*. (2014) Cancer incidence among firefighters: 45 years of follow-up in five Nordic countries. *Occup Environ Med*; **71**: 398–404.

Stec AA, Dickens KE, Salden M *et al*. (2018) Occupational exposure to polycyclic aromatic hydrocarbons and elevated cancer incidence in firefighters. *Sci Rep*; **8**: 2476.

Strandberg B, Bergemalm-Rynell K, Sallsten G. (2014) Evaluation of three types of passive samplers for measuring 1,3-butadiene and benzene at workplaces. *Environ Sci Process Impacts*; **16**: 1008–14.

Strandberg B, Julander A, Sjöström M *et al*. (2018a) An improved method for determining dermal exposure to polycyclic aromatic hydrocarbons. *Chemosphere*; **198**: 274–80.

Strandberg B, Julander A, Sjöström M *et al*. (2018b) Evaluation of polyurethane foam passive air sampler (PUF) as a tool for occupational PAH measurements. *Chemosphere*; **190**: 35–42.

Tornling G, Gustavsson A, Gustavsson P *et al*. (1994a). *Dödsorsaker bland brandmän i Stockholm/causes of death among firefighters in Stockholm*. AMF Rapporter. (in Swedish) Karolinska Institutet, Institutionen för Thoraxmedicin, Stockholm, Sweden.

Tornling G, Gustavsson P, Hogstedt C. (1994b) Mortality and cancer incidence in Stockholm fire fighters. *Am J Ind Med*; **25**: 219–28.

USEPA. (2005) Guidelines for Carcinogen Risk Assessment. EPA/630/P-03/001F Available from: http://www.epa.gov/raf/publications/pdfs/CANCER GUIDELINES FINAL 3-25-05.pdf. U.S Environmental Protection Agency.

WHO/UNEP. (2012) State of the science of endocrine disrupting chemicals—2012. An assessment of the state of the science of endocrine disruptors prepared by a group of experts for the United Nations Environment Programme (UNEP) and WHO. In Bergman Å, Heindel J, Jobling S, Kidd K, Zoeller T, editors. ISBN: 978-92-807-3274-0 (UNEP) and 978 92 4 150503 1 (WHO).

Wingfors H, Nyholm JR, Magnusson R *et al*. (2018) Impact of fire suit ensembles on firefighter PAH exposures as assessed by skin deposition and urinary biomarkers. *Ann Work Expo Health*; **62**: 221–31.