Annals of Work Exposures and Health, 2018, Vol. 62, No. 2, 221–231
doi: 10.1093/annweh/wxx097
Advance Access publication 10 December 2017
Original Article

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Original Article

Impact of Fire Suit Ensembles on Firefighter PAH Exposures as Assessed by Skin Deposition and Urinary Biomarkers

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Submitted 3 September 2017; revised 27 October 2017; editorial decision 30 October, 2017; revised version accepted 10 November 2017.

Abstract

Over the past 10 years, a number of safety measures for reducing firefighters' exposure to combustion particles have been introduced in Sweden. The most important measure was the reduction in the time firefighters wear suits and handle contaminated equipment after turn-outs involving smoke diving. This study was divided into two parts, those being to investigate the level of protection obtained by multiple garment layers and to assess exposure during a standardized smoke diving exercise. First, realistic work protection factors (WPFs) were calculated by comparing air concentrations of the full suite of gaseous and particle-bound polycyclic aromatic hydrocarbons (PAHs) inside and outside structural ensembles, including jacket and thick base layer, during a tough fire extinguishing exercise using wood as the fuel. Second, during a standardized smoke diving exercise, exposure was assessed by measuring PAH skin deposition and levels of eight urinary PAH metabolites in 20 volunteer student firefighters before and after the exercise. The average WPF for the sum of 22 PAHs was 146 ± 33 suggesting a relatively high protective capacity but also indicating a substantial enrichment of contaminants with a risk of prolonged dermal exposure. Accordingly, in the second exercise, the median levels of skin-deposited Σ14-PAHs and urinary 1-hydroxypyrene significantly increased 5-fold (21 to 99 ng/wipe) and 8-fold (0.14 to 1.1 µmol mol–1 creatinine), respectively, post exposure. Among the PAH metabolites investigated, 1-hydroxypyrene proved to be the most useful indicator of exposure, with significantly elevated urinary levels at both 6 h and 20 h after the exercise and with the strongest correlation to dermal exposure. Metabolites from two-ring and three-ring PAHs were eliminated faster while levels of 3-hydroxy-benzo[a]pyrene did not meet the detection criteria. The results from correlation studies indicated that dermal uptake was a major route of exposure in accordance with previous findings. To summarize, this study shows that some of the newly adopted protective measures were correctly implemented, and should continue to be followed and be more widely adopted.

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Keywords: biomonitoring; firefighter; GC-MS/MS; monohydroxylated PAHs; protection factor; skin wipe; urinary metabolites

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Introduction

Some 10 years ago, on a work-force initiative, firefighters in Sweden started to introduce a number of safety measures aimed at reducing exposure to combustion particles in their occupational environment (Magnusson and Hultman, 2014). A majority of the routines were focused on reducing secondary exposure by avoiding handling of used equipment and minimizing the time firefighters wore contaminated suits and base layers after fire operations. These routines were implemented by, for example, keeping used materials in separate compartments in the truck as well as changing into clean clothes before returning to the fire station. At present, newly built fire stations are designed containing zones divided according to their suspected degree of contamination, all to reduce secondary exposure while preparing for future assignments or turn-outs. Encouragingly, a majority of firefighters in Sweden adopted the routines in full, driven by an awareness that such actions reduce their risk of developing cancer. Gas and particles containing carcinogenic compounds, such as several polycyclic aromatic hydrocarbons (PAHs), have been recognized as an adverse risk for a number of occupations including asphalt workers, aluminium workers, chimney sweepers, and coal power plant workers (Boffetta *et al.*, 1997). Several of these PAHs, of which a majority are associated with airborne particles, have been assigned a toxic equivalency factor (TEF, Delistraty, 1997) or been classified by the International Agency for Research on Cancer (IARC) as either carcinogenic (Group 1), possibly carcinogenic (2A) or probably carcinogenic (2B) to humans. Quite recently, IARC also specifically evaluated firefighters' occupational exposure to be on the level "possibly carcinogenic to humans" (Group 2B) (IARC, 2010). These evaluations are not trivial since exposure dimensions are particularly difficult to assess for a workgroup involved in multiple work tasks, often part-time (e.g. volunteer firefighters), and intermittently exposed to high levels of an extremely complex composition of gases and particles produced from combustion. Note that PAHs are not the only candidates in smoke from fires that can potentially cause cancer (IARC, 2010; Tsai *et al.*, 2015). In addition, exposure may occur through both skin and lungs (Fent *et al.*, 2014) and at various phases and microenvironments during a turn-out (Baxter *et al.*, 2014), making exposure assessment a challenging task. Although being an indirect indicator of all PAHs (Jongeneelen, 2001), biomonitoring of levels of the metabolite 1-hydroxypyrene in urine has commonly been the preferred choice when assessing multi-route PAH exposure for the above-mentioned groups. For several reasons, conclusive proof of its suitability for assessing firemen's exposure has so far not been demonstrated (Caux *et al.*, 2002; Robinson *et al.*, 2008; Laitinen *et al.*, 2010; Fernando *et al.*, 2016; Oliveira *et al.*, 2016). Possibly, the optimal metabolite to represent the levels of particle-associated carcinogenic PAHs, or those being assigned TEF-values, is 3-hydroxybenzo[a]pyrene, but its levels in urine are generally very low, since the largest proportion is excreted in faeces. Alternative methods and suggestions for measuring firefighters' exposure may include monitoring of the lighter two-ring and three-ring mono-hydroxylated PAHs (Oliveira *et al.*, 2016) and methoxyphenols in urine (Fernando *et al.*, 2016), analysing skin wipes (Fent *et al.*, 2014) or by the use of biomarkers in breath samples (Pleil *et al.*, 2014). The newly adopted safety measures also involved protecting airways from inhalation exposure at all times—parking vehicles upwind and by methodical use of respirators (i.e. self-contained breathing apparatus [SCBA] or full-face filter masks) whenever smoke can be smelled. If exposure due to inhalation can be kept low, dermal uptake after passage through the fire ensemble and the base layer remains the vulnerable area that needs further investigation.

The objectives of this study were to investigate work protection factors (WPFs) for PAHs in realistic conditions with the combination of a fire jacket and base layer during an active smoke diving exercise (exercise 1), and to assess exposure by measuring skin deposition of PAHs and levels of PAH metabolites in urine during a standardized smoke diving exercise (exercise 2). The latter exercise is part of the examination at the two colleges of the Swedish Civil Contingencies Agency for prospective firefighters in Sweden, with a similar version being used as a regular yearly follow-up exercise for firefighters on active service.

Material and Methods

At the Swedish Civil Contingencies Agency colleges at Sandö and Revinge, student firefighters are trained with various exercise scenarios. During two types of exercises, measurements were made at the Sandö location.

Exercise 1: Determination of WPFs

During exercise 1, PAHs were simultaneously sampled inside and outside the protective garment layers of a firefighter instructor supervising the exercise, in order to determine WPFs. The layers consisted of a fire suit ensemble (Viking, Esbjerg, Denmark) and a thick base layer made of cotton and polyester (65:35, thickness 300 g m^{-2}).

During three successive trials on the same day, a fire was ignited in a smoke container (standard container, 12 m) using lighter fluid (hydrocarbons C_{10}–C_{13}), wood wool and untreated chipboard wood, to create a high temperature and heavy smoke. This relatively demanding exercise is to practise the use of water sprays to extinguish flames and prevent thick smoke, meaning that the instructor guides students back and forth in the container for ~30 min. Duplicate air sample pumps (Air check 2000 SKC inc., PA, USA) were mounted inside the instructor's jacket and connected to sampling heads containing a precleaned (400°C, 4 h) glass fibre filter (GFF) and two polyurethane foam plugs (PUFs). The two sampling heads were assembled on the inside of the base layer at chest height. Two temperature loggers (ACR Smartbutton, British Columbia, Canada) were mounted inside the jacket. Stationary sampling inside the container was achieved by mounting a metal T-pipe 70 cm inside the door of the container, allowing the container atmosphere to be sampled at heights of 0.5 m and 1.15 m. The hot and wet fire gases were diluted 10 times with air (Dekati Diluter DI-1000, Finland) to temperatures below 20°C before two pumps (Leland Legacy, SKC inc., PA, USA) set at 5 l min^{-1} drew the diluted fire gases through the described sample heads consisting of a GFF and PUFs. Personal pumps were set at 2.5 l min^{-1} and all flows were checked with a primary calibrator (DC-Lite, Bios, NJ, USA). The actual time the instructor spent in the container varied from 17 to 20 min during each of the three exercises. Stationary measurements were consequently matched, resulting in three duplicate paired samples. WPFs were calculated by dividing the outside concentration with the inside concentration for matched samples.

Exercise 2: Monitoring skin deposition and urine metabolites

In this qualifying exercise, instructors separately evaluated four groups (units) of students (2–3 May 2016, Monday and Tuesday) and the exercise, in principle, covered all the steps of an emergency response turn-out. Each unit consisted of six or seven students, divided into a first response group (two students) and a main group (four or five students) arriving some 5 min later, to a simulated basement. Inside the basement (a simulator for an apartment block made out of concrete and metal), fires had been lit with the aid of lighter fluid, wood wool, and chipboard wood. The whole exercise took about 3 h and the assigned tasks that involved contact with smoke i.e. fire extinguishing, evacuating dummies, initial lifesaving treatments and using roof chainsaws, lasted <1 h. Depending on the role or task during the operation, the time spent in smoke-filled compartments varied substantially for individuals (~5–30 min) using one or two air packs. Vehicles and the location for carrying out first aid medical assistance were upwind. We assume that these measures, combined with mandatory functional control and correct use of full-face positive pressure respirators, minimize exposure through inhalation.

Skin wipe samples, from individuals participating in the exercise, were collected by stroking a GFF (47 mm) which had been wetted with 500 µl of acetone, across a 30 cm^2 surface of the neck both before the exercise (pre-exposure) and after the exercise immediately after returning to the garage (post-exposure).

Three 20 ml urine samples were provided from each subject. The first was taken prior to exercise, the second and the third samples were taken at 6 h and 20 h after completion of the exercise. Urine samples were stored in a refrigerator (+8°C) and the filters kept in a freezer (–18°C) until analysis.

Study subjects

Twenty students (19–29 years old) gave their informed consent to participate in this project, approved by the regional ethics board in Umeå, Sweden (No. 2016/91-31). No smokers were included among the 20 volunteers and no test subject had a beard at the time of the exercise. They were asked to avoid other fire exercises and smoked or grilled foods over the previous weekend. These measures were taken to minimize background exposure of PAH. The students who used creatine as a dietary supplement were asked to discontinue the intake for at least 3 days prior to the examination.

Chemicals

Twenty-two (22) PAHs (including the US EPA's 16 priority PAHs) were analysed in the present study: naphthalene (NAP), 2-methylnaphtalene, 1-methylnaphtalene, biphenyl, 2,6-dimethylnaphtalene, acenaphtylene, acenaphtene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene, 1-methylphenanthrene, fluoranthene, pyrene (PYR), benz[a]anthracene, chrysene (CHR), Benzo[b+k] fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene (BaP), perylene (PER), Indeno[1,2,3-cd]pyrene, Dibenz[a,h] anthracene, and Benzo[ghi]perylene. The native PAHs,

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SRM 1491 and labelled internal standards (NAP-d_8, ACE-d_{10}, PHE-d_{10}, CHR-d_{12}, PER-d_{12}) were bought from Larodan (Malmö, Sweden) and Chiron AS (Trondheim, Norway), respectively.

Creatinine and the hydroxy-PAHs 1-hydroxynaphtalene (1-OH-NAP), 2-hydroxynaphtalene (2-OH-NAP), 1-hydroxyacenaphtene (1-OH-ACE), 9-hydroxyfluorene (9-OH-FLU), 2-hydroxyfluorene (2-OH-FLU), 9-hydroxyphenanthrene (9-OH-PHE), and 1-hydroxypyrene (1-OH-PYR) were bought from Sigma-Aldrich (Steinheim, Germany). 3-Hydroxybenzo[a]pyrene (3-OH-BaP) was bought from Toronto Research Chemicals and labelled $^{13}C_6$ 1-OH-PYR was obtained from Cambridge Isotope Laboratories.

ß-glucuronidase (type H-2 from Helix pomatia; activity 10^5 U ml^{-1}), sodium acetate, sodium sulphate, and N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1 % of trimethylchlorosilane (TMCS) were bought from Sigma-Aldrich.

Chemical analysis

GFFs and PUFs from exercise 1 were analysed for 22 PAHs (Table 1) in accordance with Wingfors *et al.* (2011). Skin wipe samples were analysed for 14 PAHs (three-ring to six-ring).

GFFs, PUFs, and skin wipe samples were individually extracted twice with dichloromethane (5 ml × 2) by ultrasonic treatment, after addition of internal standards (100 ng, NAP-d_8, ACE-d_{10}, PHE-d_{10}, CHR-d_{12}, PER-d_{12}). The volume of the combined extracts was reduced under a gentle stream of nitrogen and the solvent was changed to hexane. The extracts were cleaned on silica columns (0.6 g silica gel 60, Merck, 10% deactivated w/w with water) packed in Pasteur pipettes. After application of

Table 1. PAH air concentrations based on duplicate measurements outside and inside fire suit during exercise 1 during three similar trials and average work protection factors (WPF).

PAH (IARC group)	Outside C (µg m^{-3})			Inside C (µg m^{-3})			WPFs
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Mean
	n = 2	*n* = 2	*n* = 2	*n* = 2	*n* = 1[a]	*n* = 2	*n* = 3
	170°C	>180°C	140°C	38°C	42°C	35°C	
Naphthalene[2B]	13 000	5600	5900	190	200	120	49 ± 22
2-Methylnaphtalene	2100	1000	1000	16	20	14	84 ± 41
1-Methylnaphtalene	2300	1200	1100	16	20	14	95 ± 44
Biphenyl	1300	760	650	5.8	7.9	5.3	150 ± 66
2,6-Dimethylnaphtalene	93	72	23	4.1	3.7	3.2	16 ± 8
Acenaphtylene	6650	7300	3500	5.1	8.2	5.6	940 ± 330
Acenaphtene	670	620	350	0.66	0.81	0.35	920 ± 140
Fluorene	2400	2200	1100	1.3	0.62	1.0	2200 ± 1200
Phenanthrene	3100	3100	1400	2.2	3.5	1.4	1100 ± 270
Anthracene	1500	1400	600	0.63	0.91	0.35	1800 ± 460
1-Methylphenanthrene	210	150	90	0.21	0.28	0.11	760 ± 220
Fluoranthene	2100	2000	750	3.1	2.6	1.0	730 ± 59
Pyrene	2200	2000	760	3.8	3.1	1.4	590 ± 44
Benz[a]anthracene[2B]	360	360	150	2.2	1.8	0.85	180 ± 17
Chrysene[2B]	570	570	200	4.1	2.8	1.3	170 ± 32
Benzo[b + k]fluoranthene	550	560	320	9.0	6.5	2.7	89 ± 29
Benzo[e]pyrene[2B]	230	210	100	2.2	1.8	0.78	120 ± 11
Benzo[a]pyrene[1]	860	730	320	8.0	5.4	2.5	120 ± 14
Perylene	120	100	40	0.89	0.63	0.24	150 ± 17
Indeno[1,2,3-cd]pyrene[2B]	300	300	160	4.2	2.9	1.2	100 ± 30
Dibenz[a,h]anthracene[2A]	23	24	15	0.09	0.08	0.04	310 ± 56
Benzo[ghi]perylene	260	220	100	4.0	2.3	1.0	84 ± 18
Σ22PAH	41 000	30 000	19 000	220	240	150	146 ± 33

[a]One sampler malfunctioned.

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the sample, a fraction containing mainly alkanes was eluted from the silica column with 1.2 ml hexane (discarded), before PAHs were eluted with 5 ml dichloromethane. The extracts were concentrated, and the solvent was changed to toluene prior to GC-MS analysis. The gas chromatography mass spectrometry (GC-MS; Agilent 7890 GC, Agilent 5975C, USA) conditions were as follows: splitless injection at 250°C, GC held at 80°C for 1 min then ramped to 140°C at 20°C min^{-1}, then ramped to 300°C at 8°C min^{-1} and held for 10 min; helium was used as the carrier gas on a DB-5 MS (30 m length, 0.25 mm i.d., 0.25 µm film thickness, Agilent J&W Scientific, USA). The mass spectrometer was operated in electron ionization (EI) mode and a selected ion monitoring (SIM) program was used for the measurement of two identification ions (m/z) and one quantification ion of each analyte. A three-point calibration and quantification standard (1.8, 18 and 180 ng, $R^2 = 0.999$) was prepared in toluene from the PAH standard mixture SRM 1491 (NIST, MD, USA).

Urine samples were analysed for eight mono hydroxy-PAHs: 1-OH-NAP, 2-OH-NAP, 1-OH-ACE, 9-OH-FLU, 2-OH-FLU, 9-OH-PHE, 1-OH-PYR, and 3-OH-BaP. The analytical methods were based on publications by Campo *et al.* (2008) and Fernando *et al.* (2016). In brief, urine samples (5 ml) were transferred to a 15 ml centrifuge tube. Internal standard ($^{13}C_6$-1-hydroxypyrene, 2 ng), 2 ml acetate buffer (0.5 M, pH 5), and 20 µl ß-glucuronidase (type H-2 from Helix pomatia; activity 10^5 U ml^{-1}) were added. The samples were incubated at 37°C overnight to allow enzymatic deconjugation of hydroxyl-PAH conjugates with glucuronic acid. After incubation, the samples were extracted with hexane (5 ml × 2) after addition of sodium sulphate (1 g). Centrifugation (3000 rpm for 10 min) was used to facilitate the separation of phases. The combined organic extracts were evaporated until dry under a gentle stream of nitrogen. The residue were dissolved in 50 µl of acetonitrile and derivatized with 50 µl BSTFA (1% TMCS) in 60°C for 30 min.

Urine samples were analysed for hydroxy-PAHs with GC coupled to tandem mass spectrometry (Thermo Scientific TSQ 8000 Evo) with EI in selected reaction monitoring (SRM) mode. The transitions are shown in Table S1 (see the Online Supplementary Material, available at *Annals of Work Exposures and Health* online). The GC conditions were as follows: splitless injection at 260°C, GC held at 60°C for 1 min then ramped to 315°C at 10°C min^{-1}, and held for 4 min; helium was used as the carrier gas on a DB-5MS (30 m length, 0.25 mm i.d., 0.25 µm film thickness, Agilent J&W Scientific).

Creatinine levels in urine were determined after dilution (1000 times in purified water) and analysis with liquid chromatography coupled to tandem mass spectrometry (Waters Acquity-Xevo TQ). The analysis results for hydroxy-PAHs were normalized to creatinine concentration.

QA/QC

To ensure that contamination from the glassware, solvents or instruments did not significantly affect the results, field and laboratory blanks (non-exposed filters and purified water) were processed in parallel with the samples. A compound was considered to have been detected if the peak had a signal-to-noise ratio above 3:1, relative retention time ± 2 s compared to standard calibration solution and isotope ratio for the two most abundant ions within 20%. Correction for losses was based on the recovery of the corresponding internal standard.

Statistical analysis

The non-parametric Wilcoxon signed–rank test was carried out to test whether pre-exposure and post-exposure levels were unchanged (H_0). For the 5% level and 1% level, the critical values were 52 and 37, respectively (n = 20). Levels below the limit of detection were substituted with half the limit of detection (LOD) in statistical analysis and extreme data points were set at ±1.5 times the interquartile range but retained for statistical analysis unless otherwise described. Pearson and Spearman rank correlations were carried out to find the relationships between exposure data measured by skin wipe samples and levels of urinary exposure markers.

Results

Exercise 1: Work protection factors

During the three trials in exercise 1, the total PAH concentrations (sum of 22 PAHs) in the container ranged between 20 and 40 mg m^{-3} as shown in Table 1. The more volatile species, such as NAPs, acenapthalenes, FLU, and PHE comprised the majority of the compounds. It should be noted that the levels of benzo[a]pyrene, which has been assigned an occupational exposure limit of 2 µg m^{-3} in Sweden (8 h), showed values in the range 300–900 µg m^{-3}, illustrating that there were high levels in the container.

The total PAH concentrations inside the base layer of the instructor's jacket ranged between 150 and 240 µg m^{-3} i.e. the total concentrations were ~150 times lower inside the protective clothing. NAP was the principal compound, whereas the four-ring, five-ring, and six-ring PAHs had relatively similar levels compared to the three-ring PAHs. Average WPFs were calculated for

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each compound and the overall mean and median were 492 and 158, respectively. For the sum of 22 PAHs, the average WPF was 146 ± 33 indicating a relatively low within subject/trial variability. A somewhat unexpected pattern was found where the most volatile and the least volatile compounds had WPFs of roughly 100 and those with medium volatility, especially FLU, PHE and anthracene, had WPFs above 1000.

Temperatures at the working height (0.5 and 1.15 m) for the instructor varied between 140°C and 180°C during the three trials; temperatures inside the jacket ranged from 35°C to 42°C (Table 1).

Exercise 2: Skin deposition

PAHs with a vapour pressure of 1.6×10^{-2} Pa or lower (Arnoldsson *et al.*, 2015), thus associated with airborne particles between 20 and 100%, were investigated on the skin wipe samples. These comprised 14 PAHs, from PHE with three rings to benzo[g,h,i]perylene with six rings.

Pre-exposure skin wipe samples taken from 20 subjects showed, in general, low levels of deposited PAHs. The sum of 14 PAHs was used for box and whisker plots of pre-exposure and post-exposure levels for the 20 subjects, as seen in Fig. 1. All subjects demonstrated higher levels post-exposure compared to pre-exposure and the median value significantly increased from 21 to 99 ng/wipe (Wilcoxon Rank–sum test, $P = 0.01$). This is almost a 5-fold increase but between-individual variability was large (individual increase ranged from 1.2 to 13).

PYR was one of the predominant PAHs and the levels significantly increased from the pre-exposure median level of 4 ng/wipe to 21 ng/wipe (Fig. 1). For the heavier five-ring and six-ring PAHs, for which many have been assigned a TEF-value, the levels were low or below the limit of detection in pre-exposure samples. For instance, the BaP levels were below the limit of detection (≤0.1 ng/wipe) in 15 of the 20 pre-exposure samples whereas post-exposure BaP-levels were quantifiable in 18 of the 20 samples, at a median level of 2.8 ng/wipe. The median PAH-profile on skin wipe samples for 20 subjects collected pre-exercise and post-exercise is shown in Fig. 2.

Exercise 2: Levels of urinary hydroxy-PAHs

All subjects ($n = 20$) showed detectable levels of all metabolites, except for 3-OH-BaP, in samples taken at pre-exposure and post-exposure at 6 h and 20 h. The negative results for 3-OH-BaP were expected as the detection limit (0.18 µmol mol^{-1} creatinine) was orders of magnitude higher than concentrations reported by Barbeau *et al.* (2011) in non-smokers (0.01 nmol mol^{-1} creatinine). Average creatinine levels, used for normalization of hydroxy-PAH concentrations, ranged from 0.13 to 1.6 g l^{-1} (average 0.73 ± 0.35 g l^{-1}) which were within limits for healthy individuals. Average pre-exposure levels of 1-OH-PYR (0.21 ± 0.18 µmol mol^{-1} creatinine) corresponded to non-exposed non-smoking individuals (Bouchard and Viau, 1999).

Of all the analysed urine samples, the highest levels were observed for 1-OH-NAP and 2-OH-NAP at the 6-h sampling time (Fig. 3). It should be noted that the estimated WPF for NAP was relatively low (Table 1) and NAP also showed highest air concentrations inside and outside structural ensembles in exercise 1. One subject showed specifically high levels of 1-OH-NAP (~1000 times higher than average) but normal levels of other metabolites. This deviating value was treated as an

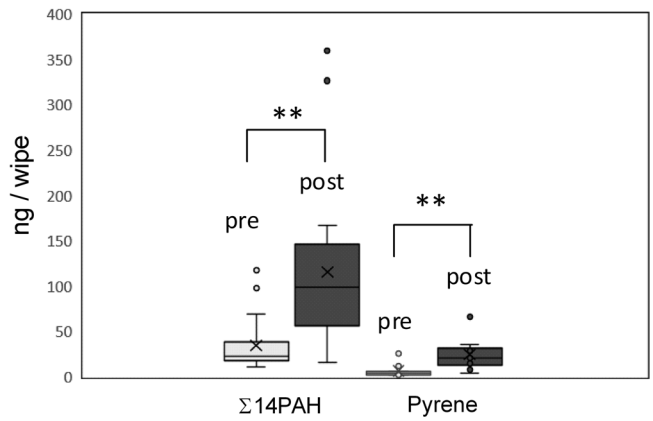

Figure 1. Box and whisker plots of PAH amounts (Σ14 PAHs and Pyrene) in skin wipe samples taken pre-exercise and post-exercise for the 20 subjects. Extreme data points are marked with dots (°) (Q1, Q3 ± 1.5 × IQR) and $^{**}P < 0.01$ (Wilcoxon rank–sum test). Abbreviation: IQR = interquartile range.

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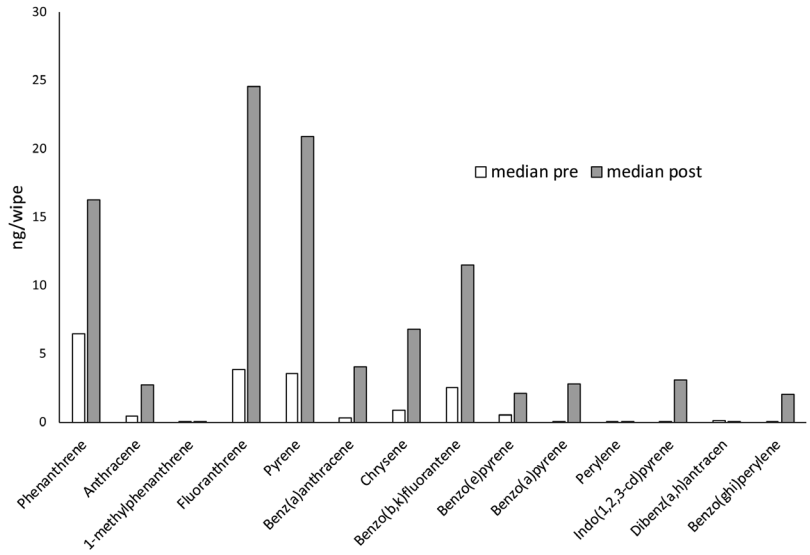

Figure 2. The median PAH-profile on skin wipe samples collected pre-exercise and post-exercise for 20 subjects.

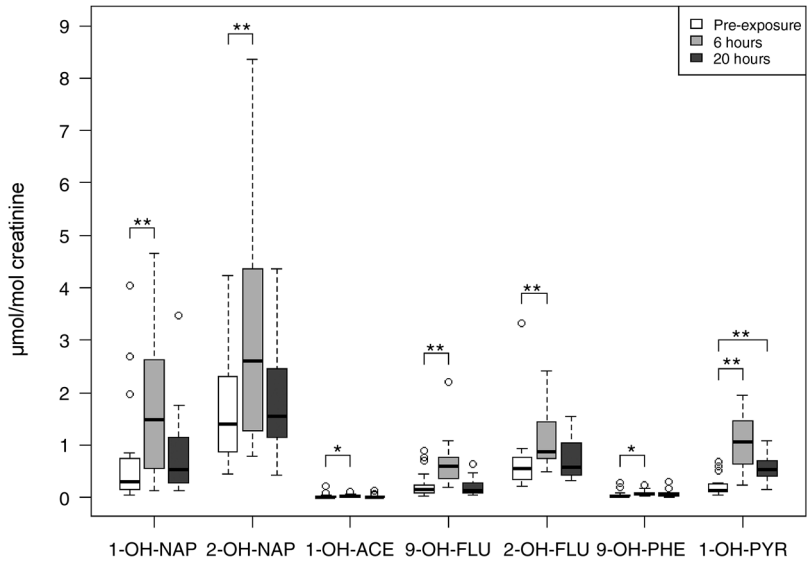

Figure 3. Box and whisker plots of urinary 1-hydroxynaphtalene (1-OH-NAP), 2-hydroxynaphtalene (2-OH-NAP), 1-hydroxyacenaphtene (1-OH-ACE), 9-hydroxyfluorene (9-OH-FLU), 2-hydroxyfluorene (2-OH-FLU), 9-hydroxyphenanthrene (9-OH-PHE), and 1-hydroxypyrene (1-OH-PYR) in samples taken pre-exercise and post-exercise for the 20 firefighter students attending an examination exercise involving live fire. Extreme data points are marked with dots (°) (Q1, Q3 ± 1.5 × IQR) and *, ** represent $P < 0.05$ and $P < 0.01$, respectively (Wilcoxon rank–sum test). Abbreviation: IQR = interquartile range.

outlier and omitted from statistical analysis as we suspected an alternative source. 1-OH-NAP is a commercial chemical that is used, for example, in dyes.

All subjects but one showed increased urinary levels of 1-OH-PYR post-exposure, in agreement with the results for skin deposition of PYR. Of all analysed metabolites, the highest relative increase was observed for 1-OH-PYR with a median increase of 7.6 times. The increases from the median baseline level of 0.14 µmol mol^{-1} creatinine to 1.1 and 0.52 µmol mol^{-1} measured

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at 6 h and 20 h post-exposure, respectively were both significant (Wilcoxon signed–rank test, $P = 0.01$). The metabolites of the two-ring and three-ring PAHs (1-OH-NAP, 2-OH-NAP, 1-OH-ACE, 9-OH-FLU, 2-OH-FLU, and 9-OH-FLU) showed the same pattern with higher median levels at 6 h than at 20 h. However, there was one major difference, in that the increased levels at 20 h were not statistically significant compared to pre-exposure levels, indicating that these urinary concentrations had returned to background levels.

Correlation studies

Two types of correlation were found relevant to study: first, which of the analysed metabolites showed the best correlation to skin-deposited PAHs (three-ring to six-ring PAHs) and second, the correlation between the relative increase of skin and urine metabolites to investigate exposure patterns among subjects. A Pearson correlation matrix was calculated based on the absolute increase for all mono-hydroxylated PAH metabolites, all deposited PAHs and their respective sum parameters. Of the analysed metabolites, 1-OH-PYR had the best correlation ($0.41 < R < 0.52$) to skin deposition of three-ring, four-ring, five-ring, and six-ring PAHs as well as the sum of 14 PAHs. The second best was 1-OH-Acenaphtylene (average $R = 0.37$) and the rest had values of R below 0.28, showing a weaker correlation with deposited PAHs. The corresponding Spearman correlation between deposited PAHs and 1-OH-PYR levels has slightly higher coefficients of 0.58 ± 0.17, which indicates the presence of monotonic and non-linear relationships. It is further likely that the exercise involved a great degree of complexity, in terms of exposure variability and patterns between individuals.

By plotting the relative increase of PYR on skin samples against its metabolite's relative increase from pre-exposure and post-exposure (at 6 h) time points, exposure patterns between subjects can be disclosed as seen in Fig. 4. Of particular interest are those subjects deviating from the unit increase line, that is assuming a perfect correlation between skin deposition and excretion of its metabolite. Three subjects showed a considerably higher relative increase in metabolite levels compared to skin deposition levels, indicating that another route of exposure, probably inhalation, played a role in their exposure (circled and marked "dermal + other" in Fig. 4). Other possibilities are that the differences were caused by disparities in contamination level of base layers at start of exercise and/or individual variability in uptake and metabolism. Apart from these three subjects, a majority appeared to be predominantly exposed by dermal uptake (circled and marked "dermal" in Fig. 4). Only one individual showed the opposite, a considerably higher increase of the skin deposition level compared to the metabolite.

Discussion

While it is obvious that firefighter's respiratory organs should have the highest possible protection level (PF ≥ 10 000) for the numerous toxic combustion products released during a fire, protection against skin contamination has been much less considered and studied. Recently, several dermal exposure assessment studies involving firefighters have demonstrated increased levels of deposited PAHs and other contaminants after smoke diving exercises (Laitinen *et al.*, 2010; Baxter *et al.*, 2014; Fent *et al.*, 2014; Fernando *et al.*, 2016). Small combustion particles (≤1 µm) and semi-volatile compounds may pass through firefighters' protective clothing layers by permeation and by penetration through gaps and other imperfections. Regarding firefighters' clothing, both types of ingress

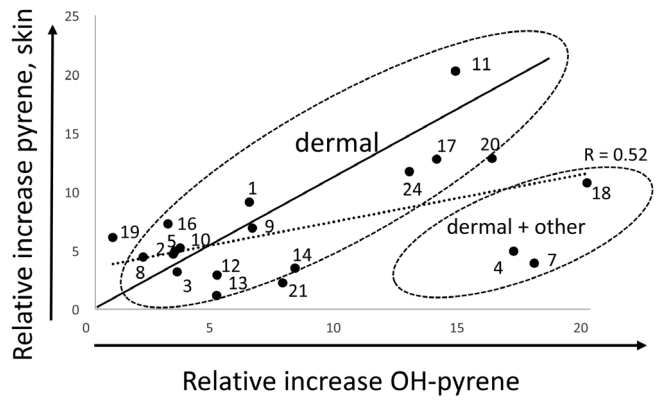

Figure 4. The relative increase in samples collected 6 h after exposure of 1-hydroxypyrene was plotted against the relative increase of deposited pyrene on the neck. A positive correlation was found with a Pearson coefficient of 0.52 (dotted line) and Spearman rank coefficient of 0.70. A unit increase line (solid) has been added.

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are relevant since there is a general lack of resistance or absorption capacity, such as active coal or non-permeable layers, to constrain the passage of airborne chemicals. Further, high ventilation rates (≤100 l min^{-1}) can be expected because of the air permeability of the fabric, and lack of seals combined with intensive body movements during exercises. One way to determine this is to generate WPFs, which is the ratio of the concentration of a contaminant on the outside and the inside of a protective barrier, in realistic whole system tests. Kirk and Logan (2015) carried out simultaneous sampling on Tenax and PUFs of PAHs directly outside on the harness at chest height and on the inside of instructors' ensembles. Using their data to calculate WPFs generates values of ~10. Their data were acquired in similar conditions and settings as in our study, yet appreciably higher protection factors of ~100–1000 were obtained in this work. Besides some methodological differences, such as use of a dilution step in our study to minimize sampling artefacts in hot temperatures of PAHs (sampling temp. 20°C instead of 180°C), the main difference was that the instructors wore a thick body base layer in addition to fire suits. Laitinen *et al.* (2010) measured a reduction of 80% of deposited PAHs when undergloves were used, highlighting how additional layers can increase the protection factors. Furthermore, in an intervention study carried out on coal liquefaction workers, the levels of both deposited PAHs and 1-OH-PYR were significantly reduced when new clothes (e.g. coveralls, shirts, trousers, undergarment) were provided daily as compared to longer use of clothes (Quinlan *et al.*, 1995). Evidently, our data and that of others show that an outer ensemble combined with additional layers may yield an improved level of protection.

However, the vast contamination being accumulated in used fabrics raises concerns for the introduction of an effective personal decontamination after finishing exercises and possibly during any turn-out involving smoke diving. The most volatile fraction can evaporate and pose a proximate inhalation threat when SCBA is removed whereas the less volatile and particle-bound PAHs may, in addition, continue to pose a risk for prolonged dermal exposure before removal of clothing. Therefore, the first step in a decontamination line, if possible even before removing respirators, is to remove the fire suit, including base layer and other contaminated fabrics that are in contact with skin. In Sweden, as per the new precautionary measures (Magnusson and Hultman, 2014), it is encouraged that this should be done before returning to the station.

Briefly, by direct contact and through the mechanism of diffusion, lipophilic compounds have been considered to be most likely to be taken up through skin. Recent studies indicate that dermal uptake from airborne chemicals may play a much larger role than previously thought (Weschler and Nazaroff, 2012; Wu *et al.*, 2016). The dermal uptake of the contextually volatile compound, 2-butoxyethanol (boiling point = 171°C and vapour pressure = 0.8 mmHg) accounted for 75% of the total uptake for whole body exposure (Johanson and Boman, 1991). Presumably, the dermal uptake of not just particle-bound PAHs but also gaseous species cannot be ignored and the 6-h post-exposure data confirm that metabolites of the more volatile species, such as NAP and FLU increased. In the absence of data based on external exposure (air or skin) for those species, it is not easy to propose an explanation of those findings. However, hot and humid conditions are known to enhance dermal uptake, conditions abundantly present during firefighting operations.

Statistical analysis of our data demonstrated, at best, medium strong positive correlations (Pearson ~0.5, Spearman rank ~0.7) between exposure data measured from skin wipe samples and levels of urinary hydroxy-PAHs. Previously reported correlations have not been substantially stronger and highly variable (Fent *et al.*, 2014; Fernando *et al.*, 2016) for similar exposure assessment studies involving firefighters. Furthermore, the assessment of exposure in industries with PAH emissions using a combination of personal air monitoring data and levels of metabolites in urine has sometimes also failed to find a positive correlation between the two data sets (Jongeneelen, 2014). If it holds true that exposure through inhalation is low, the site or methodology chosen to determine dermal exposure using skin wipes has limitations. Whereas Fent *et al.* (2014) identified the neck as a more preferable body site compared to four other sites, Fernando *et al.* (2016) found nearly equal levels of deposited PAHs at five different body sites. There may not be sufficient evidence to designate an optimal site for dermal exposure. However, wipes collected from the necks of subjects were chosen in the present study, resulting in a median 5-fold increase between pre-exposure and post-exposure for Σ14 PAHs.

Most circumstances, such as highly variable conditions, different roles of firefighters, and the possibility of secondary exposure during smoke diving exercises, all point in the direction of an internal biological indicator of exposure being more suitable than measurement of external exposure. Although being used as an aggregate indicator for all PAHs, 1-OH-PYR has, so far, been shown to be the preferred and most comprehensive carcinogenic biomarker of exposure to PAHs compared to several other hydroxylated PAHs found in urine (Jongeneelen, 2001; Käfferlein *et al.*, 2012; Yamano *et al.*, 2014). It is relatively easy to measure and applicable

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in many occupational settings where PAHs are emitted. Even though several crucial prerequisites support its use, such as evidence for multiple route exposure and difficulties in measuring external exposure, conclusive data supporting the adoption of 1-OH-PYR as a universal biomarker for firefighters' exposure are missing (Fent *et al.*, 2014; Fernando *et al.*, 2016; Oliveira *et al.*, 2016). Methoxyphenols, two-ring and three-ring mono-hydroxylated PAHs have been suggested as other complementary candidates. In accordance with Laitinen *et al.* (2010), our data support that 1-OH-PYR in urine is a useful biological indicator 6 h after smoke diving exposure, using chipboard wood, by demonstrating a significant increase for 19 out of 20 volunteer subjects. In addition to this, it was the only metabolite among six others that displayed a significant elevation in samples collected 20 h after exposure. Still, a biomarker with a stronger correlation towards particle-bound and carcinogenic PAHs found on skin samples would be desirable but, as with many other studies of firefighters' exposure, detection criteria were not met for 3-OH-BaP, due to low levels.

To overcome problems associated with a lack of an optimal indicator for carcinogenic PAHs, other strategies have been suggested. For instance, variations in the ratio of Pyrene/Benzo[a]pyrene (PYR/BaP) in air samples have been suggested as an influencing factor while calculating an adjusted guidance value (AGV) for occupational settings with expected PAH exposure (Jongeneelen, 2014). Before directly implementing this conversion in the occupational setting for firefighters, it should be emphasized that PAHs may be a fraction of the potentially carcinogenic compounds present in smoke, and highly dependent on situation. In a previous study (Laitinen *et al.*, 2012), the PYR/BaP ratio was found to be 1.3 in a conventional smoke simulator using wood and 11 in a modern simulator using propane and mineral oil as sources for heat and smoke. In this study, the ratios varied from 2.5 ± 0.2 in the outside air samples (exercise 1), 0.53 ± 0.05 inside the fabric layers and finally to 5.1 ± 2.3 on the skin samples (from exercise 2), highlighting difficulties in selecting this strategy. Nevertheless, using a ratio of 2.5 an AGV of 1 µmol 1-OH-PYR mol^{-1} creatinine would be obtained which is identical to the recommended state-of-the-art AGV proposed for coke oven workers (Jongeneelen, 2014). One exercise (exercise 2) demonstrated a group median level of 1.1 µmol mol^{-1} after 6 h and 0.52 µmol mol^{-1} after 20 h. In Sweden, there is no occupational exposure limit for levels of 1-OH-PYR in urine. In a rudimentary attempt to assess the risks, assuming that PAHs were the only group of contaminants of concern and in view of current knowledge of acceptable occupational exposure of PAHs, one exercise (similar to exercise 2) each week would probably be considered a low risk or safe. However, for instructors, exposure dimensions are usually much worse with several additional exercises each day/week and, in particular, they experience high concentrations while guiding more demanding exercises, similar to exercise 1. Unfortunately, no biological exposure monitoring data were collected during that exercise, but we consider that instructors face a greater risk and future attention should be paid to measure and possibly identify specific methods of reducing their exposure.

Conclusions

This study has shown that the addition of a base layer to a firefighter's ensemble provided significantly higher WPFs than previously demonstrated in tests carried out with just the outer ensemble. As a consequence of contaminants accumulating in the garment layers, a prompt removal of such garments can be beneficial in reducing the risk of prolonged dermal exposure.

Median levels of 1-OH-PYR were significantly increased in urine samples collected after both 6 hours and 20 hours as compared to baseline levels. The other metabolites showed significantly increased levels after 6 h but not after 20 h, indicating a faster overall metabolization and excretion. Moreover, of the quantified PAH metabolites in urine, 1-OH-PYR showed the strongest correlation to skin-deposited PAHs, and therefore it is suggested that this is a better indicator of exposure during smoke diving exercises when wood is used as fuel. Our study supports previous findings that dermal exposure is a major route of uptake for most PAHs during smoke diving exercises, when SCBA equipment is correctly used. Still, further studies are warranted to identify a marker with stronger correlation to carcinogenic PAHs. Our study failed to provide a better understanding as to the uptake route for the more volatile PAHs. Finally, this study supports the idea that some of the newly adopted protective measures were correctly implemented, and should continue to be followed and more widely used.

Supplementary Data

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

Acknowledgments

The authors are indebted to student firefighters and their instructors for their participation. Funding from the Swedish Civil Contingencies Agency and Swedish Ministry of Defence is gratefully acknowledged.

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Declaration

The authors declare no conflict of interest relating to the material presented in this Article. Its contents, including any opinions and/or conclusions expressed, are solely those of the authors.

References

Arnoldsson K, Magnusson R, Hägglund L *et al.* (2015) Initial evaluation of an axial passive sampler for PAHs and OPAHs using substrates with and without gas sampling capacity and varying diffusion distances. *Atmos Pollut Res*; **6**: 673–81.

Barbeau D, Maître A, Marques M. (2011) Highly sensitive routine method for urinary 3-hydroxybenzo[a]pyrene quantitation using liquid chromatography-fluorescence detection and automated off-line solid phase extraction. *Analyst*; **136**: 1183–91.

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.

Boffetta P, Jourenkova N, Gustavsson P. (1997) Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons. *Cancer Causes Control*; **8**: 444–72.

Bouchard M, Viau C. (1999) Urinary 1-hydroxypyrene as a biomarker of exposure to polycyclic aromatic hydrocarbons: biological monitoring strategies and methodology for determining biological exposure indices for various work environments. *Biomarkers*; **4**, 159–87.

Campo L, Rossella F, Fustinoni S. (2008) Development of a gas chromatography/mass spectrometry method to quantify several urinary monohydroxy metabolites of polycyclic aromatic hydrocarbons in occupationally exposed subjects. *J Chromatogr B Analyt Technol Biomed Life Sci*; **875**: 531–40.

Caux C, O'Brien C, Viau C. (2002) Determination of firefighter exposure to polycyclic aromatic hydrocarbons and benzene during fire fighting using measurement of biological indicators. *Appl Occup Environ Hyg*; **17**: 379–86.

Delistraty D. (1997) Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. *Toxicol Environ Chem*; **64**, 81–108.

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.

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.

IARC. 2010. *Monographs on the evaluation of carcinogenic risks to humans. Painting, firefighting and shiftwork*, vol **98**. Lyon, France: International Agency for Research on Cancer.

Johanson G, Boman A. (1991) Percutaneous absorption of 2-butoxyethanol vapour in human subjects. *Br J Ind Med*; **48**: 788–92.

Jongeneelen FJ. (2001) Benchmark guideline for urinary 1-hydroxypyrene as biomarker of occupational exposure to polycyclic aromatic hydrocarbons. *Ann Occup Hyg*; **45**: 3–13.

Jongeneelen FJ. (2014) A guidance value of 1-hydroxypyrene in urine in view of acceptable occupational exposure to polycyclic aromatic hydrocarbons. *Toxicol Lett*; **231**: 239–48.

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

Käfferlein HU, Marczynski B, Simon P *et al.* (2012) Internal exposure to carcinogenic polycyclic aromatic hydrocarbons and DNA damage: a null result in brief. *Arch Toxicol*; **86**: 1317–21.

Laitinen J, Mäkelä M, Mikkola J *et al.* (2010) Fire fighting trainers' exposure to carcinogenic agents in smoke diving simulators. *Toxicol Lett*; **192**: 61–5.

Laitinen J, Mäkelä M, Mikkola J *et al.* (2012) Firefighters' multiple exposure assessments in practice. *Toxicol Lett*; **213**: 129–33.

Magnusson S, Hultman D. (2014) (In Swedish) Friska brandmän – Skellefteåmodellen förbättrar arbetsmiljön. MSB743. Available at https://www.msb.se/RibData/Filer/pdf/27476.pdf. Accessed 27 November 2017. ISBN 978-91-7383-480-3

Oliveira M, Slezakova K, Alves MJ *et al.* (2016) Firefighters' exposure biomonitoring: Impact of firefighting activities on levels of urinary monohydroxyl metabolites. *Int J Hyg Environ Health*; **219**: 857–66.

Pleil JD, Stiegel MA, Fent KW. (2014) Exploratory breath analyses for assessing toxic dermal exposures of firefighters during suppression of structural burns. *J Breath Res*; **8**: 037107.

Quinlan R, Kowalczyk G, Gardiner K *et al.* (1995) Exposure to polycyclic aromatic hydrocarbons in coal liquefaction workers: impact of a workwear policy on excretion of urinary 1-hydroxypyrene. *Occup Environ Med*; **52**: 600–5.

Robinson MS, Anthony TR, Littau SR *et al.* (2008) Occupational PAH exposures during prescribed pile burns. *Ann Occup Hyg*; **52**: 497–508.

Tsai RJ, Luckhaupt SE, Schumacher P *et al.* (2015) Risk of cancer among firefighters in California, 1988-2007. *Am J Ind Med*; **58**: 715–29.

Weschler CJ, Nazaroff WW. (2012) SVOC exposure indoors: fresh look at dermal pathways. *Indoor Air*; **22**: 356–77.

Wingfors H, Hägglund L, Magnusson R. (2011) Characterization of the size-distribution of aerosols and particle-bound content of oxygenated PAHs, PAHs, and n-alkanes in urban environments in Afghanistan. *Atmos Environ*; **45**, 4360–9.

Wu CC, Bao LJ, Tao S *et al.* (2016) Dermal uptake from airborne organics as an important route of human exposure to e-waste combustion fumes. *Environ Sci Technol*; **50**: 6599–605.

Yamano Y, Hara K, Ichiba M *et al.* (2014) Urinary 1-hydroxypyrene as a comprehensive carcinogenic biomarker of exposure to polycyclic aromatic hydrocarbons: a cross-sectional study of coke oven workers in China. *Int Arch Occup Environ Health*; **87**: 705–13.

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