Annals of Work Exposures and Health, 2021, Vol. 65, No. 2, 148–161
doi: 10.1093/annweh/wxaa064
Advance Access publication 23 June 2020
Original Article

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Exposure and Absorption of PAHs in Wildland Firefighters: A Field Study with Pilot Interventions

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Submitted 21 January 2020; revised 29 May 2020; editorial decision 2 June 2020; revised version accepted 4 June 2020.

Abstract

Objectives: There is limited knowledge of exposure to polycyclic aromatic hydrocarbons (PAHs) in wildland firefighters, or of the effectiveness of interventions to reduce this. This study of wildland firefighters assessed whether PAHs were present and considered respiratory protection and enhanced skin hygiene as possible interventions.

Methods: 1-Hydroxypyrene (1-HP) was measured in urine samples collected pre-shift, post-shift, and next morning from wildland firefighters in Alberta and British Columbia. Skin wipes, collected pre- and post-shift, were analysed for eight PAHs. Breathing zone air samples were analysed for 11 PAHs. As pilot interventions, participants were randomized to either normal or enhanced skin hygiene. A sample of volunteers was assigned to a disposable N95 mask or a half facepiece mask with P100 organic vapour cartridge. Participants completed a brief questionnaire on activities post-shift and respiratory symptoms.

Results: Non-smoking firefighters (66 male and 20 female) were recruited from 11 fire crews. Air sampling pumps were carried for the full shift by 28 firefighters, 25 firefighters wore masks (14 N95 and 11 P100); 42 were assigned to the enhanced skin hygiene intervention. Sixty had hot spotting as their main task. Air monitoring identified PAHs (benzo(*b*,*j*,*k*)fluoranthene in particulates, phenanthrene in the gaseous phase) for 6 of the 11 crews. PAHs (largely naphthalene) were found post-shift on 40/84 skin wipes from the hand and 38/84 from jaw/throat. The mean increase in 1-HP in urine samples collected after the shift (compared with samples collected before the shift) was 66 ng g^{-1} creatinine ($P < 0.001$) with an increase over the shift found for 76% of participants. 1-HP in next morning urine samples was significantly lower than at the end of shift (a reduction of 39.3 ng g^{-1}: $P < 0.001$). The amount of naphthalene on skin wipes was greater at the end of the shift (post) than at the start (pre). The mean post–pre weight difference of naphthalene on skin wipes taken from the hand was 0.96 ng $wipe^{-1}$ ($P = 0.01$) and from the jaw/throat 1.28 ng $wipe^{-1}$ ($P = 0.002$). The enhanced skin hygiene intervention lead to a larger reduction in 1-HP between end of shift and next morning urine samples but only for those with naphthalene on skin wipes at the end of shift. The difference

in 1-HP concentration in urine samples collected before and after the shift was reduced for those wearing a mask (linear tend $P = 0.063$, one-sided). In multivariable models, 1-HP at end of shift was related to gaseous phase phenanthrene, estimated from air sampling [$\beta = 318.2$, 95% confidence interval (CI) 67.1–569.2]. Naphthalene on hand skin wipes reflected work in hot spotting during the shift ($\beta = 0.53$, 95% CI 0.22–0.86).

Conclusions: This study provided evidence of PAHs in the air and on the skin of many, but not all, fire crew. Absorbed PAHs, reflected in 1-HP in urine, increased over the shift. Results from the pilot interventions suggest that enhanced skin hygiene would reduce absorption post fire where PAHs had been accumulated on the skin, and that masks could be effective in reducing PAH inhalation exposure. Interventions to reduce PAH absorption are supported by the pilot work reported here and warrant further evaluation across a full fire season.

Keywords: 1-hydroxypyrene; intervention; PAH exposure; skin hygiene; skin wipes; wildland firefighter

Introduction

Although there have been many studies of polycyclic aromatic hydrocarbon (PAH) exposure in urban (structural) firefighters (including Fent *et al.*, 2014; Fernando *et al.*, 2016; Keir *et al.*, 2017; Oliveira *et al.*, 2017; Stec *et al.*, 2018;Wingfors *et al.*, 2018;Sjostrom *et al.*, 2019;Beitel *et al.*, 2020; Keir *et al.*, 2020) the potential exposure in wildland fighters has received less attention. Recently, papers have shown the presence of PAHs in the breathing zone of wildland firefighters (Navarro *et al.*, 2017, 2019) together with urinary PAH metabolites (Adetona *et al.*, 2017, 2019). We are not aware of studies evaluating skin deposition or absorption of PAHs in wildland firefighters, although PAHs have been found on skin wipes in studies of structural firefighters (including, e.g., Fernando *et al.*, 2016; Stec *et al.*, 2018). The route of exposure for wildland firefighters is of particular interest as both lung and skin may be important. Traditionally wildland firefighters do not use respiratory protection, tactically avoiding areas with highest smoke concentrations: Navarro *et al.* (2017) found the greatest total PAHs in the breathing zone was in those whose task during wildland fires was 'holding', walking along the active fire line to detect and suppress fire encroachments. Additionally, opportunities for skin hygiene may be limited during long rotations in camp and away from opportunities to change or clean working gear. In the Fort McMurray fire in northern Alberta in 2016, structural firefighters unable to wash or change their clothes during the first days of the fire had increased 1-hydroxypyrene (1-HP) in urine (Cherry *et al.*, 2019). With the recent upsurge in wildland fires, the prevention of long-term effects of exposures on the health of firefighters becomes an urgent question. The study reported here was designed to assess the presence of PAHs in the breathing zone and on the skin of wildland firefighters and the concentration of the PAH metabolite 1-HP in urine. It included also two pilot interventions, through use of masks and enhanced skin hygiene, to evaluate effects on absorption as reflected in urinary 1-HP.

Methods

Population and recruitment

Those taking part in the field study were wildland firefighters employed, mainly as seasonal workers, by the Alberta or British Columbia wildfire services. Crews being deployed to fires were identified by collaborators within the fire services who arranged access for the research team to meet with the firefighters the evening before the fire day of interest. The team introduced themselves to the fire crew and explained the purpose and nature of the study. They then handed out written information and consent sheets. After a period for questions, a firefighter willing to take part signed the consent form and returned it to the research team. Any smoker who consented was eligible to carry an air sampling pump, but not for biological monitoring. Among non-smokers consenting, volunteers were sought from cleanshaven men and from women to be fit tested for masks (N95 or P100). This was carried out the evening before the day (the 'fire day') identified for the research team to monitor the firefighters in the field. The following morning, all who had consented to be in the study gave a pre-shift urine sample and had skin wipes taken, as described below. Pumps for sampling particulate and vapour phase PAHs were carried by at least two volunteers during the whole shift at each site. Research team members attended the fire site and periodically checked the working of the pumps, recorded the main tasks carried out by the crew and noted the time at which any mask was removed (whether during or at the end of shift). At the

end of the fire day further urine samples and skin wipes were taken. At this time all volunteers were randomly allocated, using a random number app, to a 'normal' hygiene or 'enhanced' hygiene group, in which firefighters in the enhanced group were encouraged to shower and change into clean clothes as soon as practicable after giving the end of shift urine sample. A third urine sample was collected before the start of work the next morning. At this time the participants also completed a brief questionnaire (see Supplementary Materials) recording events since the end of shift (washing and changing clothes) and any activities (smoking, eating BBQ, and fighting other blazes) that might have provided additional PAH exposure. The participants also reported symptoms and, for those wearing masks, their perception of the experience.

Interventions

(1) Face masks: Where cleanshaven volunteers were available, one or more was allocated to, and fit tested for, either a 3M N95 particulate respirator disposable mask or a 3M rugged comfort—quick latch half facepiece mask with P100 organic vapour cartridge.
(2) Enhanced hygiene: Those randomly allocated to enhanced hygiene were instructed both verbally and by a written handout to follow the steps outlined below as soon they returned to their overnight base: "i) shower thoroughly using soap ii) wash your hair with shampoo iii) put on a full set of clean clothes iv) do not put on your nomex (fire-resistant outer clothing) or other unwashed clothing until after you provide your next morning urine sample". Those allocated to 'normal' skin hygiene followed their usual washing and clothing practice, with the understanding that, where facilities were limited, the enhanced group had first access to showers.

Collection and analysis of urine samples

Each of the three urine samples (pre- and post-shift and next morning) was collected as spot mid-flow sample into a sterile 100 ml plastic container and aliquoted into 2.0 ml microcentrifuge tubes. These were transported to the University of Alberta (Edmonton) using a portable –20°C freezer and stored at –20°C before being transported on dry ice to the Alberta Toxicology Centre in Calgary. They were analysed for 1-HP, following the liquid chromatography–tandem mass spectroscopy method previously validated (Cherry *et al.*, 2019; Gill *et al.*, 2019). Details of the method were given in an earlier publication (Cherry *et al.*, 2019) and are included here as Supplementary Material 1. Creatinine was measured on an Olympus AU480 autochemistry analyser (see Supplementary Material 2). Creatinine is excreted at a constant rate and was used here to normalize for differences in urine concentration.

Concentrations of 1-HP, corrected for creatinine, were expressed as ng g^{-1} creatinine. Samples with creatinine <30 or >300 mg dl^{-1} were excluded (WHO, 1996).

Collection and analysis of skin wipe sample

Skin wipes were taken immediately before and immediately after the fire day. Following the earlier work with urban firefighters by Stec *et al.* (2018), team members, using commercially available Loris brand prewrapped sterile 6 × 3 cm skin wipes saturated with 70% isopropyl solution, wore nitrile gloves to take wipes from the palms of the hands (from the tips of the fingers to the wrist of both palms), the throat/jaw (jawline from ear to ear, throat to shirt collar), the back of the neck (from ear to ear and hairline to collar) and the upper chest (under clothing, from area under one collarbone to the other). Additional samples were taken from the left leg (on the shin above the sock) of firefighters at some sites, following concern from firefighters that this was a source of high contamination. No attempt was made to mark out a standard area on the skin, but research staff were trained to wipe a consistent area. The research team used a fresh pair of nitrile gloves for each skin wipe to reduce cross-contamination. The wipes were unfolded and one side was used to collect the sample using firm strokes across the target area.

Wipes were sealed individually into zip top bags and placed in a larger amber bag for storage or individually in silanized amber glass tubes and conveyed to the University of Alberta (Edmonton) in a portable –20°C freezer and stored in the dark at –20°C before being transferred on dry ice to the Alberta Toxicology Laboratory at the University of Calgary, where they were stored at –18°C prior to analysis.

Samples were placed in amber silanized glass vials to which 4 ml of hexane/acetone (3:1, v/v) was added. A mixture of four deuterated PAH compounds was added as internal standard solution. Samples were sonicated for 30 min. 1.0 ml of each sample was filtered with 0.22 µM polytetrafluoroethylene syringe filters and collected in amber silanized gas chromatography (GC) glass vials.

Quantitative analysis was performed using a HP 6890 Series GC System equipped with a 5973 Mass Selective Detector (Hewlett Packard) and a J&W DB-5ms GC Column with the dimensions 30 mm × 0.25 mm ×

0.25 µm (Agilent). An injection volume of 2 µl was used with a splitless injection. Samples were analysed in SIM mode. The presence of eight PAHs was quantified: naphthalene, benz[*a*]anthracene, chrysene, benzofluoranthene isomers, benzo[*a*]pyrene, 3-methylcholanthrene, dibenz[*a*,*h*]anthracene, and dibenzo(*a*,*e*)pyrene. Full details of the method, quality control, and validation are given in Supplementary Material 3.

Collection and analysis of PAH samples as respiratory particulates and in the gaseous phase

Particulates in total dust were collected on a 37 mm, 0.8 µm, glass fibre filter (AP4003705 Millipore) and gaseous phase on XAD-2 resin (orbo 42L, Millipore) using a personal sampling pump (an SKC universal sampling pump 224-PCXR4). Sampling flow rate was set at 2 l min^{-1} with the flow rate measured immediately before and after sample collection. The pump was attached to the belt of the firefighter while the cassette and sorbent tube were clipped to the lapel of the firefighter's jacket in the breathing zone of the worker. Sampling was carried out for the length of the working shift. Once collected, samples were covered with aluminium foil to avoid sample degradation and stored at −20°C prior to being sent, on dry ice, to the Institut de recherché Robert Sauvé en Santé au Travail (IRSST) laboratory in Montreal, Quebec for analysis.

Sample preparation and analysis were performed at IRSST according to Method MA. 400—HAP 1.1 fromCentre d'expertise Environnemental du Québec (2016). Quality control of samples was done by spiking samples prior to extraction with a solution of seven PAH in isooctane. In addition, an internal standard solution of seven PAH in isooctane was added prior to analysis. Briefly, extraction on filters was performed using 5 ml of benzene in an ultrasonic bath for 30 min. Extracts were filtered and spiked with 5 µl of an internal standard containing deuterated PAHs prior to analysis. XAD-2 resin was extracted using 5 ml of a 50:50 solution of dichloromethane and benzene in a shaker for 30 min. Extracts were aliquoted prior to analysis. Each solvent fraction was analysed using GC/MS for acenaphthene, anthracene, benz(*a*)anthracene, benzo(*b*,*j*,*k*)fluoranthene, benzo(*a*)pyrene, benzo(*e*)pyrene, chrysene, fluorene, fluoranthene, phenanthrene, pyrene in both particulate and gaseous phases.

Values below the limit of detection/quantification

The beta-substitution method proposed by Ganser and Hewett (2010) was used to replace non-detected concentrations for substances found in a significant number of samples. These were: in the analyses of urine (for 1-HP), of skin wipes (for naphthalene) and PAHs from air sampling (for benzo(*b*,*j*,*k*)fluoranthene in particulates and phenanthrene in the vapour phase). The calculated beta-mean reflected both the mean of the observed values and the proportion below the limit of detection (LoD). The approach used for each type of sample is outlined below.

Urine samples: Beta-substitution was carried out separately for each time period (pre–post-shift and next morning). Where a concentration could not be detected or accurately determined, the LoD of 0.02 ng ml^{-1} for the analytical method (Supplementary Material 1) was multiplied by the beta-mean calculated using Ganser and Hewett's algorithm. This value was used to replace all values below the LoD in that time period.

Skin wipes: Beta-substitution was carried out for the two time periods (pre- and post-shift) separately. The LoD for napthalene was 2.0 ng $wipe^{-1}$ (see Supplementary Material 3) and this multiplied by the beta-mean was used to substitute values below the LoD.

Air sampling: The limits of detection for the compounds of interest were supplied by the analytical laboratory as a mass (0.15 µg) and converted to a concentration, assuming a flow rate of 2 l min^{-1} over 8 h, giving an LoD for concentration of 0.1563 µg m^{-3}. This was multiplied by the beta-mean for each compound to obtain substitute vales for those with concentrations below the LoD.

Quantification of PAH exposure

Values below the LoD were substituted for PAH compounds of interest. The mean value of the compound for pumps carried by each crew was then calculated and these crew specific values assigned to all members of that crew. If any pump carried by a crew member had a concentration above the LoD for any PAH, the whole crew was considered to have a quantifiable exposure to PAHs. The presence of PAHs deposited on the skin during the fire day was confirmed by an increase of any PAH on skin wipes, comparing mass at end of shift and pre-shift. The absorption of PAHs by either route was measured by an increase in 1-HP ng g^{-1} creatinine between post- and pre-shift urine samples.

Additional factors considered were:

- Type of task (hot spotting or 'other') on the fire day. Here 'other' was fighting active fires. Hot spotting

was a process of digging through fire debris after the initial active phase to identify and destroy 'hot spots' that were still smouldering.
- Length of shift worked on the fire day.
- Exposures to PAHs post-shift, particularly tobacco smoking.
- The sex of the firefighter.

Statistical methods

For the descriptive presentation of results, including the impact of wearing a mask, *t*-tests or analysis of variance were used to compare means and assess linearity. To evaluate the effect of the enhanced hygiene regime, data were stratified by the presence or absence of PAH on end of shift skin wipes, as the regime would only be expected to be effective if there was PAH skin contamination present. Mean changes in 1-HP from post-shift to next morning were then compared, within strata, for those in the enhanced and normal hygiene groups. A final analysis was carried out using multivariable, multilevel linear regression within STATA 14.2. The multilevel analysis allowed for clustering within work crews. Following univariate analysis allowing for clustering, all factors with $P < 0.10$ in the univariate model were entered into the multivariable one. The regression analysis considered the relation between exposure estimates from air sampling, skin wipes, and pre-exposure urine samples on end of shift 1-HP and naphthalene. It also provided a formal test, in a full model, of the effect of masks in reducing inhalation exposure. Probability $P < 0.05$ in a two-sided test was taken to indicate statistical significance. For analysis of the interventions, where the anticipated effect was in one direction only, one-sided test statistics were also assessed.

Results

In Alberta, five fire days with 36 firefighters were monitored, with a further six (covering 50 firefighters) in British Columbia, between 11 April 2019 and 28 August 2019 (see Table 1). A total of 86 firefighters gave biological samples. Of these, 20 (24.3%) were women. At one site in Alberta an additional firefighter, a tobacco smoker, carried one of the pumps. The main task was hot spotting carried out by all but four of the firefighters in British Columbia but only by 14 of those from Alberta (Table 1). Twenty-eight firefighters carried an air monitoring pump giving information on environmental air PAH concentration for all but four firefighters (at site 3) who were sent to another location without pumps but who gave urine and skin wipe samples. At site 1 the crew leader felt that the glass tubes for monitoring gaseous phase PAHs were a safety hazard and for this crew of four only particulate data are available. Twenty-five participants wore either an N95 disposable mask ($N = 14$) or a half facepiece mask with P100 organic vapour cartridge ($N = 11$). The enhanced hygiene group comprised a random 42, with 44 following normal skin hygiene.

The results of air monitoring and skin wipes for PAHs and the urinary metabolite 1-HP are summarized in Table 2. All methods confirmed the presence of PAHs in some or all of the samples.

Urine samples were analysed only for 1-HP. Few samples (six in pre-shift, one in post-shift, and three in the next morning sample) were below the level of quantification and replaced by beta-estimation. One participant had very high levels of 1-HP in all three samples, suggesting that he was a smoker and his urinary results were excluded. At each time period there were samples with creatinine outside the acceptable range (8 pre-shift, 14 post-shift, and 6 the following morning). These samples were also excluded, resulting in reduced numbers of samples, particularly for the comparison between time periods. The arithmetic mean 1-HP was lowest for samples collected pre-fire. The mean concentrations differed between time periods: there was a significant increase in 1-HP during the fire day (the difference between the end and beginning of shift), concentration of 1-HP decreased overnight but the concentration the next morning was still significantly higher than at the start of the fire day. The increase in 1-HP over the work shift was present for the means of each of the 11 work crews shown in Table 1 except site 10, with only small increases (<10 ng g^{-1} creatinine) in sites 9 and 11. The largest increases across shift were seen at site 2 (169 ng g^{-1} creatinine) and site 5 (172 ng g^{-1} creatinine). Among the 66 firefighters with acceptable creatinine concentrations both pre- and post-shift, 50 (76%) had higher 1-HP post-shift. Overall there was no significant difference between the two provinces in the rise in 1-HP across the shift (Alberta 80 ng g^{-1} creatinine; British Columbia 55 ng g^{-1} creatinine: $P = 0.291$).

Skin wipes were analysed for eight PAH compounds. Wipes were taken from five body locations of which two, the hands and jaw/throat, are considered here for 84 firefighters. The only PAH repeatedly identified in the samples was naphthalene, found on 26/84 hand wipes and 32/84 throat wipes pre-fire and on 40/84 hand wipes and 38/84 throat wipes post-fire. Other PAHs detected were as follows: benzo[*a*]anthracene on one wipe pre-fire and five post-fire; chrysene on two post-fire; benzofluoranthene isomers on three post-fire.

Table 1. Description of the sites and participants.

	Province	Date in 2019	Type of fire	Number recruited			Number hot spotting	Number of pumps	Number with N95 mask	Number with P100 mask	Number with enhanced hygiene
				M	F	All					
1	Alberta	April 11	Prescribed burn grass/muskeg	0	4	4	0	4[a]	1	1	2
2	Alberta	April 18	Prescribed burn grass	1	2	3	0	3	0	1	1
3	Alberta	July 21	Hot spotting coniferous forest	6	2	8	8	3[b]	1	1	4
4	Alberta	August 1	Hot spotting peat	6	0	6	6	2	0	1	3
5	British Columbia	August 2	Hot spotting coniferous forest	3	1	4	4	2	1	1	2
6	British Columbia	August 3	Lightning strike	3	3	6	2	2	2	0	3
7	British Columbia	August 4	Hot spotting coniferous forest	12	0	12	12	2	3	1	6
8	British Columbia	August 15	Hot spotting coniferous forest	7	3	10	10	2	2	0	5
9	British Columbia	August 16	Hot spotting coniferous forest	11	2	13	13	2	1	3	6
10	British Columbia	August 17	Hot spotting coniferous forest	4	1	5	5	2	1	0	2
11	Alberta	August 28	Extinguishing grass/ash with hose	13	2	15	0	4	2	2	8
Overall	—	—		66	20	86	60	28	14	11	42

[a]Filter cassettes for particulate matter only.

[b]Split group: four with no pump.

Table 2. Summary of results of urine, skin wipes, and air sampling for 1-HP or PAHs.

Urinary 1-HP ng g^{-1} creatinine						
	Pre-shift	**Post-shift**	**Next morning**	**Post–pre[a]**	**Post-morning[a]**	**Morning-pre[a]**
Mean	123.3	187.1	154.0	66.0	39.3	33.5
SD	68.1	107.7	101.0	92.0	58.5	86.0
N	77	71	78	66	68	74
P (ANOVA)				$P < 0.001$	$P < 0.001$	$P < 0.001$

Skin wipe naphthalene (ng $wipe^{-1}$)						
	Hands			**Jaw/throat**		
	Pre-shift	Post-shift	Post–pre[a]	Pre-shift	Post-shift	Post–pre[a]
Mean	3.27	4.24	0.98	3.89	5.16	1.28
SD	5.75	5.71	3.38	5.90	6.97	3.72
N	84	84	84	84	84	84
P (ANOVA)			$P = 0.010$			$P = 0.002$

Pumps: particulates (benzo(*b*,*j*,*k*)fluroanthene, ng m^{-3})			Pumps: gaseous phase (phenanthrene, ng m^{-3})	
	Pumps	Estimate for whole crew	Pumps	Estimate for whole crew
Mean	102.2	72.7	239.7	132.4
SD	123.2	50.5	209.1	119.7
N	28	82	24	78

ANOVA, analysis of variance; SD, standard deviation.

[a]Post–pre = difference between post-shift and pre-shift value, post-morning = difference between post-shift and next morning values, morning-pre = difference between next morning and pre-shift vales.

For naphthalene, with samples below the LoD estimated by beta-substitution, increased concentrations were found post-fire in wipes from both the hands and throat, with a somewhat bigger increase in wipes from the throat. Mean increases were found on both sets of wipes in all of the 11 sites in Table 1 except for both hands and throat for site 6 and for throat at site 4. The largest mean increase (4.4 ng $wipe^{-1}$) was seen for hand wipes at site 5. There was again no significant difference between provinces.

Analysis of particulate matter for 28 pumps identified five samples positive for benzo(*b*,*j*,*k*)fluoranthene. One of these also had detectable amounts of pyrene and benzo(*a*)pyrene. The five pumps with benzo(*b*,*j*,*k*)fluoranthene were all in Alberta (sites 1 and 2). Only phenanthrene was found in the analysis of the gaseous phase, on nine pumps, from sites 2, 3, 4, and 11 from Alberta and on one pump from site 7 in British Columbia. Samples with no concentration above the LoD were estimated by beta-substitution. Mean values for the 28 pumps for benzo(*b*,*j*,*k*)fluoranthene and 24 for phenanthrene are shown in Table 2. The concentrations for the pumps were then used to estimate exposure for the whole crew working alongside the pump carriers. The mean of all the pumps at that work site was used as an estimate of air PAH concentration. The means of these estimates are also shown in Table 2. The estimates of PAH concentration were significantly higher for the Alberta crews.

There were 42 firefighters allocated to the enhanced hygiene arm, for which the primary outcome was the change in 1-HP concentration between end of shift and next morning urine samples. PAHs that had been deposited on the skin during the fire day and which remained on the skin would continue to be absorbed between the end of shift and next morning urine sample. The 1-HP concentration in the next morning sample should be lower than the end of shift, reflecting the short first phase half-life for PAHs absorbed during the fire day, but will be increased by any post-shift skin absorption. The effect of enhanced skin hygiene would be to reduce this skin absorption post-shift and so increase the net difference between post-shift and next morning 1-HP concentrations. This analysis is summarized in Table 3 which stratifies participants into those with and without naphthalene on skin wipes taken at the end of shift: those without any PAH on their skin would be less likely to benefit from enhanced hygiene measures. One firefighter

Table 3. Effect of enhanced hygiene on next morning urinary 1-HP stratified by presence of PAH on skin wipes.

Change in 1-HP concentration (ng g^{-1}) between post-shift and next morning samples							
Enhanced hygiene	**All**	**Any naphthalene on either skin wipe**		**Any naphthalene on hands**		**Any naphthalene on throat**	
		No	**Yes**	**No**	**Yes**	**No**	**Yes**
Normal							
Mean	31.1	46.5	19.6	51.8	9.2	42.0	20.8
SD	56.1	60.6	51.0	58.3	45.2	58.4	53.5
N	35	15	20	18	17	17	18
Enhanced							
Mean	50.5	51.2	49.7	45.4	57.5	54.6	43.0
SD	61.1	65.6	53.1	73.3	40.4	62.9	59.8
N	31	16	15	18	13	20	11
Overall							
Mean	40.2	48.9	32.5	48.6	30.1	48.8	29.2
SD	58.9	64.3	53.3	65.3	49.2	60.4	56.0
N	66	31	35	36	30	37	29
P (*t*-test of difference between enhanced or not)	0.185	0.884	0.099	0.722	0.005	0.536	0.310

Table 4. Effect of respirator use on change in 1-HP (post–pre fire day) and reports of cough.

Mask worn	Change in 1-HP (post–pre) (ng g^{-1})			Bothered by cough since start of shift (visual analogue scale)		
	Mask type			Mask type		
	N95	P100	Both	N95	P100	Both
No mask						
Mean	76.1	76.1	76.1	26.3	26.3	26.3
SD	101.3	101.3	101.3	27.9	27.9	27.9
N	45	45	45	58	58	58
Mask ≤90% of shift						
Mean	63.3	54.9	57.3	15.8	15.6	15.7
SD	117.2	90.9	88.4	20.4	23.8	20.9
N	2	5	7	5	5	10
Mask >90% of shift						
Mean	27.0	33.4	29.6	14.8	12.0	13.7
SD	44.4	66.9	52.1	13.6	9.7	11.9
N	7	5	12	9	6	15
P (ANOVA)	0.461	0.614	0.305	0.360	0.350	0.147
P for linearity	0.270	0.326	0.126	0.172	0.156	0.058

who had smoked tobacco post-shift was excluded. It was observed that, overall, those in the enhanced hygiene group had a greater difference between post-shift and next morning 1-HP concentration, (normal hygiene 31.1 ng g^{-1} creatinine; enhanced hygiene 50.5 ng g^{-1} creatinine) but that this difference was significant only for those with naphthalene detected on the end of shift hand skin wipe. Those in the normal hygiene group without PAH on the skin wipe had a higher net excretion than those with positive skin wipes. In contrast, in the enhanced skin hygiene group there was no difference between those with and without PAHs on their skin at end of shift, suggesting that the hygiene measures had largely been successful in reducing post-shift skin absorption.

Firefighters had been randomly allocated to the enhanced hygiene arm when they finished their shift and in the analysis in Table 3 it was assumed that those in the two arms had similar post-shift 1-HP concentration. Overall this was the case, with the enhanced hygiene group having a mean post-shift concentration of 199.5 ng g^{-1} creatinine and the regular hygiene group 177.2 ng g^{-1} creatinine ($P = 0.395$). By chance, in the group of particular interest (those with PAHs detected on skin wipes at the end of shift) this difference was more marked, with the enhanced hygiene group having an end of shift mean of 212.1 ng g^{-1} creatinine and the regular hygiene 140.5 ng g^{-1} creatinine ($P = 0.034$). To allow for this a regression was carried out with next morning 1-HP as the dependent variable and end of shift and enhanced hygiene (yes/no) as predictors. With this allowance for end of shift concentration, the effect of the enhanced hygiene was reduced with $P = 0.073$ ($P = 0.036$ one-sided).

Among the 25 allocated to wear a mask, the outcome of prime interest was a reduction in the increase between post-shift and pre-shift 1-HP concentration, compared with those not wearing respiratory protection. Three firefighters from British Columbia who wore their own respiratory protection were omitted from this analysis. Table 4 shows changes in 1-HP post–pre shift (e.g. the difference between values at the end of shift and those before starting work) for those who were not allocated a mask, for those allocated a mask but discarded it before completing 90% of the shift and those who wore it essentially throughout. These data are shown overall and by mask type. A trend towards a lower rise in 1-HP with greater use of mask is apparent and approaches statistical significance on a one-sided test for linearity ($P = 0.063$). A similar trend is seen with reports of being troubled by cough, as reported on a visual analogue scale in the next morning questionnaire (see Supplementary Material 4). The decrease in cough overall shows a trend ($P = 0.029$, one-sided) with those wearing a mask being less bothered by coughing.

Ideally, the analysis of the impact of the mask on changes in 1-HP would have been considered separately for those crews in which PAH had been detected in air and those where it had not, with greater effect on 1-HP being expected where PAHs had been detected. The numbers of participants wearing respiratory protection were too small to allow a full analysis, but it was possible to compare changes in 1-HP for those wearing a mask (of either type) >90% of the time with all others. In firefighters from crews in which PAH had been detected by air monitoring, those with masks ($N = 6$) had lower mean changes in 1-HP (36.7 ng g^{-1} creatinine) than those with no or less mask use ($N = 27$), who had a mean change of 101.9 ng g^{-1} creatinine ($P = 0.137$). In areas in which no PAH was detected in air, a non-significant difference was again seen (masks: $N = 6$ mean 22.6 ng g^{-1} creatinine; no mask $N = 22$ mean = 45.3 ng g^{-1} creatinine $P = 0.579$).

Table 5 examines factors associated with the concentration of 1-HP in the post-shift urine sample and of naphthalene in the post-shift skin wipes, with the hand wipe data only shown in the table. In a univariate analysis, accounting for clustering within crew, post-shift urinary 1-HP was strongly related to 1-HP in pre-shift urine for the same participant. It was also related to estimated PAH concentration both in the particulate and gaseous phase. It was not associated with the other factors considered, including post-shift naphthalene on skin wipes, the task of hot spotting, length of shift, or the sex of the firefighter. In the multivariate model, only pre-shift urinary 1-HP and PAH (phenanthrene) in the gaseous phase remained significant: concentration of PAH in particulate samples did not add to the model. The multilevel model also provided a more formal evaluation of the effect of wearing a respirator. As indicated in Table 4, wearing a mask was associated with a smaller increase in urinary 1-HP post-shift but with few wearing a mask in this pilot intervention, this difference did not reach statistical significance in the full model.

The univariate analysis of post-shift naphthalene on hand skin wipes showed no relation to PAHs in the breathing zone or to post-shift urinary 1-HP. Again, the concentration was unrelated to length of shift or gender. It was related to pre-shift naphthalene on hands, to post-shift naphthalene on the jaw/throat and to the task of hot spotting. In the multivariable model all three of these factors retained or increased (hot spotting) their significance.

Table 5. Linear regression models of exposure markers related to post-shift urinary 1-HP and post-shift naphthalene on hands.

Exposure marker	Post-shift urinary 1-HP (ng g^{-1})						Post-shift naphthalene on hand skin wipe					
	Univariate[a]			Multivariable[a]			Univariate[a]			Multivariable[a]		
	β coeff	95% CI	*P*	β coeff	95% CI	*P*	β coeff	95% CI	*P*	β coeff	95% CI	*P*
Pre-shift urinary 1-HP	0.76	0.48 to 1.03	<0.001	0.77	0.43 to 1.10	<0.001	−0.00	−0.01 to 0.00	0.803	—	—	—
Post-shift urinary 1-HP	—	—	—	—	—	—	−0.00	−0.00 to 0.02	0.600	—	—	—
Pre-shift naphthalene (hands)	−1.7	−21.4 to 17.9	0.862	—	—	—	0.80	0.67 to 0.93	<0.001	0.50	0.32 to 0.68	<0.001
PAH particulates	975.7	464.6 to 1487.0	<0.001	325.1	−346.9 to 997.1	0.343	−6.1	−13.8 to 1.6	0.120	—	—	—
PAH gaseous	413.1	121.7 to 705.6	0.005	318.2	67.1 to 569.2	0.013	0.03	−3.67 to 3.72	0.988	—	—	—
End of shift naphthalene (hands)	−5.9	−25.5 to 13.6	0.552	—	—	—	—	—	—	—	—	—
End of shift naphthalene (throat)	2.3	−13.0 to 17.6	0.767	—	—	—	0.66	0.56 to 0.76	<0.001	0.29	0.14 to 0.44	<0.001
Task: hot spotting	50.6	−23.8 to 124.9	0.183	—	—	—	1.17	0.28 to 2.03	0.010	0.53	0.20 to 0.86	0.002
Length of shift (h)	−2.6	−20.5 to 15.3	0.774	—	—	—	0.02	−0.16 to 0.19	0.859	—	—	—
Gender—female	16.0	−49.6 to 81.6	0.632	—	—	—	0.02	−0.64 to 0.68	0.954	—	—	—
Mask 1—90% shift				−42.8	−122.2 to 36.5	0.290						
Mask > 90% shift				−19.0	−68.7 to 30.3	0.450						
Constant	—	—	—	−26.7	−89.8 to 36.5	0.409	—	—	—	−0.10	−0.37 to 0.18	0.492
N: participants	59–66			57			65–84			81		
N: crews	11–13			11			11–13			13		

[a]Adjusting for clustering within work crews.

Discussion

The aims of this field study were, first, to quantify PAH exposures in wildland firefighters and, second, to pilot interventions that might be used to reduce absorption of PAHs over the course of a fire season. The results demonstrate quantifiable PAHs in the breathing zone of many, but not all, of the work crews, and on the skin, post-shift, of about half. The PAHs found were comparable to those of Navarro *et al.* (2017, 2019) who reported that naphthalene, phenanthrene, and retene (not measured here) were the highest PAHs measured for wildland firefighters. Among the 66 firefighters whose urinary creatinine was within the acceptable range, 76% had a higher 1-HP at the end of shift indicating the ubiquity of exposure. It was also clear that 1-HP concentrations post-shift did not return overnight to pre-shift levels, suggesting that exposures were sufficient to accumulate over repeated days of exposure (consistent with the ACGIH (2017) PAH review). The information from the two interventions was also informative. Within the limits of sample size, there was reduced absorption of PAHs in those wearing masks and, for those with PAH skin contamination, the enhanced hygiene intervention decreased absorption post-shift.

The study has strengths in that it contributes to a sparse literature on PAH exposure in wildland firefighters, and does so by including crews working on a variety of tasks under different conditions, including prescribed burns of grass and scrub, hot spotting after a major fire in a coniferous forest, and containing active fires. A weakness is that, in a quiet fire season, advantage had to be taken of every opportunity to study an active fire crew, including some workdays that were likely to involve low exposures. The values for 1-HP found here are lower than those reported by Adetona (2019) who found mean post-shift concentration of 402.9 ng g^{-1} creatinine, more than twice the mean (187.1 ng g^{-1} creatinine) in the present study. The pre-shift concentrations in Adetona's study were high also (236 ng g^{-1} creatinine), suggesting that the 'burn days' monitored were preceded by significant PAH exposures. While the concentrations in the present study were low, their median concentration (174.3 ng g^{-1} creatinine) was higher post-shift than for the general public aged 20–39 years (smoking status unspecified) in the 2012–2013 Canadian Health Measures Survey (Health Canada) where the median concentration was 99 ng g^{-1} creatinine [95% confidence interval (CI) 87–111]. A further limitation was that it was not practicable to recruit only firefighters who came to the study after a rest period: many may have come to the study carrying, on their clothes or person, PAHs from other recent fires: the strongest predictors of post-fire 1-HP and naphthalene were the levels prior to starting the fire day. Moreover, with only 13 work crews there was considerable possibility of statistical confounding: no-one in the two crews with measured particulate PAH in air were employed in hot spotting, for example, and so this relation could not validly be explored.

A major limitation of the study lies in the relative insensitivity of the analysis of PAHs in the breathing zone. Navarro *et al.* (2017) had limits of detection of 1.71–7.14 ng m^{-3} compared with 156 ng m^{-3} in the present study. Many of the PAHs reported by Navarro *et al.* had a maximum value below our LoD and so, for these PAHs, all samples would have been non-detected had she used the analytic methods used in this study. The choice of a laboratory for analysis of the air samples was based on its excellent reputation for the analysis of workplace samples, where the prime concern is to determine whether exposure approaches current exposure limits and there is little need to detect concentrations far below these. For better quantifying exposures, lower limits of detection would have been helpful. Further, although US Environmental Protection Agency (EPA) suggests a list of 16 PAHs to be assessed (ASTDR, 1995), not all were covered in the analysis of PAHs either in the breathing zone or on skin wipes in this study. Naphthalene was not included in the panel of substances analysed in air samples. Its omission was unfortunate, given that it was the PAH most commonly found on skin wipes (and that it was detected in all air samples in the Navarro (2017) study). Conversely Navarro *et al.* did not measure phenanthrene in the gaseous phase but found it on particulates (with a LoD <1 ng m^{-3}) in all of their wildland firefighter samples. Although we have estimated exposures based on the data we have available, the high numbers below the LoD/quantification introduce uncertainty.

It should be recalled that the study was designed to demonstrate the presence of PAHs in the air and on the skin, rather than to investigate the relation between them. The analysis presented in Table 5, showing that increase in 1-HP post-shift is related to phenanthrene in the gaseous phase, was conducted to demonstrate the potential strength of such a design. It appears to be the first such analysis in wildland firefighters, with previous studies reporting either on PAH in air (Navarro 2017, 2019) or on biomarkers in urine (Adetona *et al.*, 2017, 2019), but not both. The lack of a demonstrated relationship between airborne PAH and changes in skin wipe naphthalene seems likely to reflect the insensitivity of the air sample analysis (and the absence of naphthalene from the panel of substances analysed) rather than

a true negative. Nevertheless, it is possible that particulates accumulating on the skin during hot spotting, for example, are not well represented in the breathing zone.

The long-term interest of the study is to find ways to reduce exposures to PAHs over the course of repeated deployments during a fire season. Unlike many workers exposed to PAHs and who may (at least in more affluent societies) work 8-h shifts in a 5-day work week, wildland firefighters may be required to work long shifts over many days particularly, but not only, during a season of massive poorly controlled fires. The data we have collected are relevant but almost certainly underestimate exposures under extended conditions where smoke exposure may be difficult to avoid, both while fighting fires and during rest/sleep periods and the opportunities to wash and change clothes may not be a high priority for the firefighters or management team. We have shown here that the enhanced hygiene intervention was effective in this study for those with skin contamination. With extended deployment it seems likely that all firefighters would become contaminated and benefit from better skin hygiene. The suggestion that some sort of respiratory protection worn by wildland firefighters might reduce exposures to particulates and other potential hazards, including PAHs, causes heated discussion among wildland firefighters. The data presented here, although based on small numbers, suggest that a mask, if worn, would result in lower absorption and reduced respiratory irritation, reflected in reports of less troublesome cough. In planning any larger scale trial of interventions over a complete fire season, the practicalities of the firefighters' job demands need to be considered in the recommendation of a trial of respiratory protection.

The drive to reduce PAH absorption to levels as low as reasonably practicable arises from concerns about carcinogenicity. With increasing frequency and intensity of wildfires the case for protecting firefighters from carcinogens will become more vocal. Many jurisdictions accept certain types of cancer as being occupationally related to the job of a structural firefighters, with PAH exposure as one putative cause. Although the evidence for firefighting as carcinogenic for humans was assessed as limited by the International Agency for Research on Cancer (IARC, 2010), it would be wrong to interpret this as implying no risk. PAHs are not the only hazard to wildland firefighters (e.g. repeated exposure to smoke particulates may relate to non-malignant lung disease) but interventions to reduce PAH absorption are supported by the pilot interventions reported here and warrant further evaluation across a full fire season.

Supplementary Data

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

Funding

The work in Alberta was funded by the OHS Futures Program of the Department of Employment. The work in British Columbia was funded through a grant from the BC Wildfire Service to Canada Wildfire at the University of Alberta.

Acknowledgements

The study was carried out in collaboration with Alberta Wildfire and the British Columbia Wildfire Service. The views expressed are those of the authors. Shannon McCormick, Chris Morgan, and Laura Rodgers carried out the fieldwork in Alberta, with Chris Morgan taking the lead in BC. Levi Kimble and Taryn Toic of Aura Health and Safety Corporation contributed to the fieldwork in BC. Laura Rodgers also liaised with the Alberta Centre for Toxicology for the delivery of samples from the field.

Ethical approval

The study was approved by the health ethics board of the University of Alberta (Pro00089347). All participants gave written consent.

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