Polycyclic aromatic hydrocarbons in the firefighter workplace: The results from the first in Poland short-term measuring campaign

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Abstract. The results of investigations into 15 ambient polycyclic aromatic hydrocarbons at two Polish fire stations belonging to the National Fire Service are presented. At each station, on five different days, hydrocarbons were sampled simultaneously in the changing room, garage, and exterior of the station (in the atmospheric air). The indoor and outdoor diagnostic ratios and benzo(a)pyrene carcinogenicity equivalents were computed from the measured concentrations. The former indicated the combustion of various materials and fuels as the hydrocarbons source, the latter expressed the cumulative carcinogenic hazard from the hydrocarbon mixture. Naphthalene and acenaphthene had the greatest ambient concentrations at each site. The greatest summary concentrations of the 15 hydrocarbons occurred in the changing rooms.

1 Introduction

Since the early 1980s in the United States, and since the beginning of the 21st century in other countries, the firefighter occupational health hazard has been comprehensively studied not only as direct endangerment of life and health in a firefighting situation, but also as a hazard from exposure to hazardous substances, which are often carcinogenic [1-10]. Despite the use of personal protection equipment, the danger of exposure of a firefighter to extremely high concentrations of toxic substances is great, and although its duration is usually short, it can be very intense and occur many times in the career of a firefighter. However, the cumulative health effects of such multiple acute exposures are hard to trace back to their causes, usually distant in the past and not recorded.

Smoke emitted by a fire contains carcinogens [11-15]. From among the polycyclic aromatic hydrocarbons (PAHs) released into the air in vast amounts during a fire, are benzo[a]pyrene, which is carcinogenic to humans, dibenz[a,h]anthracene which is most likely carcinogenic, and benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene,

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benzo[k]fluoranthene, chrysene, indeno[1, 2, 3-c,d]pyrene, and naphthalene which are possibly carcinogenic [16, 17]. Although direct contact with these PAHs and the presence of their metabolites in the organisms of firefighters taking part in firefighting has been proved [e.g. 6, 7, 10], the linkage of lung cancer incidence among firefighters with their occupation was considered as inconclusively proven for quite a long time [16, 17]; and only lately and cautiously, the lung cancer incidence rate among career firefighters was considered essentially higher than in the normal population [4, 5, 18-31].

A firefighter can be exposed to very high concentrations of various products of combustion and pyrolysis, including PAHs both in its gaseous phase and adsorbed on ambient particulate matter (PM-bound) not only during firefighting operations and training, but also afterwards as a result of contact with contaminated protective gear. Firefighting gear can be contaminated with combustion products whose later off-gassing can result in inhalation exposure [23]. Some volatile organic compounds, generated during controlled structure burns, can later be off-gassed by the firefighters' protective gear and be absorbed and exhaled in their breath [5, 24, 25]. Benzene and some PAHs, despite turnout gear, most likely enter firefighters' bodies through their skin. PAHs can be absorbed dermally during firefighting or inhaled during the doffing of gear that has off-gassed contaminants [5, 26]. However, even the application of cleansing wipes to PAH contaminated skin can be ineffective [27]. Therefore PAHs, mainly gaseous, contaminate firefighter turnout gear and skin and are off-gassed later in the fire truck cab and in the fire station [28]. They contribute to the occupational health hazard for firefighters on duty when they are not fighting a fire and can have long-term health effects.

The goal of the work was to determine the ambient concentrations of selected gaseous PAHs in two rooms of a fire station staffed by career firefighters, a garage and changing room, and compare them with the outdoor concentrations of these PAHs.

2 Experimental

Both fire stations of interest, one (FSS) located in the southern part of Poland and the other (FSN) in the northern part, belonged to the National Fire Service and were staffed by career firefighters. The atmospheric air quality between the location sites differ greatly [32]. At each fire station, five four-hour long air sample-takings were performed in March and April 2018. Each taking of a sample started in the morning at shift change, when one crew was leaving and the next crew was taking their gear from the changing room. A single taking of a sample consisted of drawing air at 2000 cc/min through sorption tubes filled with Amberlite XAD2 (SKC) resin using 3 GilAir® Plus Personal Air Sampling Pumps (Sensidyne, USA) simultaneously in the changing (locker) room, garage, and outside the building. In each garage the watch room was located where firefighters were on duty 24 h a day. Neither the garages nor changing rooms were equipped with air conditioning; they had gravitational ventilation. At both stations, the entrance to the gym was from the changing room.

The PAHs adsorbed on the XAD-2 bed were extracted. Each tube (sample) was broken and the exposed XAD-2 was placed in a glass vial containing 5 ml of acetonitrile (CH₃CN, J.T.Baker™) and kept in an ultrasonic bath for 30 minutes. The extract was filtered through a membrane filter (PTFE, 45µm) and the filtrate was concentrated in a nitrogen stream to 0.5 ml (MultiVap, LabTech Co.). The PAH content of the concentrated extract was determined by means of high-performance liquid chromatography (HPLC) using a Surveyor Finningan chromatograph with a UV/Vis LC detector, PAH LC Column (ID 31105-254630), and ChromQuest software (each from Thermo Scientific). The mobile

phase (acetonitrile aqueous solution 60:40 v/v) flow rate was 1.2 ml/min, the wavelength used was 254 nm.

The following 15 PAH were determined: naphthalene (Na), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (F), pyrene (Py), benzo[*a*]anthracene (BaA), chrysene (Ch), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-*c,d**]pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP). The calibration curve was plotted for each PAH separately using a standard mixture of 16 PAHs (610 PAH Calibration Mix A, RESTEK) containing each compound at a known concentration. The limit of detection for each PAH was 0.2 ng/ml.

3 Results and discussion

The means and standard deviations of all five-element PAH concentration series are presented in Table 1. In Figure 1, the PAH profiles in the rooms and in the atmospheric air at each site are presented.

At both sites, the greatest average concentration of the sum of the 15 PAHs (ΣPAH) occurred in the changing rooms. At FSN, the ΣPAH concentration was higher in the garage than outside; at FSS, the ΣPAH concentration was lower in the garage. The ambient air in the southern part of Poland is more polluted with PM-bound PAHs than the air in the northern part [32]. The values of the ΣPAH concentrations from Table 1, two times greater at FSS than at FSN, may suggest that the situation with gaseous PAHs is similar, but such a generalization is not allowed as they result from a very short measuring session. Also, the variability of the measured concentrations (great standard deviations, Table 1) means the possibility of an occurrence of entirely different PAH concentrations at both sites during another measurment period. In Poland, ambient gaseous PAHs have not been investigated, thus there are no data for comparison for the results received in this study.

Table 1. Mean indoor (changing room, garage) and outdoor (atmospheric air) concentrations of gaseous PAHs (ng/m³) at two fire stations in Poland.

FSN	Changing room		Garage		Outdoor	
	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.
naphthalene (Na)	3620	786	2764	1384	1084	1580
acenaphthene (Ace)	869	453	646	966	352	324
fluorine (Fl)	175	128	27	15	10	10
phenanthrene (Phe)	109	14	39	5	38	7
anthracene (Ant)	14	2	0	0	0	0
chrysene (Ch)	30	1	0	0	0	0
fluoranthene (F)	118	10	27	4	38	13
pyrene (Py)	49	7	16	2	4	7
benzo[<i>a</i>]anthracene (BaA)	17	2	0	0	0	0
benzo[<i>b</i>]fluoranthene (BbF),	19	2	0	0	0	0
benzo[<i>k</i>]fluoranthene (BkF)	10	1	0	0	0	0
benzo[<i>a</i>]pyrene (BaP)	3	6	1	2	3	5
dibenzo[<i>a,h</i>]anthracene (DahA),	6	6	1	2	11	19
benzo[<i>g,h,i</i>]perylene (BghiP)	0	0	0	0	0	0
indeno[<i>1,2,3-<i>c,d</i></i>]pyrene (IcdP)	10	8	0	0	0	0
ΣPAH	5047	1428	3522	2380	1540	1964
FSS	Changing room		Garage		Outdoor	
	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.
naphthalene (Na)	3327	624	1738	1151	2006	2206
acenaphthene (Ace)	1972	784	21	29	478	646

fluorine (Fl)	242	78	76	88	162	215
phenanthrene (Phe)	129	128	83	106	147	167
anthracene (Ant)	58	58	11	19	32	45
chrysene (Ch)	25	22	10	18	11	19
fluoranthene (F)	95	116	65	87	119	115
pyrene (Py)	52	46	33	31	13	23
benzo[a]anthracene (BaA)	18	16	6	11	21	20
benzo[b]fluoranthene (BbF),	7	12	5	8	0	0
benzo[k]fluoranthene (BkF)	9	8	17	7	3	6
benzo[a]pyrene (BaP)	2	4	0	0	3	5
dibenzo[a,h]anthracene (DahA),	2	2	0	0	0	0
benzo[g,h,i]perylene (BghiP)	6	10	0	0	0	0
indeno[1,2,3-c,d]pyrene (IcdP)	4	7	0	0	0	0
ΣPAH	5948	1915	2066	1556	2995	3468

Fig. 1. Mean profile of gaseous PAH in indoor (changing room, garage) and outdoor (atmospheric) air at two fire stations in Poland: FSN (a) and FSS (b).

The standard deviations of the PAH concentrations in the changing rooms are relatively small compared to those for the garages and exterior, and their proportions to the means are also small (Table 1). They allow the belief that the gaseous PAH concentrations are always relatively high in both changing rooms. Almost all the measured PAHs occurred in the gaseous phase in the changing rooms while some heavier, 4-, 5-, and 6-ring ones, were not detectable in the atmospheric air.

At FSS, the majority of the PAHs had greater concentrations and more of them were detectable, both inside and outside. Therefore, the PAH profiles differ respectively pairwise between FSS and FSN; 3-, 4-, and 5-ring PAHs had greater shares in ΣPAH at FSS than at FSN (Figure 2). Not surprisingly, the shares of 2-ring naphthalene and of all 3-ring PAHs dominated everywhere: 4-, 5-, and 6-ring PAHs occur in the air mainly as compounds bound to ambient particulate matter (PM-bound) [33], they contributed very little to the samples. However, being present in the air, they contribute to the health hazard and indicate the origins of PAH. To be able to adequately determine PAH origin, e.g. using diagnostic ratios (proportions of concentrations; DRs), and to have a comprehensive view of the health hazard from ambient PAHs in the fire stations, one should repeat the experiment and measure both gaseous and PM-bound PAHs. When only gaseous PAHs are measured, only the DRs computed from their concentrations are available, and here, three such DRs, $F/(F+Py)$, $BaA/(BaA+Ch)$, and $Ant/(Ant+Phe)$, were computed for each sampling site (Table 2). On the one hand they suffice to attribute the PAHs to the combustion of various materials and fuels proof exists that for both phases, gaseous and PM-bound, they are comparable, on the other hand $BaA/(BaA + Ch)$ can be 0.16 for gaseous PAHs and 0.33 for PM-bound PAHs [34-38].

Table 2. PAH diagnostic ratios for the the indoor and outdoor sampling points.

Diagnostic ratio	FSN			FSS			Source of PAH [33]
	Changing room	Garage	Outdoor	Changing room	Garage	Outdoor	
An/(An+Fen)	0.1	0.0	0.0	0.3	0.1	0.2	> 0,1 - petrogenic, 0,24 - coal burning
Flt/(Flt+Pyr)	0.7	0.6	0.9	0.6	0.7	0.9	< 0,4 - unburned petroleum; 0,57 - coal burning; >0,5 coal, grass, wood
BaA/(BaA+Ch)	0.4	-	-	0.4	0.4	0.7	0,46 - coal burning

The carcinogenic hazard from an ambient mixture of PAH can be expressed relative to the carcinogenicity of BaP as the BaP carcinogenicity equivalent (CEQ). CEQ is a linear combination of the ambient concentrations of PAHs from the mixture and their toxicity equivalency factors (TEFs) [39]. The CEQs computed for ΣPAH at FSS and FSN are presented in Figure 2. Although the outdoor ΣPAH concentration at FSS was two times greater than at FSN, the outdoor CEQ, i.e. the outdoor carcinogenic hazard from ΣPAH, is greater at FSN. The CEQ for the FSN changing room is greater than that for the FSS one, and at both sites the CEQ for the changing room is the greatest among all three CEQs. For the garages, conversely, the CEQ for FSS is greater (Figure 2). All this situation is controlled by the ambient concentrations of benzo(a)pyrene and dibenzo(a,h)anthracene (Table 2), which have high TEFs [39], but their occurrence in a gaseous phase can be accidental here, since their distribution between gaseous and particulate phases depends on ambient air conditions [34-38].

Fig. 2. Mean values of the BaP carcinogenicity equivalent for indoor and outdoor ΣPAH at fire stations in two Polish cities.

The firefighters' gear stored in the changing rooms after a firefighting action was the source of indoor PAHs. The firefighters' turnout clothes are washed using special chemicals in special laundries once or twice a month, therefore a majority of the contaminants are removed, but the level of gaseous PAHs in the changing room was still higher than outdoors. Firefighters usually stay in garages and changing rooms for short time, but we can suppose that PAHs from the garage and changing room can pass to adjacent or even further spaces, where people are resting, sleeping, or on duty for 24 h a day (as it is at the alarming posts in the garages).

4 Conclusions

The greatest concentrations of ambient PAHs, greater than in the garages or exterior of fire stations, occurred in the changing rooms where firefighter gear is stored after firefighting. Among the determined 15 PAHs, semivolatile naphthalene and acenaphthene had the greatest concentrations. According to the diagnostic ratios, the combustion of various materials and fuels was the PAH source at each site.

The conclusions from the investigations are following:

- Some PAHs contaminate firefighter gear during firefighting and are off-gassed while the gear is stored in a changing room. Decontamination of the firefighters' turnout gear after each action should decrease the indoor PAH levels at fire stations.
- Firefighter gear should be stored and handled in well-ventilated rooms. No turnout gear should be allowed in dormitories, gyms, kitchens, etc.
- To determine the actual risk from PAHs in firefighter stations, such measurements as presented here should be carried out in a more extensive form. The concentrations of gaseous and PM-bound PAHs should be measured in all fire station spaces where the crew spend their time, and perhaps in all seasons of the year.

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