Occupational exposure of firefighters to polycyclic aromatic hydrocarbons in non-fire work environments

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GRAPHICAL ABSTRACT

Abstract

This work aims to characterize personal exposure of firefighters to polycyclic aromatic hydrocarbons (PAHs) in non-fire work environments (fire stations), and assesses the respective risks. Eighteen PAHs (16 considered by USEPA as priority pollutants, dibenzo[a,l]pyrene and benzo[j]fluoranthene) were monitored in breathing zones of workers at five Portuguese fire stations during a normal shift. The obtained levels of PAHs fulfilled all existent occupational exposure limits as well as air quality guidelines with total concentrations (ΣPAHs) in range of 46.8–155 ng m− 3. Light compounds (2–3 rings) were the most predominant congeners (74–96% of ΣPAHs) whereas PAHs with 5–6 rings accounted 3–9% of ΣPAHs. Fuel and biomass combustions, vehicular traffic emissions, and use of lubricant oils were identified as the main sources of PAHs exposure at the studied fire corporations. Incremental lifetime cancer risks were below the recommend USEPA guideline of 10− 6 and thus negligible for all the studied subjects, but WHO health–based guideline level of 10− 5 was exceeded (9–44 times) at all fire corporations. These results thus show that even during non-fire situations firefighters are exposed to PAHs at levels that may promote some adverse health outcomes; therefore the respective occupational exposures to these compounds should be carefully controlled.

Keywords: Occupational exposure Firefighters
Polycyclic aromatic hydrocarbons (PAHs) Risk
Indoor air Legislative limits

1. Introduction

Firefighters (IARC, 2010a) represent one of the most hazardous occupation (Baxter et al., 2014). During their professional conduct, firefighters are exposed to a complex mixture of pollutants including particles (fine and respirable particulate matter) and a wide range of gaseous chemicals (such as carbon monoxide and dioxide, nitrogen oxides, carbonyls, volatile and semi-volatile organic compounds; Estrellan and Lino, 2010; Lemieux et al., 2004; Lewtas, 2007; Miranda et al., 2010; Reisen et al., 2006). Among them polycyclic aromatic hydrocarbons (PAHs) are especially relevant due to their mutagenic and genotoxic properties (Annesi-Maesano et al., 2007; IARC, 2002, 2010a, 2010b; Tuntawiroon et al., 2007), some of them being considered as endocrine disrupting chemicals (WHO, 2013). Occupational exposure to PAHs has been associated with increased risks of various cancers (lungs, bladder, skin, urinary and gastrointestinal systems; Boffetta et al., 1997; Diggs et al., 2011; Rota et al., 2014); cell damage via gene mutation (Kamal et al., 2015; Kuang et al., 2013; Poirier, 2004), oxidative stress and cardiovascular diseases (Burstyn et al., 2005; Jeng et al., 2011; Kim et al., 2013; Lee et al., 2011) and cardiovascular mortality (Brucker et al., 2014). Concerning potential exposure and adverse health effects, United States Environmental Protection Agency (USEPA) has identified 16 priority congeners (USEPA, 2014).

From chemical perspective, PAHs are compounds containing only hydrogen and carbon that are composed of multiple aromatic rings. They are abundant in soils and marine sediments, fresh water, and in atmosphere where the more health hazardous congeners (WHO, 2010) are predominantly bound to fine (i.e. $PM_{2.5}$) particles (Castro et al., 2011; Slezakova et al., 2011, 2013b). Fire emissions and smoke are the most relevant sources of PAHs exposure for firemen (Booze et al., 2004; Fent et al., 2013, 2014; Kirk and Logan, 2015a), but the compounds are formed by other man-made sources such as industrial processes, incinerators, coal-fired boilers and power plants, and last but not least, by traffic emissions (Hanedar et al., 2014; Ravindra et al., 2008; Slezakova et al., 2013a, 2013b). In confined spaces, second–hand tobacco smoke, combustion emissions (from cooking stoves and fireplaces) and infiltration of ambient air emissions are responsible for the presence of PAHs (Chen et al., 2012; Qi et al., 2014; Shen et al., 2012; Slezakova et al., 2014). The toxicity of PAHs is largely attributed to their reactive oxygenated metabolites, potential of causing oxidative stress (Kamal et al., 2015) and the adducts of their metabolites with DNA (Rengarajan et al., 2015). The DNA-binding is considered to be essential for the carcinogenic effect (Pratt et al., 2011; Tarantini et al., 2011) with DNA adducts being identified in various human tissues (Ziech et al., 2011); cancer is the primarily risk for PAHs exposure (Boström et al., 2002; Kim et al., 2013) and in that view International Agency for Research on Cancer (IARC) has categorised benzo[*a*]pyrene (B[*a*]P; a marker of PAHs exposure) as known human carcinogen (Group 1) (IARC, 2010b) whereas other congeners are classified as probable and/or possible ones (Group 2A and 2B, respectively). Further scientific evidence has also linked exposure to PAHs with cardiovascular diseases (Lewtas, 2007; Korashy and El-Kadi, 2006). Adverse health outcomes (hemotoxicity and carcinogenicity; Fabian et al., 2014; Fent and Evans, 2011; Robinson et al., 2008) and also excess morbidity and mortality have been reported for firefighters' occupational exposure, with cardiovascular diseases being the primary cause for the deaths (in approximately 45% of firefighters) and a major cause of the increased morbidity (Gaughan et al., 2014a, 2014b; Soteriades et al., 2011); the additional exposure to PAHs may promote and/or worsen the existent cardiovascular diseases of firefighters (Lewtas, 2007). Because of the relevance of this topic, data regarding firefighters' exposure to PAHs have been emerging. The most extensive studies that assessed exposures in various combat situations and scenarios (i.e. training sessions, mainly prescribed burns management, suppression and overhaul of controlled structure burns) have been conducted in USA (Baxter et al., 2014; Bolstad-Johnson et al., 2000; Booze et al., 2004; Fent et al., 2013, 2014; Fent and Evans, 2011; Pleil et al., 2014; Robinson et al., 2008) and Australia (Kirk and Logan, 2015a). In addition, some authors reported that fire-generated contaminants were tracked back to fire stations through firefighters' protective gear (gloves, boots and turnout equipment) and vehicles (Alexander and Baxter, 2014; Fabian et al., 2014; Fent et al., 2013; Kirk and Logan, 2015a, 2015b; Laitinen et al., 2010; Shen et al., 2015) but only few studies investigated occupational exposure to PAHs at fire stations (being mainly conducted in USA). Due to the geographical differences such different materials and construction techniques used for building houses and structures, and due to differences in the firefighting practices (which can influence the smoke emissions and consequently the respective exposure; Reinhardt and Ottmar, 2004; Reisen and Brown, 2009; De Vos et al., 2009), these reported exposure data may be significantly different from those of European firefighters. Furthermore, the seasonal trends of PAHs (Liu et al., 2008; Melymuk et al., 2012; Ravindra et al., 2006) may lead to further differences. This study aimed to investigate firefighters' exposure to

PAHs in work (non–fire incident) settings. The levels of 16 PAHs considered by USEPA as priority pollutants, dibenzo[*a*,*l*]pyrene (D[*a*,*l*]P) and benzo[*j*]fluoranthene (B[*j*]F; a monitoring is suggested by Directive 2004/107/EC, 2005) were measured in the breathing air zone of firefighters in five Portuguese municipalities. The potential emission sources in the work settings were identified by diagnostic ratios and the occupational risks due to PAHs exposure in the respective environments were assessed.

2. Material and methods

2.1. *Sample collection*

Portugal belongs to the five Southern European Member States which every year suffer the most forest fires (Joint Research Centre, 2011). Typically, central and northern region of the country are affected the most by forest fires; in 2014 these two regions exhibited a burnt area of 14,938 ha (~ 75% of the total) with northern region also registering the prevailing number of fire occurrences (40% of the total number of fires) (Joint Research Centre, 2015). The sample collection was thus conducted in northern region in Braganza district (Fig. 1) where annual average air temperature was 12.7 °C and precipitation was 900.2 mm (INE, 2015); summer was hot and dry (average temperature of 28.2 °C, precipitation: 3.6 mm).

The personal sampling was conducted during a period of 28 days (May–June 2014) in subjects (Table 1) who worked as professional firefighters at corporations of five different municipalities: Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), and Alfândega da Fé (AFF). All fire corporations were located in central zones of rather small towns with relatively low populations (between 1212 and 15,776 at IZD and MCC; Table 1) and were considered as urban background sites. Each fire station was composed of track/car garages that were in general indirectly connected with working areas, control room and offices, as well as with an area of living quarters (Figs. 1S and 2S). For each subject, additional information (age, weight, gender, education, duration of employment; Table 1) was collected by means of structured questionnaire (WHO, 2016). All participating firemen were non-smokers. Information on further PAH exposures such as transportation to work, smoking and diet habits were also registered (Table 1) with participants reporting the most frequently consumed meals as: boiled N roasted N grilled.

The study included 18 PM$_{2.5}$–bound PAHs, namely naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fln), pyrene (Pyr), benz[*a*]anthracene (B[*a*]A), chrysene (Chry), benzo[b + j]fluoranthene (B[b + j]F), benzo[*k*]fluoranthene (B[*k*]F), benzo[*a*]pyrene (B[*a*]P), dibenz[*a*,*h*]anthracene (D[*a*,*h*]A), benzo[*ghi*]perylene (B[*ghi*]P), indeno[1,2,3–cd]pyrene (InP), and dibenzo[*a*,*l*]pyrene (D[*a*,*l*]P). Sampling was conducted in breathing zones of the selected subjects during a continuous 4-h period of a regular shift of a single day. The personal sampling ($n = 54$) was done according to USEPA IP-10A method (USEPA, 1990) using a personal environmental monitor (PEM™; SKC Ltd., United Kingdom), i.e. single stage impactor (PM$_{2.5}$) that was placed in breading zone (at height 152–178 cm) of each subject combined with personal air sampling pump (Gilian, model GilAir-3; Sensidyne, USA; air flow rate 2 L min^{-1}) mounted at the waist (total volume of sampled air was 480 L per sample) All subjects moved freely according their needs within the stations and performed regular working tasks as usually. Polytetrafluoroethylene membrane disks (2 μm porosity, Ø37 mm; SKC Ltd., UK) were used for the collection of PM$_{2.5}$. After the sampling, filters were placed in polyethylene containers and stored (at −20 °C) for the chemical analysis.

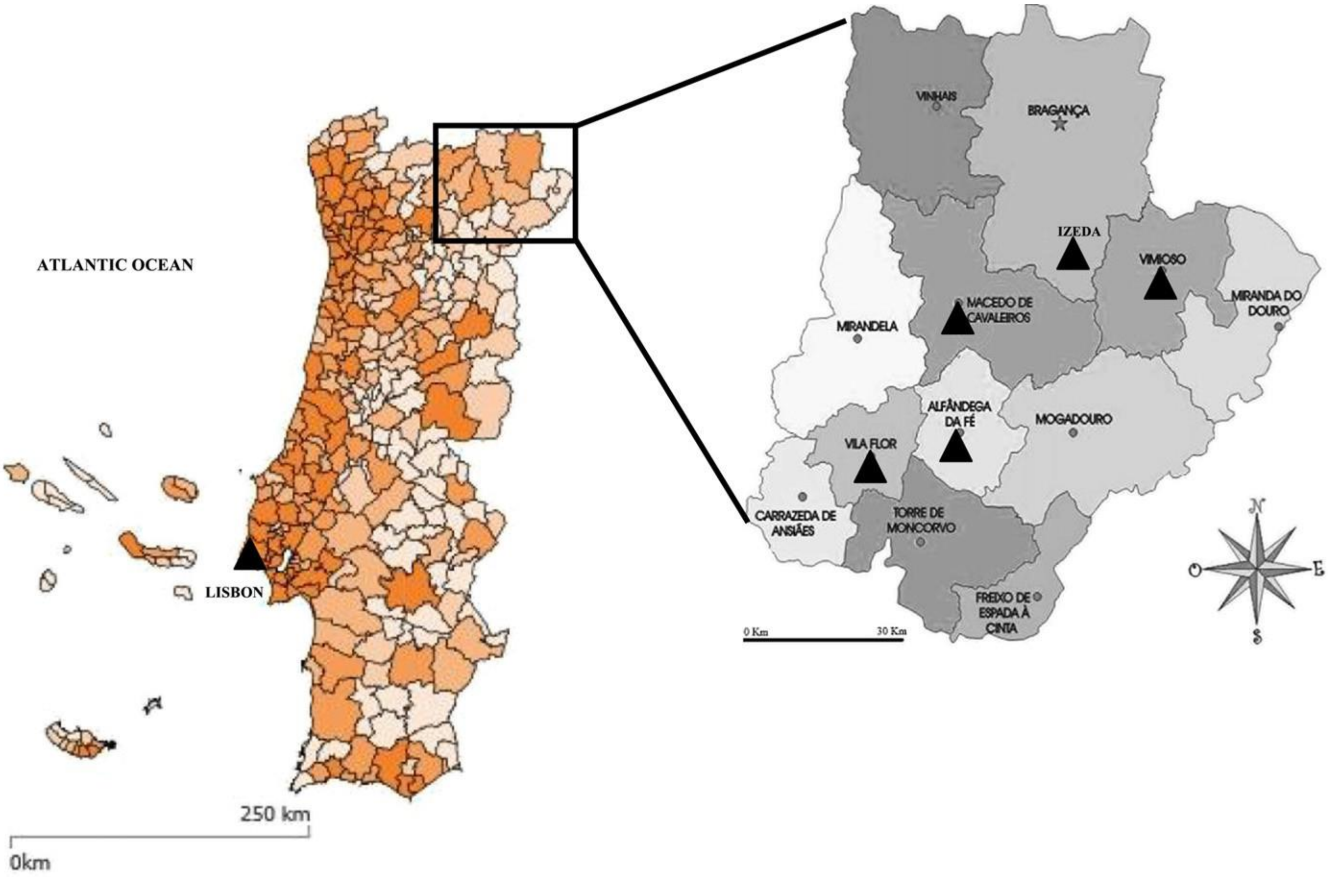


Fig. 1. Geographical representation of the study area.

All firehouses were ventilated by opening windows (when needed); air conditionings systems were not available. Smoking was prohibited in all areas of fire stations (indoor places, garages/ truck bays). During the sampling a record of potential emission sources (vehicles arrivals and/or departures, vehicles and/or equipment maintenances, use of cooking appliances, etc.), and the general activities of the study subjects were recorded (Table 1S of the Supplementary Material).

2.2. *PAHs quantification*

PAHs were determined according to Castro et al. (2009, 2011) that in details describe all steps of the validation of the used analytical method, which consisted of extraction (microwave assisted) and quantification by liquid chromatography with fluorescence (17 compounds) and photodiode array (acenaphthylene) detection. For readers convenience, the information on the analytical procedure and quality control is also presented in Supplementary Material (Section 1S and Table 2S).

2.3. *Risk assessment*

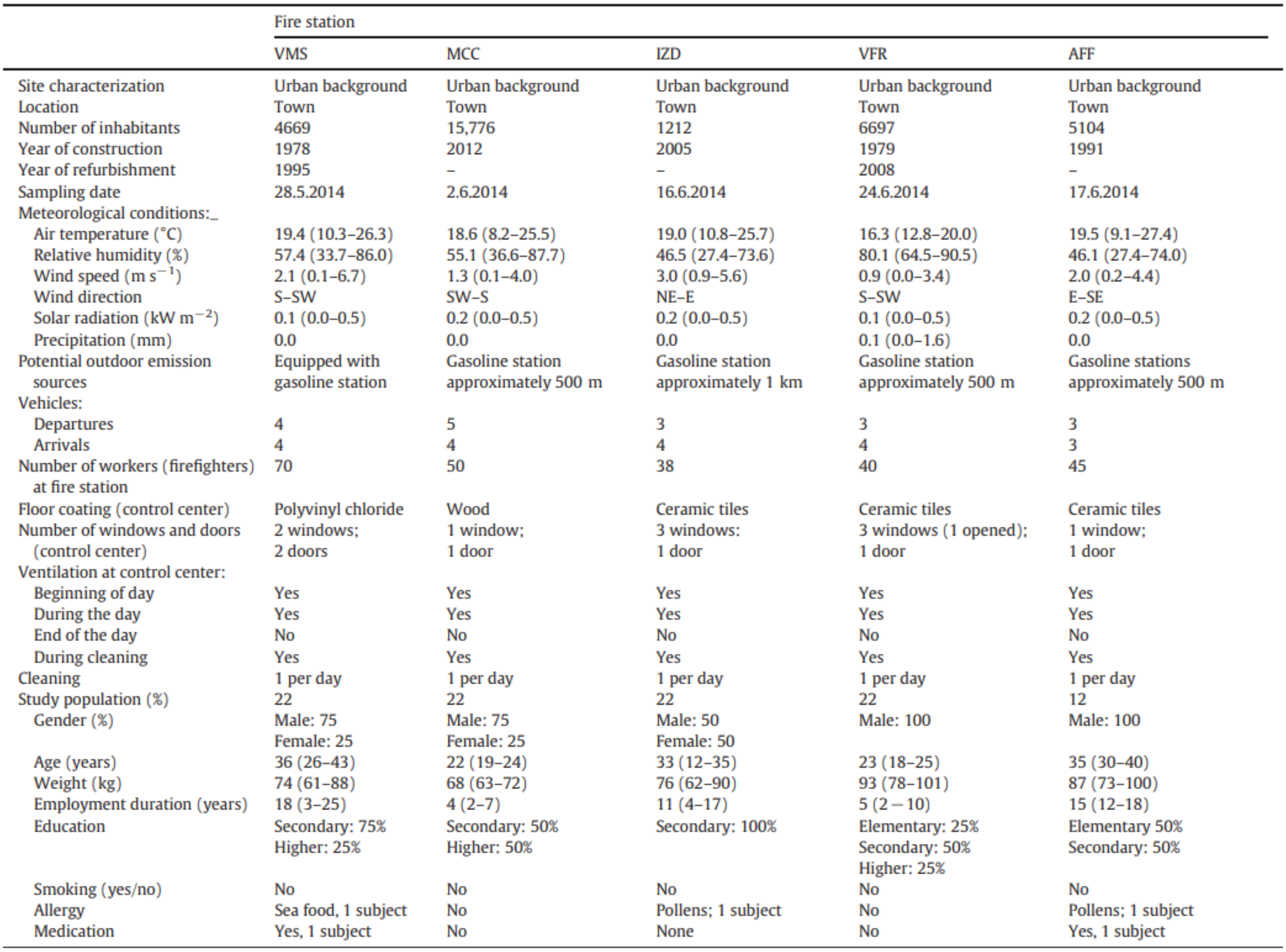
The toxicity equivalent concentrations (B[*a*]P$_{eq}$) based on the toxicity of B[*a*]P were calculated. Toxicity equivalency factors (TEF) proposed by Nisbet and LaGoy (Boström et al., 2002) were used. The excess lifetime risk of lung cancer due to PAH exposure was then estimated by quantitative risk assessment methodology (WHO, 1987, 2000) using unit risk of 8.7×10^{-5} (i.e. 8.7 cases per 100,000 people with chronic inhalational exposure to 1 ng m^{-3} of B[*a*]P over a lifetime of 70 years) and considering 8 h period for a work shift.

The incremental lifetime cancer risks (ILR) from inhalation exposure to particulate PAHs were estimated according to the USEPA methodology (Region III Risk-based Concentration Table; USEPA, 2016); ILR below 10^{-6} are denoted as safe ones, whereas potentially high risks are estimated by values N10^{-4} (USEPA, 1989). The full details of the methodology and the ILR calculations can be found in Oliveira et al. (2016a). The concentrations of PAHs (determined for each subject by personal air sampling) were used and the exposure durations (i.e. years of employment as firefighters), which were obtained for each subject. For reader's convenience, Table 3S demonstrates an example of ILR calculations; default parameters are summarized in Tables 4S and 5S.

2.4. *Statistical analysis*

Statistical analyses were done in SPSS (IBM SPSS Statistics 20), Statistica software (v. 7, StatSoft Inc., USA) and Excel (v. 16.0, Microsoft Corporation, USA). Nonparametric Mann–Whitney *U* test was used to compare the mean values once normal distribution was not observed by Shapiro–Wilk's test. Statistical significance was defined as p <0.05.

Table 1
Characterization of fire stations and the study population ($n = 54$): Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR) and Alfândega da Fé (AFF).



	Fire station				
	VMS	MCC	IZD	VFR	AFF
Site characterization	Urban background	Urban background	Urban background	Urban background	Urban background
Location	Town	Town	Town	Town	Town
Number of inhabitants	4669	15,776	1212	6697	5104
Year of construction	1978	2012	2005	1979	1991
Year of refurbishment	1995	–	–	2008	–
Sampling date	28.5.2014	2.6.2014	16.6.2014	24.6.2014	17.6.2014
Meteorological conditions:_					
Air temperature (°C)	19.4 (10.3–26.3)	18.6 (8.2–25.5)	19.0 (10.8–25.7)	16.3 (12.8–20.0)	19.5 (9.1–27.4)
Relative humidity (%)	57.4 (33.7–86.0)	55.1 (36.6–87.7)	46.5 (27.4–73.6)	80.1 (64.5–90.5)	46.1 (27.4–74.0)
Wind speed (m s^{-1})	2.1 (0.1–6.7)	1.3 (0.1–4.0)	3.0 (0.9–5.6)	0.9 (0.0–3.4)	2.0 (0.2–4.4)
Wind direction	S–SW	SW–S	NE–E	S–SW	E–SE
Solar radiation (kW m^{-2})	0.1 (0.0–0.5)	0.2 (0.0–0.5)	0.2 (0.0–0.5)	0.1 (0.0–0.5)	0.2 (0.0–0.5)
Precipitation (mm)	0.0	0.0	0.0	0.1 (0.0–1.6)	0.0
Potential outdoor emission sources	Equipped with gasoline station	Gasoline station approximately 500 m	Gasoline station approximately 1 km	Gasoline station approximately 500 m	Gasoline stations approximately 500 m
Vehicles:					
Departures	4	5	3	3	3
Arrivals	4	4	4	4	3
Number of workers (firefighters) at fire station	70	50	38	40	45
Floor coating (control center)	Polyvinyl chloride	Wood	Ceramic tiles	Ceramic tiles	Ceramic tiles
Number of windows and doors (control center)	2 windows; 2 doors	1 window; 1 door	3 windows: 1 door	3 windows (1 opened); 1 door	1 window; 1 door
Ventilation at control center:					
Beginning of day	Yes	Yes	Yes	Yes	Yes
During the day	Yes	Yes	Yes	Yes	Yes
End of the day	No	No	No	No	No
During cleaning	Yes	Yes	Yes	Yes	Yes
Cleaning	1 per day	1 per day	1 per day	1 per day	1 per day
Study population (%)	22	22	22	22	12
Gender (%)	Male: 75 Female: 25	Male: 75 Female: 25	Male: 50 Female: 50	Male: 100	Male: 100
Age (years)	36 (26–43)	22 (19–24)	33 (12–35)	23 (18–25)	35 (30–40)
Weight (kg)	74 (61–88)	68 (63–72)	76 (62–90)	93 (78–101)	87 (73–100)
Employment duration (years)	18 (3–25)	4 (2–7)	11 (4–17)	5 (2 – 10)	15 (12–18)
Education	Secondary: 75% Higher: 25%	Secondary: 50% Higher: 50%	Secondary: 100%	Elementary: 25% Secondary: 50% Higher: 25%	Elementary 50% Secondary: 50%
Smoking (yes/no)	No	No	No	No	No
Allergy	Sea food, 1 subject	No	Pollens; 1 subject	No	Pollens; 1 subject
Medication	Yes, 1 subject	No	None	No	Yes, 1 subject

Results and discussion

PAH levels

The levels of PAHs determined in the breathing air zones of studied subjects working at five fire corporations are summarized in Table 2. The total levels of PAHs (ΣPAHs) in the breathing zones of workers var- ied between the five corporations. As shown, the lowest levels (i.e. me- dian ΣPAHs) were found at VFR (46.8 ng m− 3) being significantly (p b 0.001) different than at other corporations (except for AFF; p = 0.169) whereas VMS exhibited the highest concentrations (154 ng m−3), approximately 3 times higher than at VFR. VMS corpora- tion had the highest occupancy rate (more 30–45% of workers than at the remaining firehouses) and was the only one equipped with a gaso- line station which could have caused the elevated PAH levels. For the other fire stations, similar levels of ΣPAHs were found at MCC ≈ IZD (104–107 ng m−3) being higher than those at AFF (77.3 ng m−3). It is noteworthy that, though MCC and IZD fire stations were situated in cit- ies with different populations (15,776 and 1212 inhabitants, respective- ly for MCC and IZD), the overall ΣPAHs were rather similar (p = 0.102); both firehouses were the most recently constructed ones (2005–2012 as opposed to 1978–1979 (for VMS and VFR, respectively) and 1991 (for AFF)). The building characteristics as well as other factors such as the presence of emission sources and performed activities of occupants, type of microenvironments (physical characteristics of the indoor/out- door places, occupancy, ventilation rates, etc.), and overall pollution levels (including seasonal, meteorological and geographical differences) influence the personal exposure to a pollutant (Chen et al., 2012; IARC, 2010a, 2010b; Madureira et al., 2016; Oliveira et al., 2015a).

The results in Table 2 also show that contribution profiles of PAHs at all stations were somewhat similar. Acy was the predominant PAH at all stations (except for MCC where it was the 2nd most abundant one) accounting between 44% (at VMS) and 69% (AFF) of the total PAH content (i.e. ΣPAHs). This PAH is a component of organic material such as coal tar and crude oil. The presence of Acy in air may result from evaporation from these organic materials but it may also be released into the environment during fires (Kirk and Logan, 2015a, 2015b); wood combustion results in emissions of smoke with predominant abundance of this PAH (Perwak et al., 1982). Nap was the 2nd most abundant PAH at stations IZD, VFR and AFF, accounting for 12–16% of ΣPAHs with levels much lower than those reported for fire stations in Cincinnati, USA (9.22 μg m−3 at kitchen area up to 9.24 μg m−3 at truck bay; Baxter et al., 2014). Although no specific sources of Acy and Nap were identified, higher abundance of Acy could be due secondary transfer (via contaminated protective material) whereas in indoor air Nap emissions may result from incomplete combustion (wood, tobacco) and from evaporation of Nap-containing materials (such moth repellents air fresheners, crude oil, petroleum products) (Jia and Batterman, 2010).

It is necessary to remark that Nap is recognized as relevant indoor pollutant by WHO that recommended an annual guideline value in indoor air of 10 μg m−3 (WHO, 2010). Whereas the levels reported Baxter et al. (2014) are close to that value, the concentrations in the breathing zones of the studied subjects of this work were well below the recommended guideline. However, it is necessary to remark that Nap (as well as other light–molecular weight PAHs with 2–3 aromatic rings) is predominantly found in the gas phase (Oliveira et al., 2015b, Oliveira et al., 2016b), which was not assessed in this work; thus the respective exposures of studied subjects at five fire corporations might be underestimated. Therefore, to adequately evaluate occupational exposure to PAHs (even during non-fires settings), future works should consider assessment of gaseous PAHs that are commonly not considered (Lui et al., 2017, Montaño-Soto et al., 2017, Oliveira et al., 2015a). At IZD, VFR and AFF, Phe was the 3rd (and 4th at IZD) most predominant compound (6–9% of ΣPAHs). At stations VMS and MCC, slightly different profiles of PAHs in breathing zones of workers were observed with high contributions of Ace (43% and 55% of ΣPAHs); the contribution of Nap was 6 and 10% respectively. Overall, light molecular weight PAHs (i.e. with 2–3 rings) were by far the most predominant congeners in the breathing zones of the workers at all stations, with the abundances ranging from 74% (at VFR) to 96% (at VFS) of the total PAH content. PAHs with 5–6 rings accounted for much less content (3–9% of ΣPAHs) with the exception to VFR, where heavy molecular PAHs exhibited higher proportion (21% of ΣPAHs). This occurrence was mostly due to the higher contributions of D[a,h]A (6% of ΣPAHs at VFR vs. ~ 1% at the other fire houses) and B[ghi]P (8% at VFR vs. ~ 2–4% at the remaining corporations). The higher prevalence of these two PAHs indicates a potential contribution from vehicular emissions (Ravindra et al., 2008) at this fire station.

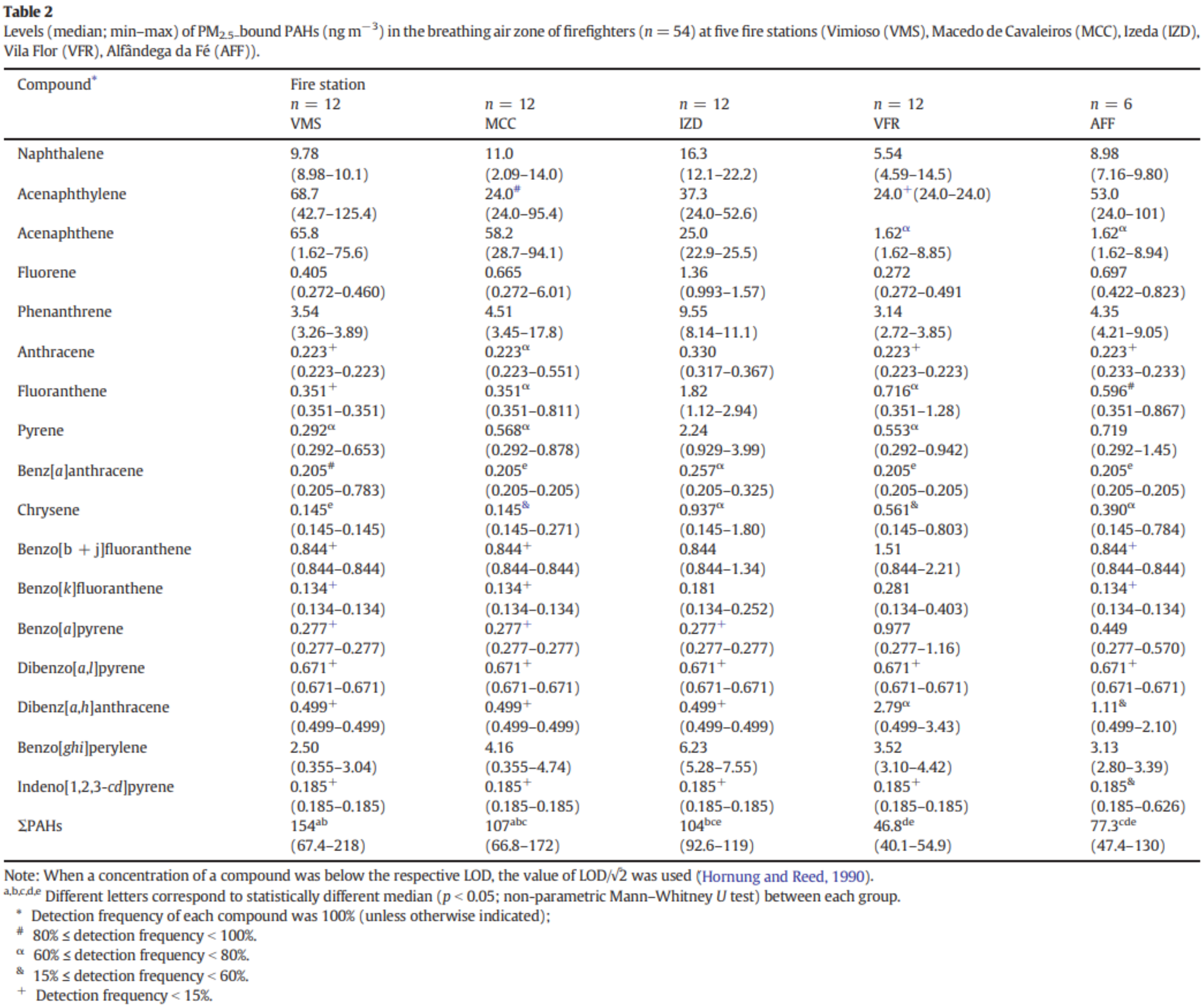


Table 2

Levels (median; min–max) of $PM_{2.5}$-bound PAHs (ng m^{-3}) in the breathing air zone of firefighters ($n = 54$) at five fire stations (Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), Alfândega da Fé (AFF)).

Compound*	Fire station $n = 12$ VMS	$n = 12$ MCC	$n = 12$ IZD	$n = 12$ VFR	$n = 6$ AFF
Naphthalene	9.78 (8.98–10.1)	11.0 (2.09–14.0)	16.3 (12.1–22.2)	5.54 (4.59–14.5)	8.98 (7.16–9.80)
Acenaphthylene	68.7 (42.7–125.4)	$24.0^{\#}$ (24.0–95.4)	37.3 (24.0–52.6)	24.0^{+}(24.0–24.0)	53.0 (24.0–101)
Acenaphthene	65.8 (1.62–75.6)	58.2 (28.7–94.1)	25.0 (22.9–25.5)	1.62^{α} (1.62–8.85)	1.62^{α} (1.62–8.94)
Fluorene	0.405 (0.272–0.460)	0.665 (0.272–6.01)	1.36 (0.993–1.57)	0.272 (0.272–0.491	0.697 (0.422–0.823)
Phenanthrene	3.54 (3.26–3.89)	4.51 (3.45–17.8)	9.55 (8.14–11.1)	3.14 (2.72–3.85)	4.35 (4.21–9.05)
Anthracene	0.223^{+} (0.223–0.223)	0.223^{α} (0.223–0.551)	0.330 (0.317–0.367)	0.223^{+} (0.223–0.223)	0.223^{+} (0.233–0.233)
Fluoranthene	0.351^{+} (0.351–0.351)	0.351^{α} (0.351–0.811)	1.82 (1.12–2.94)	0.716^{α} (0.351–1.28)	$0.596^{\#}$ (0.351–0.867)
Pyrene	0.292^{α} (0.292–0.653)	0.568^{α} (0.292–0.878)	2.24 (0.929–3.99)	0.553^{α} (0.292–0.942)	0.719 (0.292–1.45)
Benz[*a*]anthracene	$0.205^{\#}$ (0.205–0.783)	0.205^{e} (0.205–0.205)	0.257^{α} (0.205–0.325)	0.205^{e} (0.205–0.205)	0.205^{e} (0.205–0.205)
Chrysene	0.145^{e} (0.145–0.145)	$0.145^{\&}$ (0.145–0.271)	0.937^{α} (0.145–1.80)	$0.561^{\&}$ (0.145–0.803)	0.390^{α} (0.145–0.784)
Benzo[b + j]fluoranthene	0.844^{+} (0.844–0.844)	0.844^{+} (0.844–0.844)	0.844 (0.844–1.34)	1.51 (0.844–2.21)	0.844^{+} (0.844–0.844)
Benzo[*k*]fluoranthene	0.134^{+} (0.134–0.134)	0.134^{+} (0.134–0.134)	0.181 (0.134–0.252)	0.281 (0.134–0.403)	0.134^{+} (0.134–0.134)
Benzo[*a*]pyrene	0.277^{+} (0.277–0.277)	0.277^{+} (0.277–0.277)	0.277^{+} (0.277–0.277)	0.977 (0.277–1.16)	0.449 (0.277–0.570)
Dibenzo[*a,l*]pyrene	0.671^{+} (0.671–0.671)	0.671^{+} (0.671–0.671)	0.671^{+} (0.671–0.671)	0.671^{+} (0.671–0.671)	0.671^{+} (0.671–0.671)
Dibenz[*a,h*]anthracene	0.499^{+} (0.499–0.499)	0.499^{+} (0.499–0.499)	0.499^{+} (0.499–0.499)	2.79^{α} (0.499–3.43)	$1.11^{\&}$ (0.499–2.10)
Benzo[*ghi*]perylene	2.50 (0.355–3.04)	4.16 (0.355–4.74)	6.23 (5.28–7.55)	3.52 (3.10–4.42)	3.13 (2.80–3.39)
Indeno[1,2,3-*cd*]pyrene	0.185^{+} (0.185–0.185)	0.185^{+} (0.185–0.185)	0.185^{+} (0.185–0.185)	0.185^{+} (0.185–0.185)	$0.185^{\&}$ (0.185–0.626)
ΣPAHs	154^{ab} (67.4–218)	107^{abc} (66.8–172)	104^{bce} (92.6–119)	46.8^{de} (40.1–54.9)	77.3^{cde} (47.4–130)

Note: When a concentration of a compound was below the respective LOD, the value of LOD/√2 was used (Hornung and Reed, 1990).

^{a,b,c,d,e} Different letters correspond to statistically different median ($p < 0.05$; non-parametric Mann–Whitney *U* test) between each group.

* Detection frequency of each compound was 100% (unless otherwise indicated);

\# 80% ≤ detection frequency < 100%.

α 60% ≤ detection frequency < 80%.

& 15% ≤ detection frequency < 60%.

\+ Detection frequency < 15%.

Occupational Safety and Health Administration (OSHA) regulates occupational exposure to PAHs through “coal tar pitch volatiles” (ATSDR, 2016; i.e. extractable benzene soluble fraction of total particulates that includes B[a]A, B[b]F, Chry, Ant, B[a]P, Phe, Pyr and acridine) (Table 6S). The designated limit is expressed as 8–hour time-weighted average (TWA) permissible exposure limit (PEL) of 0.2 mg m− 3 (ATSDR, 2016). The National Institute for Occupational Safety and Health (NIOSH) guideline for PAHs exposure in the workplaces is set as the lowest detectable concentration of 0.1 mg m− 3 for coal tar pitch volatile agents (ATSDR, 2016). The air exposure to these seven PAHs (acridine was not considered in this work) ranged between 4.7 and 46 ng m− 3 among the investigated subjects being well below the OSHA-mandated limit and NIOSH recommendation. The permitted (0.6 mg m− 3) and maximum (1 mg m− 3) excursion limits defined by American Conference of Governmental Industrial Hygienists (ACGIH; Table 6S) were also fulfilled for total PAHs.

Occupational exposure of firefighters has been associated with increased risk of cancers (urothelial, skin, lung, kidney and testicular cancers) though some findings remain unclear (Daniels et al., 2013, LeMasters et al., 2006). Once absorbed into blood stream (by inhalation, ingestion, and dermal contact) PAHs are metabolized and distributed within the human body, being mostly eliminated through the urine in the form of glucuronide and sulphate conjugates (Kamal et al., 2015). Within this biological process, some reactive metabolites are formed and tend to bind with some macromolecules, including the DNA, thus leading to the formation of mutations and tumours that can evolve to cancer (Abdel-Shafy and Mansours, 2016). Out of 18 analysed PAHs, nine are considered as possible or probable carcinogens (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (IARC), 2002, IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (IARC), 2010b) (Nap, B[a]A, Chry, B[b]F, B[j]F, B[k]F, D[a,l]P, D[a,h]A and InP) whereas B[a]P is classified as human known (class 1) carcinogen. Regarding the obtained levels, the highest median of ΣPAHscarc was observed at IZD (20.2 ng m− 3) being rather similar (p = 0.129–0.796) at the remaining fire corporations (12.7–14.0 ng m− 3). These concentrations ranged from 8.2% (VMS) to 27% of ΣPAHs (at VFR) (Fig. 2a). Nap (Fig. 2b) was the most predominant carcinogen and accounted for 44% (IZD and VFR) to 59% of ΣPAHscarc (at MCC). The concentrations of this carcinogenic obtained in the breathing zones of the characterized firefighters were below the recommended guidelines of 50 mg m− 3 designated by NIOSH for the occupational exposure (Table 6S). D[a,h]A was the another abundant carcinogenic PAH (accounted for 9–22% of ΣPAHscarc at IZD, VFR and AFF) being followed by B[b + j]F (2–12% of ΣPAHscarc). Finally, B[a]P accounted for 2–8% of ΣPAHscarc. Its levels in breathing zone of firefighters (in non-fire settings) fulfilled the ambient air guideline of 1 ng m− 3 (Directive 2004/107/EC, 2005) (as no specific occupational guideline is established for this PAH).

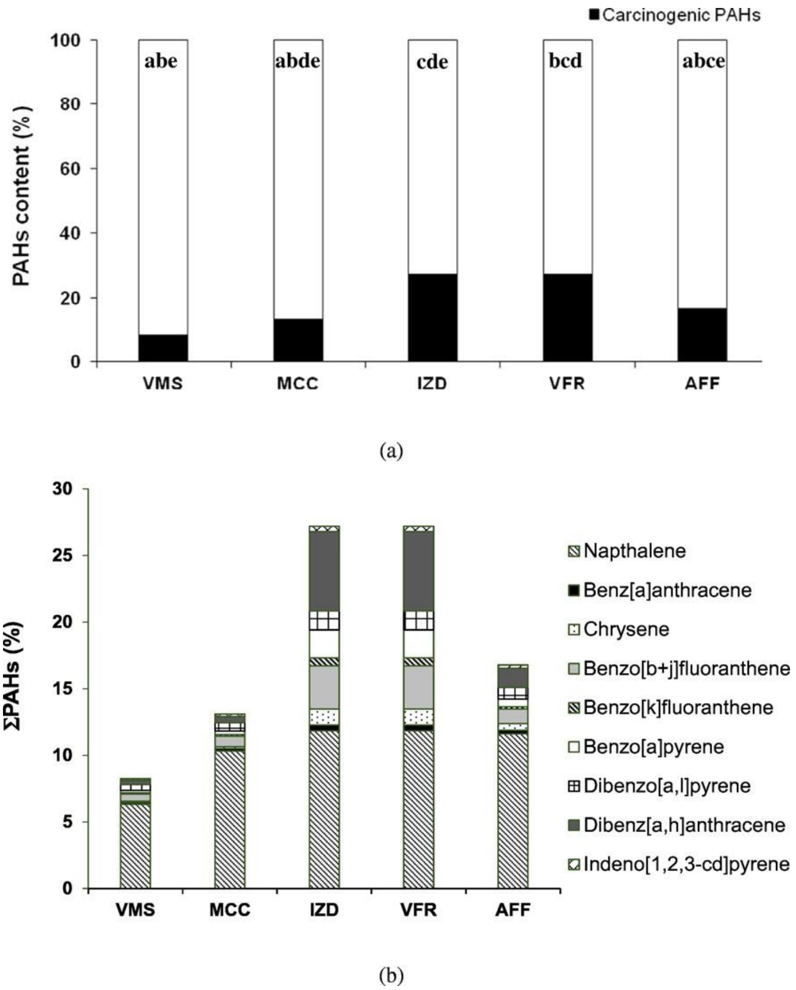


Fig. 2. Carcinogenic PAHs in breathing zones of studied population of firefighters at five fire stations (Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), Alfândega da Fé (AFF)): (a) contribution (%) of carcinogenic PAHs (ΣPAHscar) vs. total PAH (ΣPAHs) content; and (b) individual carcinogenic PAHs. a, b, c, d, e Same letters in a box plot indicate that given means are not statistically different (p > 0.05 (p < 0.05; non-parametric Mann–Whitney U test).

3.2. Source identification

Fig. 3 shows principal component analysis (PCA) for PAHs data set obtained in this work. Factors with eigenvalues > 1 were extracted and Kaiser-Meyer-Olkin measure of sampling adequacy > 0.5 was used (B[a]A was excluded as it presented value < 0.5). The PCA model resulted in two significant factors (F1 and F2) that represented 74.70% of the total variability (Table 7S). F1 contributed 42.53% of the original data with high loadings (square cosines values > 0.712) for Flu, Phe, Ant, Fln, Pyr, Chry, and B[ghi]P. This factor allowed discrimination of mainly subjects of IZD fire stations from the other corporations, and in some extend also from VMS. High loadings of Flu, Ant, Fln and Pyr indicates wood combustion or biomass burning (Deka et al., 2016, Lu et al., 2016). Coal combustion also release PAHs such as Phe and Chry (Deka et al., 2016, Harrison et al., 1996, Ho et al., 2002, Simcik et al., 1999). High loadings of Fln, Pyr and B[ghi]P were also reported for vehicular emissions (Khalili et al., 1995). The values obtained for Fln/(Fln + Pyr) diagnostic ratio (Table 3), that can differentiate between coal combustion (0.52) and vehicular emissions (0.40–0.50), points towards the latter source; the respective values ranged between 0.40 (at AFF) and 0.50 (at VMS). However, the results of InP/(InP + B[ghi]P (distinguishes between vehicular emissions, wood, and coal combustions; Kavouras et al., 2001, Rogge et al., 1993a, Sicre et al., 1987, Grimmer et al., 1983, Pio et al., 2001) and B[ghi]P/B[a]P (vehicular emissions vs. road dust; Oda et al., 2001, Rogge et al., 1993a, Rogge et al., 1993b) were inconclusive. Thus, it seems that F1 represented contributions from mixed sources. It is though necessary to remark that both these ratios contained B[ghi]P, a considered marker of vehicular (diesel) emissions. However, some studies that investigated PAHs origin in different Portuguese metropolitan areas (Alves et al., 2016, Cachada et al., 2012, Castro et al., 2009, Slezakova et al., 2010, Slezakova et al., 2011, Slezakova et al., 2013a, Slezakova et al., 2013b), did not report B[ghi]P as the predominant compound (though it was abundant, and traffic emissions were identified as the major source). Instead, the authors reported higher abundances of other indicators: Pyr, B[b + j]F, D[a,h]A (Callén et al., 2013, Ravindra et al., 2008).

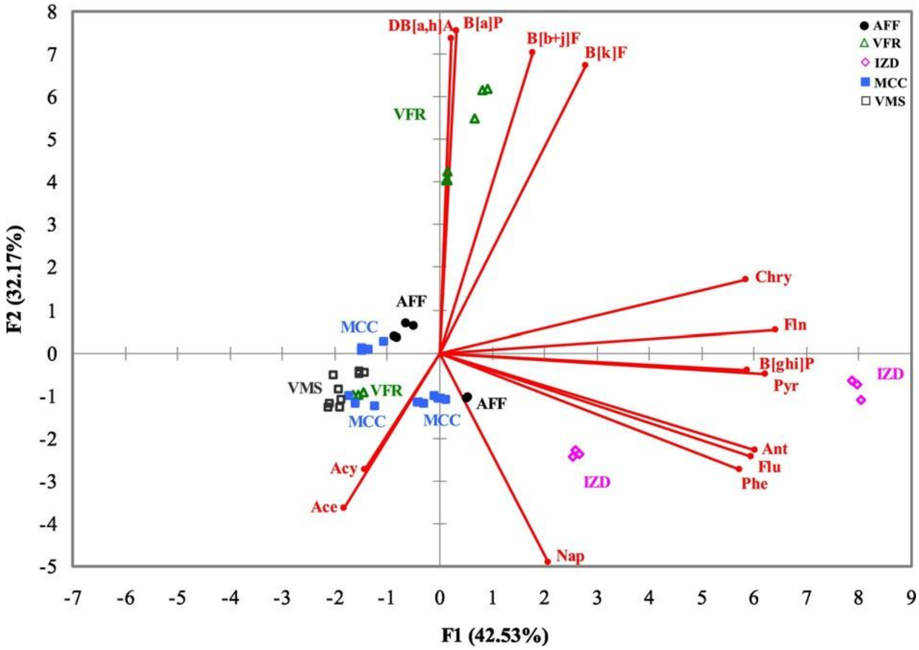


Fig. 3. Principal components analysis (PCA) of the data set at five characterized corporations (Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), Alfândega da Fé (AFF))) based on concentrations of selected PAHs.

Table 3
Diagnostic ratios for $PM_{2.5}$–bound PAHs in the breathing zone of firefighters at five fire stations (Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), Alfândega da Fé (AFF)).

Ratio	This study					Value	Source	Reference
	VMS	MCC	IZD	VFR	AFF			
$\Sigma PAHs_{LMW}/\Sigma PAH_{sHMW}$[a]	30.9 ± 13.5	16.1 ± 6.8	7.0 ± 4.3	5.8 ± 4.0	9.3 ± 4.4	>1 <1	Petrogenic Pyrogenic	(Zhang et al., 2008)
Fln/(Fln + Pyr)	0.50 ± 0.09	0.46 ± 0.09	0.48 ± 0.07	0.44 ± 0.26	0.40 ± 0.16	0.40–0.5 >0.5 0.42, 0.52	Vehicular traffic Coal combustion Road dust	(Kavouras et al., 1999; Yunker et al., 2002; Zencak et al., 2007; Rogge et al., 1993a; Oda et al., 2001)
InP/(InP + B[*ghi*]P)	0.06 ± 0.04	0.05 ± 0.03	0.03 ± 0.01	0.10 ± 0.08	0.07 ± 0.06	0.21–0.22 0.35–0.70 0.56 0.62 0.36	Gasoline cars Diesel emissions Coal combustion Wood combustion Road dust	(Gogou et al., 1996; Grimmer et al., 1983; Kavouras et al., 2001; Pio et al., 2001; Ravindra et al., 2008; Rogge et al., 1993a; Sicre et al., 1987)
B[*ghi*]P/B[*a*]P	12.6 ± 9.6	13.4 ± 4.6	22.7 ± 4.5	6.0 ± 3.9	8.0 ± 2.2	1.2–2.2 2.5–3.3 0.86, 0.91	Diesel cars Gasoline cars Road dust	(Oda et al., 2001; Rogge et al., 1993a, 1993b)
B[*a*]A/Chry	2.36 ± 1.88	1.25 ± 0.32	0.80 ± 0.87	0.87 ± 0.63	0.64 ± 0.56	>0.35	Fuel combustion	(Krugly et al., 2014)
B[*b*]F/B[*k*]F	8.1 ± 3.6	6.3 ± 2.3	5.5 ± 1.18	6.3 ± 1.1	6.0 ± 0.5	>0.5	Diesel	(Ravindra et al., 2008)
B[*a*]A/(B[*a*]A + Chry)	0.64 ± 0.13	0.55 ± 0.07	0.38 ± 0.31	0.41 ± 0.20	0.40 ± 0.19	0.40, 0.38–0.64 0.76 0.43	Diesel Gasoline Wood combustion	(Li and Kamens, 1993; Manoli et al., 2004; Sicre et al., 1987)
B[b + k]F/B[*ghi*]P	0.41 ± 0.15	0.30 ± 0.15	0.19 ± 0.01	0.45 ± 0.12	0.30 ± 0.04	1.60 0.33 2.18	Diesel cars Gasoline cars Wood combustion	(Li and Kamens, 1993)
B[*a*]P/(B[*a*]P + Chry)	0.71 ± 0.11	0.66 ± 0.07	0.49 ± 0.37	0.72 ± 0.17	0.52 ± 0.22	0.5 0.73	Diesel Gasoline	(Ravindra et al., 2008)
Flu/(Flu + Pyr)	0.59 ± 0.22	0.60 ± 0.19	0.53 ± 0.16	0.39 ± 0.11	0.44 ± 0.08	>0.5 <0.5	Diesel Gasoline	(Ravindra et al., 2008)
Phe/(Phe + Ant)	0.95 ± 0.03	0.95 ± 0.01	0.97 ± 0.01	0.95 ± 0.03	0.96 ± 0.01	>0.7	Lubricant oils and fossil fuels	(Mirante et al., 2013)

Nap – naphthalene, Acy – acenaphthylene; Ace – acenaphthene, Flu – fluorene, Phe – phenanthrene, Ant – anthracene, Fln – fluoranthene, Pyr – pyrene, B[*a*]A – benz[*a*]anthracene, Chry – chrysene, B[b + j]F – benzo[b + j]fluoranthene, B[*k*]F – benzo[*k*]fluoranthene, B[*a*]P – benzo[*a*]pyrene, D[*a,h*]A – dibenz[*a,h*]anthracene, B[*ghi*]P – benzo[*ghi*]perylene, InP – indeno[1,2,3-cd]pyrene;

[a] Total concentration of 2– and 3–rings PAHs ($\Sigma PAHs_{LMW}$), and 4–6–rings PAHs ($\Sigma PAHs_{HMW}$);

F2 represented 32.17% of the original data variance and allowed the discrimination of VFR individuals from the others. F2 was highly loaded (square cosines > 0.747) for B[b + j]F, B[k]F, B[a]P and DB[ah]A), and much less for Nap (square cosines value of 0.389). The high loadings of B[b]F and B[a]P were reported for gasoline emissions (Chen et al., 2016, Guo et al., 2003), whereas high loadings of B[k]F, B[a]P and DB[ah]A are indicative of diesel emissions (Ravindra et al., 2008, Teixeira et al., 2013). In general, vehicular emissions are a common major source of PAHs in ambient air (Slezakova et al., 2010, Slezakova et al., 2013a, Slezakova et al., 2013b) and indoor infiltrations result from poorly fitted windows, doors, building cracks, and ventilation systems (WHO, 2010). In agreement, B[a]A/Chry (> 0.35 at all fire houses) indicated fuel combustion and car exhausts (Krugly et al., 2014) and the values of B[b]F/B[k]F ratios (> 0.5 at all fire corporations) also pointed towards impacts of traffic emissions at the fire houses, specifically from diesel emissions (Ravindra et al., 2008). These findings were expected. Firstly, diesel is the most used car fuel in Portugal (~ 80% of the total car fuel consumption; INE, 2015), and secondly it was the fuel used for vehicles and firefighting trucks in all fire facilities. The ambient air emissions and car exhausts (from garages/truck bays) may infiltrate indoors (to living quarters, common areas and control centers). Nevertheless, B[b + k]F/B[ghi]P that can differentiate between various vehicle emissions (1.60: diesel; 0.33: gasoline; Li and Kamens, 1993) indicated a contribution mostly from gasoline exhausts at all fire corporations. In addition, B[a]P/(B[a]P + Chry) and Flu/(Flu + Pyr) ratios that can also be used to distinguish between both types of exhausts (Ravindra et al., 2008) suggested predominance of gasoline emissions at VFR, diesel emissions at IZD, and mixed contribution from both diesel and gasoline emissions at firehouses VMS, MCC and AFF.

Nap results from unburned fossil derived fuel or alkyl substituted PAHs and indicates petrogenic source (Chen et al., 2016). In addition, petrogenic origin of unburned petroleum, gasoline and diesel emissions have been reported for dominant 2– and 3–ring PAHs (Yunker et al., 2002). In agreement, the diagnostic ratios of low molecular PAHs vs. high molecular weight congeners (Table 3) were > 1 indicating contributions of petrogenic sources at all fire corporations. Petrogenic sources were also identified with Phe/(Phe + Ant) values > 0.7, implying the use of lubricant oils (Mirante et al., 2013). F2 thus represented a mixed contribution of petrogenic and pyrogenic sources. Still, it is necessary to emphasize that diagnostic ratios are merely rudimentary indicators of PAHs origin (Galarneau, 2008). Numerous studies have highlighted the limitations of this method as values can be altered to a different extent due to environmental degradation and phase transfers (Dvorská et al., 2011, Galarneau, 2008, Katsoyiannis et al., 2007, Katsoyiannis et al., 2011, Tobiszewski and Namieśnik, 2012, Usenko et al., 2010) and/or reactions between PAHs and other gaseous pollutants (ozone, nitrogen oxides; Ravindra et al., 2008). Some of the technical literature concerning PAHs emission signatures is rather old and lacks information on molecular signatures of new generation vehicles, biomass burning technologies, boilers and waste treatment plants (Finardi et al., 2015); the available reference values of currently used diagnostic ratios may be unusable to clearly assign PAHs to specific sources.

3.3. Risk assessment of PAHs

Because of its high TEF, D[a,h]A was the predominant PAH to ΣB[a]Peq (~ 80% at VMS, MCC and IZD; ~ 90% at VFR and AFF; Table 4) being followed by B[a]P (6–7% at VFR and AFF; 9% VMS, MCC and IZD). B[a]Peq were also assessed using TEF values by Muller (Boström et al., 2002; Table 8S) who included D[a,l]P (TEF of 100); this PAH was the largest contributor (95–99%) to ΣB[a]Peq. Despite strong arguments that support monitoring and assessment of D[a,l]P (Boström et al., 2002, Okona-Mensah et al., 2005), these findings need to be carefully implied as at all fire stations D[a,l]P levels were below its LOD (Table 2). Nap (~ 6–16% of ΣPAHs; Table 2) contributed < 1% to ΣB[a]Peq (Table 4 and 8S).

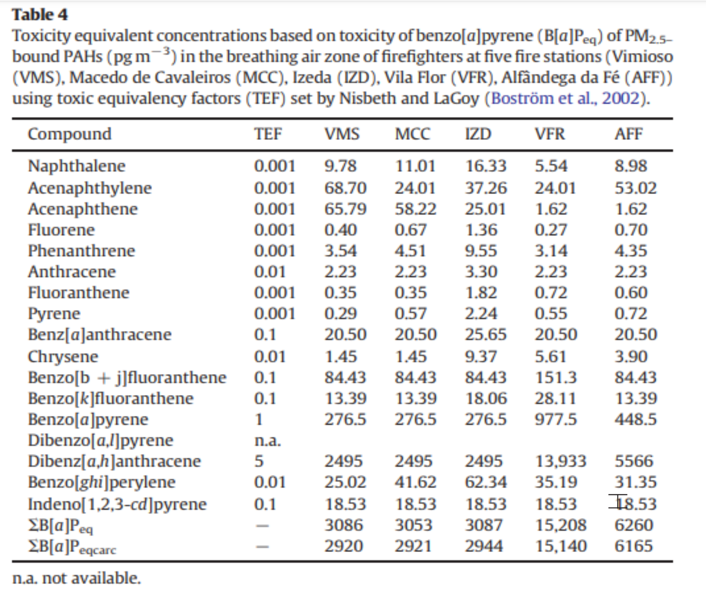


Table 4

Toxicity equivalent concentrations based on toxicity of benzo[*a*]pyrene ($B[a]P_{eq}$) of $PM_{2.5}$-bound PAHs ($pg\ m^{-3}$) in the breathing air zone of firefighters at five fire stations (Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), Alfândega da Fé (AFF)) using toxic equivalency factors (TEF) set by Nisbeth and LaGoy (Boström et al., 2002).

Compound	TEF	VMS	MCC	IZD	VFR	AFF
Naphthalene	0.001	9.78	11.01	16.33	5.54	8.98
Acenaphthylene	0.001	68.70	24.01	37.26	24.01	53.02
Acenaphthene	0.001	65.79	58.22	25.01	1.62	1.62
Fluorene	0.001	0.40	0.67	1.36	0.27	0.70
Phenanthrene	0.001	3.54	4.51	9.55	3.14	4.35
Anthracene	0.01	2.23	2.23	3.30	2.23	2.23
Fluoranthene	0.001	0.35	0.35	1.82	0.72	0.60
Pyrene	0.001	0.29	0.57	2.24	0.55	0.72
Benz[*a*]anthracene	0.1	20.50	20.50	25.65	20.50	20.50
Chrysene	0.01	1.45	1.45	9.37	5.61	3.90
Benzo[b + j]fluoranthene	0.1	84.43	84.43	84.43	151.3	84.43
Benzo[*k*]fluoranthene	0.1	13.39	13.39	18.06	28.11	13.39
Benzo[*a*]pyrene	1	276.5	276.5	276.5	977.5	448.5
Dibenzo[*a,l*]pyrene	n.a.					
Dibenz[*a,h*]anthracene	5	2495	2495	2495	13,933	5566
Benzo[*ghi*]perylene	0.01	25.02	41.62	62.34	35.19	31.35
Indeno[1,2,3-*cd*]pyrene	0.1	18.53	18.53	18.53	18.53	18.53
$\Sigma B[a]P_{eq}$	–	3086	3053	3087	15,208	6260
$\Sigma B[a]P_{eqcarc}$	–	2920	2921	2944	15,140	6165

n.a. not available.

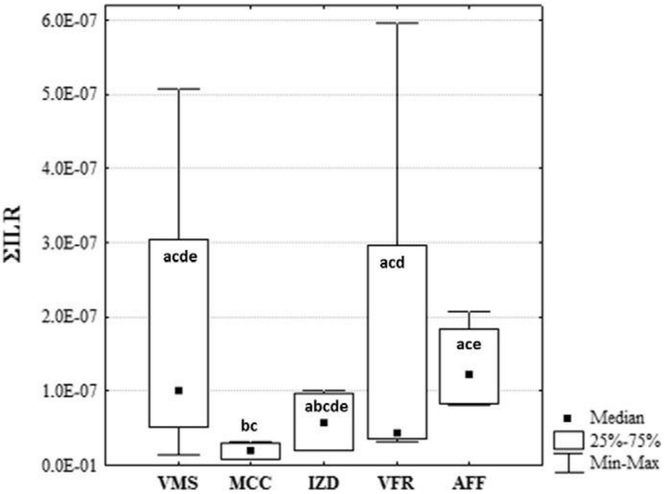


Fig. 4. Incremental lifetime cancer risks (ΣILR; ■ Median; □ 25-75%, and range) in breathing zones of studied population of firefighters at five fire stations (Vimioso (VMS), Macedo de Cavaleiros (MCC), Izeda (IZD), Vila Flor (VFR), Alfândega da Fé (AFF)). $^{a,\ b,\ c,\ d,\ e}$ Same letters in a box plot indicate that given means are not statistically different (p N 0.05; non-parametric Mann-Whitney U test).

Nap should be routinely monitored when assessing the respective risks. Finally, the risk analysis of Nap might be underestimated to some ex- tent; unlike other considered PAHs (B[a]A, Chry, B[b]F, B[k]F, B[a]P, D[a,h]A and InP) Nap is predominantly present in vapour phase (Castro et al., 2011; Ravindra et al., 2006, 2008; Slezakova et al., 2011) which was not included in this work.

4. Conclusions

This study reports information concerning occupational exposure to PAHs for firefighters in non-fire settings once limited information (and from non-European) settings exists. The obtained levels of PAHs fulfilled all existent occupational exposure limits as well air quality guidelines. Light molecular weight PAHs (2–3 rings) were the most predominant congeners (74–96% of ΣPAHs) whereas compounds with 5–6 rings accounted for much less content (3–9% of ΣPAHs). The source analysis indicated mixed contributions from pyrogenic and petrogenic sources (fuel and wood combustions, vehicular emissions from both diesel and gasoline fuelled cars, and usage of lubricant oils) for personal PAHs exposure at the studied fire corporations.

The incremental lifetime cancer risks (based on USEPA methodology) due to exposure to airborne PAHs were below the recommend guideline of 10^{-6} and thus can be considered as negligible for studied subjects. However, WHO health–based guideline level of 10^{-5} was exceeded at all five fire corporations (9–44 times). Therefore, the respective exposures to these compounds should be carefully controlled for these occupational settings. From the health perspective, monitoring of the potential occupational health effects should be carried on in order to better understand PAH quantitative exposure–response relationships.

Finally, the present study included assessment of occupational exposure to PAHs during a summer season when the risks and frequency of forest fires are the highest. However, as demonstrated, atmospheric emissions impacted on background levels of occupational exposure of firefighters. Therefore, future studies evaluating occupational exposure should be also conducted during cold seasons when concentrations of ambient PAHs are increased, typically due to house heating emissions.

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