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Polycyclic aromatic hydrocarbons at fire stations: firefighters' exposure monitoring and biomonitoring, and assessment of the contribution to total internal dose

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HIGHLIGHTS

- Firefighters exposure to PAHs was assessed by personal monitoring and biomonitoring.
- Airborne PAHs with 2–3 rings were the most abundant at all fire stations.
- 1-hydroxynaphthalene and 1-hydroxyacenaphthene were the predominant metabolites.
- Naphthalene contributed the most to carcinogenic PAHs in majority of firehouses.
- Significant correlations were found among urinary OH-PAH excretion and inhaled PAHs.

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ABSTRACT

This work characterizes levels of eighteen polycyclic aromatic hydrocarbons (PAHs) in the breathing air zone of firefighters during their regular work shift at eight Portuguese fire stations, and the firefighters' total internal dose by six urinary monohydroxyl metabolites (OH-PAHs). Total PAHs (ΣPAHs) concentrations varied widely (46.4–428 ng/m^3), mainly due to site specificity (urban/rural) and characteristics (age and layout) of buildings. Airborne PAHs with 2–3 rings were the most abundant (63.9–95.7% ΣPAHs). Similarly, urinary 1-hydroxynaphthalene and 1-hydroxyacenaphthene were the predominant metabolites (66–96% ΣOH-PAHs). Naphthalene contributed the most to carcinogenic ΣPAHs (39.4–78.1%) in majority of firehouses; benzo[a]pyrene, the marker of carcinogenic PAHs, accounted with 1.5–10%. Statistically positive significant correlations ($r \geq 0.733$, $p \leq 0.025$) were observed between ΣPAHs and urinary ΣOH-PAHs for firefighters of four fire stations suggesting that, at these sites, indoor air was their major exposure source of PAHs. Firefighter's personal exposure to PAHs at Portuguese fire stations were well below the existent occupational exposure limits. Also, the quantified concentrations of post-shift urinary 1-hydroxypyrene in all firefighters were clearly lower than the benchmark level (0.5 μmol/mol) recommended by the American Conference of Governmental Industrial Hygienists.

1. Introduction

Firefighting, along with construction, mining, and agriculture, ranks among the most dangerous professions, with its occupational exposure being regarded as possible carcinogen to humans by the International Agency for Research on Cancer (IARC) and the US National Institute for Occupational Safety and Health (NIOSH) [1,2]. Firefighting is among the most hazardous yet the least studied occupations in terms of exposures and their relationship to occupational diseases.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds that are released during the incomplete combustion or pyrolysis of organic material. PAHs are well known for their cytotoxic and mutagenic properties [3,4], with some

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of them being recognized as endocrine disrupting chemicals [5]; USEPA listed 16 priority PAHs [6]. PAHs possess an undeniable role in the induction of human carcinogenesis [7], especially if benzo[a]pyrene (known human carcinogenic) and benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, indeno[1,2,3-cd]pyrene, and naphthalene (possible human carcinogens; [4,8] are present. Dibenzo[a,l]pyrene and dibenz[a,h]anthracene have been also under scrutiny because they are regarded as probable carcinogens to humans due to their higher carcinogenic potency than benzo[a]pyrene [9–12]. Electrophilic compounds such as PAHs play a key role in environmental cancer and some recent evidences associate their role in cardiovascular disease [13]. Firefighters' occupational exposure has been associated with excess morbidity and mortality with cardiovascular disease being considered as the leading cause of death in approximately 45% of firefighters and a major cause of their morbidity [14–16]. As a consequence firefighters' occupational exposure to PAHs may promote the development or aggravation of cardiovascular illnesses. Fires are the major contributor to occupational exposure to PAHs [17–20]. Other relevant sources include motor-vehicle exhaust (especially diesel), industrial emissions, residential and commercial heating with wood, coal, or other biomass fuels, and tobacco smoke [21–23]. Despite some available information regarding firefighters' occupational exposure to PAHs during live fire combat activities in Australia [20] and USA [17–19,23–27], firefighters may also be exposed to PAHs when they are at fire stations. Recently some studies revealed that chemical contaminants from fires were tracked back to fire stations via fire vehicles and principally through firefighters' personal equipments such as boots, gloves, and turnout gear [18,20,28–31]. Only two studies were found regarding firefighters' occupational exposure to PAHs at fire stations [23,32], both performed in USA. No information exists concerning other countries, even though the available exposure data may not be directly applicable.

Biological monitoring is an important tool in the prevention of occupational diseases related to those exposed chemicals on a regular basis, particularly when multi-route exposure (inhalation, dermal, ingestion) or abnormal exposure takes place. 1-hydroxypyrene (1OHPy) is the most widely used biological indicator of internal dose of PAHs exposure [33,34]; 3-hydroxibenzo[a]pyrene (3OHBaP) is the main metabolite of the known human carcinogenic benzo[a]pyrene. Acenaphthene, fluorene, and phenanthrene are common PAHs in different matrices [10,35,36] and their major urinary metabolites are 1-hydroxylacenaphthene (1OHAce), 2-hydroxylfluorene (2OHFlu), and 1-hydroxyphenanthrene (1OHPhen), respectively. Regarding naphthalene there are more than thirty

Table 1
Concentrations of $PM_{2.5}$-bound PAHs (median[a]; min-max; ng/m^3) in the breathing air zone of firefighters at the fire stations (Miranda do Douro (MRD), Torre Dona Chama (TDC), Sendim (SDM), Mirandela (MDL), Torre de Moncorvo (TMC), Vinhais (VNH), Bragança (BRG), and Freixo de Espada à Cinta (FEC)).

Compound	Fire station							
	MRD	TDC	SDM	MDL	TMC	VNH	BRG	FEC
Naphthalene	12.2 (8.51–15.1)	6.67 (5.61 – 6.99)	7.95 (6.04 – 10.3)	11.5 (10.9 – 13.5)	4.95 (4.27 – 8.74)	7.19 (5.95 – 8.53)	9.21 (4.23 – 13.0)	35.5 (33.4 – 38.6)
Acenaphthylene	110 (75.6 – 208)	24.0[a]	56.4 (27.8 – 86.9)	125[**] (24.0 – 198)	24.0[a]	43.9[***] (24.0 – 89.1)	27.2[***] (24.0 – 111)	199 (60.3 – 352)
Acenaphthene	88.5 (56.1 – 111)	2.48[**] (1.62 – 4.26)	18.7 (18.4 – 20.8)	97.3[**] (1.62 – 121)	10.3 (9.11 – 16.2)	1.62[a]	8.54[***] (1.62 – 18.2)	4.33[***] (1.62 – 8.02)
Fluorene	1.05 (0.540 – 1.49)	0.272[***] (0.272 – 0.588)	0.272[a]	1.86 (1.62 – 3.53)	0.446[**] (0.272 – 0.528)	0.272[a]	0.272[***] (0.272 – 0.450)	6.73 (3.13 – 9.94)
Phenanthrene	6.07 (3.74 – 7.27)	4.08 (3.71 – 5.97)	2.88 (2.76 – 3.00)	9.45 (6.83 – 9.88)	3.99 (3.39 – 4.42)	4.32 (3.42 – 5.01)	3.63 (2.97 – 4.84)	28.5 (21.0 – 35.9)
Anthracene	0.223[a]	0.223[***] (0.223 – 0.364)	0.223[a]	0.223[***] (0.223 – 1.59)	0.223[a]	0.223[***] (0.223 – 0.657)	0.223[a]	0.636 (0.601 – 0.675)
Fluoranthene	0.351[***] (0.351 – 0.603)	0.351[***] (0.351 – 0.592)	0.351[a]	1.50 (0.968 – 2.16)	0.351[***] (0.351 – 0.589)	0.596[**] (0.351 – 1.02)	0.351[***] (0.351 – 0.631)	1.88[***] (0.351 – 3.88)
Pyrene	1.24[**] (0.292 – 1.34)	0.292[a]	0.292[a]	2.28 (1.76 – 2.77)	0.473[**] (0.292 – 0.755)	0.582[**] (0.292 – 1.09)	0.292[a]	3.41 (2.01 – 4.92)
Benz[a]anthracene	0.205[a]	0.205[a]	0.205[a]	0.205[***] (0.205 – 0.866)	0.205[a]	0.205[***] (0.205 – 0.452)	0.205[***] (0.205 – 0.324)	0.446[***] (0.205 – 0.824)
Chrysene	0.145[***] (0.145 – 0.358)	0.145[a]	0.145[a]	0.145[***] (0.145 – 2.01)	0.365[**] (0.145 – 0.475)	0.196[***] (0.145 – 0.743)	0.145[a]	2.41 (2.01 – 3.08)
Benzo[b+j]fluoranthene	0.844[a]	0.844[a]	0.844[a]	0.844[***] (0.844 – 3.55)	0.844[a]	2.31[**] (0.844 – 3.51)	0.844[a]	24.5 (15.5 – 33.9)
Benzo[k]fluoranthene	0.238[**] (0.134 – 0.642)	0.134[a]	0.134[a]	0.134[***] (0.134 – 0.412)	0.134[a]	0.399[**] (0.134 – 0.594)	0.134[a]	3.84 (2.50 – 5.15)
Benzo[a]pyrene	0.277[***] (0.277 – 1.02)	0.277[***] (0.277 – 0.398)	0.277[a]	0.277[***] (0.277 – 1.24)	0.277[a]	1.22[**] (0.277 – 2.45)	0.277[a]	15.1 (9.76 – 20.5)
Dibenzo[a,l]pyrene	0.671[a]	0.671[a]	0.671[a]	0.671[a]	0.671[a]	0.671[a]	0.671[a]	0.671[a]
Dibenz[a,h]anthracene	3.97[**] (0.499 – 13.9)	0.499[***] (0.499 – 1.66)	0.499[a]	0.767[**] (0.499 – 3.63)	0.499[a]	5.85[**] (0.499 – 9.96)	0.499[a]	51.1 (38.1 – 65.5)
Benzo[ghi]perylene	3.09[**] (0.355 – 4.48)	5.08 (2.66 – 6.78)	1.66 (1.44 – 1.88)	3.80 (2.86 – 11.8)	3.17 (1.98 – 4.00)	4.83 (3.06 – 8.53)	2.29 (1.55 – 4.18)	32.9 (27.9 – 40.8)
Indeno[1,2,3-cd]pyrene	0.185[***] (0.185 – 1.18)	0.185[a]	0.185[a]	0.185[a]	0.185[a]	0.185[a]	0.185[a]	17.6 (13.9 – 23.3)
ΣPAHs	229 (200 – 296)	46.4 (44.0 – 49.4)	91.7 (64.5 – 124)	256 (77.6 – 352)	51.1 (48.8 – 57.5)	74.6 (44.4 – 125)	55.0 (49.8 – 137)	428 (250 – 631)
$\Sigma PAHs_{carc}$	20.8 (15.8 – 26.0)	9.82 (8.57 – 11.1)	10.9 (9.00 – 13.3)	16.8 (13.9 – 23.9)	8.24 (7.45 – 11.7)	19.6 (9.43 – 23.6)	12.2 (7.19 – 16.1)	150 (122 – 186)

Note: Detection frequency of each compound was 100% unless otherwise indicate.
[*] 80% ≤ detection frequency <100%.
[**] 60% ≤ detection frequency <80%.
[***] 15% ≤ detection. frequency <60%.
[a] When the concentration was below the LOD, the value of the respective LOD/$\sqrt{2}$ was used [50].