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Níveis de exposição de bombeiros portugueses a hidrocarbonetos aromáticos policíclicos em ambiente de quartel

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Exposure Levels of Portuguese Firefighters to Polycyclic Aromatic Hydrocarbons at Fire Stations

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Abstract

Firefighting activity is among the most dangerous occupations, being classified as a possible carcinogen to humans by the International Agency for Research on Cancer. Polycyclic aromatic hydrocarbons (PAHs), organic pollutants classified as priority pollutants by the Environmental Protection Agency of the United States of America (US EPA), are among the most characterised compounds in the occupational exposure of firefighters. However, the existing information is still very limited, particularly in a fire station environment.

This main objective of this study was to characterize the occupational exposure of firefighters to 18 PAHs through personal air monitoring during the regular work shift. Firefighters from three fire corporations from the Bragança district (Bragança, Macedo de Cavaleiros and Torre de Moncorvo) were invited to collect a fraction of particulate matter, $PM_{2.5}$ - particles with diameter ≤ 2.5 µm, for further analysis regarding its composition in PAHs.

The concentrations of total PAHs (ΣPAHs) ranged from 2.23 ng/m^3 (Macedo de Cavaleiros) to 486.25 ng/m^3 (Torre de Moncorvo). The compounds with 2 and 3 aromatic rings were the predominant ones in the samples collected in the Bragança (82.7%) and Macedo de Cavaleiros (79.3%) corporations while the PAHs with 5 and 6 rings predominated in the $PM_{2.5}$ samples collected in the Torre de Moncorvo fire station (55.3%). The risk assessment performed with the determined PAHs concentrations revealed a higher prevalence of possible/probable carcinogenic compounds in the breathing air of firefighters from Torre de Moncorvo corporation (72% *versus* 14% in Bragança and Macedo de Cavaleiros). Among the compounds under study, the prevalence of dibenzo(a,h)anthracene in samples of personal air collected in Torre de Moncorvo (median 62.67 ng/m^3; range 0.72-195.06 ng/m^3) and Bragança (0.95 ng/m^3; range 0.91-12.69 ng/m^3) should be highlighted. In fact, from those fire stations presented a higher lifetime risk of developing cancer during their life (3.55×10^{-7} and 6.05×10^{-9}, respectively for Torre de Moncorvo and Bragança). However, the values determined are clearly below the guideline recommended by the US EPA (10^{-6}). Thus, it can be concluded that exposure to PAHs (through $PM_{2.5}$ inhalation) represents no risk in the characterized fire stations is safe for these operational forces.

Keywords: Polycyclic aromatic compounds, Firefighters, Occupational exposure, Personal air monitoring

Resumo

A atividade de combate a fogos está entre as profissões mais perigosas, sendo classificada como possível agente cancerígeno para o Homem pela Agência Internacional de Investigação para o Cancro (IARC). Os hidrocarbonetos aromáticos policíclicos (PAHs), poluentes orgânicos classificados como poluentes prioritários pela Agência de Proteção Ambiental dos Estados Unidos da América (US EPA), estão entre os compostos mais caracterizados na exposição ocupacional dos bombeiros. No entanto, a informação existente ainda é muito limitada, em particular em ambiente de quartel.

Este estudo teve como objetivo principal a caracterização da exposição ocupacional dos bombeiros a 18 PAHs através da monitorização do ar pessoal durante o turno de trabalho regular. Bombeiros de três corporações do distrito de Bragança (Bragança, Macedo de Cavaleiros e Torre de Moncorvo) foram convidados a recolher uma fração de matéria particulada, $PM_{2.5}$ – partículas com diâmetro aerodinâmico ≤ 2.5 µm, para posterior análise quanto à sua composição em PAHs.

As concentrações totais de PAHs (ΣPAHs) variaram entre 2,23 ng/m^3 (Macedo de Cavaleiros) e 486,25 ng/m^3 (Torre de Moncorvo). Os compostos com 2 e 3 anéis aromáticos foram os predominantes nas amostras recolhidas nas corporações de Bragança (82,7%) e Macedo de Cavaleiros (79,3%), enquanto os PAHs com 5 e 6 anéis dominaram nas amostras de $PM_{2.5}$ recolhidas na corporação de Torre de Moncorvo (55,3%). A avaliação de risco demonstrou uma maior prevalência de compostos possivelmente/provavelmente cancerígenos no ar respirável de bombeiros da corporação de Torre de Moncorvo (72% *versus* 14% em Bragança e Macedo de Cavaleiros). Entre os compostos em estudo, destaca-se a prevalência do dibenzo(a,h)antraceno em amostras de ar pessoal recolhidas nas corporações de Torre de Moncorvo (mediana 62,67 ng/m^3; gama 0,72-195,06 ng/m^3) e de Bragança (0,95 ng/m^3; gama 0,91-12,69 ng/m^3). Com efeito, foram os indivíduos destas corporações que apresentaram um maior valor de risco de desenvolvimento de cancro ao longo da vida ($3,55\times10^{-7}$ e $6,05\times10^{-9}$, respetivamente para Torre de Moncorvo e Bragança), porém os valores determinados encontram-se claramente abaixo da diretriz recomendada pela US EPA (10^{-6}). Assim, conclui-se que a exposição a PAHs (através da inalação de $PM_{2.5}$) nos quarteis caracterizados não representa um risco acrescido para a saúde destes operacionais.

Palavras-Chave: Hidrocarbonetos aromáticos policíclicos; Bombeiros; Exposição ocupacional; Monitorização de ar pessoal

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List of Symbols and Abbreviations

AOSR	Athabasca Oil Sands Region
ACN	Acetonitrile
BaP	Benzo[a]pyrene
EU	European Union
IARC	International Agency for Research on Cancer
PPE	Personal protective equipment
NIOSH	National Institute for Occupational Safety and Health
1OH-Ace	1-Hydroxyacenaphthene
3OH-B[a]P	3-Hydroxybenzo[a]pyrene
2OH-FLU	2-Hydroxyfluorene
1OH-Naph	1-Hydroxynaphthalene
1OHPy	1-Hydroxydixypyrene
OHCA	Out-of-Hospital Cardiac Arrest
PAHs	Polycyclic Aromatic Hydrocarbons
PCA	Principal Component Analysis
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
$PM_{2.5}$	Particulate matter with an aerodynamic diameter of less than 2,5 µm
PM_{10}	Particulate matter with an aerodynamic diameter of less than 10 µm
SCBA	Self-contained Breathing Apparatus
SCF	EU Scientific Committee for Food
US-EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds
WHO	World Health Organization

1. Introduction

1.1. The impact of climate changes in the occurrence of forest fires

Climate changes is an undeniable reality that has been causing an increase in the frequency and intensity of extreme weather events (Oliveira et al., 2020). Global warning has substantially contributed to increase episodes of forest fires, with longer fire seasons and more severe fire incidents, which has contributed to the changes observed in climate as well as the impact on the various terrestrial ecosystems (Oliveira et al., 2020). The exacerbation of climate changes favours the increase of forest fires with severe consequences for the affected populations and surrounding environment (Schmuck et al., 2015).

Forest fires are uncontrolled and unstructured fire events that occur in rural areas (forests and woodlands). These fires act as a catalyst for the needed environmental change, causing the chemical renewal of soil and air and the recycling of available nutrients. Forest fires cause the replenishment of riparian vegetation and the dispersal of plants adapted to fire. Also, they remove undergrowth, clean the forest floor of debris, and promote its natural fertilization. Indeed, forest fires are an essential ecological process in nature, which occurrence is promoted by the existence of forest land with a high coverage of dry foliage, litter, and herbaceous plants. This effect combined with the increase in demand for forest products, results in a loss of ecological stability, increased occurrence of floods, droughts, and desertification, which promotes the occurrence of forest fires (Singh, 2018). Planned and intentional burning are a widely used forest management tool to control vegetation, increase productivity and biotic diversity, control diseases and insects' plagues, and reduce fuel accumulation (Zielinska et al., 2019). Thus, prescribed fires are a valuable tool for fuel management in forests and for ecosystems restoration.

The analysis of the occurrence of forest fires in the European territory during the last 30 years showed an increase in the duration of fire seasons and the existing projection points to progressive increases as the average annual temperature increases, particularly, in the Mediterranean countries (Figure 1.1). In recent years, some Northern European countries have experienced unprecedented forest fires, such as Scandinavia (Schmuck et al., 2015).

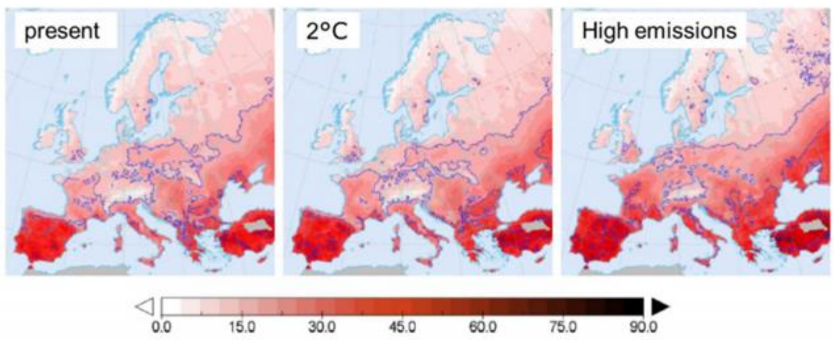


Figure 1.1 Global Forest fire danger caused by weather (score from 0 to 90) at ent, at 2°C and high emissions (Schmuck et al., 2015).

Several reports indicate that forest fires are increasingly frequent, and their severity has increased significantly in European Mediterranean countries, Australia and North America (Bassi & Kettunen, 2008; JRC Technical Report, 2021; Tedim et al., 2015; Oliveira et al., 2020).

Weather and climate are among the main factors influencing the potential of forest fires. In Mediterranean areas of Europe, precipitation and soil moisture appear among the most relevant factors, associated with spatial patterns of fire occurrence (Rigo et al., 2017). Large fires and extreme fires, in general, are complex and dynamic events that have become a central concern of policy and decision-making committes. However, the study of their characteristics, factors and impacts has been neglected, especially in Europe (Fernandes et al., 2016). Fernandes et al. (2016) correlated large forest fires in Portugal with forest areas subjected to extreme weather conditions, combined with subsequent rapid fire spread (Fernandes et al., 2016). The results of Ruffault et al., 2017 revealed that wind conditions were the main factor for the size of large summer fires in Mediterranean France between 1973-2013 (Ruffault et al., 2017). Current trends in Greece indicate longer and more intense summer droughts that extend even out of season. As such, the frequency and the intensity of forest fires are increasing. The impact of high temperature and wind speed on the critical fire danger was underlined (Karali et al., 2014). The analysis of Founda et al. (2009) revealed that the maximum temperatures recorded in Athens have a high similarity with the temperatures predicted for the second half of the century (2071-2100). Analysis of the temperatures of two other regions close to Athens, but less affected by urbanisation, indicated that the urban heat effect in the city of Athens contributed positively to the anomalies of night temperatures, making the heat wave even more unbearable (Founda & Giannakopoulos, 2009). Heat wave events cause recognised adverse impacts on agriculture, forests, and economic activities. Cardil et al. (2014) analysed the relationship between high temperatures (air temperature above 25°C at 850 hPa) and large forest fires in Sardinia (Italy) during the period 1991-2009 (Cardil et al., 2014; Founda & Giannakopoulos, 2009).

In the period of 2000-2017, forest fires were responsible for 8.5 million ha burned (approximately 480 800 ha/year), the death of 611 firefighters and civilians, as a loss of more than 54 billion euros in European territory (European Commission, 2018). Between 2010 and 2016, more than 40 000 fires per year were reported in Greece, Spain, France, Italy and Portugal, countries burnt areas represented about 85% of the total burn in Europe.

Portugal has been experiencing a progressive reduction in forest area over time, with losses of 4.6% between 1995 and 2010 (approximately 104 ha per year) (Turco et al., 2019). This reduction occurs due to a decrease in the area covered by maritime pine (*Pinus pinaster*) (Turco et al., 2019). This species has physical characteristics that allow its survival after low intensity fires, such as thick bark and reproductive processes that facilitate its recovery. However, its structural arrangement, quantity and quality also makes it highly flammable (Fernandes & Rigolot, 2007). The time intervals observed between fires (< 20 years) do not allow this species to reach the necessary maturity and to produce seed essential for its reproduction, which compromises its regeneration (Fernandes & Rigolot, 2007). As an economic alternative, forest owners have replaced pine plantations with eucalyptus (Eucalyptus globulus), a species with a shorter life cycle, so, it makes its plantation compatible with recurrent forest fires (Turco et al., 2019). The forest fires that occurred between 2010 and 2017 represented a cumulative loss of 37% of the Portuguese forest area. Since 2010, the northern and central regions of the country have continuously been the most affected areas by forest fires, with a total annual area burnt between 15-59% and 35-73%, respectively; the total area burnt in the southern region ranged between 3-31% (Oliveira et al., 2020).

Recent studies reveal that high temperatures and drought are both important factors for the increase of burned area in Portugal. The solid association between burned area and these factors allows to conclude that drier and hotter conditions result in larger forest fires (Oliveira et al., 2020; Turco et al., 2019). In 2017, Portugal recorded a burnet area of 539 921 ha, 598% of the previous decennium average (90 269 ha), owing to 21 006 occurrences. Pine and eucalyptus forest areas were the most affected by the 2017 fires (Schmuck et al., 2015). Approximately 90% of forest fires are caused by human activity, mostly through negligence/accident or criminal actions (agricultural crop alteration, property enhancement and environmental crime) (Satendra Ashutosh Dev Kaushik, 2014).

Major forest fires cause serious ecological, economic, and social problems in the affected areas. The European Union has estimated an average annual loss of €140.8 million due to the occurrence of forest fires (European Commission, 2018).

1.2. Pollutants released by forest fires

The occurrence of forest fires has a negative impact on the air quality of the affected sites and surrounding areas. Thus, it becomes necessary to understand the impact on public health due to exposure to emissions from fires (forest or controlled ones).

In a forest and/or prescribed fire, the burning of wood results in the emissions of carbon dioxide and water vapour according to the following chemical equation (eq. 1):

$$n\,CH_2O + n\,O_2 \longrightarrow n\,CO_2 + n\,H_2O + Heat \qquad \text{(eq. 1)}$$

This combustion reaction, when incomplete, releases carbon monoxide (CO). In addition to carbon monoxide and carbon dioxide, fires release into the atmosphere large amounts of particulate matter (PM) and various pollutants gases such as nitrogen oxides (NOx), volatile organic compounds (VOCs) and semi-volatile ones, such as polycyclic aromatic hydrocarbons (PAHs), acetaldehyde, formaldehyde, benzene, toluene, among many other substances (Jaffe et al., 2020; Liu et al., 2014; Oliveira et al., 2020). PM consists of a complex mixture of solid and liquid particles suspended in air that vary in size, shape, origin, and composition. PM is either emitted directly into the atmosphere (primary source) or is formed through chemical reactions between different gases (secondary source) (Kaulfus et al., 2017). PM can absorb/adsorb at its surface other substances such as elemental carbon, metals, and inorganic ions (e.g., sulphates, nitrates, ammonia, and soluble metals), VOCs including PAHs (Navarro 2018) (Zhang et al., 2015). VOCs released by fires, upon the presence of nitrogen oxides generate tropospheric ozone precursors (Zielinska et al., 2019).

In late June 2017, a forest fire occurred in the Doñana Natural Park, in Spain, which is in southwestern Europe. This forest fire occurred under exceptional weather circumstances. When the fire started, record high values were measured for all monitored gases at this site (specifically, peaks of 99,995 $\mu g/m^3$ for CO, 951 $\mu g/m^3$ for O_3, 478 $\mu g/m^3$ for NO_2, 116 $\mu g/m^3$ for SO_2 and 1000 $\mu g/m^3$ for PM_{10} – particulate matter with an aerodynamic diameter of 10 µm). Some species, such as CO, SO_2 and PM_{10} remained at high levels for several hours. Emissions from wildfires can account for 20% of total daily fine PM emissions during the fire season (Adame et al., 2018). Pollutants released during forest fires can persist for long periods and accumulate in the environment and food chain, thus affecting humans and animals through multiple exposure pathways (European Environment Agency, 2019). According to the temporal evolution patterns of a burnt area, it can recover to initial atmospheric levels between 48 and 96h after an event (Adame et al., 2018). McClure et al., (2018) concluded a decline in the overall decrease in $PM_{2.5}$

at monitoring sites in rural areas, this being a direct result of reduced anthropogenic emissions (McClure & Jaffe, 2018). During May 2016, a large boreal fire occurred across the Athabasca Oil Sands Region (AOSR) in central Canada and near an extensive air quality monitoring network. Wentworth et al., (2018) examined integrated polycyclic aromatic hydrocarbons and the sum of PAHs (ΣPAH) was, on average, 17 times higher in fire-influenced samples compared to non-fire influenced samples from air monitoring stations. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are unintentional by-products of combustion and industrial processes. PCDD/Fs can be produced by the combustion of excess air, water, carbon dioxide, hydrogen chloride, and chlorinated materials (Hsu et al., 2011). Hsu et al., (2011) performed congener-specific analyses of 17 PCDD/Fs in 20 serum samples collected from firefighters and researchers. PCDD/F concentrations in helmets that were contaminated when worn during fires were 63-285 times higher than in a clean helmet (Hsu et al., 2011).

Some authors have reported the significant impact of the fires that occurred in Chile in 2017, with important environmental consequences: i) the impact of emissions from the fires on the increased levels of PM found in cities near and bordering the burned areas; ii) increased risk of landslides and flooding in populated areas downstream of the burned sites (de la Barrera et al., 2018). de la Barrera et al. (2018) also observed a significant impact of emissions from the fires in Chile on air quality in cities more than 100 km from the burned area (de la Barrera et al., 2018). A systematic review by Reid et al. (2016) and based on epidemiological studies showed significant associations between exposure to smoke from forest fires and declines in lung function in asthmatic children (Reid et al., 2016). These authors also found evidence that smoke from forest fires can be associated with increased respiratory morbidity, including chronic obstructive pulmonary disease (Naeher et al., 2007) . Another study also found that the presence of PM from forest fires, resulting from an impactful episode in Southeast Asia, was associated with increased cardiopulmonary mortality (Naeher et al., 2007). Recently, Oliveira et al. (2020) assessed the health effects on populations exposed to the 2017 forest fires in Portugal, with an estimated occurrence of more than 450 hospital admissions due to cardiovascular diseases and 3500 cases with asthma incidence symptoms per 100000 individuals at risk. These authors found a positive and direct association between exposure to PM released by forest fires with all-cause mortality and respiratory morbidity, including bronchitis, asthma, chronic obstructive pulmonary disease, and pneumonia (Oliveira et al., 2020). Emissions from forest fires also have a significant impact on the physico-chemical properties of the atmosphere, alter visibility and the microclimate of affected locations.

Emissions from fires (forest and prescribed) contribute to increased air pollution. Air pollution is a globally recognised threat to quality of life and human health, particularly in urban areas (Oliveira et al., 2020). The World Health Organization (WHO) estimated a total of 12.6 million deaths worldwide due to environmental diseases, representing 23% of global mortality and 26% of deaths in young children (WHO, 2016). Studies show that this type of pollution has an impact on reducing the average life span, increasing medical costs, and reducing the productivity of the population. Air pollution is also related to several adverse risks to human health such as reproductive effects, cardiovascular diseases, and a higher incidence of oncological diseases (Lewtas, 2007). Although occupational exposure to coal combustion products by inhalation is known to cause lung cancer, many studies, mostly from China, show similar effects from domestic coal use (Straif et al., 2006). In Xuan Wei County, Yunnan Province, lung cancer mortality is among the highest in China and, especially in women, is more closely associated with "smoked" indoor coal burning, as opposed to "smokeless" wood or coal burning, than with tobacco smoke. Mumford et al., (1987) suggested an aetiological link between domestic burning of smoked coal and lung cancer in Xuan Wei (Mumford et al., 1987). The study by de Lan et al. (2002) assessed if incidence of lung cancer decreased after changing cooker equipment. Unvented domestic burning of coal and biomass fuel is very common in developing countries, particularly in rural areas. Switching from unvented to vented cookers appears to benefit the health of people in China (Lan et al., 2002). A case-control study of female lung adenocarcinoma in Harbin, China, involving interviews with 120 cases of non-smoking women, showed that high charcoal use, indoor air pollution, exposure to charcoal dust, frequent frying and deep frying, and a family history of lung cancer are statistically significant risk factors for female adenocarcinoma. High personal income, spacious housing, and frequent consumption of carrots were protective factors for adenocarcinoma (Dai et al., 1996). Colon cancers are most common in the Western world. In most of these cases, there is no family history and sporadic gene damage appears to play an important role in the development of colon tumours (Diggs et al., 2011). Bonner et al. (2005) conducted a population-based case-control study of environmental exposure to PAHs in early life in relation to breast cancer risk. The study suggested that early life exposure to high levels of PAHs may increase the risk of postmenopausal breast cancer (Bonner et al., 2005). Nie et al. (2007) Bonner et al. (2005) conducted a population-based case-control study of environmental exposure to PAHs in early life in relation to breast cancer risk (Nie et al., 2007).

It's known that millions of people can potentially be exposed to smoke from forest fires which makes an important public health problem. As such, Dennekamp (2015), from July 2006 through June 2007, collected data with the aim to measure the association between out-of-hospital cardiac arrest (OHCA) and forest fire smoke exposures in a large city (Melbourne) during a severe forest fire season. Their study was able to find an association between exposure to forest fire smoke and an increase in the rate of OHCA (Dennekamp et al., 2015).

Rappold et al. (2017) developed a Community Health-Vulnerability Index (CHVI) that included different factors such as, the prevalence of asthma (in children and adults), the prevalence of hypertension, diabetes, and obesity and indicators of socio-economic status such as poverty, education, and unemployment level. This index was based on factors that are known to increase the risk of the health effects of air pollution. With this index, it was possible to identify which states (in the US) had the highest smoke exposure and were therefore the most vulnerable. Using a simulation of air quality in the USA between 2008 and 2012, it was possible to verify that 10% of the population (30.5 million people) lived in the areas where the contribution of fire-$PM_{2.5}$ to annual average ambient $PM_{2.5}$ was high (>1.5 μg/m^3). And yet, that 10.3 million subjects experienced unhealthy air quality levels for more than 10 days due to smoke (Rappold et al., 2017).

To improve air quality in Europe, the European Commission has published the Clean Air Policy Package for Europe, which aims to reduce to half the number of premature deaths by 2030 compared to 2005 data (European Environment Agency, 2019). In this context, the European Union agreed on a revision of the National Emission Ceilings Directive and set commitments to reduce emissions of sulphur dioxide, ammonia, NO_x, PM, and some VOCs by 2030. In addition, the Directive requires Member States to develop National Air Pollution Control Programmes which should contribute to the successful implementation of the air quality plans established under the EU Air Quality Directive (European Environment Agency, 2019).

It is important to understand the risk related to fire management actions to promote the informed protection of public health. It thus becomes imperative the need to develop awareness and self-protection programmes for populations, especially the most susceptible groups (children, pregnant women, the elderly and the chronically ill).

1.2.1. Polycyclic aromatic hydrocarbons

PM and PAHs are one of the most relevant air pollutants to human health due to their contribute to the degradation of air quality. The effects of PM depend on the concentration, size, and chemical composition of the aerosols. Particles between 5 and 10 µm, in size, are retained in the tracheobronchial tree, while the lighter ones (PM < 2.5µm in size) are deposited in the bronchi and pulmonary alveoli where gas exchange takes place. PM with size less than 0.1 µm behave similarly to gas molecules and therefore penetrate the respiratory system to the lung alveoli, manage to transpose cell membranes to reach the blood circulation (Kim et al., 2015).

PAHs are organic substances made of carbon and hydrogen atoms grouped in at least two, condensed or fused, aromatic ring structures. Table 1.1 presents the chemical structures of PAHs that are frequently monitored, according to the recommendations of the EU Scientific Committee for Food (SCF), the European Union and the United States Environmental Protection Agency (US-EPA) (Lerda, 2010). At room temperature, PAHs are usually coloured and crystalline solids (Kim et al., 2013). PAHs are light-sensitive lipophilic compounds, and their water solubility decreases with the increase in the number of aromatic rings (Table 1.2). Low molecular mass compounds (up to three rings) are more volatile (with low condensation temperatures) and exist mainly in the gas phase while heavier compounds prevail adsorbed to PM (Kim et al., 2013).

Table 1.1 Chemical structure of frequently monitored PAHs, according to SCF, US-EPA and EU mmendations (Lerda, 2010).

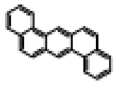
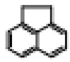
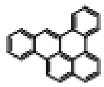
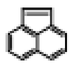
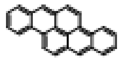
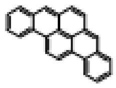
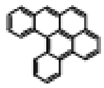
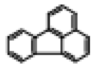
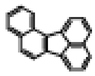
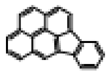
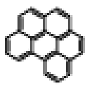
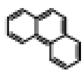
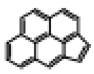
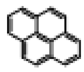
List	Common Name	Structure	List	Common Name	Structure
EPA, SCF, EU	Benzo[*a*] pyrene		EPA, SCF, EU	Dibenz[*a*,*h*] anthracene	
EPA	Acenaphthene		EU+SCF	Dibenzo [*a*,*e*]pyrene	
EPA	Acenaphthylene		EU+SCF	Dibenzo [*a*,*h*]pyrene	
EPA	Anthracene		EU+SCF	Dibenzo [*a*,*i*]pyrene	
EPA, SCF, EU	Benz[*a*] anthracene		EU+SCF	Dibenzo [*a*,*l*]pyrene	
EPA, SCF, EU	Benzo[*b*] fluoranthene		EPA	Fluoranthene	
SCF, EU	Benzo[*j*] fluoranthene		EPA	Fluorene	
EPA, SCF, EU	Benzo[*k*] fluoranthene		EPA, SCF, EU	Indeno[1,2,3-*cd*]pyrene	
EU	Benzo[*c*]fluorene		EU+SCF	5-Methyl chrysene	
EPA, SCF, EU	Benzo[*ghi*] perylene		EPA	Naphthalene	
EPA, SCF, EU	Chrysene		EPA	Phenanthrene	
SCF, EU	Cyclopenta [*cd*]pyrene		EPA	Pyrene	

Table 1.2 Physico-chemical properties of the 16 priority PAHs, as well as dibenzo[a,l]pyrene and benzo[j]fluoranthene (WHO, 1998) (Maria & Castro, 2010).

Compound	Abbreviation	Condensed formula	Molar mass (g/mol)	Melting point (°C)	Boiling point (°C)	Log K_{ow*}	Vapour pressure at 25 °C (Pa)	Water solubility at 25 °C (µg/L)	Henry's constant at 25 °C (kPa)
Naphtalene	Naph	$C_{10}H_8$	128.17	81	218	3.40	10,4	3.17 × 104	4.89 x 10-2
Acenaphtylene	Aci	$C_{12}H_8$	152.19	92 - 93	265	4.07	8.9 × 10-1	3.93 × 103	1.14 × 10-3
Acenaphthene	Ace	$C_{12}H_{10}$	154.21	95	279	3.92	2.9 × 10-1	3.4 × 103	1.48 × 10-2
Fluorene	Fl	$C_{13}H_{10}$	166.22	115 - 116	295	4.18	8.0 × 10-2	1.98 × 103	1.01 × 10-2
Anthracene	Ant	$C_{14}H_{10}$	178.23	216	342	4.50	8.0 × 10-4	73	7.3 × 10-2
Phenanthrene	Phe	$C_{14}H_{10}$	178.23	100	340	4.60	1.6 × 10-2	1.29 × 103	3.98 × 10-2
Fluoranthene	Ft	$C_{16}H_{10}$	202.25	109	375	5.22	1.2 × 10-3	260	6.5 × 10-4
Pyrene	Pyr	$C_{16}H_{10}$	202.25	150	393	5.18	6.0 × 10-4	135	1.1 × 10-3
Benzo[a]anthracene	B[a]A	$C_{18}H_{12}$	228.29	161	400	5.61	2.8 × 10-5	14	----------
Chrysene	Chr	$C_{18}H_{12}$	228.29	254	448	5.91	8.4 × 10-5	2.0	----------
Benzo[b]fluoranthene	B[b]F	$C_{20}H_{12}$	252.31	167	357	5.80		1,2	----------
Benzo[k]fluoranthene	B[k]F	$C_{20}H_{12}$	252.31	216	480	6.84	1.3 × 10-7	0.76	4.4 × 10-5
Benzo[a]pyrene	B[a]P	$C_{20}H_{12}$	252.31	178	496	6.50	7.3×10^{-7}	3.8	3.4 × 10-5 (20 °C)
Dibenz[a,h]anthracene	DB[a,h]A	$C_{22}H_{14}$	278.35	267	524	6.50	1.3×10^{-8} (20 °C)	0.5 (27 °C)	7.0 × 10-6
Indeno[1,2,3-cd]pyrene	InP	$C_{22}H_{12}$	276.33	164	536	6.58	1.3×10^{-8} (20 °C)	62	2.9 × 10-5 (20 °C)

Benzo[g,h,i]perylene	B[g,h,i]P	$C_{22}H_{12}$	276.33	278	545	7.10	1.4×10^{-8}	0.26	2.7 × 10-5 (20 °C)
Benzo[j]fluoranthene	B[j]F	$C_{20}H_{12}$	252.31	165	480	6.12	2.0×10^{-6}	2.5 (20 °C)	----------
Dibenzo[a,l] pyrene	DB[a,1] P	$C_{24}H_{14}$	302.36	-------	--------	------	---	-----------	----------

PAHs are formed mainly during combustion processes of natural and anthropogenic origin where burning of organic matter occurs (e.g., wood, coal, peat, fossil fuels, and waste) (Samburova et al., 2016). Naturally happening included volcanoes, disintegration of sedimentary rocks, among others. From anthropogenic source it includes tar deposits, wood cookers, cigarette smoking, huge flames, among others. There are three primary wellsprings of PAHs in the climate: pyrogenic, petrogenic and organic. Momentarily:

I) Pyrogenic: In pyrolysis, pyrogenic PAHs are shaped when natural substances are presented to high temperatures without even a trace of oxygen or in low amount. Pyrogenic cycles happen at temperatures going from 350ºC to over 1200ºC, for example, in the burning of vehicles, inadequate ignition of wood (as in timberland fires) and surprisingly deficient burning of oils in warming frameworks. These PAHs are normally present in metropolitan conditions.

II) Petrogenic: Unlike pyrogenic PAHs, these can frame at 100-150 ºC, just like the instance of their development during the development of raw petroleum. In this sort of compound cycle, PAHs are found in raw petroleum items. Subsequently, their fundamental sources are oil slicks in seas and fresh waters; spills from underground stores; aggregation from petroleum and engine oil releases.

III) Biological: PAHs can likewise be integrated by explicit plants and microorganisms or through the degradation of vegetative matter.

In any case, it ought to be referenced that the source perceived as the biggest contributors of PAHs to atmosphere, regardless of whether normally happening or from anthropogenic sources, is incomplete combustion (Abdel-Shafy & Mansour, 2016).

Sharma et al. (2007) assessed the presence of PAHs in PM from the campus of Jawaharlal Nehru University, an urbanized site at New Delhi, India. The results of principal component analysis indicated that diesel and petrol vehicles are the major sources of PAHs in all seasons. In winter, coal and wood combustion also contribute significantly to the levels of PAHs. This is not unexpected, considering that wood and coal are widely used by an appreciable fraction of the population of Delhi to meet their heating/energy needs (Sharma et al., 2007). Marr et al. 2004 aimed to describe the concentrations of PAHs associated with vehicle traffic and installations using diesel vehicles. Median total particulate PAH concentrations along Mexico City roads ranged from 60 to 910 ng m^{-3}. These levels are approximately 5 times higher than concentrations measured in the United States and among the highest measured ambient values reported in the literature. These results indicate that exposure to vehicle-related emissions of PAHs on Mexico City roads may present an important public health risk (Marr et al., 2004). Becker at al., 2006 through air measured during the period 1992-2000 at the High Arctic Warning Station in Canada verified an increase in the concentration of PAHs in the atmosphere, associated with regional combustion events during summer, namely from forest fires (Becker et al., 2006). PAHs from East Asia are transported to the west coast of the United States under certain meteorological conditions (Zhang & Tao, 2009). Xu et al. (2006) estimated that the total emission of PAHs in China was 25 300 tons in 2003. Among various sources, biomass burning, and domestic coal combustion contributed 60% and 20% of total emissions, respectively. Although energy consumption in China has increased continuously during the past two decades, the annual emission of PAHs has fluctuated depending on the amount of coal consumed nationally and energy efficiency (Xu et al., 2006).

The behaviour of these compounds in the atmosphere depends on the occurrence of complex physico-chemical reactions through interactions with other pollutants and photochemical transformations (Kim et al., 2013). Once released into the atmosphere, PAHs are transported over long distances before deposition through atmospheric precipitation onto soils, vegetation, or water cycles.

PAHs are thus widely distributed in the environment. Several studies report the levels of PAHs in air, water, sediment, and food samples (Santos et al., 2019). Although low molecular mass compounds are considered less toxic, they can react with other pollutants (such as sulphur dioxide and ozone) to form compounds such as diones and nitro-PAHs, which exhibit more pronounced toxicity (Kim et al., 2013).

Exposure to PAHs occurs through different exposure routes, namely through inhalation, ingestion, and dermal contact (Agency for Toxic Substances and Disease Registry, 2012). Although there are several hundred of PAHs, scientific attention has been focused on sixteen compounds recognised by the United States Environmental Protection Agency as priority pollutants (USEPA - U.S, 2005). Table 1.2 visualises some relevant physico-chemical characteristics to understand the environmental and toxicological behaviour of the 16 priority PAHs, as well as dibenzo[a,l]pyrene and benzo[j]fluoranthene (Maria & Castro, 2010). Due to the presence of aromatic rings, some PAHs exhibit high toxicity, mutagenic and carcinogenic characteristics. Benzo[a]pyrene is classified as carcinogenic to humans by IARC (group 1; IARC, 2010), while naphthalene, benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene and indeno[1,2,3-cd]pyrene are considered as possible carcinogens to humans (group 2B; IARC 2002, 2010). The compounds dibenzo[a,l]pyrene and dibenzo[a,h]anthracene are also considered probable carcinogens for humans (group 2A; IARC 2010) due to their greater carcinogenic potency than benzo[a]pyrene (Oliveira et al., 2016). The acute effects of PAHs on human health are mainly associated with the extent of exposure, their concentration and route of exposure. Acute exposure has been associated with worsening of cardiorespiratory function in people with diagnosed associated pathologies (asthma, hypertension, coronary heart disease, etc). Prolonged exposure has been associated with an increased risk of cancer of the skin, lung, bladder, and gastrointestinal tract (Kim et al., 2013).

When absorbed by the human body, PAHs are biotransformed by complex enzymatic mechanisms to facilitate their excretion from the human body mostly through urine. However, many of the metabolites of PAHs, after biotransformation, exhibit mutagenic properties, which is due to the formation of various reactive intermediates (Kim et al., 2013). The toxicity of PAHs, especially those with high molecular mass, is largely attributed to the ability of these species to react with DNA giving rise to adduct formation and mutation. Consequently, structure change mutation, chromosomal aberrations and mutations are the main products of the biological response to exposure to mutagenic species, enhancing genetic effects that may cause damage to the respiratory, cardiovascular, and reproductive systems, as well as promoting the development of cancer (Lewtas, 2007).

The most used instrumental methods for the analysis and detection of PAHs and OH-PAHs are gas chromatography (GC) coupled with tandem mass spectrometry (MS/MS); liquid chromatography (LC) coupled with fluorescence detection (FLD) and MS/MS. However, extensive sample cleaning must still be performed beforehand to reduce as much interference as possible, simultaneously reducing the detection limits (Gill & Britz-McKibbin, 2020).

1.3. Human biomonitoring

Through biological fluid analysis, human biomonitoring allows to quantify chemical substances concentrations, their metabolites, or the products reaction with the human organism, thus resulting in the assessment of total individual exposure to chemicals or their effects on the human organism. The increasing occurrence of forest fires dramatically increases the amount of air pollutants, thereby putting the population (general and occupational) at greater risk of exposure to toxic chemicals. The biomonitoring is mostly performed through the analysis of urine, blood, saliva, breath, placenta, hair, breast milk, and cerebrospinal fluid samples. Thus, the use of human biomonitoring is a valuable tool because, in addition to estimating the total internal dose, regardless of the source, route and duration of exposure, it also assists in determining the adverse effects associated with toxic exposure (Oliveira et al., 2017b).

Whilst PAHs tend to be persistent in the environment, once in the body they behave as non-persistent chemicals because they are rapidly metabolised, eliminated mostly through urine and faeces, and only small amounts are deposited in biological tissues. Biomonitoring of PAHs by determining their major metabolites in biological matrices allows a more accurate estimation of total exposure to these pollutants, regardless of the route of exposure. 1-Hydroxypyrene (1OHPy) the main metabolite of pyrene, is the most frequently used biomarker in the biomonitoring of PAHs (Oliveira et al., 2017b). 3-Hydroxybenzo[a]pyrene (3OH-B[a]P) is one of the metabolites of benzo[a]pyrene and is considered a biomarker of carcinogenic PAHs exposure (Oliveira et al., 2017b). Due to the abundance of PAHs from different routes of exposure, the use of more than one biomarker more adequately characterises total individual exposure (Oliveira et al., 2017b). However, the combination with data obtained from environmental monitoring (air and dermal exposure) should not be excluded to obtain a more complete characterisation (Oliveira et al., 2019). Additionally, taking into consideration that biological matrices are complex, it is of utmost importance to use extremely sensitive and efficient techniques, such as liquid and gas chromatography techniques (Santos et al., 2019).

Biomonitoring of PAHs is mostly performed in urine. Although the use of urine samples to determine OH-PAHs is widespread due to the sampling being non-invasive, there are still no standardized protocols to standardize the results reported in the literature. The main advantages of using urine samples lie in the possibility of collecting a large amount of sample, with a matrix that is easy and quick to process (Santos et al., 2019). In contrast, urine has as disadvantages the "matrix effect" which includes the low solubility of compounds that can lead to low concentrations and the possible interference of compounds that are in higher concentrations. If it is necessary to determine the metabolites produced after the reaction of the primary compounds, the rate of metabolism in everyone must also be considered (Santos et al., 2019). Urine sampling typically requires 24 h collection or concentration adjustment, as analytes can be highly diluted or highly concentrated relative to fluid intake. This problem can be overcome by measuring and normalising the results to the individual values of creatinine excreted in urine. Creatinine is eliminated from the human body at a constant rate and is therefore widely used to minimise the variability of parameters such as individual fluid intake, body temperature, exercise, and ambient temperature, which varies between individuals (Oliveira, et al., 2017a).

Regarding blood, because the half-life of PAHs in blood is short (hours), PAH concentrations in blood are typically three orders of magnitude lower than urinary metabolite levels (Santos et al., 2019). Consequently, most biomarker studies analysing exposure to PAHs in blood have simultaneously measured PAHs metabolites in urine (Sexton et al., 2011). The collection of a blood sample is difficult and invasive, requires needle handling and storage with additional care, relative to urine, during transport to the time of analysis (Santos et al., 2019). As such, blood may be a useful matrix to assess the internal dose of PAHs only upon recent exposure (Santos et al., 2019).

In the literature, the use of other matrices for the biomonitoring of PAHs has been discussed. Saliva is an alternative non-invasive sampling medium for screening and determination of PAHs (Santos et al., 2019). The collection and manipulation of saliva is quick and easy. However, the volume of saliva available may be limited depending on different physiological factors. In addition, the concentration of the compounds of interest can be affected by food ingestion (Santos et al., 2019). Regarding exhaled air, it seems to be a useful sample for recent exposure to PAHs with low molecular mass. Although collection is non-invasive, there is a need for specific systems to ensure the integrity of the collected sample (Santos et al., 2019). Human hair has also been considered to determine PAHs as an indicator of long-term exposure, since samples are not affected by extreme intra- or inter-day variations. The main advantage of this type of samples is that they are easy to collect (non-invasive and accessible) and transport before analysis (Santos et al., 2019). Other biological samples explored include placenta, breast milk and cerebrospinal fluid (Santos et al., 2019). The first two have been used to study prenatal exposure to PAHs, and this exposure may have health effects on newborns (Fernández-Cruz et al., 2017). Cerebrospinal fluid was used to monitor PAHs in patients with amyotrophic lateral sclerosis (Vinceti et al., 2017).

1.4. Non-occupational exposure: general population

The biomonitoring of the general population is challenging which explains the small number of studies. Although there are already several studies monitoring atmospheric concentrations of pollutants emitted by forest fires and discussing their socioeconomic, environmental and health impacts on the population, the use of biological samples to assess the specific exposure of forest fire emissions in the general population has not yet been reported.

In the human population**,** children and the elderly stand out as the most vulnerable groups. In the case of children (age below 18; (UNICEF, 2018)), their systems (respiratory, immune, reproductive, central nervous and digestive) are still developing, therefore, children constitute a subgroup of the population substantially susceptible and vulnerable to the potential health effects of air pollution (Oliveira et al., 2019). Additionally, children's airway epithelium is more permeable to air pollutants and their lung defences against these particles are not yet fully effective (Salvi, 2007). Forest fire emissions alter the composition and quality of atmospheric air which can lead to air contamination inside and outside the school environment. Oliveira et al. (2019) summarised information from studies addressing childhood biomonitoring and environmental exposure to fine PM and PAHs in school microenvironments (indoor and outdoor) (Oliveira et al., 2019). Although forest fires occur more frequently in rural areas due to the high amount of vegetation, children attending schools in polluted urban environments and in industrial areas are exposed to higher levels of PM and PAHs. Oliveira et al. (2019) concluded that there is a clear need to improve indoor air quality in schools and establish guidelines for exposure limits in these environments (Oliveira et al., 2019).

Electronic waste is currently one of the main sources of pollution. Almost 50 million tonnes of electronic waste are generated worldwide every year. A large proportion of this waste is shipped to China, where it is often processed using primitive methods to recover useful materials. A variety of toxic contaminants, including PAHs, are released into the surrounding environment during the recycling of this electronic waste, for example during burning. Consequently, employees who are not properly protected and residents living near these e-waste processing facilities are exposed to these pollutants (Zhu et al., 2018). Luo et al. (2015) determined the cancer risks promoted by exposure to PAHs in e-waste recycling areas and examined the size distribution of particle-bound PAHs. The estimated results by incremental inhalation of cancer risk suggested that particle-bound PAHs posed a serious threat to human health within the e-waste recycling zone and Guangzhou (Luo et al., 2015).

Strong evidence has demonstrated associations between environmental exposure to PM and PAHs with various health effects, including an increased risk of asthma, lung infections, skin diseases and allergies (Oliveira et al., 2019). Emissions from forest fires contribute strongly to pollutant concentrations in the atmosphere, which intensifies the need to explore the impact of these emissions on the population.

1.5. Occupational exposure: firefighters

Of the various occupational groups, firefighters are at higher risk of suffering potential health effects due to chronic exposure to a high number of air pollutants, which are released during fires (Oliveira et al., 2016). Occupational exposure of firefighters is classified by the International Agency for Research on Cancer (IARC) and the National Institute for Occupational Safety and Health (NIOSH) as possible carcinogenic for humans (IARC monograph (n 98), 2010). Exposure to hazardous pollutants can induce the formation of reactive oxygen species and cause the activation of oxidative pathways that can culminate in inflammatory lung and cardiovascular diseases (Oliveira et al., 2020). Monitoring firefighters' exposure during firefighting is a very complex task due to the unpredictability and challenges of the environment, such as weather conditions and hazardous situations. Although firefighting is among the most dangerous occupations, it is one of the least studied in terms of exposure and its relationship with occupational diseases (Oliveira et al., 2017). As such, biomonitoring of firefighters is an effective assessment tool to understand total exposures, especially to compounds such as PAHs that are not exclusively absorbed by inhalation and ingestion but also through dermal contact (Oliveira et al., 2017a).

The biomonitoring of firefighters has been reported in countries that are most frequently affected by forest fires namely, USA, Canada, Portugal. When comparing firefighters from different nationalities it is necessary to consider geographical, climatic, and seasonal differences, as well as the materials (such as vehicles or firefighters' protective equipment) and firefighting techniques used. In Portugal, biomonitoring studies in firefighters are scarce. Only in 2016 was published the first study assessing the total internal dose of PAHs in Portuguese firefighters, using six urinary OH-PAHs, namely: 1-hydroxynaphthalene, 1-hydroxyacenaphthene, 2-hydroxyfluorene, 1-hydroxyphenanthrene, 1-hydroxypyrene (1OHPy) and 3-hydroxybenzo[a]pyrene (3OHB[a]P). In this study, urinary concentrations and distribution profiles of individual OH-PAHs were determined in unexposed and exposed firefighters from six different corps. It should be noted that gender influence was accounted for in two fire brigades (Oliveira et al., 2016). Additionally, Oliveira et al. (2020) characterised the impact of firefighting activities on occupational exposure of Portuguese firefighters through exposure and effect biomarkers. To this end, six urinary biomarkers of exposure to PAHs and two biomarkers of genotoxicity (baseline DNA damage and oxidative DNA damage) were determined in firefighters from eight different corporations. Cardiorespiratory parameters were also monitored and correlated with the levels of the selected biomarkers (Oliveira et al., 2020). Urinary concentrations of total OH-PAHs, 1-hydroxynaphthalene (1OH-Naph), 1-hydroxyacenaphthene (1OH-Ace) and 2-hydroxyfluorene (2OH-FLU) were significantly higher in exposed than in unexposed individuals. Also, Oliveira et al. (2020) reported an association between heart rate, OH-PAHs, and blood biomarker of stress oxidative DNA damage in non-smoking firefighters (unexposed and exposed). However, this cross-sectional study cannot lead to a causal relationship (Oliveira et al., 2020).

On the other hand, tobacco consumption is a possible biasing factor when interpreting biomonitoring results of PAHs in occupational context. In order to identify the impact of tobacco consumption on the levels of OH-PAHs in the urine of firefighters, six metabolites were determined in three different groups: i) non-exposed non-smoking firefighters, i.e., who were not involved in firefighting activities in the week prior to urine sampling; ii) smoking firefighters who were not exposed to any type of fire emissions; iii) exposed smoking firefighters who actively participated in firefighting activities in the 48 h prior to urine collection. Oliveira et al. (2017b), found that individuals who smoke and were in contact with fire activities, presented OH-PAHs levels 355-3237% higher than individuals who neither smoked nor were exposed. Tobacco users not exposed to fires showed 76-412% higher levels of OH-PAHs compared to the control group (Oliveira et al., 2017b). These results indicate that individual and cumulative exposure to PAHs occurs through participation in firefighting activities and tobacco consumption (Oliveira et al., 2017b). Thus, to consider only occupational exposure as a source of exposure to PAHs, it is crucial to exclude the influence of tobacco consumption on the levels of OH-PAHs in the urine of firefighters. This influence can be assessed by determining the levels of cotinine, a metabolite of nicotine, in the urine samples of the participants before each occupational exposure (Rossbach et al., 2020).

In order to assess the working conditions of firefighters as comprehensively as possible, environmental monitoring should be complemented by biological monitoring. Only a few studies have investigated occupational exposure to PAHs in fire stations, being mainly conducted in the United States (Reinhardt & Ottmar, 2004). In Portugal, Oliveira et al. (2017a) identified the exposure of firefighters to PAHs under normal working conditions without fire incidents. Only this study simultaneously reported the environmental exposure in the fire brigade and the levels of PAHs metabolites in the urine of firefighters. Oliveira et al., 2017a evaluated the levels of 18 PAHs in the breathing air zone during their work shift in fire stations and the total internal dose of firefighters by quantifying six OH-PAHs in urine samples normalizing with individual creatinine values (Oliveira et al., 2017a). Oliveira et al. (2017) reported significant positive correlations between monitored PAHs in air and metabolites in urine ($r \geq 0.733$, $p \leq 0.025$). The concentrations of OH-PAHs in the urine of firefighters were inversely related to the size of the compounds, i.e., the higher the molecular weight, the lower the detected (Oliveira et al., 2017a). These results suggest that the air inside the fire stations is also a major source of occupational exposure in firefighters. However, it is important to note that the values of PAHs in air and the reported levels of 1-hydroxypyrene (1OHPy) were below the recommended reference values (Oliveira et al., 2017a).

In addition to direct exposure to emissions from forest fires and on the premises of the corporation, firefighters can be indirectly exposed through contamination of personal protective equipment (PPE) and vehicles used during firefighting. Several studies have identified the presence of PAHs in firefighters' PPE (Fent et al., 2015; Kirk & Logan, 2015). Occupational exposure of firefighters can also occur in phases considered safe (training, overhaul, cleaning, and maintenance of equipment) (Abrard et al., 2019). After a training session, benzo[a]pyrene (BaP), a biomarker of exposure to carcinogenic PAHs, was found on the surfaces of fireproof jackets and firefighters' tools (Abrard et al., 2019). A single training session accounted for a BaP deposition of 113.75 ± 45.03 μg m^2 on fire-exposed jacket material. After several training sessions, a cumulative effect on the deposition of this PAH was suspected. The estimated dose of BaP present in fireproof jackets can promote potential acute and chronic effects when absorbed into the body (Abrard et al., 2019). Current cleaning and maintenance procedures for protective materials do not appear to effectively reduce contamination (Abrard et al., 2019). To identify ways to reduce the internal dose of PAHs in firefighters, Cherry et al. (2019) determined 1OHPy in the urine of firefighters by assessing the relationship between estimated environmental exposures, the use of respiratory protective equipment and the use of mitigation measures that mitigate exposure via dermal absorption. Although an effect of respiratory protective equipment use was not observed on PAHs exposure metabolite levels, 1OHPy levels were significantly lower in firefighters who made greater use of mitigation measures including, changing clothes, showering, and washing during training intervals (Cherry et al., 2019). Additionally, using baby wipes to clean the face and neck during rehabilitation may mitigate dermal exposure (Beitel et al., 2020). Firefighter training and education should consider exposure risks since, in addition to inhalation and ingestion, exposure occurs through the dermal route (Fent et al., 2019). Combining the analysis of dermal wipe extracts and urine samples collected from firefighters may be a good strategy to ascertain the contribution of dermal exposure to the total internal dose of PAHs (Beitel et al., 2020).

The biomonitoring of firefighters in their occupational context is necessary and will bring immense advantages to this group of workers, namely, i) improvement of the occupational risk assessment, ii) identification of all exposure pathways contributing to the total internal dose; iii) evaluation of the efficacy of the PPE used; iv) complement of the environmental monitoring. However, there are still some important limitations, namely the usefulness of the data obtained, since reference values or occupational guidelines have not yet been defined for most pollutants emitted during forest fires. Furthermore, the half-life values of most biomarkers of these pollutants have not yet been established, which makes the organisation of biomonitoring studies difficult, namely the sampling times. This limitation may be reflected in a decrease in reproducibility and significance of the data obtained. Therefore, the development of standardized methodologies for the correct biomonitoring in the population and in firefighters is crucial.

The standardization will enable the establishment of the basis for systematic and legislated biomonitoring that will contribute to a comprehensive risk assessment and consequent proposal of mitigation policies and strategies to mitigate the impact of forest fire emissions on at-risk populations (occupational and non-occupational).

The standardization will enable the establishment of the basis for systematic and legislated biomonitoring that will contribute to a comprehensive risk assessment and consequent proposal of mitigation policies and strategies to mitigate the impact of forest fire emissions on at-risk populations (occupational and non-occupational).

2. Research aim

The main aim of this study was to characterize firefighters exposure to eighteen PAHs (sixteen classified as priority pollutants by the United States Environmental Protection Agency, benzo(j)fluoranthene, and dibenzo(a,l)pyrene) by personal air monitoring. This study also aimed to assess the health risks based on US-EPA methodology. Considering the importance of forest fires in the Northeastern of Portugal (REA, 2021), the collection of samples was conducted in three corporations in the district of Bragança.

3. Materials and methodologies

3.1 Characterization of the sampling sites

In 2019 the Portuguese mainland registered a total of 10 832 rural fire occurrences, responsible for the burning of 42 084 ha of forest, shrub, and agricultural land. About 65% of the total burned area corresponded to 62 registered large fires which burned more than 100 ha. Compared with 2018, there was a decrease of 6% and comparing to the average of fires in the last decade, there was a decrease of 49% (San-Miguel-Ayanz et al., 2020).

The Institute for Nature Conservation and Forests (ICNF) carried out the 8th provisional report on rural fires for the year 2020 and reported a total of 9 394 rural fires burning 65 887 ha in the period between 1 January and 15 October (Da et al., 2020). Since 2010, the year 2020 presented the 2nd lowest number of fires and the 4th lowest value of annual burnt area (Da et al., 2020).

In this period, 65 large fires, i.e., fires with a total burnt area equal or higher than 100 ha, occurred and burned 55218 ha of land including forests (84% of the total annual burnt area). Bragança, a district located in the region of Trás-os-Montes (located in northeastern Portugal), was the second most affected district, with the burning of 6522 ha (10% of the total burnt area) (Da et al., 2020).

In Bragança, summer is short, warm, dry and with almost cloudless skies; winter is very cold, with precipitation and partly cloudy skies. Throughout the year, in general the temperature varies from 1 °C to 29 °C and is rarely below -4 °C or above 35 °C (Instituto Nacional de Estatística, 2012). Sampling was performed at three different fire stations: Bragança (BRG), Macedo de Cavaleiros (MCC) and Torre de Moncorvo (TMC), as it can be seen in Figure 3.1.

Figure 3.1 Geographical location of the monitored fire stations in the district of Bragança.

3.2 Sample collection

The population under study are professional and voluntary firefighters, daily attending the pre-selected fire stations of Bragança (BRG), Macedo de Cavaleiros (MCC) and Torre de Moncorvo (TMC). Each firefighter filled a structured questionnaire adapted from a validated questionnaire (World Health Survey B - Individual Questionnaire., 2002). The questionnaire characterizes each participant regarding his socio-demographic data (gender, age, weight) and number of years working as a firefighter.

The sampling campaign took place on a single working day, during a continuous 227-317-min period of a given shift (Table 3.1) and firefighters were encouraged to move freely around the unit, as in a regular working day. Air sampling was carried out using personal constant flow samplers (Gilian, models GilAir3 and ProValue3; Sensidyne, USA) positioned at the waist of each firefighter taking part in the study. Air sampling was done with an airflow rate of 2 L/min and the inlet of the pump was positioned at the breading air zone of firefighters (Castro et al., 2009).

Air samples were collected on filters with a polytetrafluoroethylene membrane with a polymethylpentene support ring (porosity 2 m, Ø47 mm, SKC Ltd., UK). After sampling, the filters were stored in a freezer at -20 ◦C until chemical analysis was performed (Oliveira et al., 2017a).

Table 3.1 Air sampling conditions

Corporation	Subject ID	Duration (min)	V_{air} 25°C (m^3)	Notes
Bragança	1	240	0.486	
	2	240	0.483	
	3	233	0.466	Left to an electric fire incident (10:43-13:30)
	4	240	0.483	
	5	240	0.481	
Macedo de Cavaleiros	6	227	0.458	
	7	232	0.465	
	8	193	0.387	
	9	223	0.448	
Torre de Moncorvo	10	305	0.611	
	11	317	0.634	
	12	10	0.020	Smoker; 3-4 cigarettes
	13	310	0.619	

3.3 Extraction of PAHs

$PM_{2.5}$ filters were extracted with a MARS-X 1500W Microwave Accelerated Reaction System for Extraction (CEM, Mathews, NC, USA) configured with a 14-position carousel. Temperature and pressure were monitored in one of the positions (the control). Magnetic stirrers were also used, which were placed inside each extraction vessel and a sensor was placed inside the microwave oven to record solvent leakage (Castro et al., 2009).

Inside each extraction container, filters were immersed on 30 mL of acetonitrile (ACN). Extraction of PAHs was performed at 110°C during 20 min. After the containers cooled to room temperature, the extracts were reduced to a small volume using a rotavapor (Buchi Rotavapor, R-200) at room temperature. The residue obtained was then redissolved in 300 µL of ACN (purity 99.9%; Riedel-de Han), stirred in a vortex (Analog vortex mixer, Model 945304, VWR International) and filtered using a PTFE membrane filter with a porosity of 0.45 µm 0.20 µm for a chromatographic vial. Extracts of collected $PM_{2.5}$ filters were stored in the freezer (-20ºC) till chromatographic analysis. All glassware was washed with detergent and water, rinsed with commercial acetone and n-hexane, and dried at 50 °C before use (Castro et al., 2011).

3.4 PAHs chromatographic analysis

The quantification of 18 PAHs, 16 US EPA priority pollutants, benzo[j]fluoranthene (B[j]F), and dibenzo[a,l]pyrene (D[a,l]P) was performed according to Castro et al. (2011). Briefly, extracts were analysed by a Shimadzu LC system (Shimadzu Corporation, Kyoto, Japan) equipped with an LC-20AD pump, DGU-20AS degasser and SPD-M20A photodiode (PAD) and RF-10AXL (FLD) in-line fluorescent detectors. The separation of the compounds occurred on a C18 column (CC 150/4 Nucleosil 100-5C18 PAH, 150 x 4.0 mm; 5 µm particle size; Macherey-Nagel, Duren, Germany) maintained at room temperature (25 ± 1 °C). The injected volume was 15.0 µL. A mixture of water and acetonitrile was used as the mobile phase (Oliveira et al., 2017) (Oliveira et al., 2017a). Ultra-pure water was prepared by a Milli-Q simplicity 185 system (Millipore, Molsheim, France) (Oliveira et al., 2017) (Oliveira et al., 2020).

Initially, the mobile phase composition consisted of 50% acetonitrile and 50% ultrapure water and a linear gradient till 100% acetonitrile was programmed to be achieved in 15 minutes, followed by a gradient at 100% acetonitrile during 13 minutes before returning to the initial chromatographic conditions (50% acetonitrile and water). Initial conditions took 1 minute to reach and were maintained for 6 minutes before the next run. The total run time for each run was 40 minutes at a flow rate of 0.8 mL min^{-1} (Oliveira et al., 2017) (Oliveira et al., 2017a).

As each compound has its own optimal excitation/emission wavelength pair, the fluorescence wavelength was programmed to achieve best sensitivity and minimal interference. Table 3.2 presents the optimal pairs of excitation and emission wavelengths for each compound under study. The PAH acenaphthylene, which shows limited fluorescence, was analysed at 254 nm in photodiode array detector.

Table 3.2 Optimal excitation/emission wavelength pair of the PAHs in study.

PAH	Excitation/emission wavelength pair (nm)
naphthalene, acenaphthene and fluorene	260/315
phenanthrene	260/366
anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo [b + j] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and dibenzo[a,l]pyrene	260/430
indeno[1,2,3-cd]pyrene	290/505

Calibration curves with ten standard solutions were prepared by dilution of stock solutions with acetonitrile. A certified standard mixture containing the 16 USEPA PAHs [naphthalene (Naph) 1000 µg /mL, acenaphthylene (Ace) 2000 µg/mL, acenaphthene (Ace) 1000 µg/mL, fluorene (Flu) 199. 9 µg/mL, phenanthrene (Phe) 99.8 µg/mL, anthracene (Ant) 100.0 µg/mL, fluoranthene (Fln) 200.1 µg/mL, pyrene (Pyr) 99.9 µg/mL, benzo(a)anthracene (B(a)A) 100. 1 µg/mL, chrysene (Chry) 100.0 µg/mL, benzo(b)fluoranthene (B(b)Ft) 200.2 µg/mL, benzo(k)fluoranthene (B(k)Ft) 99.9 µg/mL, benzo(a)pyrene (B(a)P) 100. 0 µg/mL, dibenzo(a,h)anthracene (DB(a,h)A) 200.0 µg/mL, benzo(g,h,i)-perylene (B(g,h,i)P) 200.0 µg/mL, and indeno(1,2,3-cd)pyrene (InP) 100.1 µg/mL] as well as the individual standard of dibenzo(a,l)pyrene DB(a,l)P and benzo(j)fluoranthene (2000 µg/mL) were purchased from Supelco, Bellefonte, PA, USA. Standards were stored at -20 ºC, in the dark, to avoid volatilization and photodegradation (Castro et al., 2011).

Calibration curves were linearly fitted with correlation coefficients always higher than 0.9979. RSD values ranged from 1.8% (dibenzo[a,l]pyrene) to 9.1% (naphthalene) for PAHs extraction from filters. Limits of detection (LODs) and quantification (LOQs) were calculated as the minimum detectable amount of analyte with a signal-to-noise ratio of 3:1 and 10:1, respectively. LODs between 0.077 µg/L (for benzo[a]pyrene) and 24.8 µg/L (for acenaphthylene), while the other PAHs had a LOD below 1.0 µg/L.

Each analysis was performed in triplicate. Whenever necessary, sample dilution was done to ensure that the signal from the sample was within the linear range of the method (Oliveira et al., 2017) (Oliveira et al., 2017a).

3.5 Health risk analysis

Based on the toxicity equivalency factors (TEF) proposed by Nisbet and LaGoy (Boström et al., 2002), the toxicity equivalent concentrations (B[a]Peq) were calculated using equation 3.1.

The quantitative risk assessment methodology was used to estimate the excess lifetime risk of lung cancer (equation 3.2) due to exposure to PAHs (WHO, 1987; WHO, 2000) using the unit risk of 8.7×10^{-5} (i.e. 8.7 cases per 100000 people with chronic inhalation exposure to 1 ngm^{-3} of B[a]P over a lifetime of 70 years) and considering 8 h period for a work shift (Table 3.3). The concentrations of PAHs (determined for each individual by personal air sampling) and the exposure durations (i.e., years of work as a firefighter; Table 3.3) were used. ILR below 10^{-6} are denoted as safe ones, whereas potentially high risks are estimated by values higher than 10^{-4} (US EPA, 1989). The full details of the methodology and the ILR calculations can be found in Oliveira et al. (2017).

$$\mathbf{B(a)P_{eq} = C_{PAH} \times TEF_{PAH\ specific}} \qquad \mathbf{(3.1)}$$

$B(a)P_{eq}$: Toxicity equivalent concentration

$TEF_{PAH\ specific}$: Specific toxic equivalency factor for each PAH proposed by Nisbet and LaGoy (Boström et al., 2002).

C_{PAH}: PAH concentration obtained (µg/m³)

$$\mathbf{ILR = (EFr \times ED \times ET \times C_{PAH} \times IUR) / AT} \qquad \mathbf{(3.2)}$$

Table 3.3 Information used for the calculation of the incremental lifetime cancer risk (ILR) for chronic inhalation of 1 µg/m³ of PAHs (Oliveira et al., 2017b).

SYMBOL	DEFINITION	UNIT	VALUE
EFR	Frequency of exposure	Days/Year	250
ED	Duration of exposure	Years	3
ET	Time of exposure	Hours/Day	0.33 (8 h/24 h)
AT	Average time	Days	25 500
C_{PAH}	Concentration of PAHs (µg/m³)	*	
IUR	Chronic Inhalation Risk Unit	$(\mu g\ m^{-3})^{-1}$	**
NAPH		$(\mu g\ m^{-3})^{-1}$	3.4×10^{-5}
B(A)A		$(\mu g\ m^{-3})^{-1}$	6.0×10^{-5}
CHRY		$(\mu g\ m^{-3})^{-1}$	6.0×10^{-7}
DB(A, H)A		$(\mu g\ m^{-3})^{-1}$	6.0×10^{-4}

* Calculated for each sample and PAH individually; **(USEPA - U.S, 2021)

3.6 Statistical analysis

Concentrations of $PM_{2.5}$-bound PAHs were presented as median, minimum, and maximum. Data were treated with Microsoft Excel. When levels were below the LOD, the value of the respective LOD/√2 was used (Taylor et al., 1990).

4. Results and discussion

4.1 PAHs levels

A total of 13 male firefighters collected their personal air samples during a regular working day at the fire station. Among the 18 PAHs under study, naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, and chrysene were detected in all the air samples; acenaphtylene, benzo(b)fluoranthene+benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,l)pyrene , and indeno(1,2,3, c-d)pyrene were never detected.

Table 4.1 presents the median concentrations of $PM_{2.5}$-bound PAHs and the range of variation of the individual concentrations of the 11 detected PAHs, as well as the median total concentration of PAHs (∑PAHs) for each fire station.

Firefighters from the fire station of Macedo de Cavaleiros presented levels of ΣPAHs ranging from 2.23-53.06 ng/m^3 (median 15.05 ng/m^3), with fluorene ranging from 0.09-16.12 ng/m^3 (median 3.73 ng/m^3), phenanthrene ranging from 0.04-16.94 (median 2.70 ng/m^3), and naphthalene ranging from 0.94-4.53 ng/m^3 (median 2.82 ng/m^3) as the most abundant compounds. The compounds benzo(a)anthracene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were not detected.

In Bragança fire station, concentrations of ∑PAHs ranged from 9.15 to 129.08 ng/m^3 (median 18.59 ng/m^3), being acenaphthene the compound that presented the maximum values, ranging between 5.06-42.77 ng/m^3 (median 9.07 ng/m^3), followed by fluorene ranging from 1.87-38.91 ng/m^3 (median 2.53 ng/m^3) and phenanthrene ranging from 0.30-23.74 ng/m^3 (median 1.39 ng/m^3).

At Torre de Moncorvo, levels of ΣPAHs ranged between 3.69-486.25 ng/m^3 (median 74.24 ng/m^3) with dibenzo(a,h)anthracene (median 62.67 ng/m^3) showing the highest concentration; acenaphthene and fluorene were not detected.

Table 4.1 Concentrations (median; Min.-Max.) of $PM_{2.5}$-bound PAHs (ng/m^3) in the breathing air zone of firefighters (n = 13) in three fire stations Bragança, Macedo de Cavaleiros and Torre de Moncorvo)

Station	**Bragança (n=5)**		**Macedo de Cavaleiros (n=4)**		**Torre de Moncorvo (n=4)**	
PAH	**Median**	**Min.-Max**	**Median**	**Min.-Max.**	**Median**	**Min.-Max.**
Naph	1.54	0.56-3.14	2.82	0.94-4.53	4.44	2.26-182.99
Ace	9.07	5.06-42.77	1.45	0.35-5.31	n.d.	n.d.
Flu	2.53	1.87-38.91	3.73	0.09-16.12	n.d.	n.d.
Phe	1.39	0.30-23.74	2.70	0.04-16.94	0.24	0.03-44.86
Ant	0.10	0.10-1.95	0.32	0.11-1.46	0.08	0.08-5.49
Fln	1.50	0.11-2.00	1.76	0.08-3.91	0.05	0.03-6.92
Pyr	1.34	0.07-2.04	1.73	0.50-3.18	0.20	0.06-13.82
B(a)A	0.04	0.04-0.06	n.d.	n.d.	0.48	0.03-2.72
Chry	0.12	0.12-1.50	0.52	0.13-1.61	0.09	0.09-21.45
DB(a,h)A	0.95	0.91-12.69	n.d.	n.d.	62.67	0.72-195.06
B(g,h,i)P	n.d.	n.d.	n.d.	n.d.	5.97	0.40-12.94
ΣPAHs	18.59	9.15-129.08	15.05	2.23-53.06	74.24	3.69-486.25

Ace: Acenaphthene; Ant: Anthracene; B(a)A: Benz(a)anthracene; B(a)P: Benzo(a)pyrene; B(g,h,i)P: Benzo(g,h,i)perylene; Chry: Chrysene; DB(a,h)A: Dibenz(a,h)anthracene; Fln: Fluoantene; Flu: Fluorene; Naph: Naphthalene; PAHs: Polycyclic Aromatic Hydrocarbons; Phe: Phenanthrene; Pyr: Pyrene; ΣPAHs: Sum of all Polycyclic Aromatic Hydrocarbons. n: number of samples; n.d.: not detected.

Figure 4.1 presents the distribution of PAHs (in percentage) by the number of aromatic rings in the three fire corporations under study. At the fire stations of Macedo de Cavaleiros and Bragança, low molecular weight PAHs, i.e., compounds with 2 and 3 aromatic rings were the predominant in the personal air of firefighters (79.3 and 82.7%, respectively). Regarding participants from the fire station situated in Torre de Moncorvo, it was found that the heavier compounds (PAHs with 5-6 aromatic rings) represented 55.3% of ΣPAHs, in opposite to what was observed in the other two stations.

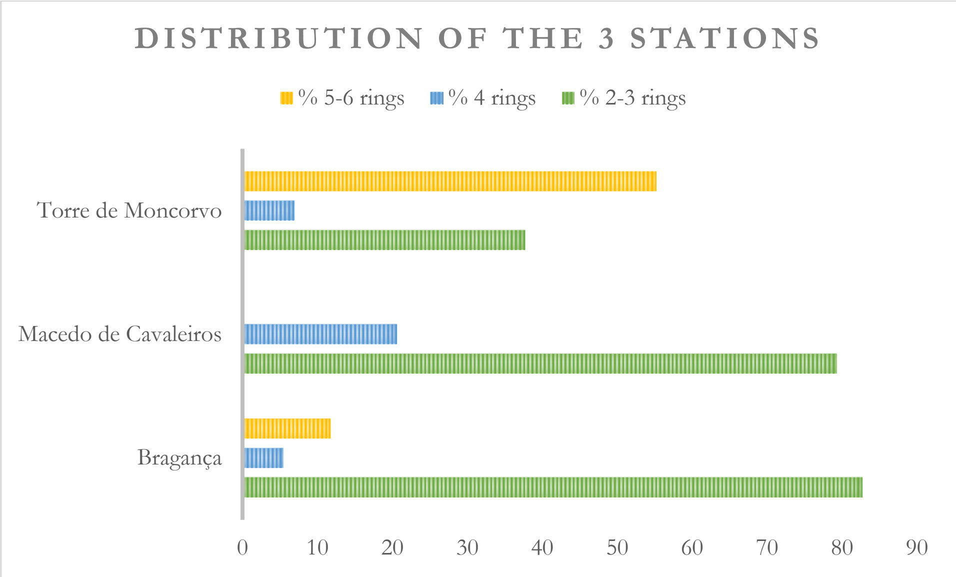


Figure 4.1 Distribution (%) of the PAHs detected according to the number of aromatic rings (2-3 rings, 4 rings or 5-6 rings) for each of the corporations under study.

Individually analysing the Bragança fire station (Figure 4.2 a)), in the $PM_{2.5}$ fraction of the breathing air of 3, there is a predominance of lighter compounds (2-3 rings) representing 95.7% of the total observed. On the other hand, $PM_{2.5}$ fraction of the breathing air of 1 is the one that contains the lowest percentage of lighter compounds 51.6%. Possibly, individual 3 presents this profile because he left the station to participate in an electrical fire during the study.

Regarding PAHs of 4 aromatic rings, they prevail in personal air of subject 1 holding 17.5% of the total of PAHs detected, and in less dominance in subject 2 being only 1.5% of the total.

The $PM_{2.5}$ fraction of breathing air of individual 2 is the one that presents in its constitution a higher percentage of PAHs constituted by heavy aromatic rings (31.0%) and the one that presents the lowest is the 3 (0.87%).

Figure 4.2 Distribution (%) of the PAHs according to the number of aromatic rings (2-3 rings, 4 rings or 5-6 rings) detected in the $PM_{2.5}$ fraction of the breathing air of each individual of the several corporations under study: a) Bragança, b) Macedo de Cavaleiros

In the Macedo de Cavaleiros station, there is a common point: the non-detection of heavy PAHs, i.e., composed of 5-6 aromatic rings (Figure 4.2 b). This can be justified by the absence of traffic (being located in a more rural area) and the inexistence of smoking firefighters. Lighter compounds with 2-3 aromatic rings predominated in the 4 individuals, representing between 73.8% and 83.0% (median 79.1%) of the total detected.

In the Torre de Moncorvo station, the characterized firefighters under study showed quite different distribution profiles (Figure 4.2 c). A composition of lighter PAHs (2-3 rings) predominates in the $PM_{2.5}$ fraction of the breathing air of subjects 10 and 12, with 81.0% and 47.9%, respectively. However, data from subjects 11 and 13 show that the heavier compounds (5-6 rings) prevail, with 96.1% and 85.1%, respectively. It was found in the questionnaires that firefighter 12 smoked *ca*. 3-4 cigarettes during the study, which may justify this distribution.

In agreement with Figure 4.2 a, the compound more detected in the personal air of the characterized subjects of Braganca was acenaphthene (Figure 4.3 a) with a concentration between 5.06 and 42.77 ng/m^3 (median 9.07 ng/m^3). Also, fluorene was detected with a concentration between 1.87 and 38.91 ng/m^3 (median 2.53 ng/m^3); these two compounds being low molecular weight PAHs. Analysing the total amount of detected PAHs, it is clear that individual 3 is the more exposed to PAHs with a concentration of 109.29 ng/m^3, while the one with the lowest exposure is firefighter 5 (14.64 ng/m^3). The concentration of total PAHs detected in the $PM_{2.5}$ fraction of the breathing air of individual 3 supports the need of characterization of firefighter's exposure to fire emissions.

Regarding participants from the fire station of Macedo de Cavaleiros (Figure 4.3 b), the most abundant PAHs in the personal air of firefighters are phenanthrene, fluorene and acenaphthene, with ranges between 0.038 ng/m^3 - 16.94 ng/m^3 (median 2.70 ng/m^3), 0.087 ng/m^3-16.12 ng/m^3 (median 3.73 ng/m^3) and 0.35 ng/m^3 - 5.31 ng/m^3 (median 1.45 ng/m^3), respectively. Looking at the individual levels, in the breathing zone of firefighters 8 and 9, naphthalene prevails with 64.16 and 67.0%, respectively. In the air $PM_{2.5}$ fractions of individuals 7 and 6, a completely different profile was found, with the predominance of phenanthrene with 35.6% and fluorene with 25.1%, respectively.

In the personal air of participants from Torre de Moncorvo fire station (Figure 4.3 c)), there is a predominance of dibenzo(a,h)anthracene, naphthalene and phenanthrene with concentrations ranging from 0.72 ng/m^3 to 195.06 ng/m^3 (median 62.67 ng/m^3), 2.26 ng/m^3 to 182.99 ng/m^3 (median 4.44 ng/m^3) and 0.09 to 44.86 ng/m^3 (median 0.24 ng/m^3), respectively. $PM_{2.5}$ fractions collected in Torre de Moncorvo had the highest total concentration of PAHs among the three characterized ranging from 3.69 to 486.25 ng/m^3 (median 74.24 ng/m^3). Firefighter 12 is a smoker, and the highest total concentration of PAHs was detected in his personal air, with a total value of 455.36 ng/m^3. Analysing altogether the profiles of firemen 11, 12 and 13, it can be observed that the heavy compound dibenzo(a,h)anthracene predominates with 84.0, 41.1 and 84.3%, respectively. In the $PM_{2.5}$ fraction of the breathing air of firefighter 10, the lighter compound naphthalene prevails with 79.5%.

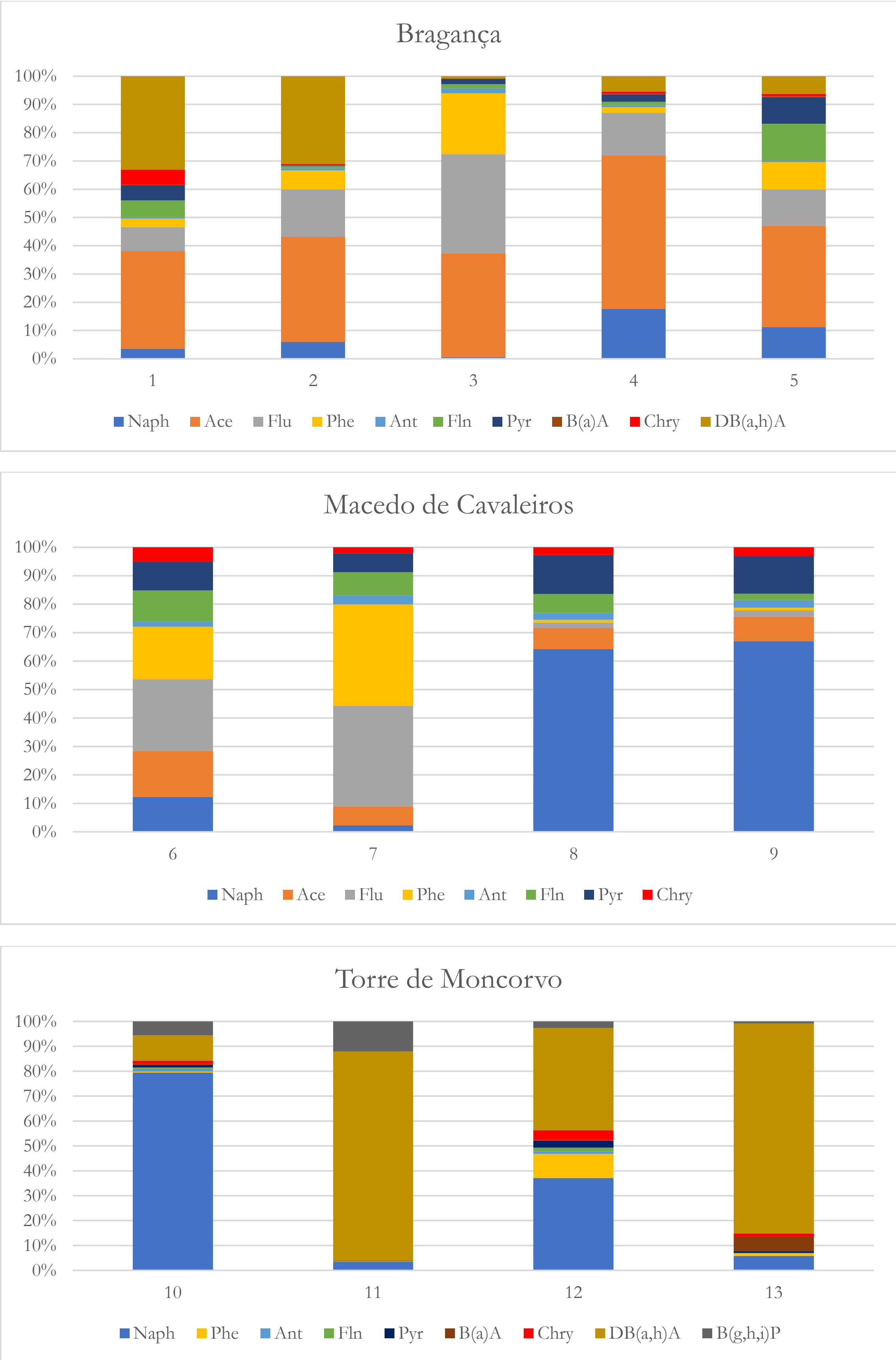


Figure 4.3 Distribution profile (%) of PAHs in the $PM_{2.5}$ fraction of the breathing air of each firefighter from the fire stations of a) Bragança, b) Macedo de Cavaleiros, and c) Torre de Moncorvo.

According to IARC and USEPA, the compounds considered as priority carcinogens and pollutants are naphthalene, benzo(a)pyrene, chrysene and dibenzo(a,h)anthracene (group 2B; IARC 2002, 2010) (USEPA - U.S, 2021). To this end, Figure 4.4 consolidates the distribution of PAHs with carcinogenic properties present in the breathing zone of the firefighters of the three corporations under study. Performing the calculation of the percentage of carcinogenic PAHs detected in each personal air, it was found that from Torre de Moncorvo corporation present the highest percentages of possible/probable carcinogenic compounds ranging between 82.3 and 97.1%. In the air sampling campaign of Macedo de Cavaleiros, benzo(a)anthracene and dibenzo(a,h)anthracene were not detected, oppositely to Bragança and Torre de Moncorvo. Bragança was the corporation that presented the lowest percentages of carcinogenic compounds, with levels ranging from 1.98 - 44.1%.

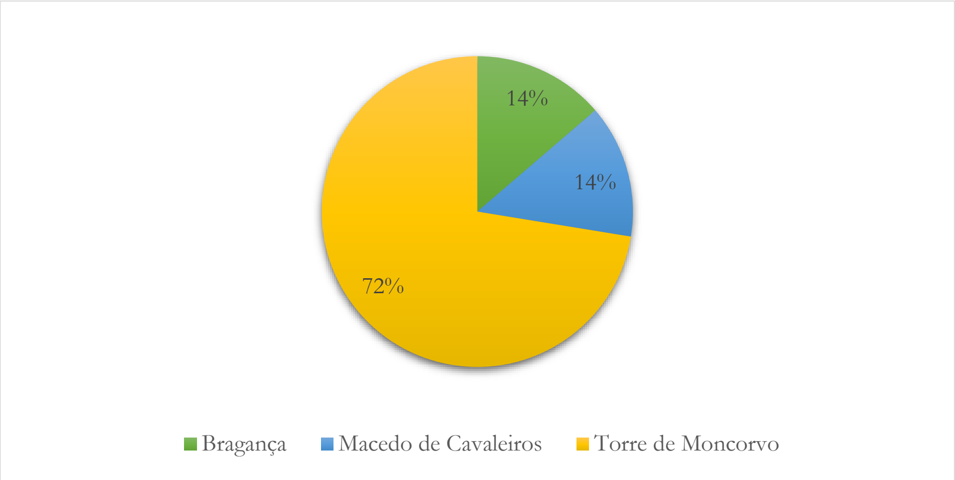


Figure 4.4 Percentage of carcinogenic PAHs determined in the $PM_{2.5}$ fraction of the breathing air of firefighters from the study corporations.

Figure 4.5 displays the individual distribution profiles of the PAHs with carcinogenic properties in each characterized firefighter. Specifically, in the $PM_{2.5}$ fraction of the breathing air of firefighters 1, 2, 3, 11, 12 and 13, dibenzo(a,h)anthracene predominates, compared to the other detected carcinogenic PAHs, with percentages of 79.3, 82.6, 52.32, 95.9, 49.9 and 86.8%, respectively, while data concerning the remaining firefighters (from 4 to 10) naphthalene predominates, with 73.3, 60.3, 70.4, 50.6, 95.9, 95.5 and 87.0%.

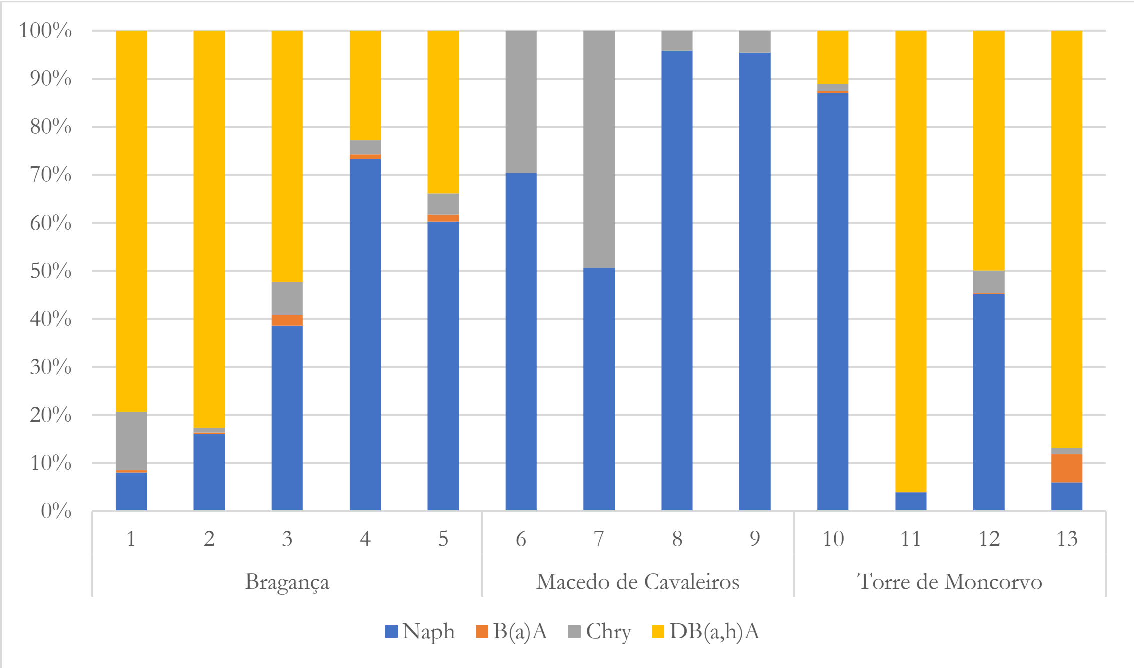


Figure 4.5 Distribution profile of PAHs with carcinogenic properties (possible/probable) in the $PM_{2.5}$ fraction of the breathing air of each characterized firefighter from Bragança, Macedo de Cavaleiros and Torre de Moncorvo fire brigades.

4.2 Risk assessment of PAHs

The risk of exposure to particles depends on their dose, which is dependent on the concentration and size of the particles and on the characteristics of each individual, such as breathing rate, age and body weight. Table 4.2 shows the toxicity equivalent concentrations (B(a)Peq) of the PAHs under study, based on benzo(a)pyrene toxicity, in the breathing air zone of firefighters. Given its carcinogenic potential, benzo[a]pyrene has traditionally been the marker of choice for measuring the level of risk and human exposure to mixtures of PAHs in ambient air (WHO, 2015).

The total toxicity equivalent concentrations were clearly different in the breathing air zone of the firefighters of the three fire stations, being by descending order: 6.07×10^{-2} µg/m^3 (Torre de Moncorvo) >> 9.53×10^{-4} µg/m^3 (Bragança) >> 2.35×10^{-6} µg/m^3 (Macedo de Cavaleiros). Dibenz(a,h)anthracene was the compound that contributed the most to these discrepancies.

Table 4.2 Toxicity equivalent concentrations (B(a)Peq; µg/m^3) of $PM_{2.5}$ bound PAHs in the breathing air zone of firefighters in three fire stations (Bragança, Macedo de Cavaleiros and Torre de Moncorvo) using specific toxic equivalence factors (TEF) of each PAH defined by the World Health Organization (WHO, 2015) and applying equation (3 .2).

Station		**Bragança (n=5)**	**Macedo de Cavaleiros (n=4)**	**Torre de Moncorvo (n=4)**
PAH	**TEF** (WHO, 2015)	**$B(a)P_{eq}{}^a$**	**$B(a)P_{eq}{}^a$**	**$B(a)P_{eq}{}^a$**
Naph	0.0001	1.54×10^{-7}	3.06×10^{-7}	4.61×10^{-7}
Ace	0.0001	9.07×10^{-7}	1.45×10^{-7}	n.d.
Flu	0.0001	2.53×10^{-7}	3.74×10^{-7}	n.d.
Phe	0.0001	1.39×10^{-7}	2.75×10^{-7}	2.57×10^{-8}
Ant	0.001	1.03×10^{-7}	3.24×10^{-7}	8.04×10^{-8}
Fln	0.0001	1.50×10^{-7}	1.76×10^{-7}	1.10×10^{-8}
Pyr	0.0001	1.34×10^{-7}	1.85×10^{-7}	2.01×10^{-8}
B(a)A	0.1	3.88×10^{-6}	n.d.	4.82×10^{-5}
Chry	0.001	1.2×10^{-7}	5.66×10^{-7}	4.5×10^{-7}
DB(a,h)A	1	9.48×10^{-4}	n.d.	6.06×10^{-2}
B(g,h,i)P	0.001	n.d.	n.d.	6.32×10^{-6}
Σ $B(a)P_{eq}$	--	9.53×10^{-4}	2.35×10^{-6}	6.07×10^{-2}

a: Median; n: number of samples; n.d.: not detected.

Ace: Acenaphthene; Ant: Anthracene; B(a)A: Benz(a)anthracene; B(a)P: Benzo(a)pyrene; B(g,h,i)P: Benzo(g,h,i)perylene; Chry: Chrysene; DB(a,h)A: Dibenz(a,h)anthracene; Fln: Fluoanthene; Flu: Fluorene; Naph: Naphthalene; PAHs: Polycyclic Aromatic Hydrocarbons; Phe: Phenanthrene; Pyr: Pyrene; Σ B(a)Peq: Total Benzo(a)Pyrene toxicity equivalence amount of all PAHs; Σ B(a)Peq: Total toxicity equivalence quantity to Benzo(a)Pyrene of the PAHs classified by the International Agency for Research on Cancer (IARC) as possible/probable carcinogens (Naph, B(a)A, Chry, B(b)F, B(j)F, B(k)F, B(a)P, DB(a,h)A and Indeno(1,2,3, c-d)Pyrene).

In addition, and as expected based on the high contribution of dibenz(a,h)anthracene, the same pattern of variation was observed concerning the total estimated incremental lifetime cancer risks, i.e., 3.55×10^{-7} (Torre de Moncorvo) >> 6.05×10^{-9} (Bragança) > 1.01×10^{-9} (Macedo de Cavaleiros) (Table 4.3). This profile is in agreement with the fact that the Torre de Moncorvo corporation is the one that presents the highest percentage of carcinogenic compounds. Still, all determined incremental lifetime cancer risks were below 10^{-6} indicating that firefighters are not exposed to significant carcinogenic risks through exposure to $PM_{2.5}$ bound PAHs at the characterized fire stations.

Table 4.3 - Incremental lifetime cancer risks (ILRs; median) in the breathing air zone of firefighters in three fire stations (Bragança, Macedo de Cavaleiros and Torre de Moncorvo), estimated according to the United States Environmental Protection Agency (USEPA) methodology (Region III risk-based concentration table; USEPA, 2021) (USEPA - U.S, 2021)

	Bragança (n=5)	**Macedo de Cavaleiros (n=4)**	**Torre de Moncorvo (n=4)**
PAH	**ILR [a,b]**	**ILR [a,b]**	**ILR [a,b]**
Naph	5.09×10^{-10}	1.01×10^{-9}	1.52×10^{-9}
B(a)A	2.26×10^{-11}	n.d.	2.81×10^{-10}
Chry	7.00×10^{-13}	3.30×10^{-12}	2.62×10^{-12}
DB(a,h)A	5.52×10^{-9}	n.d.	3.53×10^{-7}
Σ ILRs	6.05×10^{-9}	1.01×10^{-9}	3.55×10^{-7}

B(a)A: Benz(a)anthracene; B(a)P: Benzo(a)pyrene; Chry: Chrysene; DB(a,h)A: Dibenz(a,h)anthracene; Naph: Naphthalene; PAHs: Polycyclic Aromatic Hydrocarbons; IUR: Chronic Inhalation Risk Unit. a: Median; b: ILR was estimated only for PAHs for which IUR values are available (USEPA 2021_THQ 0.1.), namely: Naphthalene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenz(a, h)anthracene and Indeno(1,2,3-cd)pyrene.n.d.: not detected.

5. Conclusions and future perspectives

Out of the 18 PAHs monitored through the personal air of firefighters during their regular work shift in three fire stations, six compounds were never detected: acenaphthylene, benzo(b)fluoranthene+benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,l)pyrene, and indeno(1,2,3, c-d)pyrene. Overall, $PM_{2.5}$-bound ΣPAH concentrations ranged from 2.23-486.25 ng/m^3, with 2-3 aromatic rings accounting with 79.3 and 82.7%, in Macedo de Cavaleiros and Bragança, respectively. Compounds with 5-6 aromatic rings represented 55.3% of ΣPAH in Torre de Moncorvo.

The health risk assessment performed with the concentrations of PAHs determined in the personal air of firefighters during regular working days demonstrated that individuals from Torre de Moncorvo presented the highest percentage of possible/probable carcinogenic compounds (72% of ΣPAH) comparatively with subjects from the fire corporations of Bragança and Macedo de Cavaleiros (14% of ΣPAH). Also, these subjects presented higher levels of total incremental lifetime cancer risk (3.55×10^{-7}) than firefighters working at the fire station of Bragança (6.05×10^{-9}) and Macedo de Cavaleiros (1.01×10^{-9}). However, the determined health risks due to personal exposure at fire stations were well below the recommend USEPA guideline of 10^{-6}.

In general, the execution of this study was important to understand that firefighters, even during their shift in the corporation and not intervening in fires, are exposed to these pollutants that can compromise the quality of their health in the long term.

In a future perspective, it would be important to perform personal monitoring including the monitorization of other health-relevant pollutants such as carbon monoxide and nitrogen dioxide in the personal air of firefighters. Also, the inclusion of biomonitoring studies, through the collection of biological fluids (e.g., urine and blood) would be crucial to determine firefighters' total internal exposure to PAHs. Data generated with this work are necessary for a better evaluation of firefighters' occupational exposure at fire stations and will contribute to complement the so much needed information to characterize and understand the complex exposure during firefighting period.

6. References

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