Assessment of exposure to fine and ultrafine particulate-bound polycyclic aromatic hydrocarbons during prescribed burns

TEIXEIRA J., MORAIS S., RODRIGUES F., DELERUE-MATOS C., OLIVEIRA M.[*]

REQUIMTE/LAQV-Instituto Superior de Engenharia, Instituto Politécnico do Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015, Porto, Portugal

*corresponding author:

e-mail: marta.oliveira@graq.isep.ipp.pt

Abstract Portugal is one of the most affected countries in southern Europe by wildfires. The human exposure characterization to fine particulate matter (PM) during fires remains limited; no information is available for ultrafine particles nor their composition on polycyclic aromatic hydrocarbons (PAHs). This work assesses fine and ultrafine PM levels and their composition on 18 PAHs during two prescribed burns performed in Porto (North of Portugal). A low-pressure impactor was used to collect 14 PM fractions (PM_{15nm} to $PM_{10\mu m}$) at the firefighting area. Concentrations of PM were determined by gravimetry, and its PAHs content was determined with a microwave-assisted extraction and analyzed by liquid chromatography with fluorescence/UV-Vis detectors. Total cumulative concentrations of collected PM varied between 0.34 to 1.41 mg/m^3 with fine (PM_{156nm} to $PM_{2.5\mu m}$) and ultrafine (PM_{15nm} to PM_{95nm}) PM accounting for 48.6-63.1% and 11.7-31.4% of total PM, respectively. Benzo(a)pyrene, carcinogenic PAH, was detected in all PM fractions with values ranging from 5.72×10^{-5} to 2.63×10^{-3} µg/m^3. The PM-bound possible or probable carcinogenic PAHs represented up to 7.62% of total PAHs. Further studies concerning humans, *e.g.*, firefighting forces and local population exposure to fine/ultrafine PM and PAHs are urgently needed to pursue preventive measures to promote human health.

Keywords: Human exposure; Fire emissions; Particulate matter; PAHs; Health risks.

1. Introduction

During their daily routine, firefighters perform different activities (*e.g.*, emergency medical and pre-hospital support, rescue, and firefighting) that can comprise a variety of health risk factors. Firefighters' occupational exposure, including fire combat, was recently evaluated as carcinogenic to humans (Group 1, IARC) [1] with demonstrated sufficient scientific evidence that this activity can trigger the development of bladder cancer and mesothelioma [1]. Firefighters present increased rates of mortality and morbidity [2,3]. A wide variety of health-hazardous pollutants including carbon monoxide, metals, particulate matter (PM), volatile and semi-volatile organic compounds (VOCs)) are emitted during fire events [4,5], contributing to the adverse effects on firefighters' health. PM consists on a suspension of solid particles and liquid droplets with different sizes and shapes [6,7], being

classified as coarse (PM > 2.5 µm of aerodynamic diameter), fine (PM ≤ 2.5 µm), and ultrafine (PM ≤ 0.1 µm) [6,7]. Ambient PM causes cancer (Group 1, IARC) with demonstrated evidence for lung cancer, being this classification also based on results obtained from experiments with animal models [8]. Different compounds (*e.g.*, metals and polycyclic aromatic hydrocarbons (PAHs)) can be bound to PM. The presence of PAHs, a class of VOCs, in the ambient air during fire events was already demonstrated by different authors [9,10]. The United States Environmental Protection Agency (USEPA) introduced 16 PAHs to the list of priority pollutants [11]. Regular exposure to PAHs promotes adverse health impacts on human wellbeing due to the toxic, teratogenic, and mutagenic properties of these compounds [12,13]. Benzo(a)pyrene (BaP) is carcinogenic to humans whereas some other PAHs are classified as possible (anthracene, naphthalene, benzo(a)anthracene, chrysene, indeno(1,2,3-c,d)pyrene and benzofluoranthene isomers) or probable (dibenzo(a,h)anthracene and dibenzo(a,l)pyrene) carcinogenic to humans [14-16]. Although the information related to occupational exposure of firefighters to PM and PAHs is well documented in the literature, the data concerning the exposure of firefighters to fine and ultrafine PM-bound PAHs continues absent. For the first time, this study assessed the levels of different fine/ultrafine PM fractions and their PAHs' composition during two controlled forest fires that occurred in the North of Portugal.

2. Materials and methods

2.1. Sampling campaigns and gravimetric analysis

Air sampling campaigns were performed during two prescribed burns that occurred in Marco de Canaveses (Oporto, Portugal) with a Dekati Low Pressure Impactor in January 2022. Air samples were collected with the equipment placed at the breathable zone of participants in a secure area close to the ignition point. PM fractions were collected onto aluminium filters (Ø25 mm; Dekati®, Finland) previously covered with a substrate grease (Apiezon®-L, Sigma-Aldrich). A total of 14 PM fractions with a specific stage cut-off diameter (D_p) [0.0149 µm (stage 0), 0.031 µm (stage 1), 0.054 µm (stage 2), 0.095 µm (stage 3), 0.156 µm (stage 4), 0.256 µm (stage 5), 0.382 µm (stage 6), 0.603 µm (stage 7), 0.947 µm (stage 8), 1.63 µm (stage 9), 2.47 µm (stage 10), 3.65 µm (stage 11), 5.36

μm (stage 12), 9.88 μm (stage 13)] were sampled during all fires events. The impactor worked with a vacuum pump (Leybold, Sogevac, Germany) at predefined conditions (40 mbar and 9.96 L/min). Quality control was guaranteed by a calibration of the equipment according to the specifications of the supplier. Relative humidity and temperature were monitored with a portable device (HygroLog SERIE HL20; Rotronic, Switzerland). All filters were conditioned at a constant relative humidity and temperature before being weighted on an analytical balance (MS205DU, Metler Toledo). The mass of each PM fraction was determined by gravimetric analysis.

2.2. *PAHs' extraction and chromatographic analysis*

PAHs were extracted from the aluminium filters by ultrasonic extraction (Sonorex Digital 10P, Bandelin, Germany) with acetonitrile and evaporated till dryness at 20 °C. The obtained residue was redissolved in acetonitrile, filtered (0.45 μm PTFE filter), and frozen (-20 °C). PAHs were quantified by liquid chromatography with a photodiode array and fluorescence detectors online [17]. The chromatographic separation was achieved with a C18 column (CC 150/4 Nucleosil 100-5C18 PAH; Macherey-Nagel, Duren, Germany) at controlled temperature (25 ± 1 °C) and flow rate (0.8 mL/min) during a 40 min run time. Extraction and quantification methods were previously validated. The limits of detection and quantification ranged between 0.06 to 37.2 μg/L and from 0.22 to 124.1 μg/L, respectively. Standards and blank filters extracts were daily analyze; all extracts were analyzed in triplicate.

2.3. *Data analysis*

PM levels were determined considering the specifications of the impactor supplier and accounting for the temperature and relative humidity monitored during the sampling campaign. The determined concentrations were normalized for a temperature of 21 ºC and the atmospheric pressure. The levels of total cumulative PM were determined for each fire event by the sum of all non-cumulative fractions collected. The statistical analysis was performed with SPSS (IBM SPSS Statistics 20) and Excel (v.16.0. Microsoft Corporation, USA). A statistical significance of $p < 0.05$ was assumed.

3. Results and Discussion

Fourteen PM fractions were quantified being the levels of total cumulative PM ranged between 0.34 to 1.41 mg/m^3. Concentrations of fine (0.23 – 1.13 mg/m^3), and ultrafine (0.11 – 0.17 mg/m^3) particles accounted for 48.6 – 63.1% and 11.7 – 31.4% of total cumulative concentrations, respectively. Fine and ultrafine PM represented more than 90% of total PM in both fire events. The levels of coarse particles (0.06 – 0.1 mg/m^3) accounted for 2.86 – 3.35% of total cumulative PM. Non-cumulative concentrations of PM for each fire event are presented in Table 1. The highest median non-cumulative concentrations were observed for fire event 1.

Table 1. Median PM concentrations (mg/m^3) for each stage at the fire events.

Stage	Fire 1	Fire 2
0	0.06	0.03
1	0.13	0.04
2	0.23	0.08
3	0.30	0.33
4	1.14	0.27
5	1.78	0.28
6	1.28	0.25
7	0.56	0.05
8	0.37	0.04
9	0.39	0.16
10	0.37	0.12
11	0.28	0.06
12	0.15	n.d.
13	0.03	n.d.

n.d. – non-detected

Median levels of PAHs in both fire events are represented in Figure 1. Among the 18 compounds under study, acenaphthene was not detected in the two prescribed burns. Anthracene, benz(a)anthracene, and benzo(g,h,i)perylene were only observed in event 1 whereas dibenzo(a,l)pyrene was only detected in event 2. Concentrations of total PAHs were increased in fire event 1 than in event 2 (0.16 *versus* 0.07 μg/m^3). Acenaphthylene was the predominant compound (0.057 – 0.063 μg/m^3), followed by pyrene (1.36×10^{-4} – 0.077 μg/m^3), naphthalene (1.61×10^{-3} – 1.92×10^{-3} μg/m^3), and fluoranthene (9.03×10^{-5} – 8.40×10^{-3} μg/m^3). In prescribed burn 1, benz(a)anthracene (1.76×10^{-3} μg/m^3), dibenzo(a,h)anthracene (1.38×10^{-4} – 1.79×10^{-3} μg/m^3) and indeno(1,2,3-c,d)pyrene (1.72×10^{-4} - 1.40×10^{-3} μg/m^3) were also prevalent compounds . The other prevalent compounds in filters collected during fire event 1 were benzo(b+j)fluoranthene (2.95×10^{-3} μg/m^3), chrysene (2.08×10^{-3} μg/m^3) and phenanthrene (2.01×10^{-3} μg/m^3). Benzo(a)pyrene, known carcinogenic PAH, was detected in all PM fractions with concentrations ranging between 5.72×10^{-5} to 2.63×10^{-3} μg/m^3. Other carcinogenic compounds represented up to 7.62% of total PAHs levels during controlled fires.

PAHs with 2 and 3 aromatic rings (LMW) were the dominating compounds (98.5%) during fire event 2 while PAHs with 4 rings were the prevalent PAHs in prescribed burn 1 (55.8%).

The characterization of emissions of PM in the ambient air during forest fires was already assessed by different authors [18,19]. Those authors emphasized the negative impact of PM on air quality with potential health risks for firefighters and exposed populations [20,21]. Other studies also described high levels of PAHs during fire events [22,23], being similarly described the prevalence of LMW PAHs (*e.g.*, naphthalene, phenanthrene, fluoranthene, and pyrene) during fire events [31,32].

4. Conclusions

The exposure levels to fine and ultrafine PM and its content in PAHs were for the first time evaluated during prescribed burns. Fine and ultrafine fractions represented more than 90% of the total PM released in both fires. LMW PAHs were the prevalent compounds in fire 2 while 4 rings compounds dominated in the first prescribed burn. This study emphasized the importance of characterization of firefighters' occupational exposure to allow the implementation of preventive and mitigated measures. Further studies considering a superior number of events and the determination of additional PM-bound health-relevant pollutants should be addressed.
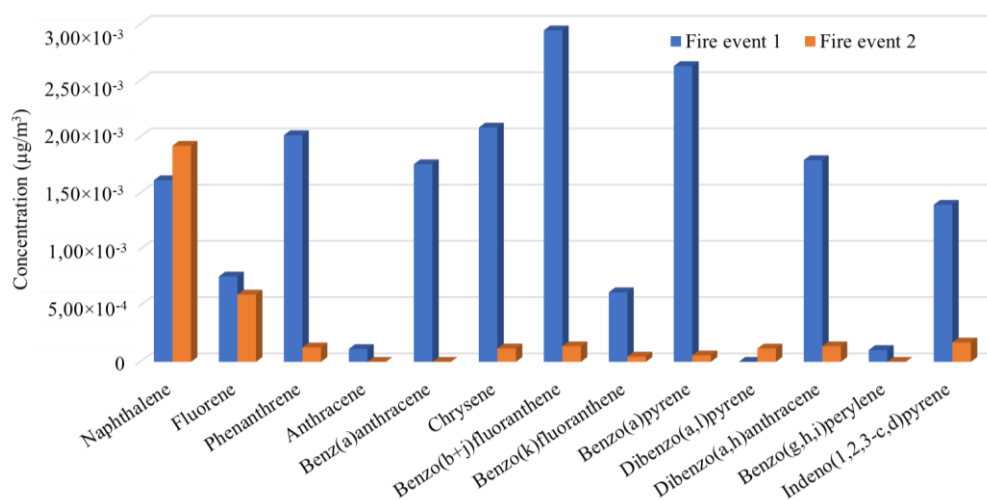
Figure 1. Median levels ($\mu g/m^3$) of PAHs (except acenaphthylene, fluoranthene, and pyrene) during the controlled fire events.

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