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Health Exposure Assessment of Firefighters Caused by PAHs in PM4 and TSP after Firefighting Operations

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Abstract: Among the many different chemicals in the air, polycyclic aromatic hydrocarbons (PAHs) pose a serious threat to human health. Firefighters are exposed to them both during fire suppression and in fire vehicles and fire stations due to inhalation of the fumes from contaminated clothing and personal protective equipment. This study aimed to estimate the exposure and cancer risk caused by suspended particulate matter and PAHs present in these particles. Air samples were collected for 4 months in a garage of the fire station in a small town, located in an urban–rural area. PAH concentrations were measured using the gas chromatography method with mass spectrometry (GC/MS). The concentration of PM4 (particulate matter with a diameter below 4µm) and TSP (total suspended particulate) in the fire station garage was 7 and 9 times higher than outside, respectively. The calculated values of health hazard risks associated with the exposure to PAHs in PM4 and TSP are: a toxic equivalent (TEQ) up to 10.36 and 23.3, incremental lifetime cancer risk (ILCR) up to 3.45 and 4.65 and hazard quotient (HQ) up to 0.42 and 0.57, respectively. A significantly increased risk of cancers in the professional group of firefighters was found.

Keywords: polycyclic aromatic hydrocarbons (PAHs); particulate matter (PM); occupational exposure; firefighter; (non)cancer risk assessment

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds containing only hydrogen and carbon that are composed of two or more fused aromatic rings [1]. They are abundant in soils and marine sediments, fresh water, and in the atmosphere, where they are predominantly bound to fine particles [2]. PAHs are persistent compounds, having a wide range of toxicity with all environmental elements. In 1983, the United States Environmental Protection Agency (USEPA) declared 16 PAHs as priority pollutants due to their high concentration, long persistence and toxicity [3]. Several PAHs exhibit carcinogenic activity: benzo[a]pyrene is carcinogenic to humans (Group 1); cyclopenta[c,d]pyrene, dibenz[a,h]anthracene and dibenzo[a,l]pyrene are probably carcinogenic (Group 2A); and naphthalene, benz[j]aceanthrylene, benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[c]phenanthrene, chrysene, dibenzo[a,h]pyrene, dibenzo[a,i]-pyrene, indeno[1,2,3-cd]pyrene and 5-methylchrysene are possibly carcinogenic (Group 2B) [4]. The carcinogenicity of PAHs in humans has been evidenced in cases of colon, skin, lung, bladder and kidney cancer [5]. Studies have shown that the risk of developing multiple myeloma and prostate, colon, rectum, bladder, skin, lung and testicular cancer is higher in firefighters than in other professional groups [6–11]. PAHs are also considered to be mutagenic, teratogenic, genotoxic and endocrine-disrupting chemicals, and they have important cardiovascular implications [4,12–14].

The sources of PAH pollution are anthropogenic and natural emissions [15–17], mainly combined with incomplete combustion [17–21]. The phenomenon of incomplete combustion occurs during all fires and can release significant quantities of harmful substances such as trace gases and particulate matter into the atmosphere [20,22,23]. Large fires, both those resulting from industrial accidents and natural fires, especially wildfires, often deteriorate

air quality in large areas leading to noticeable health and environmental effects [24–27]. Depending on the type of materials burned (e.g., wood, grass, cars, buildings with all equipment incl. flooring, upholstery, paints and coatings, bedding, draperies, etc.), and the conditions and phase of the fire, the type and amount of the produced substances may differ significantly [7]. Additionally, the smoke produced during a fire is a mixture of many compounds, and its toxicity is very diverse because each combustion condition and type of material burnt generate a unique composition [7,20,24].

Toxic and carcinogenic substances such as heavy metals or organic compounds, including both gaseous-phase and PM-bound PAHs, are released during combustion [24]; thus, firefighters are at risk of inhaling them during fire suppression. These compounds also deposit on firefighters' clothing and personal protective equipment (PPE) and are then released into the air in fire vehicles, and later, in fire brigade buildings. Firefighters inhale these hazardous compounds long after the end of firefighting activities while on duty at the fire station [6,12,13,22,28–32]. Moreover, in fire stations, diesel exhaust fumes may occur [33,34], especially when garages do not have appropriate ventilation systems and contaminants are deposited on equipment used during rescue operations, e.g., rescue spreaders, saws, and cutters. Thus, firefighting is considered a very high-risk profession and carcinogenic PAHs are an occupational health hazard for firefighters [4,31,35–41].

Unfortunately, firefighters' risk of exposure to PAHs is likely to increase, as new compounds such as modern synthetic materials produce PAHs when burned. Moreover, firefighters are not only exposed to PAHs through inhalation, but also through dermal contact with PAHs from a build-up of soot and debris [42]. However, there is little research on the types and sources of PAHs in fire stations and it is insufficient for a comprehensive risk assessment.

The PAH pollution level has become a significant issue due to health concerns, particularly in fire stations, where the risk of human exposure to atmospheric PAHs appears to be higher. PAHs in the particulate phase pose the greatest threat to health in fire brigades' garages [41]. Studies indicated that PAHs with the highest toxicity equivalent factor (TEF), containing 5–6 rings, are mainly in the solid phase [15,43–45]. Therefore, this study aimed to: (1) measure concentrations of different PM fractions in a fire station unit garage, (2) characterize PAH air pollution in PM4 and TSP and (3) evaluate the associated firefighters' carcinogenic risks. Identification of possible emission sources of PAHs using statistical analyses is an additional goal of the research.

2. Materials and Methods

2.1. Sampling Site

The fire station is located in southwest Poland (51.520044; 17.286005) beyond the central zones of a small town with a population of 11,500 and was considered an urban–rural community. The atmospheric air quality in the studied municipality is better than the average in Poland and is mainly shaped by emissions from households and individual conventional heating sources. Outdoor air quality around the nearest firehouse is influenced by traffic emissions from the national road passing through the town. The expressway is about 25 km away.

The firefighting and rescue unit (FRU) is located in a building with two aboveground stories. On the first floor, there are FRU garages, a hall, a control station, a police station and utility rooms. The social rooms of the FRU are located on the upper floor above the garages. The garage hall is about 45 m in area. The height of this room is about 5 m. There are 8 vehicles in the garage and hangers for the firefighters' special clothes.

The fire station is ventilated by a compulsory mechanical system that opens doors on departure/arrival and, if needed, opens windows. Smoking is prohibited in the entire area of the fire station. During the sampling, records of potential emission sources were recorded (vehicle arrivals/departures, vehicle and equipment maintenance, exercises, etc.).

2.2. PM Sampling

Optical and gravimetric measurements were performed simultaneously. Measurements were carried out in the fire station garages from August to December 2021, 10 times every month. Each 24 h long air test started in the morning at shift change and finished the next morning. For optical tests (PM1, PM2.5, PM4, PM7, PM10 and TSP), the particulate matter monitor Met One Aerocet LS 531 was used. The device was programmed to repeat 1 min measurements every 15 min. In the methods based on optical detection, aerosol particles are illuminated by a light beam, which scatter this light in all directions. Some of this light is absorbed at the same time. The difference between the incident and the transmitted light is converted into an electrical signal and recorded in the meter's memory.

In the gravimetric method, all PM samples were collected within 24 h in the garage of the fire station after the day the firefighters had participated in a firefighting operation. PM sampling was carried out simultaneously using two GilAir-3 personal aspirators: one with a respirable fraction (PM4) collection head, and the other with an inhalable fraction (TSP) collection head. The airflow was 2 L/min for TSPs and 2.2 L/min for PM4. Glass filters with a diameter of 25 mm were placed in the heads, on which PM4 or TSP particulate matter was deposited, depending on the mounted head. Before the measurements, the filters were conditioned for 48 h at 22 °C and 38% humidity and weighted. After PM collecting, filters were again conditioned and weighted.

PM gravimetric sampling in the garage was performed at the same time as the optical measurement method.

Health legislation does not include demands for particles above 10µm, whereas the exposure to PM in the occupational environment is based on the concentration of particles not larger than 4 µm [46–49]. For this reason, our studies took into account PM4. TSP are not considered a health risk factor as they are filtered out through the nose and throat. However, TSP cover the full range of particle sizes including PM10, PM7, PM4, PM2.5 and smaller, which pose hazards such as severe respiratory and circulation problems; therefore, they were also included in our research.

2.3. Chemical Analysis

The PAH fractions were extracted from 88 filters by ultrasonification with dichloromethane three times for a total of 45 min. The obtained extract was cleaned up using a column with sodium sulfate, activated silica and activated alumina. The final extracts were concentrated under a helium stream.

Chemical characterization of the collected PM samples was performed to determine the concentration of PAHs by the GC/MS method. The apparatuses used for gas chromatography with mass spectrometry analysis were the Agilent GC 6890A and MS 5973. For the separation of the compounds, an HP–5ms (5%-phenyl)-methylpolysiloxane column that is 30 m × 0.25 mm and 0.15 µm was used. The injection volume was 2.0 µL and the injector temperature was 275 °C. The GC oven temperature program started from 50 °C (hold 1 min) and went to 150 °C at 25 °C/min; next, it went from 150 °C to 280 °C at 5 °C/min (hold 9 min). The carrier gas was helium with a flow of 1.4 mL/min.

For the analysis, selective ion monitoring (SIM) mode was used. An external standard (M–610A, AccuStandard Inc., New Haven, USA) was used in every analysis. The external standard mixture also included the compounds in the internal standard. Possible sample losses that occurred in the evaporation or the other phases of the sample handling were managed by using the relation of the response factors of a native compound and a deuterated compound analyzed in the external standard mixture in the quantitative analysis. Recoveries of PAH internal standards were 78 ÷ 92%. Limits of detection (LOD) and limits of quantification (LOQ), calculated as three times the standard deviation for the blanks, were 0.005 ppb and 0.015 ppb, respectively. PAH concentration in blanks was below the detection limit for all targeted compounds.

2.4. Health Risk Analysis

Health risk assessment was performed based on the 15 PAHs listed as priority by the US EPA [50]. Their carcinogenic potency was estimated as toxic equivalency factors (TEFs), of which the values are specified in Table 1. To evaluate the toxicity and assess the risks of a mixture of structurally related chemicals, the toxicity or toxic equivalent (TEQ) of the carcinogenic PAHs can be determined for each day by multiplying the concentration of the individual PAH (C_{PAHn}) with its toxic equivalent factor (TEF_{PAHn}); values given by the US EPA were chosen for calculations [3]:

$$TEQ = \Sigma\, C_{PAHn} \times TEF_{PAHn} \quad (1)$$

Table 1. The toxic equivalent factor (TEF) for individual PAHs.

PAH	Nisbet & LaGoy [1]	EPA [3]	Clement Associates [51,52]	Chen et al. [53]
Dibenzo[a,h]anthracene	5	1	1.11	0.69
Benzo[a]pyrene	1	1	1	1
Benzo[a]anthracene	0.1	0.1	0.145	0.013
Benzo[b]fluoranthene	0.1	0.1	0.140	0.08
Benzo[k]fluoranthene	0.1	0.1	0.066	0.004
Indeno[1,2,3-cd]pyrene	0.1	0.1	0.232	0.017
Anthracene	0.01	0.01		
Benzo[g,h,i]perylene	0.01	0.01	0.022	
Chrysene	0.01	0.01	0.0044	0.001
Acenaphthene	0.001	0.001		
Acenaphthylene	0.001	0.001		
Fluoranthene	0.001	0.001		
Fluorene	0.001	0.001		
Naphthalene	0.001	0.001		
Phenanthrene	0.001	0.001		
Pyrene	0.001	0.001	0.081	

The obtained TEQ values depend not only on the concentration of pollutants but also on the adopted TEF coefficients, which may have the values presented in Table 1. The toxicity equivalent (TEQ) was calculated by adding together the TEQ values obtained for the individual PAHs.

Additionally, the incremental lifetime cancer risk (ILCR) and the non-cancerogenic hazard quotient index (HQ) from PAH inhalation over the period of professional activity (Equations (2) and (4), respectively) were calculated [54,55].

$$ILCR = EC \times UR \quad (2)$$

$$EC = (C \times ED \times EF)/AT \quad (3)$$

$$HQ = EDI/RfD \quad (4)$$

$$EDI = (C \times IR \times ED \times EF)/(AT \times BW) \quad (5)$$

EC is the exposure concentration, UR is the cancer inhalation unit risk (8.7×10^{-2} µg/m^3 [56]), C is the PAH concentration, ED is exposure duration in years, EF is exposure frequency in days/year, AT is the number of days over which the exposure is averaged, EDI is the estimated daily intake of PAHs, IR is the inhalation rate (16 m^3/day), RfD is the reference and BW is body weight (75 kg). Due to the fact that occupational exposure is investigated, a 4 h period of exposure to PAHs lasting 3 days a week (EF—26 days) for 20 years of work (ED) was assumed (a firefighter spends only part of the working day in a garage). For the calculations, life expectancy was assumed to be 70 years (AT).

2.5. Calculations and Data Analysis

Statistical analysis was performed. For data evaluation and presentation, the basic statistical functions of mean, minimum and maximum values of obtained results were used. Additionally, factor analysis was applied to interpret results and explain variations in the data. Median values of individual and Σ-PAHs were compared to calibration curves including standards of analyzed PAHs. The correlation coefficients for the concentration range ranged from 0.98 to 0.99. Statistical significance was defined as $p \leq 0.05$.

3. Results and Discussion

3.1. PM Concentrations

The use of an optical detection method in the research made it possible to measure the particle concentration in the air in real time and to determine the size distribution of particles present in the tested rooms. Gravimetric tests made it possible to verify the results of photometric tests, and next, the submission to chemical analysis of the collected aerosols made it possible to determine the concentrations of compounds, i.e., polycyclic aromatic hydrocarbons adsorbed on fine particles [57].

The average hourly concentrations of PM in the air in the investigated fire station in Poland during the considered periods (VIII, X, XI and XII, 2021) are presented in Figure 1.

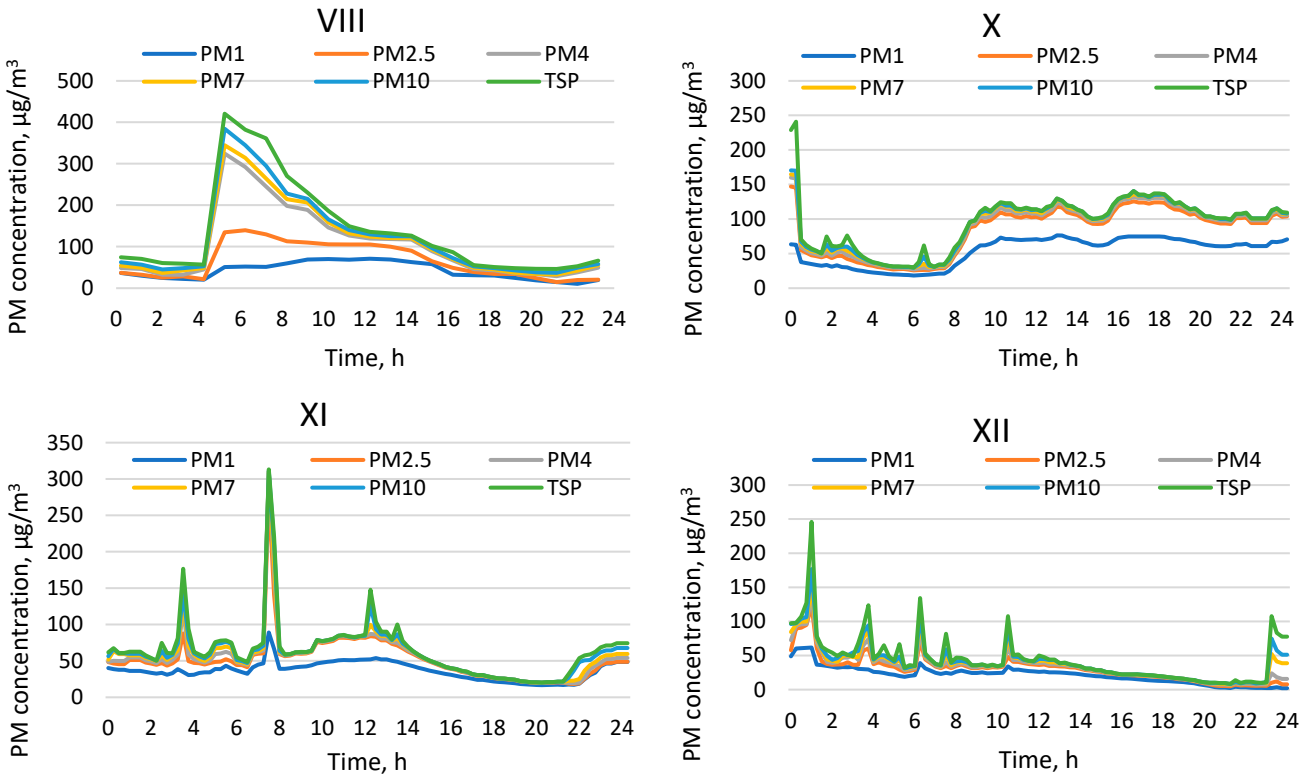


Figure 1. The hourly average concentrations of particulate matter in the air of the fire brigade unit in Poland in the analyzed periods: August, October, November and December (VIII, X, XI, XII) 2021.

On observed days, the concentration of all PM fractions was higher when the traffic in the garage was the greatest because, during this period, cleanup work, sports exercises and checking the equipment of vehicles are carried out. In addition, an increase in the concentration of particulate matter in the indoor air was observed, related to the departure of rescue vehicles to the incidents and then the return to the garage. The statistics for the mean, minimum and maximum values for the hourly concentrations of PM fractions of each month are presented in Table 2. For example, the maximum recorded concentration of PM4 in the garage of the fire brigade unit on the days of the investigation ranged from 138.3 µg/m^3 to 324.7 µg/m^3 in December and August, respectively. The mean value of

PM4 concentration on the individual days was 65.7; 55.3; 85.8 and 34.9 $\mu g/m^3$ for each of the months (August–December 2021). The maximum recorded concentration of PM10 in the garage at the same time ranged from 169.8 $\mu g/m^3$ to 384.7 $\mu g/m^3$ in October and August, respectively. The mean value of PM10 concentration was 121.3; 40.5; 61.2 and 89.6 $\mu g/m^3$ for each of the months (August–December 2021). Every day between 6.00 a.m. and 9.00 a.m. an increase in PM concentration was observed due to the increased activity of firefighters caused by the work shift. In turn, from 9:00 p.m., the concentration of PM in the garage started to decline until 5:00 a.m. due to the very low activity of firefighters in the garage during this time. Moreover, periodic increases in PM concentrations occurred during the times of intervention departures and return after the actions, e.g., at 1 p.m. (the sixth hour of measurement) there was a departure from the garage, and then a return at 2 p.m. (Figure 1XII).

Table 2. The statistics for the mean, minimum and maximum values ($\mu g/m^3$) for the hourly concentrations of PM fractions in the selected months in the garage of the tested fire station.

Month	PM1	PM2.5	PM4	PM7	PM10	TSP
			Mean value			
August	41.5	65.7	104.6	112.0	121.3	136.2
October	52.4	81.3	85.8	88.9	90.5	93.9
November	36.1	51.9	55.3	58.2	61.2	64.1
December	22.1	31.4	34.9	37.9	40.5	44.7
			Minimum value			
August	10.4	14.6	28.8	32.7	37.2	46.4
October	18.4	25.7	27.2	29.0	29.3	29.9
November	16.6	18.3	19.4	20.2	20.2	20.2
December	2.1	5.0	6.8	7.4	8.1	8.6
			Maximum value			
August	71.0	139.7	324.7	344.6	384.7	420.7
October	76.5	145.3	158.6	163.4	169.8	240.8
November	89.1	280.2	308.5	310.7	311.0	313.2
December	61.9	123.3	138.3	153.6	176.8	246.1

It is difficult to compare our results with findings from previous studies as only a few studies regarding air pollution at fire station garages have been conducted [5,12,34,41]. The available research relating to PM in the fire station confirms the problem of air contamination in various fire station rooms, especially in garages [12,23,41,58].

It is assumed that the source of contamination of high concentrations of PM occurring in fire brigade garages and changing rooms is primarily PM from firefighting activities lasting on uniforms and other equipment that are stored in changing rooms and garages between rescue operations. An additional factor is the burning of fuels by fire trucks and other devices powered by liquid fuel.

The harmfulness of particulate matter to human health was proven. PM is included in the group of non-threshold harmful substances, i.e., it has not been found that they do not cause diseases below a certain value (threshold). To protect human health, the WHO has established permissible dust concentrations in the air, both outside and inside. According to WHO guidelines, the daily concentration of PM2.5 should not exceed 15 $\mu g/m^3$, whereas the daily concentration of PM10 should not exceed 45 $\mu g/m^3$ [56].

During the research on the concentration of suspended particulate matter in the garage of the fire service unit, the level of air pollution recorded at the environmental monitoring station 1 km away from the fire station was much lower. Detailed data are presented in Table 3. A comparison of the data from Tables 2 and 3 allows us to conclude that the contamination in the firehouse garage comes from fires and other firefighter rescue activities and service works.

Table 3. The statistics for the PM concentration values (μg/m^3) for the months August–December 2021 at the air monitoring station [59].

Month	Value of PM2.5 Concentration, μg/m^3			Value of PM10 Concentration, μg/m^3		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
August	3.5	27.5	9.2	4.9	27.7	13.2
October	3.2	36.3	18.2	8.8	40	23.4
November	3.8	63.6	25.9	6.9	73.3	28.3
December	6.3	57.1	9.0	7.5	68.7	31.4

3.2. PAH Concentration

The concentrations of 15 PAHs in PM4 and TSP vary widely, from 1.74 to 130.56 ng/m^3 and from 1.58 to 45.77 ng/m^3 in the case of TSP and PM4, respectively (Table 4). Benzo[k]fluoranthene, chrysene, acenaphthylene, naphthalene and benzo[g,h,i]perylene were at the lowest concentration in the investigated samples. The most toxic, benzo[a]pyrene, was found in almost all samples. The most abundant were PAHs with the highest toxic equivalent factor (0.1–1.0; Table 1): dibenzo[a,h]anthracene, benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and anthracene, which occurred mainly in TSP fractions. The highest amount of organic pollutants was absorbed on the third day of measurements and the least on the second day. It was probably influenced by the activity of firefighters and their participation in fire suppression, as well as the outdoor air quality and weather conditions. However, the relationship between temperature and PAH concentrations was not found, because on the second and third day an equal temperature was noticed (4.7 °C and 4.6 °C, respectively). At the same time, no clear correlation was found between the concentration of PAH in the garage and the amount of PM outdoors. Comparing obtained data with the study on Portuguese firehouses, the sum of PAHs is a little bit higher in the fire station garage in Poland. The differences exist only in the case of participating PAHs with different amounts of aromatic rings. In Portugal, PAHs with 2–3 rings had the largest share, and in the Polish samples, 4-ring PAHs dominated [36].

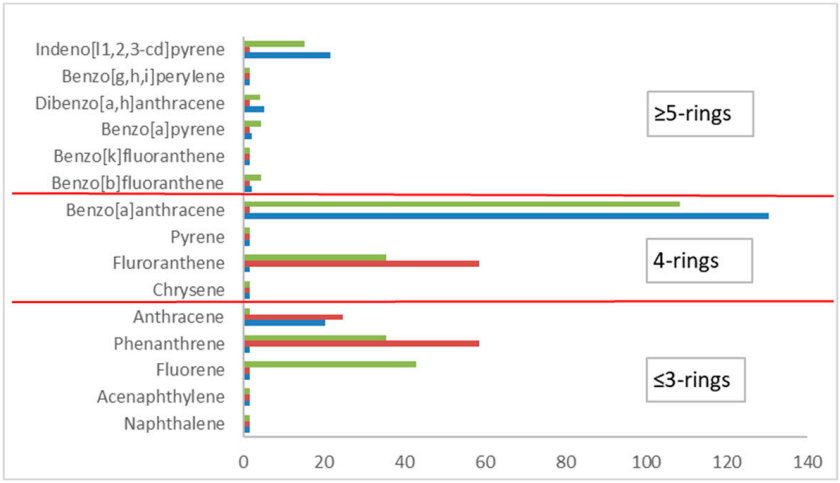
Table 4. The concentration of individual PAHs (ng/m^3) in TSP and PM4 samples collected in the garage of the fire station unit.

	28/29.10.21		10/11.11.21		1/2.12.21	
PAH	TSP	PM4	TSP	PM4	TSP	PM4
Dibenzo[a,h]anthracene	5.21	1.58	1.74	1.58	4.17	1.58
Benzo[a]pyrene	2.08	1.58	1.74	2.21	4.51	7.89
Benzo[a]anthracene	130.56	1.58	1.74	1.58	108.33	1.58
Benzo[b]fluoranthene	2.08	1.58	1.74	2.21	4.51	1.58
Benzo[k]fluoranthene	1.74	1.58	1.74	1.58	1.74	1.58
Indeno[1,2,3-cd]pyrene	21.53	1.58	1.74	1.58	15.28	1.58
Anthracene	20.49	20.52	24.65	4.10	1.74	1.58
Benzo[g,h,i]perylene	1.74	1.58	1.74	1.58	1.74	1.58
Chrysene	1.74	1.58	1.74	1.58	1.74	1.58
Acenaphthylene	1.74	1.58	1.74	1.58	1.74	1.58
Fluoranthene	1.74	39.77	58.68	1.58	35.42	45.77
Fluorene	1.74	41.67	1.74	1.58	43.06	1.58
Naphthalene	1.74	1.58	1.74	1.58	1.74	1.58
Phenanthrene	1.74	39.77	58.68	1.58	35.42	45.77
Pyrene	1.74	37.56	1.74	30.93	1.74	1.58
Sum of PAHs	197.57	195.08	162.85	56.82	262.85	118.37

Many studies have focused on the distinction and identification of sources of PAHs based on the molecular weight, and the number of benzene rings or ratios between amounts of different PAHs. Differences in PAH concentration in TSP and PM4 depend on the number

of benzene rings (Figure 2). In TSP samples, the contribution of PAHs with two to six rings is observed, with a predominance of compounds with four rings, whereas in the case of PM4 there are PAHs with four and fewer rings in significantly higher amounts. This distribution of PAHs indicates that the heaviest PAH fractions are associated with the coarser PM fractions. In finer PM there are lighter PAHs, similar to ambient air [5,43–45].

(**a**)



(**b**)

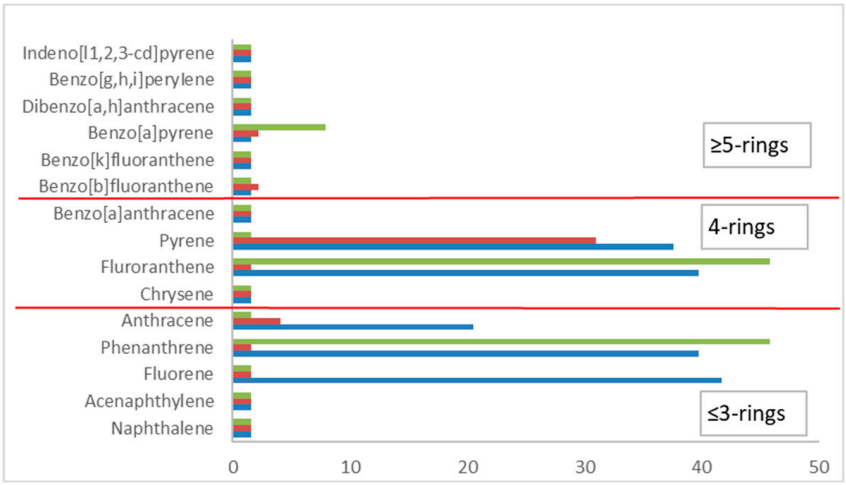


Figure 2. The PAH concentration dependent on the number of the benzene rings in: (**a**) TSP samples and (**b**) PM4 samples. The red lines are the borders between the PAH groups with different number of rings.

The source analysis was performed using diagnostic ratios computed on the basis of specific PAH concentrations [41,60]. The relatively high ratio PAH(3 + 4)/PAHs(5 + 6) indicates long-distance transportation of pollutants, which in this case may suggest their translocation from the place of fire into the garage (Table 5). Another ratio, anthracene/(anthracene + phenanthrene), ranged from 0.03 to 0.92, fluoranthene/(fluoranthene + pyrene) varied from 0.05 to 0.97 and benzo[a] anthracene/(benzo[a] anthracene + chrysene) in the range of 0.50–0.99, indicating both pyrogenic and petrogenic sources. This means that besides incomplete combustion of fossil fuels and organic matter (grass, wood, coal), vehicular emissions from diesel engines are the significant sources of PAHs in the garage. Only in December 2021 was the contribution of petroleum combustion sources suggested by the ratio anthracene/(anthracene + phenanthrene) below 0.1 [41].

Table 5. The PAH diagnostic ratios in TSP and PM4 samples collected in the garage of the fire station unit.

Diagnostic Ratios *	28/29.10.21		10/11.11.21		1/2.12.21	
	TSP	PM4	TSP	PM4	TSP	PM4
PAHs(3 + 4)/PAHs(5 + 6)	4.70	19.43	14.47	4.15	7.17	6.40
Ant/(Ant + Phe)	0.92	0.34	0.30	0.72	0.05	0.03
Flt/(Flt + Pyr)	0.50	0.51	0.97	0.05	0.95	0.97
BaA/(BaA + Chr)	0.99	0.50	0.50	0.50	0.98	0.50

* PAH abbreviations are as follows: PAHs(3 + 4) means sum of PAHs with 3 and 4 rings, PAHs(5 + 6) means sum of PAHs with 5 and 6 rings, phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA) and chrysene (Chr).

3.3. Health Risk Assessment

The toxicity equivalent (TEQ) of the carcinogenic PAHs varies from 4.38 to 23.33 ng/m^3 when taking into account PM fractions, but when comparing these values for days, the highest TEQ was obtained for the measurement day in October, whereas the highest values of the incremental lifetime cancer risk (ILCR) and the non-cancerogenic hazard quotient index (HQ) were obtained for TSP samples collected in December 2021 (Table 6). Results indicated that the smallest health risk caused by exposure to PAHs occurred in November 2021. TEQs in the studied fire station were much higher than in selected public bars from the southern part of Nigeria due to tobacco smoke [54], and simultaneously, significantly lower than values obtained from the Portuguese fire stations (several thousand) [12]. The difference may result from the different functions of the rooms in the fire stations and the number of departures to fires and other rescue actions. Moreover, the authors used different TEF values for their calculations [1,12]. Values of carcinogenic risk, where the ILCR ranged from 1.01×10^{-4} to 4.65×10^{-4}, are much higher than the permissible limit of 10^{-5} set by the WHO [58]. The HQ varied from 0.12 to 0.57 and it indicated a quite high non-carcinogenic risk for firefighters. Generally, the occupational exposure of firefighters is in fact much higher; however, this study concerned only air pollutants in the garage, and the calculated indices assumed the firefighters stayed in it for only a few hours for an average of 3 days a week and only studied the related risk of the absorption of pollutants through the respiratory tract; dermal contact and ingestion was not taken into account. The health of firefighters is also at risk when staying in other rooms of fire brigades, which, as studies show, are also heavily contaminated [12,41]. However, the greatest risk of inhaling carcinogenic compounds contained in fumes, dust and soot is associated with participation in firefighting operations.

Table 6. The toxicity indices: the toxic equivalent (TEQ, ng/m^3), the incremental lifetime cancer risk (ILCR) and the non-cancerogenic hazard quotient index (HQ) calculated based on individual dust fractions and measurement days.

PAH	28/29.10.21		10/11.11.21		1/2.12.21	
	TSP	PM4	TSP	PM4	TSP	PM4
TEQ	23.33	4.38	4.74	4.65	22.10	10.36
ILCR ($\times 10^{-4}$)	3.50	3.45	2.88	1.01	4.65	2.10
HQ	0.43	0.42	0.35	0.12	0.57	0.26

To summarize, the investigation showed that staying in the garage and inhaling the air polluted with dust emitted by protective clothing and firefighting equipment poses a high risk to the health of firefighters, both carcinogenic and non-carcinogenic, which increases even more when they come into contact with the skin of exposed parts of the body. The results are similar or even higher than the results obtained by several studies on the harmful effects of inhaling poor air quality caused by enhanced PAH concentrations [31,32,36,41–43,54,55].

4. Conclusions

Our study presents the results of occupational exposure to PM and PM-bound PAHs for firefighters in the workplace when performing tasks other than firefighting or rescue operations. The obtained data on the PM fractions and PAH concentrations indicate the existing occupational exposure of firefighters due to bad air quality in fire stations. The occupational exposure of firefighters was assessed in an urban–rural commune, where outdoor air pollution is relatively low and the number of departures was small compared to large cities and highly urbanized areas. The conducted research allows identifying several problems impacting the air quality in garages of fire brigades. One of them is the introduction to a firehouse of contamination deposited on vehicles, equipment and clothes of firefighters. Particles present on the surface of vehicles, equipment, clothes and flooring could be resuspended as a result of the movement of people during the maintenance of PPE or technical rescue equipment. This phenomenon is related, among others, to the number of departures and arrivals of the crew while on duty, which causes a temporary increase in the PM concentrations. Air pollution in the fire brigade unit influenced the occupational exposure of firefighters. Health hazard indices such as the total toxicity equivalent concentration (TEQ), the incremental lifetime cancer risk (ILCR) and the non-cancerogenic hazard quotient (HQ) indicated that firefighters are a group with very high health risk exposure, especially to neoplastic diseases caused by inhalation of carcinogenic PAHs.

Taking into account the significantly increased risk of certain cancers in the professional group of firefighters, research should be continued on the determination of the sources of harmful pollutants, the effectiveness of the methods used to eliminate them, and more accurate and in-depth exposure assessments.

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