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Evaluation of the PAH Content in Soot from Solid Fuels Combustion in Low Power Boilers

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Abstract: The emission of carbon compounds (in the form of soot) to the atmosphere has a significant impact on the environment and human health. Air pollution with combustion products, having a unique combination of physical and chemical properties, is an important component of very fine suspended dust, which is emitted from various sources related to combustion processes. The carbon compounds in aerosol form and deposited in the substrate are found all over the Earth. The paper presents results of comparative research on the content of 16 polycyclic aromatic hydrocarbons (PAH) in soot samples obtained as a result of combustion of solid fuels such as hard coal with granulation above 60 mm, coal with a grain size of 25–80 mm, coal with a grain size of 8–25 mm, pellets and dry wood. On the basis of the conducted tests, it was found that the soot obtained in the combustion of coal in different granulation contains more cytotoxic PAH in comparison to the combustion of wood pellets or dry firewood.

Keywords: solid fuels; combustion; soot; PAH

1. Introduction

Emission of carbon compounds in the form of soot to the atmosphere has a significant impact on the environment and human health. Soot is a form of air pollution that has a unique combination of physical and chemical properties. It is also an important component of very fine suspended dust, which is emitted from various sources related to combustion processes [1]. Often in literature, soot compounds are referred as elemental carbon (EC); alternative names are black carbon (BC) or black smoke. Soot is a toxic waste produced mainly as a result of low emissions, i.e., in the combustion processes of solid fuels and waste in individual heat sources. Here, the term 'low emissions' is used to describe harmful dust and gas emissions at low altitude. These are emitters such as chimneys and other emission sources located at a height not exceeding 40 m [2,3]. Other sources of soot in the environment include emission of pollutants from vehicles and vessels with diesel engines, production of energy and heat in the power industry, production of heat in industry, forest fires and biomass burning in agriculture [1,4–8]. This waste consists of highly toxic, carcinogenic or mutagenic compounds, including amorphous carbon, graphite-like connections, fullerenes, ashes, and metal compounds, including heavy metals and metalloids. In addition, hydrocarbons, in particular aliphatic and aromatic hydrocarbons, including large amounts of polycyclic aromatic hydrocarbons (PAH), constitute a large proportion of the soot [4,5].

Chemical composition of soot depends on the fuel composition and the physicochemical conditions of the combustion process [9–11].

The formation of soot begins with the reaction of the decomposition of fuel molecules, i.e., the pyrolysis and oxidation reactions. Then, there are recombination and cyclization reactions that lead to the formation of polycyclic aromatic hydrocarbons. On the other hand, the increase in PAH

in flames occurs through the repetitive hydrogen abstraction and acetylene addition, known as the hydrogen and acetylene addition mechanism (HACA) [5,6]. The soot particles under the microscope resemble a layer structure formed from condensed six- and five-membered rings. The presence of these rings causes the expanding layers to develop into spherical structures with a diameter of several dozen nanometers. Research conducted by the group of Schultz confirms the large variety of aromatic compounds involved in the formation of the initial soot particles. In addition, Schultz proved that penta rings often occur during black carbon formation and that non-aromatic side groups such as cycloaliphatic moieties, methyl groups and alkyl chains also occur [5]. In contrast, Commodo and others confirmed that in the black carbon formed at the beginning of soot creation process there are molecules containing condensed six-ring units (formed in the flame) organized in almost completely peri-condensed structures and several molecules showing aliphatic side groups—mainly methyl groups ($-CH_3$) [6].

A well-developed specific surface of soot translates into a high adsorption capacity. Along with soot, other toxic substances are transferred. Due to its very low density (1.3 g/cm^3 [12]), it can persist in the atmosphere for a long time. Small size of soot particles (soot is part of the PM10 and PM2.5 dust) makes it able to penetrate the body's barrier, penetrating not only through the airways, but sometimes even through the skin [13–15]. Medical research conducted in this direction has shown that it can cause mutagenic and carcinogenic changes in the human body, as well as cardiovascular and respiratory diseases [16,17].

In addition, soot is considered a factor affecting the climate of the Earth. Initially, the share of soot in this area was treated very slightly, and all attention was focused mainly on carbon dioxide as the main factor contributing to global warming. Recent scientific studies show that soot is the second most important factor that influences the current climate change after carbon dioxide. An additional feature of BC is that it absorbs sunlight [18–29]. Absorbed energy is released in the form of heat and thus contributes to the warming of air, which results in the acceleration of melting ice and snow [5]. In addition, soot affects the climate change through such processes as cloud formation, water evaporation and disappearance, or precipitation [18–20].

According to researchers' forecasts and trends of changes obtained in international research centers, the soot emission in Europe has significantly decreased, based on inventory and measurements from soot emission sources, but the structure of emission sources has changed. An increase in emissions in the municipal and household sector in the overall carbon pollution balance was observed. This phenomenon is caused by a greater share of organic carbon in the dust emitted from the combustion of solid fuels in energy and emission inefficiencies in installations. This is connected with the dominating share of solid fuels, i.e., coal and biomass in the fuel structure of the municipal sector in Eastern Europe and a large share of diesel-powered vehicles in Western Europe [20]. However, in Poland, according to the report prepared by The National Centre For Emissions Management of The Institute of Environmental Protection—National Research Institute (IEPNRI), published in 2018, the volume of emissions of the BC dust soot fraction increased in 2015–2016. The emission of BC dust fractions in 2016 increased by approximately 7% compared to 2015, mainly due to higher consumption of fuels in the sector of combustion processes outside the industry and in road transport [21].

In connection with the above, this research was undertaken to assess the content of 16 individual representatives of the polycyclic aromatic hydrocarbons (PAH) group in soot from the combustion of various solid fuels in the low power boilers. Therefore, samples of soot selected for testing were from the combustion of imported hard coal with dimensions over 60 mm, hard coal with a grain size of 25–80 mm, bituminous coal with a grain size of 8–25 mm, pellets with a grain size of 6 mm and mixed firewood. The content of the ΣLMW (low molecular weight polycyclic aromatic hydrocarbons) fraction containing the hydrocarbons containing in their structure from two to four aromatic rings, ΣHMW (high molecular weight polycyclic aromatic hydrocarbons with concentrations of five- and six-ring hydrocarbons) and Σ16PAH (total content of 16 polycyclic aromatic hydrocarbons in the sample) were taken into account. This measure of the content of the 16 compounds from the PAH

group is recommended for monitoring in the environment by Environmental Protection Agency (EPA) as it encompasses the most potent carcinogenic and mutagenic properties. Therefore, it was decided to evaluate the content of PAH in soot samples from the combustion of solid fuels in a low power class 5 boiler that met the eco-design standards. The potential for reducing emissions of soot and its components depends on technical and non-technical solutions that should be applied in the sector of human activity bringing the largest load of soot to the air [20].

In addition, the carcinogenicity equivalent (CEQ) and selected mutagenic and toxic equivalents of the TCDD-TEQ (the 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) toxic equivalent quantity) interaction of the PAH mixture and the $\Sigma PAH_{carc}/\Sigma PAH$ ratio (ratio of the sum of carcinogenic PAH to the sum of PAH determined) for all types obtained from the combustion of solid carbonaceous fuels were calculated.

2. Materials and Methods

The tests were carried out by burning the following fuels: hard coal with a size of over 60 mm, hard coal with a grain size of 25–80 mm, hard coal with a granulation of 8–25 mm, pellets with a grain size of 6 mm and mixed firewood. The combustion process was carried out on a laboratory bench [22] (Figure 1) consisting of Moderator Unica Vento Eko boiler 25 kW with an automatic feeder equipped with a manual and retort grate. The temperature of the feed water (at the boiler's outlet) was about 70–80 °C, while at the return it was not less than 50 °C.

The moderator is a boiler with a transverse circulation chamber working with upper combustion. The walls are water cooled and made of quality 5/6 mm sheet steel and a 4 mm outer shell. The cubical exchanger consists of a chamber with a self-cleaning retort furnace, above which there is a flue gas deflector (Figure 1). The deflector is an essential element of the retort furnace—it serves as a "flue gas accelerator". The remaining part of the exchanger consists of heat plates which effectively receive the heat from the flowing flue gases. The boiler is thermally insulated and has a chassis. In addition, it has a retort furnace door and loading door (for alternative fuel). Soot for further testing was taken from the door for cleaning the boiler chambers, located on the front wall of the boiler. Next to the boiler there is a fuel container mounted on the feeder unit. The feeder unit is powered by a motoreducer via an electrical motor (Figure 1). Mounted on the boiler there also is an electronic controller, which allows for a fully automatic control of the boiler operation. The engine powering the screw via the motoreducer is turned on and off by the controller based on the temperature read from sensors; the blow fan is activated accordingly. The screw transports the fuel to the boiler where it is burned in the furnace with a supply of air through the openings in the top.

Three events of combustion were carried out for each of the five solid fuels selected for testing, collecting measurements each day from the heat exchanger (Figure 1). Each time, 15 kg of each fuel was burned, maintaining the same combustion conditions, i.e., temperature of the fumes.
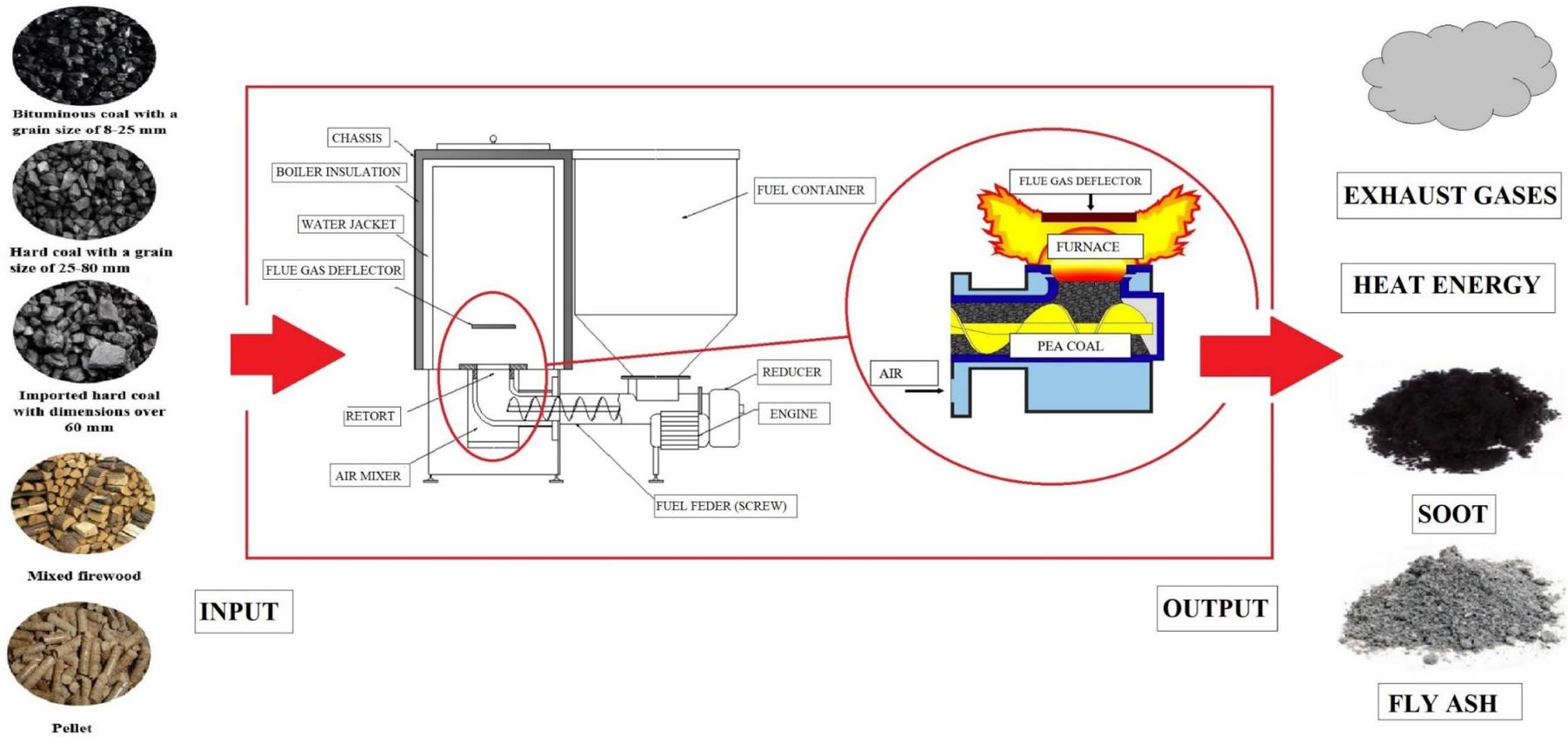
Figure 1. Scheme of testing system with all key elements.

Then, after the combustion of the individual types of fuels, soot samples were collected. The soot is a side effect of the combustion process. About 3 g of soot was taken from the heat exchanger. The soot was extracted twice with a mixture of hexane-acetone solvents (20 mL/5 mL) for 2 h to elute the PAH tested therein, i.e., naphthalene, acenaphthalene, anthracene, benzo(a)anthracene, benzo(b)fluoroanthrone, benzo(k)fluoroanthrone, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibano(a,h)anthracene, fluoroanthene, fluoren, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene and pyrene. Acetone and polar compounds extracted from it were removed by washing twice with 10 mL of deionized water. The remaining organic phase was dried over anhydrous sodium sulfate (anhydrous, ACS reagent, ≥99% Sigma-Aldrich). The extracts were then concentrated on a Turbo-Vap apparatus under an inert gas ie. nitrogen atmosphere, to a volume of 1 mL. The solutions prepared in this way were subjected to chromatographic analysis for the presence of aromatic hydrocarbons mentioned above. A gas chromatograph coupled with a mass spectrometer (Agilent GC/MS Triple Quad 7000 C) was used, equipped with a split/splitless dispenser and an HP-5MS capillary column measuring 30 m × 0.25 mm with a film thickness of 0.25 μm. Working conditions of the apparatus during the analysis shown in Table 1.

Table 1. Chromatograph working conditions during polycyclic aromatic hydrocarbons (PAH) determination.

Working Conditions	Value
carrier gas	helium with purity 6.0
carrier gas flow rate through the column	1 mL/min (splitless)
volume of the injected sample	1 μL
dispenser temperature	260 °C
ion source temperature	230 °C
transfer line temperature	300 °C
quadrupole temperature	150 °C
scanning mode	single ion monitoring (SIM—selected ion monitoring)
The temperature program was set as follows	
initial temperature of the column furnace	60 °C, 2 min isothermal
temperature increase	30 °C/min to 120 °C, from 120 °C temperature increase 5 °C/min to 300 °C
end temperature of the column furnace	300 °C, isothermal 15 min

During the extraction, no internal standard addition was used, whereas the method control was carried out by simultaneous execution of the entire analytical procedure for a sample of certified reference material—Clean soil Reference Material EDF-5183 (CERILLIANT Analytical Reference Standards). The tests used external calibration with calibration curves for individual compounds. Calibration solutions were prepared from a standard of 16 PAH mixture (AccuStandard, Z-014G).

In order to determine the harmfulness of the 16 PAH examined, indicators were used which define the toxicity of individual PAH and the whole group as well. A universal method for calculating the risk related to exposure to PAH mixture was adopted. B(a)P (benzo(a)pirene) is assumed to be a reference compound. The carcinogenic potential, called the toxicity equivalence factor (TEF) of other compounds is calculated relative to B(a)P. The toxicity equivalent value (TEQ—toxic equivalent) is the sum of the products of the concentrations of individual PAH and their relative toxicity coefficients TEQ = CEQ [23]:

$$
\begin{aligned}
\text{TEQ} = \text{CEQ} = &\ 0.001 \times [\text{Nap}] + 0.001 \times [\text{Acy}] + 0.001 \times [\text{Ace}] + 0.001 \times [\text{Fl}] + 0.001 \times [\text{Phe}] + \\
& 0.01 \times [\text{Ant}] + 0.001 \times [\text{Flu}] + 0.001 \times [\text{Pyr}] + 0.1 \times [\text{B(a)A}] + 0.01 \times [\text{Chr}] + 0.1 \times [\text{B(b)F}] + 0.1 \times \\
& [\text{B(k)F}] + 1 \times [\text{B(a)P}] + 5 \times [\text{D(ah)A}] + 0.1 \times [\text{B(ghi)P}] + 0.1 \times [\text{I(cd)P}].
\end{aligned} \tag{1}
$$

Durant and others [25] reported mutagenic coefficients for individual PAH. Wilellet and others [26] proposed that the carcinogenic potential of PAH may be calculated with respect to

dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin—TCDD), for which the carcinogenicity coefficient value is equal to 1. To assess the harmfulness of PAH, in addition to the CEQ toxicity equivalent (TEQ) given by Nisbet and LaGoy [23], the mutagenicity equivalent (MEQ) and carcinogenicity (TCDD-TEQ) are also used [24]. The mutagenicity factors [25] and carcinogenicity factors [26] were selected which refer to the 16 priority PAH according to the EPA list. The mutagenicity equivalent was given as the sum of the product of the concentration of individual PAH and their relative mutagenicity coefficients [24]:

$$MEQ = 0.00056 \times [Acy] + 0.082 \times [B(a)A] + 0.017 \times [Chr] + 0.25 \times [B(b)F] + 0.11 \times [B(k)F] + 1 \times [B(a)P] + 0.31 \times [I(cd)P] + 0.29 \times [D(ah)A] + 0.19 \times [B(ghi)P]. \tag{2}$$

On the other hand, the equivalent of carcinogenicity is the sum of the products of the concentrations of individual PAH and their relative carcinogenicity coefficients:

$$TCDD\text{-}TEQ = 0.000025 \times [B(a)A] + 0.00020 \times [Chr] + 0.000354 \times [B(a)P] + 0.00110 \times [I(cd)P] + 0.00203 \times [D(ah)A] + 0.00253 \times [B(b)F] + 0.00487 \times [B(k)F]. \tag{3}$$

The harmfulness of PAH is also expressed as the ratio of PAH considered carcinogenic to the sum of all PAH determined [27]:

$$\Sigma PAHcarc/\Sigma PAH = ([B(a)A] + [B(a)P] + [B(b)F] + [B(k)F] + [Chr] + [D(ah)A] + [I(cd)P])/([\Sigma16PAH]). \tag{4}$$

Based on the calculated carcinogenicity and mutagenicity indicators, the toxicity of the tested types of solid fuels was determined. It was assumed that when the value of the ratio $\Sigma PAH_{carc}/\Sigma PAH$ is closer to 1, the PAH pose a greater threat to the population.

3. Results and Discussion

Table 2 shows the basic properties of the analyzed 16 polycyclic aromatic hydrocarbons: naphthalene, acenaphthalene, anthracene, benzo(a)anthracene, benzo(b)fluoroanthrone, benzo(k)fluoranthrene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoroanthene, fluoren, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene and pyrene. The studied hydrocarbons were divided into three groups: ΣLMW (hydrocarbons containing from two to four aromatic rings in their structure: naphthalene, acenaphthene, acenaphthalene, fluorene, phenanthrene, anthracene); ΣHMW (five- and six-ring compounds: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene) and the total of 16 aromatic hydrocarbons—Σ16PAH.

Table 3 presents results of PAH content analysis in the studied soot samples from the combustion of selected fuels. PAH are the most frequently tested pollutants in environmental samples, which is dictated primarily by their negative impact on health, including toxicity, carcinogenicity and mutagenicity [25,30,31].

Table 2. ΣPAH included hydrocarbons containing from two to six rings in their structure.

Ordinal Number	Polycyclic Aromatic Hydrocarbons	Short Name	Structure (Number of Rings)	Molecular Weight (g/mole)	Solubility (mg/L)	Vapor Pressure (mm Hg)
1	Naphthalene	Nap	2	128.17	31	8.89×10^{-2}
2	Acenaphthylene	Acy	3	152.20	16.1	2.90×10^{-2}
3	Acenaphthene	Ace	3	154.21	3.8	3.75×10^{-3}
4	Fluorene	Flu	3	166.22	1.9	3.24×10^{-3}
5	Phenanthrene	Phe	3	178.23	1.1	6.80×10^{-4}
6	Anthracene	Ant	3	178.23	0.045	2.55×10^{-5}
7	Fluoranthene	Flr	4	202.26	0.26	8.13×10^{-6}
8	Pyrene	Pyr	4	202.26	0.132	4.25×10^{-6}
9	Benzo(a)anthracene	B(a)A	4	228.29	0.011	1.54×10^{-7}
10	Chrysene	Chr	4	228.29	0.0015	7.80×10^{-9}
11	Benzo(b)fluoranthene	B(b)F	5	252.32	0.0015	8.06×10^{-8}
12	Benzo(k)fluoranthene	B(k)F	5	252.32	0.0008	9.59×10^{-11}
13	Benzo(a)pyrene	B(a)P	5	252.32	0.0038	4.89×10^{-9}
14	Indeno[1,2,3-cd]pyrene	I(cd)P	6	276.34	0.062	1.40×10^{-10}
15	Dibenz(a,h)anthracene	D(ah)A	6	278.35	0.0005	2.10×10^{-11}
16	Benzo(g,h,i)perylene	B(ghi)P	6	276.34	0.00026	1.00×10^{-10}

Source: Own elaboration on [28,29].

Table 3. Results of PAH determinations in soot samples from the combustion of solid fuels.

mg/kg DM	Pellet 6 mm	Hard Coal > 60 mm	Hard Coal 25–80 mm	Hard Coal 8–25 mm	Mixed Firewood
Naphthalene	0.50 ± 0.20	2.52 ± 3.04	1.20 ± 0.04	2.17 ± 0.46	1.33 ± 0.08
Acenaphthylene	0.63 ± 0.07	10.77 ± 4.46	4.48 ± 0.45	13.01 ± 5.83	3.05 ± 0.33
Acenaphthene	0.05 ± 0.002	1.28 ± 1.62	0.29 ± 0.03	0.59 ± 0.26	0.15 ± 0.02
Fluorene	0.07 ± 0.002	9.62 ± 13.34	0.86 ± 0.08	7.71 ± 9.23	0.27 ± 0.02
Phenanthrene	2.87 ± 0.12	50.05 ± 12.44	47.5 ± 5.69	52.49 ± 11.67	18.82 ± 2.45
Anthracene	0.78 ± 0.05	13.56 ± 5.95	17.49 ± 2.15	19.28 ± 6.44	4.39 ± 0.57
Fluoranthene	5.06 ± 0.30	17.95 ± 5.03	46.34 ± 6.25	36.38 ± 9.06	14.18 ± 2.23
Pyrene	5.23 ± 0.61	16.42 ± 2.51	41.12 ± 5.39	32.01 ± 9.68	11.84 ± 1.90
Benzo(a)anthracene	3.70 ± 0.09	13.05 ± 9.14	26.17 ± 3.86	18.84 ± 5.65	8.44 ± 1.27
Chrysene	4.52 ± 0.11	12.04 ± 7.09	24.07 ± 3.61	17.09 ± 5.07	8.73 ± 1.24
Benzo(b)fluoranthene	13.07 ± 3.97	22.40 ± 7.40	33.09 ± 5.78	29.04 ± 8.70	32.87 ± 5.29
Benzo(k)fluoranthene	15.58 ± 0.55	27.02 ± 12.85	49.58 ± 7.77	44.49 ± 12.95	28.03 ± 4.50
Benzo(a)pyrene	12.67 ± 0.06	30.87 ± 6.71	60.48 ± 10.05	58.55 ± 17.84	36.53 ± 5.72
Indeno[1,2,3-cd]pyrene	16.54 ± 2.69	20.42 ± 6.35	36.70 ± 6.02	44.82 ± 9.48	33.94 ± 2.56
Dibenz(a,h)anthracene	1.32 ± 0.15	2.45 ± 0.97	6.69 ± 0.99	6.06 ± 2.42	4.39 ± 0.33
Benzo(g,h,i)perylene	13.01 ± 1.95	12.93 ± 2.63	22.12 ± 3.19	30.16 ± 5.60	23.48 ± 1.50
Σ16PAH	95.62 ± 6.44	263.36 ± 91.00	418.21 ± 61.03	412.70 ± 127.16	230.44 ± 28.62
ΣLMW	4.90 ± 0.42	87.81 ± 24.89	71.86 ± 6.24	95.26 ± 32.92	28.01 ± 2.81
ΣHMW	90.72 ± 5.99	175.55 ± 60.16	346.35 ± 52.67	317.43 ± 58.32	188.26 ± 25.31

As a result of chromatographic analysis of extracts from black carbon samples, it was found that the sum of 16 determined hydrocarbons included in the PAH group depends significantly on the type of fuel burned while maintaining the same combustion conditions. The total PAH content in fuel samples ranged from 95.62 ± 6.44 mg/kg DM in the case of combustion of pellets with a grain size of 6 mm to 418.21 ± 61.03 mg/kg DM in the case of coal combustion with a grain size of 25–80 mm. Relative uncertainty of each of the PAH sum assays within the framework of separate combustion for individual fuels was estimated from 6% to 34%, which means that the combustion process is characterized by high variability and nonlinearity, even while maintaining the same fuel and combustion parameters [32].

Analyzing the content of the sum of 16 PAH (Figure 2), the smallest content in the soot in the samples was from pellet combustion and was found to be 95.62 ± 6.44 mg/kg DM. Another fuel, which was characterized by the second lowest PAH content, was mixed wood fuel, for which 230.44 ± 28.62 mg/kg DM was obtained. The remaining three analyzed fuels were hard coal with different granulation. Soot samples from the combustion of selected hard coals were characterized by much higher PAH content as compared to soot samples from the combustion of pellets and mixed

wood fuel. In the group of coals, the highest total PAH content was found in soot samples from the combustion of coal with a grain size of 25–80 mm, which was 418.21 ± 61.03 mg/kg DM, while the smallest content was characterized by soot samples from coal combustion granulation >60 mm, which was 263.36 ± 91.00 mg/kg DM. Soot from coal combustion with large irregular cubes over 60 mm was characterized by a lower content of PAH not only from black carbon from 25–80 mm granulation, but also from coal with 8–25 mm granulation.
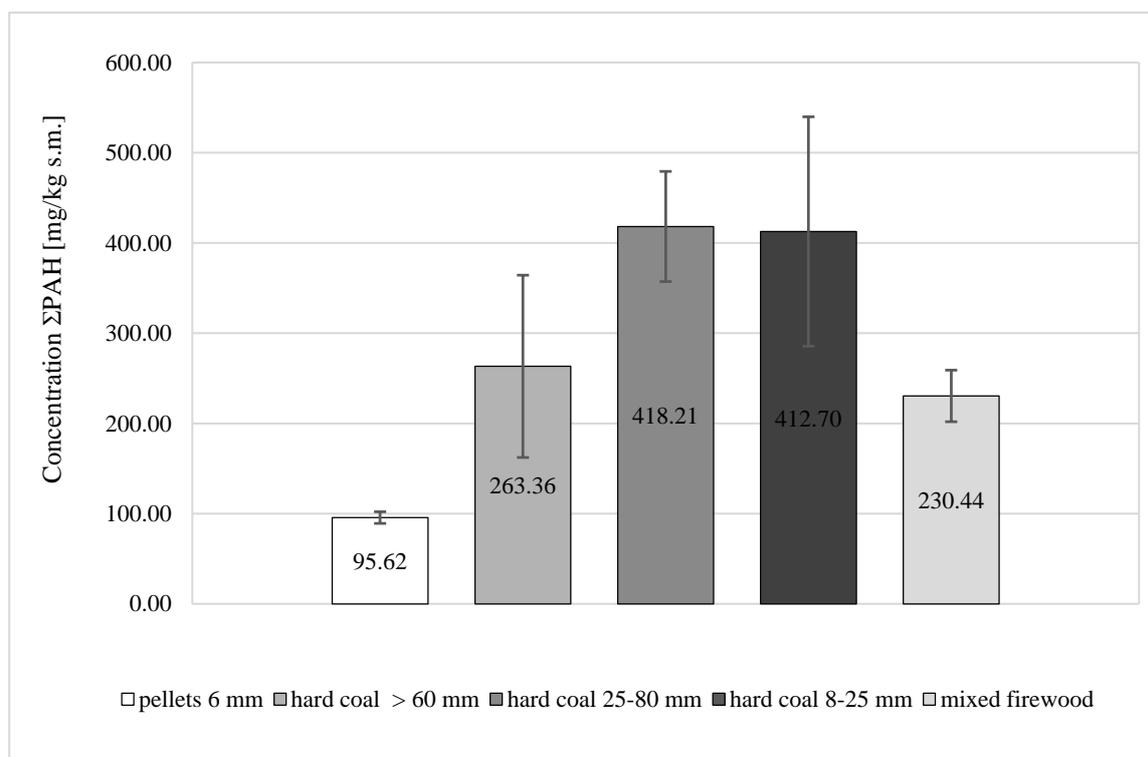
Figure 2. Average content of ΣPAH in soot samples from the combustion of selected fuels.

Research conducted by Kakareka on the emission of polycyclic aromatic hydrocarbons (PAH) from several types of solid fuel combustion in various low power boilers in Belarus proved that the highest PAH emissions were detected in waste gases from the incineration of household waste and wood waste. The lowest PAH emissions originated from the combustion of peat briquettes. A difference was observed in the concentrations of the total PAH in the waste gases from the combustion of solid fuels depending on the type of boiler. The PAH content from birch wood combustion was higher than in the case of pine wood emissions [33].

When analyzing the compactness of light PAH fraction, determined with the abbreviation LMW (Figure 3) and containing hydrocarbons consisting of two and three aromatic rings, it was found that soot from the combustion of pellets and mixed fuel wood contains, as in the case of a total of 16 PAH, the least LMW; these values were 4.90 ± 0.42 mg/kg DM and 18.01 ± 2.81 mg/kg DM, respectively. These values represented only 5% of the total PAH content for pellets and 12% for firewood. The content of ΣLMW in soot samples from hard coal combustion was much higher than in the case of pellets and firewood. The highest content of ΣLMW was obtained in soot samples from the combustion of coal with 8–25 mm granulation and it amounted to 95.26 ± 32.92 mg/kg DM, which constituted 23% of the total PAH content. However, in the samples after combustion of coal with a granulation of 25–80 mm and coal with a granulation above 60 mm, the ΣLMW contents were 71.86 ± 6.24 mg/kg DM and 87.81 ± 24.89 mg/kg DM, respectively. These contents for coal of 25–80 mm granulation and coal of >60 mm granulation constituted 17% and 33% of their total PAH content, respectively.
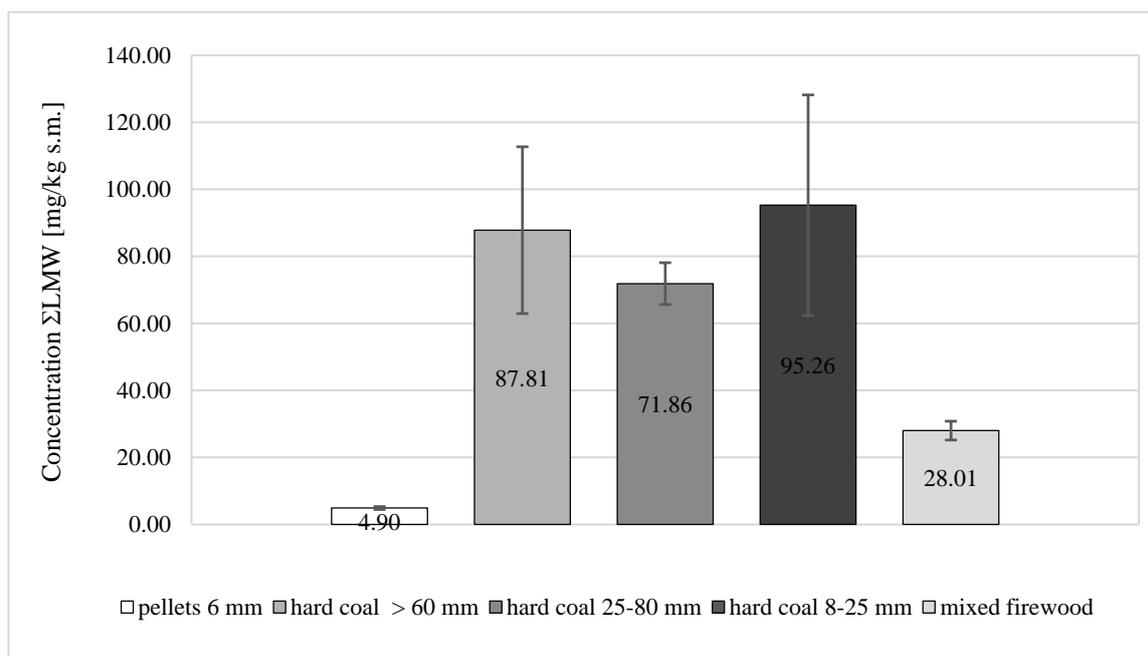
Figure 3. Average content of ΣLMW in soot samples from the combustion of selected fuels.

This information indicates that among the coals, the combustion of bituminous coal with a grain size of 25–80 mm is the most advantageous as it contains the largest percentage of light aromatic hydrocarbons, yet the highest ΣPAH. Thus, it contains the lowest percentage of light aromatic hydrocarbons. Compounds from the PAH group are the more biodegradable the easier their construction is [34].

Results of the heavier PAH fraction, the so-called HMW (Figure 4) which includes hydrocarbons with four or more rings [35], showed that the percentages of HMW in the case of samples of solid fuels from wood biomass were 95% for pellets and 88% for mixed firewood. In the case of coal samples, the percent contents of heavier PAH were 67% for hard coal with a grain size exceeding 60 mm, 83% for hard coal with a grain size of 25–80 mm and 77% for hard coal 8–25 mm. A higher percentage of PAH with higher molecular weights, i.e., having at least four aromatic rings in their molecule, accounted for more than 50% in each of the analyzed solid fuels. These hydrocarbons are characterized by higher durability in the environment compared to hydrocarbons with lower masses. This property is related to their lower solubility in water as well as the volatility described by Henry's constant. Both values decrease with the increase of molecular mass, while their value depends on the intensity of PAH elimination through biochemical changes and evaporation [36].

From Figures 2–4, hard coals 25–80 mm and 8–25 mm have very similar performance in ΣPAH, ΣLMW and ΣHMW. It seems that within the whole grain size range of 8–80 mm, soot emission does not depend on grain size. While on the other hand, grains >60 mm have clearly lower ΣPAH and ΣHMW. It is possible that these differences result from the properties of hard coal, e.g., the moisture content of coal.
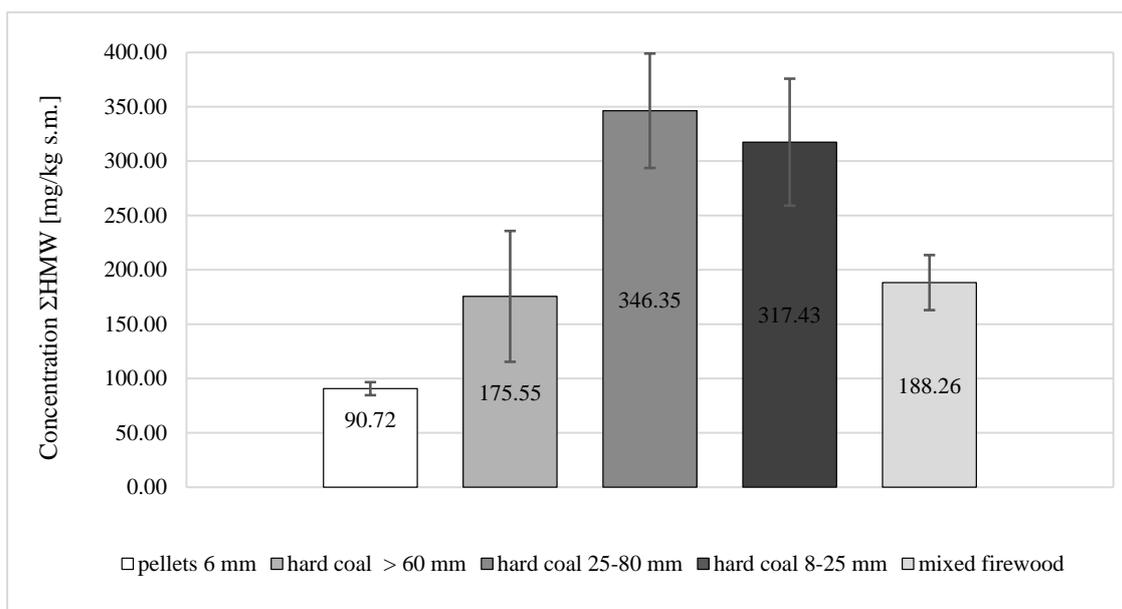
Figure 4. Average content of ΣHMW in soot samples from the combustion of selected fuels.

In addition, taking into account that individual PAH show very diversified degrees of carcinogenicity, the equivalent values of TEQ toxicity were determined (Table 4), which characterize the total toxicity of the test compounds relative to the indicator benzo(a)pyrene. The value of the TEQ toxicity equivalent depends primarily on the PAH content with high TEF toxicity ratios [37]. The highest equivalents of toxicity characterized soot from the combustion of hard coal with a grain size of 25–80 mm and hard coal of 8–25 mm, amounting to 158.76 ± 23.34 mg/kg DM and 158.53 ± 31.77 mg/kg DM, respectively. This means that although both soot types have similar contents of 16 PAH, the soot from combustion of coal with a granulation of 25–80 mm contains more carcinogenic homologs. Whereas, the soot coming from the combustion of wood pellets with a grain size of 6 mm had the smallest value of toxicity equivalent, which was 28.39 ± 1.19 mg/kg DM. The highest mutagenic equivalent (Table 3) was also obtained for soot derived from the combustion of bituminous coal 80 mm (94.28 ± 15.47 mg/kg DM) and hard coal 9–25 mm (93.93 ± 16.65 mg/kg DM), and the lowest was for soot obtained from the combustion of pellets (26.02 ± 1.68 mg/kg DM).

Table 4. Mean values of the four risk indicators (CEQ, MEQ, TCDD-TEQ and ΣPAH$_{carc}$/ΣPAH) in soot samples.

Indicator	Pellet 6 mm	Hard Coal > 60 mm	Hard Coal 25–80 mm	Hard Coal 8–25 mm	Mixed Firewood
TEQ = CEQ	28.39 ± 1.19	103.06 ± 37.95	158.76 ± 23.34	158.53 ± 31.77	90.16 ± 11.12
MEQ	26.02 ± 1.68	50.22 ± 13.47	94.28 ± 15.47	93.93 ± 16.65	64.93 ± 8.56
TCDD-TEQ	0.19 ± 0.01	0.33 ± 0.06	0.61 ± 0.09	0.55 ± 0.11	0.39 ± 0.06
ΣPAH$_{carc}$/ΣPAH	0.70 ± 0.02	0.60 ± 0.15	0.56 ± 0.01	0.53 ± 0.01	0.66 ± 0.02

The fuels selected for the analysis of PAH emission differed in their calorific value, i.e., in the amount of heat emitted during combustion of a mass unit or a volume unit of fuel during its total and complete combustion. According to producers of examined fuels: hard coal with dimensions over 60 mm emits 29 MJ/kg, hard coal with a grain size of 25–80 mm emits 26 MJ//kg, bituminous coal with a grain size of 8–25 mm emits 23 MJ/kg, pellets with a grain size of 6 mm emits 17 MJ/kg and mixed firewood emits 15 MJ/kg. Calculation of PAH emission from soot for the unit (MJ) of released energy during combustion of tested fuels reached such values as: hard coal with dimensions over 60 mm, 9.08 mg PAH/MJ; hard coal with a grain size of 25–80 mm, 16.09 mg PAH/MJ; bituminous coal

with a grain size of 8–25 mm, 17.91 mg PAH/MJ; pellets with a grain size of 6 mm, 5.58 mg PAH/MJ; and mixed firewood, 15.36 mg PAH/MJ. The lowest PAH emissions per calorific value were obtained for pellets and the highest were obtained in the case of bituminous coal with a grain size of 8–25 mm.

On the other hand, when comparing the toxicity equivalent of soot samples with combustion of fuels, the highest one was obtained for soot samples from hard coal combustion with granulation of 25–80 mm (0.61 ± 0.09 mg/kg DM). The next largest was the equivalent calculated for soot samples from the combustion of black coal 8–25 mm (0.55 ± 0.11 mg/kg DM), then for samples from burning mixed fuel wood (0.39 ± 0.06 mg/kg DM) and further for combustion samples of the hard coal >60 mm (0.33 ± 0.06 mg/kg DM). The smallest TCDD-TEQ was obtained in the case of samples from 6-mm pellet combustion, which was 0.19 ± 0.01 mg/kg DM. Analyzing the ratio of PAH considered carcinogenic to the sum of all PAH (Table 3) in the soot samples, it was found that the soot from the combustion of 6-mm pellets had the highest ratio (0.70 ± 0.02), with the soot from the combustion of mixed fuel wood classified as the next highest (0 66 ± 0.02). The smallest ratio $\Sigma PAH_{carc}/\Sigma PAH$ was obtained in the case of soot samples from the combustion of black coal 8–25 mm (0.53 ± 0.01). Despite the lowest TEQ, MEQ and TCDD-TEQ coefficients for soot from the combustion of pellets with a grain size of 6 mm, the highest ratio of carcinogenic PAH to the total PAH was obtained for this soot, which proves that the more carcinogenic PAH homologues are predominant.

Research results presented in this manuscript show a very significant impact on the content of mutagenic and toxic compounds such as PAH in soot, which is affected by the type of solid fuel burned in household furnaces. Reduction of PAH emissions in soot particles is extremely important due to the occurrence of adverse health effects [29]. The National Agency for Research on Cancer (IARC) has identified benzo(a)pyrene as a group of compounds with proven carcinogenicity (IARC 2012). Carcinogenic compounds are non-threshold substances, which entail the risk of cancer changes upon exposure to any substance concentration [38]. It is necessary to conduct activities to limit the exposure of the population to these compounds. The most effective process could be the elimination of low-emission sources by changing the way apartments and houses are heated, because coal burning in the municipal sector is still the most important source of PAH emissions. On the basis of the conducted research, it was stated that hard coal, regardless of the form in which it is adapted for combustion, whether it is in a form of large cubes with granulation over 60 mm or walnut-type fine coal with granulation of 25–80 mm or also eco-pea coal, which is adapted to combustion in boilers equipped with an automatic feeder, which evenly dispenses the material, generates higher amounts of PAH in soot than the combustion of biomass in the form of mixed firewood or 6-mm pellets.

4. Conclusions

1. Among the examined soot samples from the combustion of solid fuels, the lowest PAH concentration was obtained in soot samples from combustion of 6-mm pellets (95.62 ± 6.44 mg/kg DM), and the highest was obtained for 25–80 mm coal (418.21 ± 61.03 mg/kg DM), which was over 4 times higher than in the case of 6-mm pellets.
2. Analysis of the compactness of the light LMW fraction showed that the smallest share of this fraction in the total concentration was recorded in samples of 6-mm pellets, representing only 5% of the total PAH total. This fraction was measured to be 12% for firewood. In the case of coals, much higher percentages of the LMW fraction were obtained.
3. Higher percentages of PAH with higher molecular weights, i.e., the HMW fraction, accounted for more than 50% in each of the analyzed solid fuels.
4. Considering the calculated TEQ = CEQ, MEQ and TCDD-TEQ indicators, it was found that the most toxic and carcinogenic is black carbon with the granulation of 25–80 mm, while soot samples from combustion 6-mm pellets.
5. The largest ratio of $\Sigma PAH_{carc}/\Sigma PAH$ was obtained in the case of soot samples from the combustion of 6-mm pellets, while the smallest was from the combustion of coal with a granulation of 8–25 mm.

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