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Article

Evaluation of the PAHs 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 the aerosol 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 (PAHs) 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 PAHs in comparison to the combustion of wood pellets or dry firewood.

Keywords: solid fuels, combustion, soot, PAHs

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 an 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 to as EC (elemental carbon), alternatively the name is black carbon (BC) or black smoke. The 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. 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 [1-3]. This waste consists of highly toxic, carcinogenic or mutagenic compounds, including: amorphous carbon, graphite-like connections, fullerenes, metal compounds, including heavy metals and metalloids and ashes. In addition, hydrocarbons, in particular aliphatic and aromatic hydrocarbons, including large amounts of PAHs, constitute a large proportion of the soot. Chemical composition of soot depends on the fuel composition and the physicochemical conditions of the combustion process [4-6].

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. 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, 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 [7-9]. Medical

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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 [10-11].

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. 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. In addition, soot affects the climate change through such processes as cloud formation, water evaporation and disappearance or precipitation [12-14].

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 [14]. 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 [15].

In connection with the above, the research was undertaken to assess the content of individual 16 representatives of the PAH group (polycyclic aromatic hydrocarbons) 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, pellet with a grain size of 6 mm and mixed firewood. The content of the ΣLMW fraction containing the hydrocarbons containing in their structure from 2 to 4 aromatic rings, ΣHMW, in which the concentrations of 5 and 6-ring hydrocarbons and ΣWWA was taken into account, takes into account the total concentration of 16 compounds from the PAH group, the content of which is recommended for monitoring in the environment by EPA. In addition, the carcinogenicity equivalent and selected mutagenic and toxic equivalents of the TCDD-TEQ interaction of the PAH mixture and the ΣWWAcarc/ΣWWA ratio 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, pellet with a grain size of 6 mm and mixed firewood. The combustion process was carried out on a laboratory bench [16] (Figure 1) consisting of Moderator Unica Vento Eko boiler 25 kW with an automatic feeder equipped with a manual and retort grate. Three events of combustion were carried out each of 5 solid fuels selected for testing, collecting 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 and the temperature of the feed water (at the boiler's outlet), which was about 70-80 °C, while at the return not less than 50 °C.

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Figure 1. Laboratory stand for fuel combustion with a soot collection point.

Then, after the combustion of 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 hours to elute the PAHs tested therein, i.e.: 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 - 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 7000C) was used, equipped with a split/splitless dispenser and an HP-5MS capillary column measuring 30 m x 0.25 mm and a film thickness of 0.25 μm. Working conditions of the apparatus during the analysis were as follows:

- carrier gas - helium with purity 6.0;
- carrier gas flow rate through the column - 1ml/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).
- gaz nośny - Hel o czystości 6.0;

The temperature program was set as follows:

- initial temperature of the 60 °C column furnace, 2 min isothermal;
- temperature increase 30 °C/min to 120 °C;
- from 120^{o}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 Analitical Reference Standards). The tests used external calibration with calibration curves for individual compounds. Calibration solutions were prepared from a standard of 16 PAHs mixture (AccuStandard, Z-014G).

In order to determine the harmfulness of the 16 PAHs examined, indicators were used which define the toxicity of individual PAHs and the whole group as well. A universal method for calculating the risk related to exposure to PAH mixture was adopted. BaP is assumed to be a reference compound. The carcinogenic potential, called the Toxicity Equivalence Factor (TEF) of other

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compounds is calculated relative to BaP. The RTBaP toxicity equivalent value (TEQ - Toxic Equivalent) is the sum of the products of the concentrations of individual PAHs and their relative toxicity coefficients [17]:

$$\begin{gathered}RTBaP = 0{,}001 \times [Nap] + 0{,}001 \times [Acy] + 0{,}001 \times [Ace] + 0{,}001 \times [Fl] \\ + 0{,}001 \times [Phe] + 0{,}01 \times [Ant] + 0{,}001 \times [Flu] + 0{,}001 \times [Pyr] + 0{,}1 \times [B(a)A] \\ + 0{,}01 \times [Chr] + 0{,}1 \times [B(b)F] + 0{,}1 \times [B(k)F] + 1 \times [B(a)P] + 5 \times [D(ah)A] + 0{,}1 \times \\ [B(ghi)P] + 0.1 \times [I(cd)P] \qquad (1)\end{gathered}$$

Durant and others (1996) reported mutagenic coefficients for individual PAHs. Wilellet and others. (1997) proposed that the carcinogenic potential of PAHs 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 PAHs, in addition to the CEQ toxicity equivalent (RTBaP) given by Nisbet and LaGoy (1992), the mutagenicity equivalent (MEQ) and carcinogenicity (TCDD-TEQ) is also used [18]. Using the mutagenicity factors [19] and carcinogenicity factors [20], those were selected, which refer to 16 priority PAHs according to the EPA list. The mutagenicity equivalent was given as the sum of the product of the concentration of individual PAHs and their relative mutagenicity coefficients [18]:

$$\begin{gathered}MEQ = 0{,}00056 \times [Acy] + 0{,}082 \times [B(a)A] + 0.017 \times [Chr] + 0.25 \times [B(b)F] \\ + 0{,}11 \times [B(k)F] + 1 \times [B(a)P] + 0{,}31 \times [I(cd)P] + 0{,}29 \times [D(ah)A] + 0{,}19 \times [B(ghi)P] \qquad (2)\end{gathered}$$

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

$$\begin{gathered}TCDD\text{-}TEQ = 0{,}000025 \times [B(a)A] + 0{,}00020 \times [Chr] + 0{,}000354 \times [B(a)P] + \\ 0{,}00110 \times [I(cd)P] + 0{,}00203 \times [D(ah)A] + 0{,}00253 \times [B(b)F] + 0{,}00487 \times [B(k)F] \qquad (3)\end{gathered}$$

The harmfulness of PAHs is also expressed as the ratio of PAHs considered carcinogenic to the sum of all PAHs determined [21]:

$$\begin{gathered}\Sigma WWAcarc/\Sigma WWA=([B(a)A]+[B(a)P]+[B(b)F]+[B(k)F]+[Chr]+[D(ah)A]+ \\ [I(cd)P])/([SWWA]) \qquad (4)\end{gathered}$$

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

3. Results and discussion

Table 1 shows the basic properties of the analyzed 16 polycyclic aromatic hydrocarbons: acenaphthalene, anthracene, benzo(a)anthracene, benzo(b)fluoroanthrone, benzo(k)fluoroanthrene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenzo(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 (*Low Molecular Weight*) (hydrocarbons containing from 2 to 4 aromatic rings in their structure: naphthalene, acenaphthene, acenaphthalene, fluorene, phenanthrene, anthracene); ΣHMW (*High Molecular Weight*), (5, 6-ring compounds: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene and a total of 16 aromatic hydrocarbons - ΣWWA.

Table 1. ΣPAHs included hydrocarbons containing from 2 to 6 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	8.89E−02
2	Acenaphthene	Ace	3	154.21	3.8	3.75E−03
3	Acenaphthylene	Acy	3	152.20	16.1	2.90E−02
4	Anthracene	Ant	3	178.23	0.045	2.55E−05
5	Phenanthrene	Phe	3	178.23	1.1	6.80E−04
6	Fluorene	Flu	3	166.22	1.9	3.24E−03
7	Fluoranthene	Flr	4	202.26	0.26	8.13E−06
8	Benzo(a)anthracene	B(a)A	4	228.29	0.011	1.54E−07
9	Chrysene	Chr	4	228.29	0.0015	7.80E−09
10	Pyrene	Pyr	4	202.26	0.132	4.25E−06
11	Benzo(a)pyrene	B(a)P	5	252.32	0.0038	4.89E−09
12	Benzo(b)fluoranthene	B(b)F	5	252.32	0.0015	8.06E−08
13	Benzo(k)fluoranthene	B(k)F	5	252.32	0.0008	9.59E−11
14	Dibenz(a,h)anthracene	D(ah)A	6	278.35	0.0005	2.10E−11
15	Benzo(g,h,i)perylene	B(ghi)P	6	276.34	0.00026	1.00E−10
16	Indeno[1,2,3-cd]pyrene	I(cd)P	6	276.34	0.062	1.40E−10

Source: Own elaboration on [22-23].

Table 2 presents results of PAH content analysis in the studied soot samples from the combustion of selected fuels. PAHs are the most frequently tested pollutants in environmental samples. It is dictated primarily by their negative impact on health, including toxicity, carcinogenicity and mutagenicity [19, 24-25].

Table 2. Results of PAH determinations in soot samples from the combustion of solid fuels

mg/kg s. m.	pellet 6 mm	hard coal > 60 mm	hard coal 25-80 mm	hard coal 8-25 mm	mixed firewood
Naftalen	0,50±0,20	2,52±3,04	1,20±0,04	2,17±0,46	1,33±0,08
Acenaftylen	0,63±0,07	10,77±4,46	4,48±0,45	13,01±5,83	3,05±0,33
Acenaften	0,05±0,002	1,28±1,62	0,29±0,03	0,59±0,26	0,15±0,02
Fluoren	0,07±0,002	9,62±13,34	0,86±0,08	7,71±9,23	0,27±0,02
Fenantren	2,87±0,12	50,05±12,44	47,5±5,69	52,49±11,67	18,82±2,45
Antracen	0,78±0,05	13,56±5,95	17,49±2,15	19,28±6,44	4,39±0,57
Fluoranten	5,06±0,30	17,95±5,03	46,34±6,25	36,38±9,06	14,18±2,23
Piren	5,23±0,61	16,42±2,51	41,12±5,39	32,01±9,68	11,84±1,90
Benzo[a]antracen	3,70±0,09	13,05±9,14	26,17±3,86	18,84±5,65	8,44±1,27
Chryzen	4,52±0,11	12,04±7,09	24,07±3,61	17,09±5,07	8,73±1,24
Benzo[b]fluoranten	13,07±3,97	22,40±7,40	33,09±5,78	29,04±8,70	32,87±5,29
Benzo[k]fluoranten	15,58±0,55	27,02±12,85	49,58±7,77	44,49±12,95	28,03±4,50
Benzo[a]piren	12,67±0,06	30,87±6,71	60,48±10,05	58,55±17,84	36,53±5,72
Indeno[1,2,3,c,d]piren	16,54±2,69	20,42±6,35	36,70±6,02	44,82±9,48	33,94±2,56
Dibenzo[a,h]antracen	1,32±0,15	2,45±0,97	6,69±0,99	6,06±2,42	4,39±0,33
Benzo[g,h,i]perylen	13,01±1,95	12,93±2,63	22,12±3,19	30,16±5,60	23,48±1,50
ΣWWA	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 soot 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 [26].

Analyzing the content of the sum of 16 PAHs (Figure 2), the smallest content in the soot in the samples from pellet combustion was found, which was 95.62 ± 6.44 mg/kg DM. Another fuel, which was characterized by the second lowest PAH content, was wood mixed 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 fuel wood. 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 the combustion of coal with large irregular cubes over 60 mm was characterized by a smaller content not only from the combustion of coal with a grain size of 25-80 mm, but also from hard coal granulation 8-25 mm, as a result of which PAH content was obtained amounting to 412.70 ± 127.16 mg/kg DM.

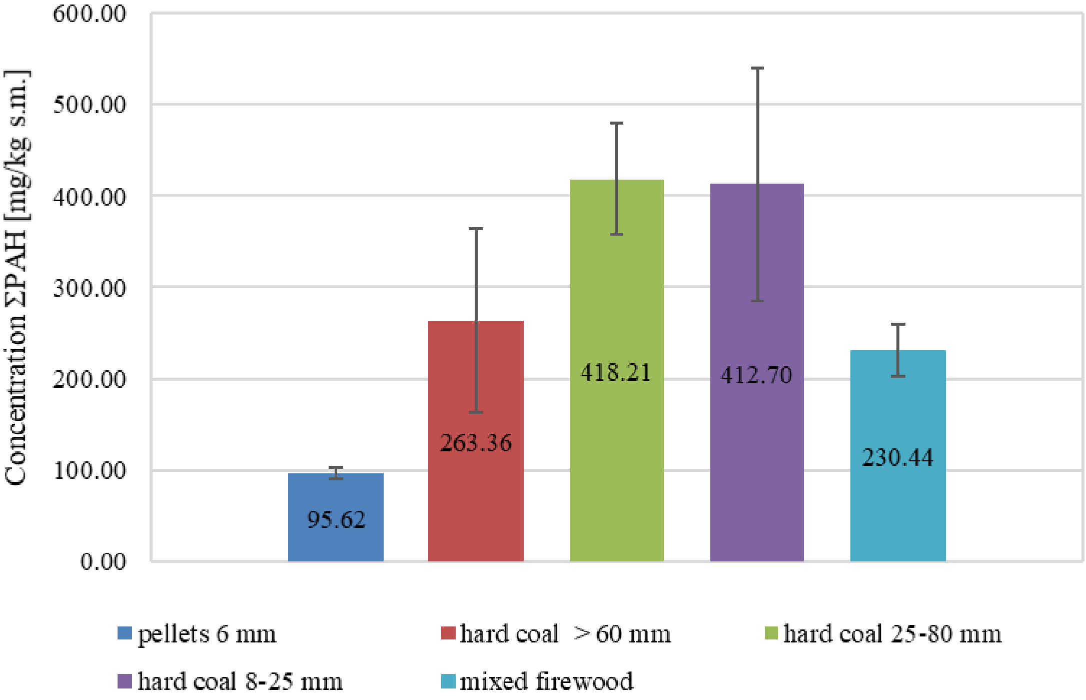

Figure 2. Average content of ΣPAH in soot samples from the combustion of selected fuels.

Research conducted by Kakareka and others (2005) on the emission of polycyclic aromatic hydrocarbons (PAHs) 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. PAH concentrations in flue gases from solid fuel combustion differed significantly more than PAH concentrations depending on the type of boiler, in which the fuel was burned. The PAH content from birch wood combustion was higher than in the case of pine wood emissions [27].

When analyzing the compactness of light PAH fraction determined with the abbreviation LMW (*Low Molecular Weight*) (Figure 3) containing hydrocarbons consisting of 2 and 3 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 PAHs, the least LMW; these values were 4.90 ± 0.42 mg/kg DM and 18.01 ± 2.81 mg/kg DM, respectively. It was only 5% of the total PAH content for pellets and 12% for firewood. The content

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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. Compared with samples after combustion of coal with a grain size of 25-80 mm and coal with a grain size of over 60 mm, the ΣLMW content was: 71.86 ± 6.24 mg/kg DM and 87.81 ± 24.89 mg/kg DM. These contents constituted respectively: 17% and 33% of the total PAH content. 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. Compounds from the PAH group are the more biodegradable the easier their construction is [28].

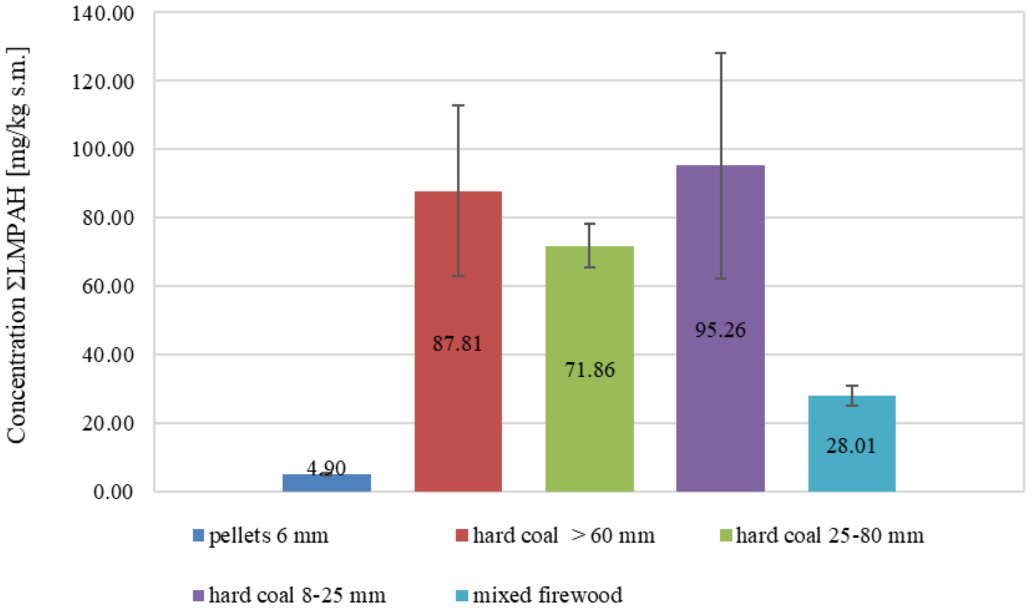

Figure 3. Average content of ΣLMW in soot samples from the combustion of selected fuels.

Results of heavier PAH fraction of the so-called HMW (Figure 4) (*High Molecular Weight*), which includes hydrocarbons with four or more rings [29] showed that the percentage of HMW was in the case of samples of solid fuels from wood biomass, i.e. 95% of pellets and 88% of mixed firewood. Considering the percentage share of heavier PAH fraction, it is more beneficial to burn mixed firewood than pellets. In the case of coal samples, the per cent content of heavier PAHs was 67% for hard coal with a grain size exceeding 60 mm, for hard coal with a grain size of 25-80 mm - 83%, and 77% for hard coal 8-25 mm. A higher percentage of PAHs 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 PAHs elimination through biochemical changes and evaporation [30].

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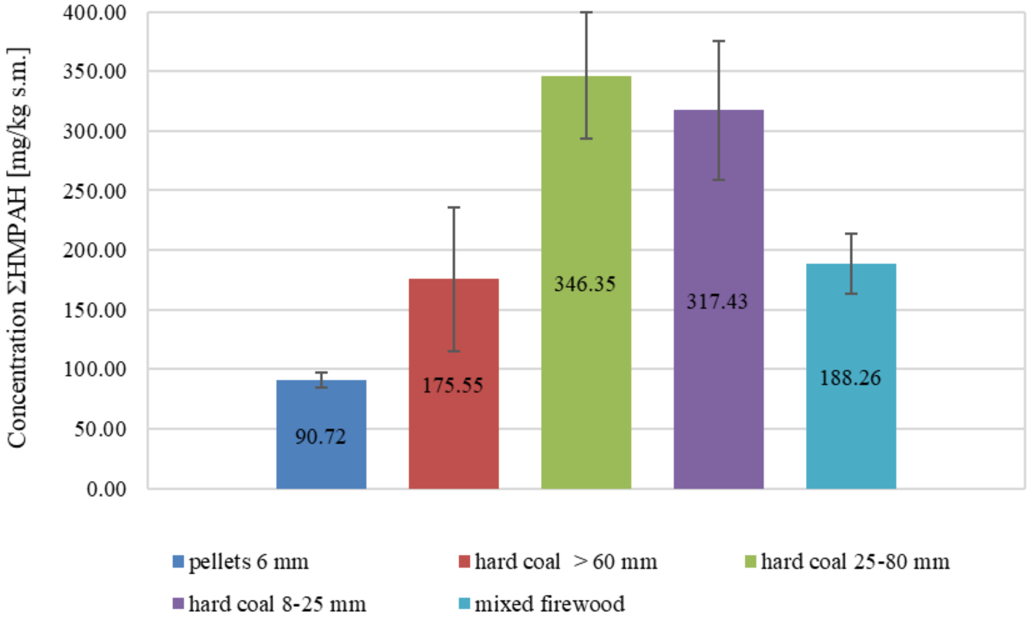

Figure 4. Average content of ΣHMW in soot samples from the combustion of selected fuels.

In addition, taking into account that individual PAHs show very diversified degree of carcinogenicity, the equivalent value of TEQ toxicity was determined (Table 3), which characterizes the total toxicity of the test compounds relative to the indicator benzo[a]pyrene. Value of the TEQ toxicity equivalent depends primarily on the PAH content with high TEF toxicity ratios [31]. The highest equivalent of toxicity characterized soot from the combustion of hard coal with a grain size of 25-80 mm and hard coal of 9-25 mm. It amounted 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 for soot obtained from the combustion of pellets (26.02 ± 1.68 mg/kg DM).

Table 3. Mean values of the four risk indicators (CEQ, MEQ, TCDD-TEQ and $PAH_{canc}/ΣPAH$) at 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
ΣWWAcarc/ΣWWA	0,70±0,02	0,60±0,15	0,56±0,01	0,53±0,01	0,66±0,02

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), further for combustion samples 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 PAHs considered carcinogenic

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to the sum of all PAHs (Table 3) in the soot samples, it was found that the highest ratio had the soot from the combustion of pellets 6 mm (0.70 ± 0.02), then the soot from the combustion of mixed fuel wood was classified (0 66 ± 0.02). The smallest ratio $\Sigma WWA_{carc}/\Sigma WWA$ 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 PAHs to the total PAH was obtained for this soot, which proves that the more carcinogenic PAH homologues are predominant.

Of approximately 100 PAHs present in the environment, the US Environmental Protection Agency (US EPA 2015) paid particular attention to 16 hydrocarbons with the most potent carcinogenic and mutagenic properties [30]. Therefore, it was decided to evaluate the content of PAHs in soot samples from the combustion of solid fuels in a low power class 5 boiler that met the eco-design standards. Soot is a carbonaceous matter that is contained in atmospheric aerosols, i.e. suspended solid particles with a characteristic size of 0.01-10 µm and a retention time in the atmosphere of at least a few hours [32]. Soot, as a product of incomplete combustion of fuels mainly from stationary sources, i.e. household furnaces used in the housing sector, causes climate change [33]. 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 [14]. Research results presented in this article show that a very significant impact on the content of mutagenic and toxic compounds such as PAHs in soot 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 [23]. 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 entails the risk of cancer changes when exposed to any substance concentration [34].

It is necessary to conduct activities aimed at limiting the exposure of the population to these compounds. The most effective action would be the elimination of low-emission sources by changing the way apartments 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 large cubes with granulation over 60 mm or fine coal walnut-type 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 pellets 6 mm. According to the Wielgosiński et al. (2017), who studied the combustion of seven types of biomass (basket willow, primitive willow, rape straw briquettes, granules of cakes and sawdust, fuel wood chips, oak bark), the emission of organic compounds in many cases was unexpectedly higher than in the case of hard coal. It is difficult to recognize biomass as a truly ecological fuel, although it is undoubtedly a renewable fuel. Due to significant differences in the chemical composition (elemental), calorific value, volatile content and properties of biomass and coal emissions, biomass combustion should be carried out under different technological conditions (temperature, excess air, etc.) than combustion of fossil fuels (e.g. coal [35]. According to the research by Horak and others (2017), the issue of PAHs is influenced not only by the type of fuel, but also by the type of boiler, in which this fuel is combusted. To burn biomass, in order to achieve low PAH emissions, more oxygen should be supplied than coal, i.e. the combustion parameters should be selected accordingly and then lower PAH emissions will be obtained than in the case of hard coal combustion [36].

4. Conclusions

1. Among the examined soot samples from the combustion of solid fuels, the highest PAH concentration was obtained in soot samples from combustion of 6 mm pellets (95.62 ± 6.44 mg/kg DM), and the largest of 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 pellets 6 mm; it was only 5% of the total PAH total, and 12% for firewood. In the case of coals, much higher percentages of the LMW fraction were obtained, which indicates a greater share of more biodegradable compounds from the PAH group.
3. Higher percentage of PAHs with higher molecular weights, i.e. HMW fraction, 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.
4. Considering the calculated TEQ = CEQ, MEQ and TCDD-TEQ indicators, it was found that the most toxic and carcinogenic is carbon black with the granulation of 25-80 mm, while soot samples from combustion 6 mm pellets were the least affecting living organisms and the environment.
5. The largest ratio of ΣWWAcarc/ΣWWA was obtained in the case of soot samples from the combustion of pellets 6 mm, while the smallest from the combustion of coal with a granulation of 8-25 mm

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