

Article

Effect of Composting Ashes from Biomass Combustion on Polycyclic Aromatic Hydrocarbon Content

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Abstract: The safe management of waste from biomass combustion is a global problem, as the use of biomass for energy purposes is increasing around the world. Many rapidly developing countries in Asia, Africa, and South America have weak legal regulations regarding the composition of biomass combustion waste, such as ashes. As a result of the improper management of ashes, some of the pollutants may enter agricultural soils and pose a long-term risk to human health through the accumulation of harmful compounds in food. For this reason, research was carried out on the possibility of reducing harmful contaminants contained in ash in the composting process. The work presents the results of the content of 16 polycyclic aromatic hydrocarbons (PAHs) in the created composts, followed by an analysis of the toxicity, mutagenicity, and carcinogenicity of the created fertilisers. Based on the results obtained, a positive impact of the composting process on the reduction in PAHs contained in ash was found. Composting the mixture at 20 °C resulted in a slight decrease in the ΣPAH_{16} content from 2185.46 $\mu\text{g}\cdot\text{kg}^{-1}$ to 2063.48 $\mu\text{g}\cdot\text{kg}^{-1}$. A greater reduction in ΣPAH_{16} was obtained in the mixture incubated at 40 °C, where an overall decrease in the ΣPAH_{16} content was recorded from 2185.46 $\mu\text{g}\cdot\text{kg}^{-1}$ to 1372.38 $\mu\text{g}\cdot\text{kg}^{-1}$. The composting process also had a positive impact on the TEQ = CEQ, MEQ, and TCDD-TEQ coefficients, causing their decrease.

Keywords: PAH migration; fly ash; composting

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1. Introduction

In recent years, Europe's energy sector has been greatly influenced by the European Union through the adoption by the Council of Europe and the European Commission of policies to reduce greenhouse gas emissions to at least 55% by 2030 and to achieve climate neutrality by 2050 [1–3]. The result of the slow elimination of energy production from the combustion of fossil fuels is the increase in renewable energy sources (RESs).

Energy production in Poland is still mainly based on coal combustion (80%), generating 10.6 million tonnes of ash–slag mixtures per year, of which 8.9 million tonnes are untreated and deposited in landfills [4]. The prevailing trend in Europe of the closure of coal mines and coal-fired power plants has resulted in a decrease in the production of combustion by-products (UPS) in individual EU countries, making Poland, which still uses energy from the combustion of fossil fuels, the main producer of UPS in the European Union [5].

In 2019, fly ash production in Poland reached 2.4 million tonnes (CSO). Fly ash has pozzolanic properties; therefore, it is used in roads, construction, mining, and engineering works [6]. Despite this, more than 100,000 tonnes of fly ash were transferred to landfills in 2018 as a result of a higher production over demand, with 25.5 million tonnes of undeveloped fly ash currently in storage [7].

The problem with ash management stems from its chemical composition. Ash from biomass as well as ash from coal both contain trace amounts of toxic metals. The first one

has much higher concentrations than those found in ash from coal combustion. In addition, these elements tend to occur in more mobile and hazardous compounds than in coal ash [8].

Particularly, hazardous pollutants found in fly ash also include polycyclic aromatic hydrocarbons (PAHs), which belong to the so-called persistent organic pollutants with mutagenic, toxic, and carcinogenic properties. PAHs are formed during the incomplete combustion of organic mass in natural and anthropogenic processes [9,10]. Anthropogenic sources include combustion processes of organic materials such as liquid and solid fossil fuels used mainly in the energy sector [11]. PAHs present in the air seep into soils, waters, and living organisms. The concentration of PAHs in water and soil is dependent on reaction, temperature, and the presence of other chemicals, such as organic pollutants. Polycyclic aromatic hydrocarbons easily decompose when exposed to UV radiation, ozone, or dioxygen [12].

Polycyclic aromatic hydrocarbons have been classified as a group of compounds dangerous to human health and are included in the list of hazardous substances. Their recognition as toxic substances depends on many factors, such as the duration of the exhibition, the path of exposure, and the amount of substance adopted. PAHs can enter to the body through the digestive system by consuming foods that have been in contact with PAHs and through the respiratory tract [13].

The concentration of PAHs in waters and soils is regulated by the ordinance of the Ministry of the Environment. The regulation on sewage discharged into the environment (Journal of Laws 2009 No. 27) refers to a limit values for BTX (benzene, toluene, xylene) and petroleum hydrocarbons and adsorbed organochlorine compounds (AOX), while no limit values have been set for PAHs. Due to their confirmed carcinogenic properties, they should be included in the group of pollutants that are harmful to the environment [14,15].

One way of utilising fly ash is through the cementing process [16,17]. The cementing process uses the ash to create cement mortars and concretes. This method uses ash from the combustion of conventional fuels and ash from the co-firing of biomass with conventional fuels. In a study by Jura and Ulewicz, mortars with the addition of ash instead of normal sand obtained better results when tested for compressive strength, and also obtained better frost resistance [18].

Another method of ash disposal is through the geopolymerisation process [19–21]. In the geopolymerisation process, waste that comes from biomass combustion is neutralised through a physical process of encapsulating heavy metals in the material [22]. Several studies have been carried out on the possibilities of disposing fly ash by geopolymerisation [23–25], and a positive effect of geopolymerisation on the immobilisation of most heavy metals was confirmed. In a study by Ahmari and Zhang, through to the use of appropriately selected geopolymer matrix compositions, a material resistant to adverse weather conditions and with improved mechanical properties was obtained [26].

Biomass ashes can also be used as a substitute or component of mineral fertilisers [27–29]. They contain nutrients that are a valuable source of elements necessary for the proper growth of plants. The type of fuel burned as well as the design of the boiler influences their chemical composition [30]. According to Uliasz-Bocheńczyk et al., the ashes contain K_2O , MgO , Na_2O , P_2O_5 , CaO , and SO_3 ; however, they are characterised by a negligible content of nitrogen and organic matter [31]. There are also metals and toxic substances in their composition. The requirements concerning their permissible content were specified in the Act of 10 July 2007 on fertilisers and fertilisation (Journal of Laws of 2007, No. 147, item 1033) [32] and in the regulation by the Ministry of Agriculture and Rural Development of 18 June 2008 on the implementation of certain provisions of the Act on fertilisers and fertilisation (Journal of Laws of 2008, No. 119, item 765) [33]. Due to their alkaline reaction, ash used as a fertiliser also exhibits soil deacidification properties. Additionally, the use of biomass combustion by-products in agriculture is important due to their relatively low risk to the surrounding environment [34,35].

Another way to manage ashes is composting. During the composting process, there are mechanical stages, including preparing the raw material and maintaining optimal conditions, as well as biochemical stages, based on the decomposition of organic substances by microorganisms [36]. The mechanical stages include the pre-treatment of the raw material and the necessary activities related to the control of biochemical processes, and also, if necessary, the post-treatment of the compost. In turn, biochemical processes involve the decomposition of organic substances by bacteria, fungi, and actinomycetes, with the participation of moisture and the presence of oxygen. Within these processes, mineralisation and humification play key roles. Mineralisation is the process of breaking down organic matter into simpler forms. This process is important to obtain pathogen- and seed-free compost. In turn, humification is a process during which the organic components of biomass are transformed into humus compounds. The latter, due to their sorption and ion exchange abilities, contribute to improving the properties of the soil. As a final result, composting can generate a high-quality product, free of harmful pathogens and seeds, which means it can be effectively used to improve the structure and composition of the soil [37].

Therefore, the present study attempts to utilise ash from biomass combustion for fertiliser purposes. Green waste compost with ash was prepared and incubated under preset temperature conditions. Then, the PAH content was determined in the prepared composts, and the TEQ toxicity equivalent, MEQ mutagenicity equivalent, and carcinogenicity equivalent were determined (equivalent amount of toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)). The use of ash for fertiliser purposes is to enrich organic fertiliser (compost) with nutrients (micro and macro elements) and, through its management, to reduce the amount of stored ashes. The innovation of preliminary research lies in the possibility of developing organic fertilisers enriched with nutrients, and at the same time to reduce the content of PAHs, which could penetrate the environment in uncontrolled conditions.

2. Materials and Methods

2.1. Materials

Green waste compost and ash from biomass combustion was used in the study. The research materials were obtained in-house. Compost was made from green waste obtained from the home garden. The waste included grass, small branches, and waste from fruit trees growing in the garden, such as cherry pits which can be seen in Figure 1b. The ash was collected from a boiler operating in a single-family house fuelled by pine sawdust pellets (Figure 1).



Figure 1. Raw materials used in the study: (a) ash, (b) compost.

2.2. Incubation Process

The incubation process was carried out in a POL-EKO climatic chamber, model 750 KK smart pro, to maintain constant, controlled temperature and humidity. The climatic chamber is equipped with several safeguards that control the compliance of the temperature and humidity inside the working chamber with the desired temperature programmed by the user.

Samples of ripening compost with the addition of ash from biomass combustion in a ratio of 4:1 were incubated at temperatures of 20 °C and 40 °C; the constant parameters were humidity, at 60%, and fan speed at 40%.

2.3. Determination of PAH Content

The procedure for extraction and chromatographic analysis of PAHs was carried out according to the methodology described in Smolewska et al. [38]. An analysis of the obtained extracts was performed using an Agilent GC System 7890B gas chromatograph coupled to an Agilent GC/MS Triple Quad 7000C mass spectrometer. The instrument was equipped with an Agilent 7693 automatic sample feeder and a split/splitless dispenser. Chromatographic separation of analytes was performed on an Agilent HP-5MS-fused silica capillary column (polydimethylsiloxane with 5% phenyl groups) of 30 m × 0.25 mm × 0.25 µm film thickness at a constant helium flow rate (99.9999%) of 1 mL/min. Detection was carried out in selected ion monitoring (SIM) mode, and the selected ion values corresponded to the molecular ions of each of the 16 PAH congeners analysed.

2.4. PAH Toxicity Analysis

Indicators determining the toxicity of both individual PAHs and the entire group were used to assess the harmfulness of 16 tested PAHs. A universal approach to calculate the risk associated with exposure to a mixture of PAHs was adopted. Benzo(a)pyrene (B(a)P) was considered as the reference compound. The carcinogenic potential, known as the toxic equivalence factor (TEF) for other compounds, was calculated in relation to B(a)P. The toxic equivalent value (TEQ—toxic equivalent) was determined as the sum of the products of the concentrations of individual PAHs and their respective toxicity coefficients, according to the formula $TEQ = CEQ$ [39]:

$$TEQ = CEQ = 0.001 \times [NAP] + 0.001 \times [ACY] + 0.001 \times [ACE] + 0.001 \times [FLU] + 0.001 \times [PHE] + 0.01 \times [ANT] + 0.001 \times [FLA] + 0.001 \times [PYR] + 0.1 \times [BaA] + 0.01 \times [CHR] + 0.1 \times [BbF] + 0.1 \times [BkF] + 1 \times [BaP] + 5 \times [DBA] + 0.1 \times [BgP] + 0.1 \times [InP]. \quad (1)$$

In addition to the CEQ toxicity equivalent (TEQ), the mutagenicity equivalent (MEQ) and carcinogenicity equivalent (TCDD-TEQ) were also calculated [40]. The carcinogenic potential was calculated in relation to dioxins (2,3,7,8-tetrachlorodibenzo-p-dioxin—TCDD), for which the carcinogenicity coefficient value is 1 [41]. The total mutagenicity equivalent (MEQ) was determined by calculating the sum of the products of the concentrations of individual PAHs and their corresponding mutagenicity coefficients [40]:

$$MEQ = 0.00056 \times [ACY] + 0.082 \times [BaA] + 0.017 \times [CHR] + 0.25 \times [BbF] + 0.11 \times [BkF] + 1 \times [BaP] + 0.31 \times [InP] + 0.29 \times [DBA] + 0.19 \times [BgP] \quad (2)$$

The totality of WWA carcinogenicity can be expressed as the combined result of multiplying the concentrations of individual polycyclic aromatic hydrocarbons (PAHs) by their respective coefficients, indicative of relative carcinogenicity:

$$TCDD-TEQ = 0.000025 \times [BaA] + 0.00020 \times [CHR] + 0.000354 \times [BaP] + 0.00110 \times [InP] + 0.00203 \times [DBA] + 0.00253 \times [BbF] + 0.00487 \times [BkF] \quad (3)$$

The overall harmfulness of polycyclic aromatic hydrocarbons (PAHs) was expressed as the proportion of PAHs considered to be carcinogenic to the total sum of all established PAHs [42]:

$$\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH} = ([\text{BaA}] + [\text{BaP}] + [\text{BbF}] + [\text{BkF}] + [\text{CHR}] + [\text{DBA}] + [\text{InP}]) / ([\Sigma 16\text{PAH}]) \quad (4)$$

Calculation of the harmfulness factor $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$ is very important to determine the risk to the population. The closer the $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$ ratio is to 1, the greater the risk a given substance poses to the population.

3. Results and Discussion

3.1. PAH Content in Biomass Ash

Despite its high fertilising properties, ash can pose a threat to the environment and humans due to its high content of heavy metals and PAHs. As a result of a secondary carbon aromatisation reaction in the pyrolysis phase of incomplete combustion at temperatures higher than 400 °C, polycyclic aromatic hydrocarbons (PAHs) are formed in biomass combustion. According to Masto [43], the grade of wood burned is less important in the amount of PAHs formed than the operating conditions of the boiler. The high PAH content of ash often prevents it from being used as a fertiliser. This study therefore attempts to assess the PAH content of ashes from biomass combustion and mixtures prepared for composting at 20 °C and 40 °C.

Considering the proportion of individual PAHs in the ash samples, naphthalene was found to be the most abundant, with 6795.772 $\mu\text{g}\cdot\text{kg}^{-1}$, representing 87% of the total PAHs in the ash. The second most abundant compound was benzo(a)pyrene at 343.295 $\mu\text{g}\cdot\text{kg}^{-1}$ (4.4% of the total PAH content), which is considered the most carcinogenic congener. The rest of the compounds were present in small amounts, below 100 $\mu\text{g}\cdot\text{kg}^{-1}$. The total content of all 16 congeners in wood ash was 7674.44 $\mu\text{g}\cdot\text{kg}^{-1}$ (Table 1). A study by Masto [43] showed that the PAH content of biomass ash was 3588 $\mu\text{g}\cdot\text{kg}^{-1}$, where naphthalene also accounted for a significant proportion in wood ash at 1870 $\mu\text{g}\cdot\text{kg}^{-1}$, while benzo(a)pyrene was much lower at 88 $\mu\text{g}\cdot\text{kg}^{-1}$, representing 2.45% of the content of all 16 congeners. In contrast, in a study conducted by Zhai et al. [44], the PAH content of biomass-derived ash averaged 12,000 $\mu\text{g}\cdot\text{kg}^{-1}$.

Table 1. PAH content in the tested samples.

Compound Name	Biomass Ash	Biomass Ash + Compost	Biomass Ash + Compost after Incubation at 20 °C	Biomass Ash + Compost after Incubation at 40 °C
			[$\mu\text{g}\cdot\text{kg}^{-1}$ DM]	
Nafthalen (NAP)	6795.77	1492.99	995.34	604.94
Acenaftylen (ACY)	9.922	8.898	3.1	3.54
Acenaften (ACE)	67.299	18.725	41.77	48.51
Fluoren (FLU)	5.666	4.936	4.28	4.14
Fenantren (PHE)	45.949	43.473	119.41	120.15
Antracen (ANT)	7.565	4.764	7.94	6.81
Fluoranten (FLA)	51.489	51.098	192.88	90.97
Pirene (PYR)	55.63	50.937	242.3	99.43
Benzo(a)antracen (BaA)	23.791	20.087	28.44	19.23
Chrysen (CHR)	52.55	49.11	47.76	41.3
Benzo(b)fluoranten (BbF)	101.331	94.586	57.45	51.46
Benzo(k)fluoranten (BkF)	69.817	63.471	61.19	28.52
Benzo(a)piren (BaP)	343.295	249.609	234.7	232
Indeno(1,2,3-c,d)piren (InP)	6.58	2.34	1,27	0.57
Dibenzo(a,h)antracen (DBA)	7.88	4.72	2.47	2.18
Benzo(g,h,i)perylen (BgP)	29.907	25.72	23.18	18.63
Total PAHs	7674.44	2185.46	2063.48	1372.38
ΣLMW	7115.631	1745.02	1683.22	1039.02

Σ HMW	558.81	440.446	380.26	333.36
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3.2. PAH Content of the Tested Mixtures after the Incubation Process

Mixing ash from biomass combustion with maturing compost resulted in a significant decrease in total PAH content from 7674.44 $\mu\text{g}\cdot\text{kg}^{-1}$ to 2185.46 $\mu\text{g}\cdot\text{kg}^{-1}$ (Table 1). The combination of ash and compost resulted in a decrease in indeno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene content to almost 0. A significant decrease in acenaphthene of 72.18% and benzo(k)fluoranthene of 40.11% was also observed. In contrast, naphthalene content decreased from 6795.77 $\mu\text{g}\cdot\text{kg}^{-1}$ to 1492.988 $\mu\text{g}\cdot\text{kg}^{-1}$.

Subjecting the mixture to an incubation process at 20 °C resulted in a decrease in the content of most congeners, with the greatest decrease recorded in the content of naphthalene, where the content of this congener decreased from 1492.99 $\mu\text{g}\cdot\text{kg}^{-1}$ to 995.34 $\mu\text{g}\cdot\text{kg}^{-1}$. There was also a slight increase in some congeners such as acenaphthene, anthracene, and benzo(a)anthracene. In contrast, phenanthrene increased by 175% and fluoranthene and pyrene by 277% and 375%, respectively. The total content of all 16 congeners decreased by 5.58%, from 2185.46 $\mu\text{g}\cdot\text{kg}^{-1}$ to 2063.48 $\mu\text{g}\cdot\text{kg}^{-1}$.

The incubation process at 40 °C resulted in a significant decrease in the PAH content of the mixture compared to pre-incubation values. The higher temperature of the process carried out (40 °C) resulted in a much more noticeable reduction in PAH content than at 20 °C. The only congener that reacts negatively to incubation temperature is acenaphthene, whose content increases with incubation temperature. In contrast to incubation at 20 °C, the content of the following congeners anthracene and benzo(a)anthracene increased compared to the initial content, but to a lesser extent than during incubation at 20 °C. Fluoranthene content increased by 78% while pyrene content increased by 95%. The phenanthrene content increased identically to the incubation at 20 °C. The sum of all congeners decreased by 37.11% from 2185.46 $\mu\text{g}\cdot\text{kg}^{-1}$ to 1372.38 $\mu\text{g}\cdot\text{kg}^{-1}$. Comparing the results obtained from the studies of Mackiewicz-Walec and Krzebietke, the PAH content of the tested mixture is four times higher than in cattle manure [45]. The results obtained by Poluszyńska, on the other hand, indicate a positive effect of the process of composting sewage sludge with sawdust on the PAH content, where the average reduction was 74.2% [46].

The obtained reduction in the total PAH content is much lower than the results reported by Antizar-Ladislao, Lopez-Real, and Beck [47], who examined the impact of composting soil contaminated with coal tar and green waste in a ratio of 0.6:1, at a reduction of 76.2% at 38 °C. The increase in temperature had a negative impact on the reduction in PAHs, reducing it to 52.2% at a temperature of 55 °C, while at a temperature of 70 °C, only 22.3% of PAHs were reduced.

The lightest restrictions on organic fertilisers containing ash are enforced in the Czech Republic, where the maximum content of PAH₁₆ is 20 $\text{mg}\cdot\text{kg}^{-1}$ [48]. The latest European Union proposal regarding the content of PAH₁₆ in fertilisers containing ash is 6 $\text{mg}\cdot\text{kg}^{-1}$ [49]. In Sweden, the limit for PAH₁₆ is 2 $\text{mg}\cdot\text{kg}^{-1}$ [50]. The obtained fertilisers before and after composting are within the limits of the Czech and European Union standards. The fresh compost and ash mixture as well as the one incubated at 20 °C slightly exceeds the limit in force in Sweden. In the case of ash from biomass combustion, it only meets the requirements set by the Czech Republic.

The content of the light fraction of PAHs (abbreviated as LMW, i.e., the group of PAH congeners made up of a smaller number of rings (2–4)) in the ash studied was 7115.631 $\mu\text{g}\cdot\text{kg}^{-1}$ [Figure 2]. In a study by Szatyłowicz and Skoczko, the Σ LMW content in ash from wood and pellet combustion was 18010 $\mu\text{g}\cdot\text{kg}^{-1}$ and 4090 $\mu\text{g}\cdot\text{kg}^{-1}$, respectively [51]. Co-composting the ash resulted in a decrease in Σ LMW from 1745.02 $\mu\text{g}\cdot\text{kg}^{-1}$ to 1683.22 $\mu\text{g}\cdot\text{kg}^{-1}$ when composted at 20 °C and to 1039.02 $\mu\text{g}\cdot\text{kg}^{-1}$ when incubated at 40 °C.

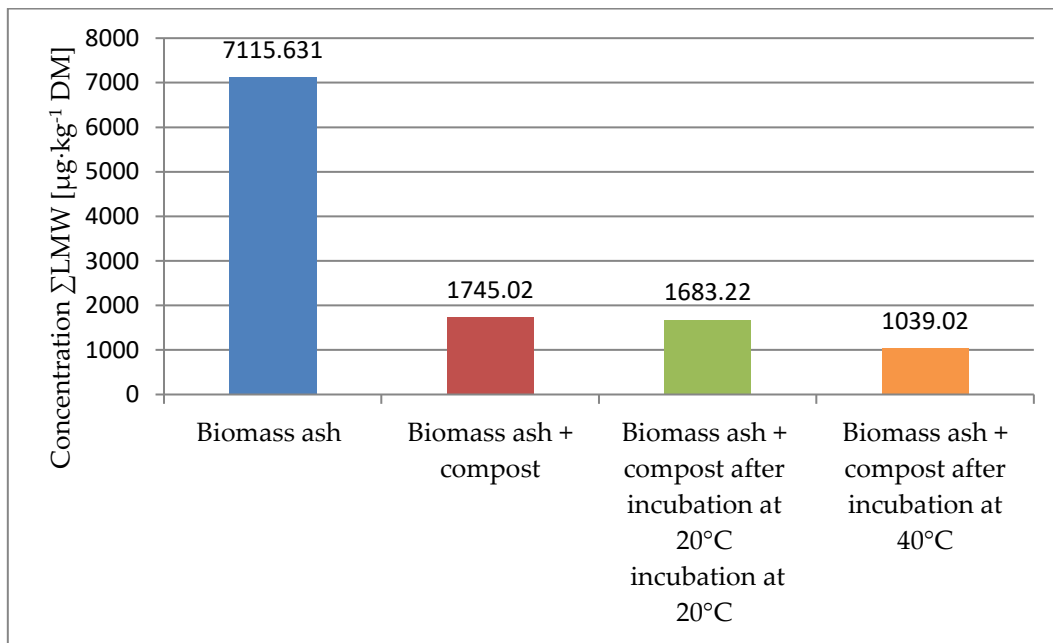


Figure 2. Average ΣLMW content in the tested samples.

3.3. Risk Indicators in the Tested Samples (CEQ, MEQ TCDD-TEQ, $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$)

The content of the heavy fraction of PAHs abbreviated as HMW consisting of hydrocarbons containing five or more aromatic rings in the tested ash was $558.81 \mu\text{g}\cdot\text{kg}^{-1}$ [Figure 3]. In contrast, the results obtained by Košnář et al. showed the content of ΣHMW in ash-fertilised soil to be $508 \mu\text{g}\cdot\text{kg}^{-1}$ [52]. The composting process at 20°C reduced ΣHMW from $440.446 \mu\text{g}\cdot\text{kg}^{-1}$ to $380.26 \mu\text{g}\cdot\text{kg}^{-1}$, while increasing the incubation temperature resulted in a greater decrease in HMW to $333.36 \mu\text{g}\cdot\text{kg}^{-1}$.

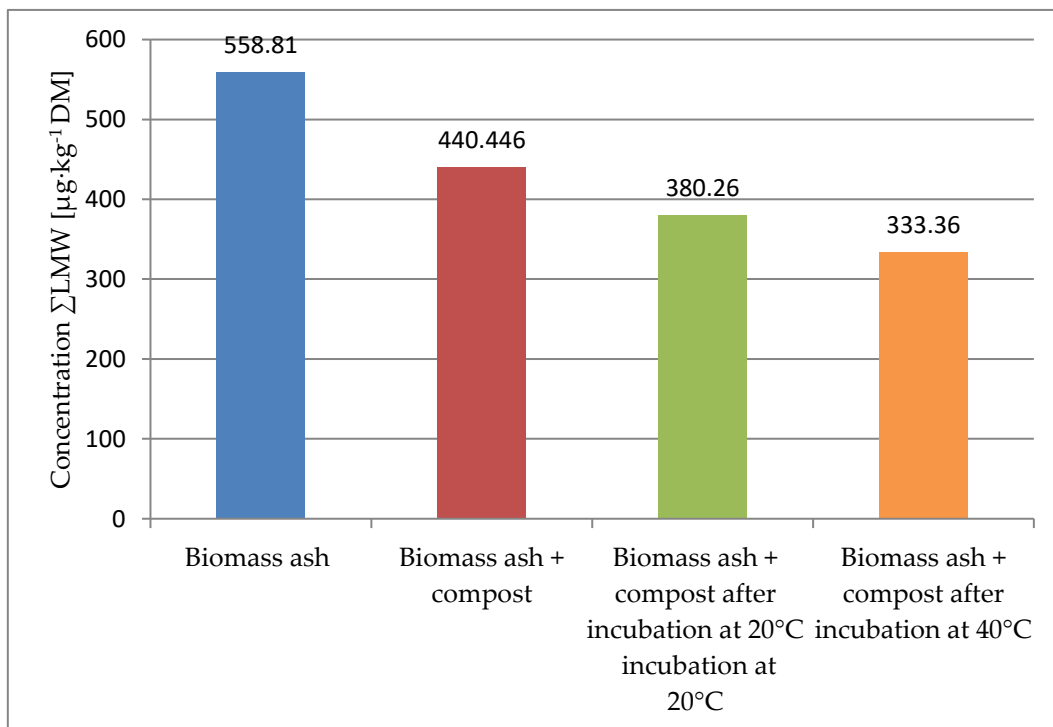


Figure 3. Average ΣHMW content in the tested samples.

Considering the wide-ranging levels of carcinogenicity exhibited by individual polycyclic aromatic hydrocarbons (PAHs), values of toxicity equivalent (TEQ) were calculated (Table 2). These values depict the overall toxicity of the examined compounds in relation to the specified indicator benzo(a)pyrene.

Table 2. Contents of indicators (CEQ, MEQ TCDD-TEQ, Σ PAH_{carc}/ Σ PAH) in the tested samples.

Indicator	Biomass Ash	Biomass Ash + Compost	Biomass Ash + Compost after Incubation at 20 °C	Biomass Ash + Compost after Incubation at 40 °C
			[$\mu\text{g}\cdot\text{kg}^{-1}$ DM]	
TEQ = CEQ	413.47	296.04	266.36	256.19
MEQ	389.16	289.71	264.45	254.63
TCDD-TEQ	0.75	0.66	0.54	0.36
Σ PAH _{carc} / Σ PAH	0.08	0.22	0.21	0.27

The toxicity equivalent (TEQ) for ash was $413.47 \mu\text{g}\cdot\text{kg}^{-1}$. In a study by Kozielska et al., the TEQ for ash from wood combustion was $603 \mu\text{g}\cdot\text{kg}^{-1}$ [53]. Co-composting the ash at 20 °C resulted in a 35.58% decrease in TEQ. Increasing the temperature to 40 °C increased the TEQ reduction by 38.04%.

The tested ash is characterised by a mutagenicity index (MEQ) of $389.16 \mu\text{g}\cdot\text{kg}^{-1}$. Charcoal is characterised by varying MEQ levels ranging from $2600 \mu\text{g}\cdot\text{kg}^{-1}$ to $984,980 \mu\text{g}\cdot\text{kg}^{-1}$ [54]. In a study by Szatyłowicz and Skoczko, the MEQ for ash from wood pellet combustion was $26,020 \mu\text{g}\cdot\text{kg}^{-1}$ [51]. Incubation of the ash together with compost at 20 °C resulted in a decrease in the mutagenicity factor to $264.45 \mu\text{g}\cdot\text{kg}^{-1}$, while increasing the temperature to 40 °C slightly decreased the MEQ to $254.63 \mu\text{g}\cdot\text{kg}^{-1}$.

The carcinogenicity factor (PCDD-TEQ) for the tested ash was $0.75 \mu\text{g}\cdot\text{kg}^{-1}$. The co-composting process of the ash significantly affected the carcinogenicity of the tested samples. Composting at 20 °C resulted in a decrease in the PCDD-TEQ to $0.54 \mu\text{g}\cdot\text{kg}^{-1}$; an increase in temperature had a positive effect on the carcinogenicity factor level, reducing it to $0.36 \mu\text{g}\cdot\text{kg}^{-1}$, which is a decrease of 51.09%.

The total harmfulness of PAHs (Σ PAH_{carc}/ Σ PAH) for the ash was 0.08. According to the research of Szatyłowicz and Hawrylik, the harmfulness coefficient Σ PAH_{carc}/ Σ PAH for ash from pellet combustion was 0.7, while for coal, it was 0.6 [55]. The composting process negatively affected the amount of this ratio, which increased to 0.21 when incubated at 20 °C, while it reached 0.27 at 40 °C. The increase in the Σ PAH_{carc}/ Σ PAH ratio is due to the fact that hydrocarbons made up of fewer rings (LMW) are mainly reduced during the composting process.

4. Conclusions

Based on the research conducted, the following conclusions were drawn:

1. An analysis of the content of a group of hydrocarbons consisting of a smaller number of aromatic rings (2–4) showed a huge impact of the temperature of the composting process on the reduction in PAHs. The highest degree of degradation was obtained for indeno(1,2,3-c,d)pyrene (InP), where the content of this congener decreased by approximately 46% during incubation at 20 °C, and by 76% at 40 °C.
2. In both composting methods, acenaphthene turned out to be the most resistant to degradation, the content of which decreased significantly after mixing with compost, but increased during incubation. After incubation at 20 °C, its content increased by 123.07%, and after incubation at 40 °C, it increased by 159.07%.
3. The composting process has a beneficial effect on reducing the total number of polycyclic aromatic hydrocarbons in ash from biomass combustion. As a result of the co-composting of ashes, a decrease in PAH₁₆ content was found by 37.2%.

4. Analyzing the calculated TEQ = CEQ, MEQ, and TCDD-TEQ indicators, a significant decrease was found in the composting process. The TCDD-TEQ carcinogenicity index decreased the most (45.45%).
5. The harmfulness of the tested Σ PAH_{carc}/ Σ PAH samples was minimally reduced from 0.22 to 0.21 when composted at 20 °C, but increased to 0.27 when composted at 40 °C.
6. The Σ PAH_{carc}/ Σ PAH coefficient for the test samples was well below 1, which means that the resulting composts do not pose a threat to humans.
7. To sum up, it was concluded that the research results showed a positive effect of co-composting ashes on the content of PAHs. Reducing the content of Σ PAH₁₆ and reducing the overall harmfulness of Σ PAH_{carc}/ Σ PAH means that ash from biomass combustion has great potential for use as a fertiliser. Therefore, the management of waste from biomass combustion in the form of compost in agriculture would enable an effective and very simple reduction of PAHs entering the environment.

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