

Article

# Influence of Biomass Incineration Temperature on the Content of Selected Heavy Metals in the Ash Used for Fertilizing Purposes

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**Abstract:** This article presents the influence of ash-forming temperature on ash content and the content of selected heavy metals. The biomasses most commonly used in low-power heating boilers, such as miscanthus, oak, pine, sunflower husk, wheat straw and willow, were selected for the research. The biomass was incinerated at temperatures of 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C, using the X-ray Fluorescence Spectrometer (XRF) for the measurement of element content. The results show that the content of heavy metals in the examined ash was not excessive and could not be considered as potentially dangerous. As the ash-forming temperature increased, the content of Zn, Cd, Cu and Pb decreased, which indicates that, at higher temperatures, they went into the gas phase. Cr, Ni and Fe were thermally stable and less volatile, thus the ashes were enriched with them as the ash-forming temperature increased.

**Keywords:** biomass ash; elements; ash-forming temperature

## 1. Introduction

Growing environmental problems, especially those related to the use of fossil fuels, have made it necessary to look for new solutions that would limit the greenhouse effect. The problem is also related to economic and political issues.

Among all the available methods of reducing the greenhouse effect, i.e., the use of hydro, solar or wind energy [1], the use of biomass in combustion processes is one of the most promising options, especially compared to coal-based, dispersed power industry. Biomass has numerous advantages over fossil fuels—primarily, it is regarded as a renewable energy source with zero or low CO<sub>2</sub> emissions if it is produced in a sustainable way. Additional benefits are low SO<sub>2</sub> emissions and possibly low NO<sub>x</sub> emissions [2].

The use of biomass in the European Union (EU) has grown significantly over the last decades and the EU's ambition for biomass use is high. Solid biomass covers a wide range of materials including: wood, straw, and agricultural residues. A large variety of raw materials and, consequently, varied properties make biomass a complex and difficult fuel [3–5].

The process of producing energy by combustion has the disadvantage of generating large amounts of ash, which is a solid combustion residue. Biomass ash accounts for 2–20% of the input material [6,7]. Since the production of energy from biomass combustion is constantly growing, the processing and disposal of the generated ash has become an environmental and economic problem. Landfilling is traditionally the most widely used method of storage in waste management, but it causes significant

costs for users [6]. Ash from biomass incineration, however, has many potential applications: in forest ecosystems, for agricultural and horticultural purposes as a fertilizer [8], as a building material [9,10] or as an ingredient in the process of building materials production. It is particularly attractive to use as a fertilizer due to the high content of valuable macro- and micronutrients. The composition of ash from biomass is very diverse and depends to a large extent on the type of plant, its origin, incineration system, process parameters and storage conditions.

Another problem that may limit the use of ashes as fertilizers is the presence of trace elements in the ash [11,12]. The opinion that biomass is relatively low in hazardous elements is not supported by detailed analyses. The concentration of toxic (or potentially toxic) trace elements is usually lower in biomass than in coal, with the exception of Zn, Mn and Cu. However, the toxic elements contained in the biomass are more mobile during incineration compared to coal and are also more susceptible to leaching from the ash [13]. In the case of biomass grown on contaminated sites, the content of various heavy metal elements in ash may be very high. According to Kovacs et al. [14], ash from plants cultivated in contaminated mining areas should be treated as toxic waste. In addition, biomass usually exhibits higher chlorine concentrations, which, according to the thermodynamic equilibrium calculations, are believed to particularly improve the mobilization of a number of metals from fuel particles, particularly under reducing conditions. At the same time, it should be borne in mind that the behavior of trace elements, i.e., volatilization or retention in the ash during incineration, is quite a complex problem. It will depend on the mode of occurrence of trace elements in the materials, physicochemical interactions between the components as well as the ash-forming temperature.

The chemical degradation of biomass during incineration, i.e., pyrolysis, leads to the formation of a solid residue in the form of ash. Bottom and volatile ash are usually two types of ash produced and may differ in properties due to different types of biomass burned, operating conditions and type of system used. High ash content significantly reduces the energy efficiency obtained from a specific source of biomass. The ash-forming temperature and speed are influenced by the ash properties and composition [15,16].

The aim of the work was to assess the impact of biomass type and ash-forming temperature on ash and selected heavy metals contents in view of sustainable management of biomass ashes through their use for fertilizing purposes. The toxic elements contained in biomass are more mobile during incineration than those in coal, therefore, from the point of view of ecological safety, it is important to know the content of heavy metals in biomass ash in order not to introduce excessive and potentially dangerous amounts into the environment.

Realizing the aim of the work, in the laboratory conditions, at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C, the incineration of biomasses used most commonly in the processes of thermal-chemical conversion was performed: miscant, oak, pine, sunflower husk, wheat straw, and willow. The contents of ash and selected trace elements (Cd, Cr, Cu, Ni, Cu, Pb, Zn, and Fe) were determined.

## 2. Materials and Methods

Six solid biomass fuels were selected for this study. They are typical materials used in a domestic boiler. The selection included forestry biomass (oak wood pellets and pine wood pellets); energy crops (miscant pellets and willow pellets); and agricultural residues (sunflower husk and wheat straw). Thus, a range of differing ash compositions was provided.

The pellets from oak, pine, and sunflower husk came from pellet producers and were purchased in retail chains, while the remaining material came from own experimental crops. The samples were milled in the analytical mill (IKA A11, IKA-Werke GmbH & Co.KG, Staufen, Germany) and then sieved. Only the fraction retained on the 1.0–2.5 mm sieve was used.

Temperatures for various chemical-thermal conversion technologies of biomass are generally controlled in the range 250–1200 °C [17]. However, the combustion of biomass at high temperatures often leads to slagging, while at low temperatures it is ineffective due to insufficient incineration. Accordingly, the temperature range of 500–1000 °C with 100 °C intervals was selected for the experiment.

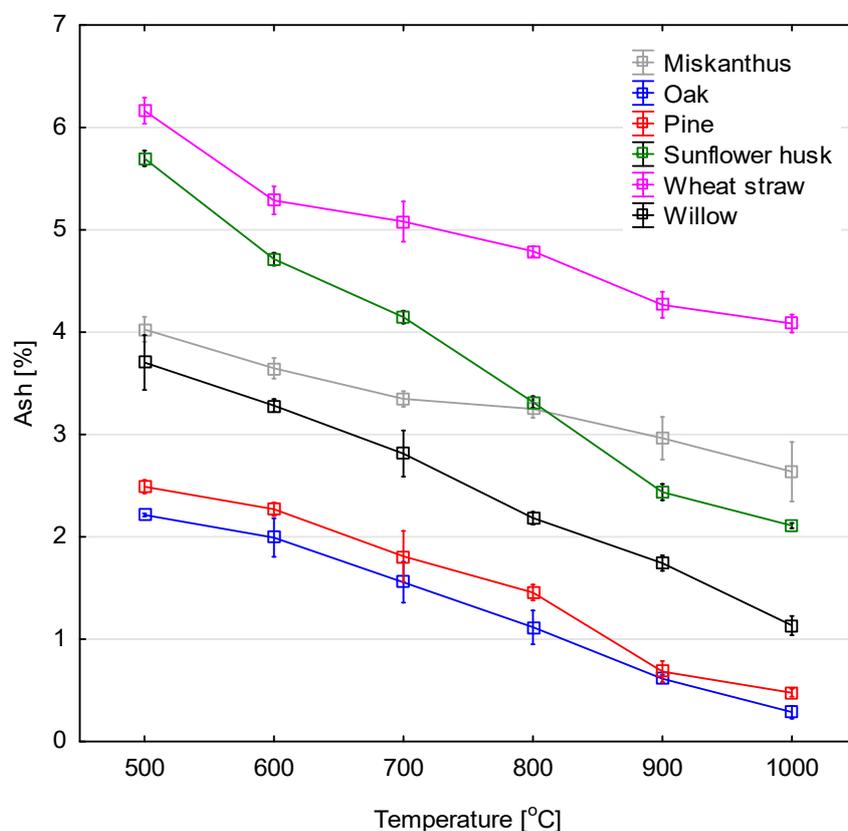
The thermogravimeter (TGA 701, LECO Corporation, Saint Joseph MI, USA) was used for the incineration. About 2 g of the biomass was weighed into a ceramic crucible and heated from ambient temperature to ash-forming temperature at the heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  in the air stream. Then, it was kept at the ash-forming temperature for 4 h. After the temperature dropped to about  $100\text{ }^{\circ}\text{C}$ , the ash was removed, placed in a desiccator and cooled to ambient temperature.

The XRF technique was used to determine the content of trace elements. The research was carried out using the Multi-Element Analyzer (HDMaxine, XOS, East Greenbush, NY, USA). Because the apparatus did not require sample preparation, it was dispensed directly into measuring cups. The apparatus software allowed analyzing the acquired oscillograms. The work presents and discusses the results of tests for Cd, Cr, Cu, Ni, Cu, Pb, and Zn. Fe was also included in the analysis. Fe is a metal rarely included in the balance sheets of thermal biomass processes, but, due to its high content in biomass, it was included in this analysis. Other toxic elements included in the list of contaminants in the European incinerator directive such as As, Hg and Sb were below the limit of detection and were not analyzed. The quality of analytical results regarding their accuracy was verified using standard certified materials. To obtain accurate and stable experimental data, each experiment was repeated at least three times.

The statistical analysis was carried out in the Statistica program (Dell Inc. (2016). Dell Statistica (data analysis software system), version 13, Tulsa, OK, USA) using a two-way ANOVA analysis of variance.

### 3. Results and Discussion

The ash content found in the examined biomass was generally dependent on the biomass type and ash-forming temperature (Figure 1). The lowest ash content was found for oak and it ranged from 0.29% at the temperature of  $1000\text{ }^{\circ}\text{C}$  to 2.21% at  $500\text{ }^{\circ}\text{C}$ , while the highest ash content was found for wheat straw, from 4.08% at  $1000\text{ }^{\circ}\text{C}$  to 6.16% at  $500\text{ }^{\circ}\text{C}$ .



**Figure 1.** Changes in ash content in the examined biomass depending on ash-forming temperature.

The obtained test results indicate that the compactness of ash in the studied biomass was relatively low and typical for a given raw material [18,19], regardless of ash-forming temperature. In wood, ash accounted for less than 2%, whereas in agricultural crops it could amount from 5–10% to as much as 30–40% [18]. The ash content in biomass depends on the sampling site, harvesting time and harvest conditions. Thus, for example, its content in wood and woody biomass was below 1%, in energy crops from 1.79% to 5.38%, in agricultural biomass from 6.88% to 9.2%, in forest residue from 6.27% to 10.44% and in agri-food industry wastes from 1.06% to 9.98%.

The changes in the ash content in the examined biomass depending on ash-forming temperature (Figure 1) clearly indicated that it dropped with increasing temperature, with the largest differences for ash from wood biomass (above 70–80%). As the temperature increased, the percentage of content drop went lower for ash from miscanthus and wheat straw (34%). This is the result of the volatilization of most of the components contained in the biomass to the gas phase during incineration. The observed differences may be related to the higher content of mineral compounds in the biomass of grass plants.

The content of heavy metals in the studied biomass varied within very wide limits. Differences between particular types of organic material, even of the same type, were of the order of magnitude. The results of the determinations are collected in together with statistical analysis of the results are collected in Tables 1–4 together with statistical analysis of the results.

The highest Cr content was found in sunflower husk ash, on average 67.8 ppm, obtained at all considered temperatures, except for the temperature of 1000 °C, for which the highest Cr content was found in willow ash (97.1 ppm) (Figure 2). The lowest content of this element was found in miscanthus ash, on average 34.1 ppm. In all studied biomass types, the content of Cr in ash increased with ash-forming temperature, but with different dynamics—the interaction effect occurred, among others, for willow, oak and pine, where, for samples incinerated at 1000 °C, a significant increase in Cr was observed.

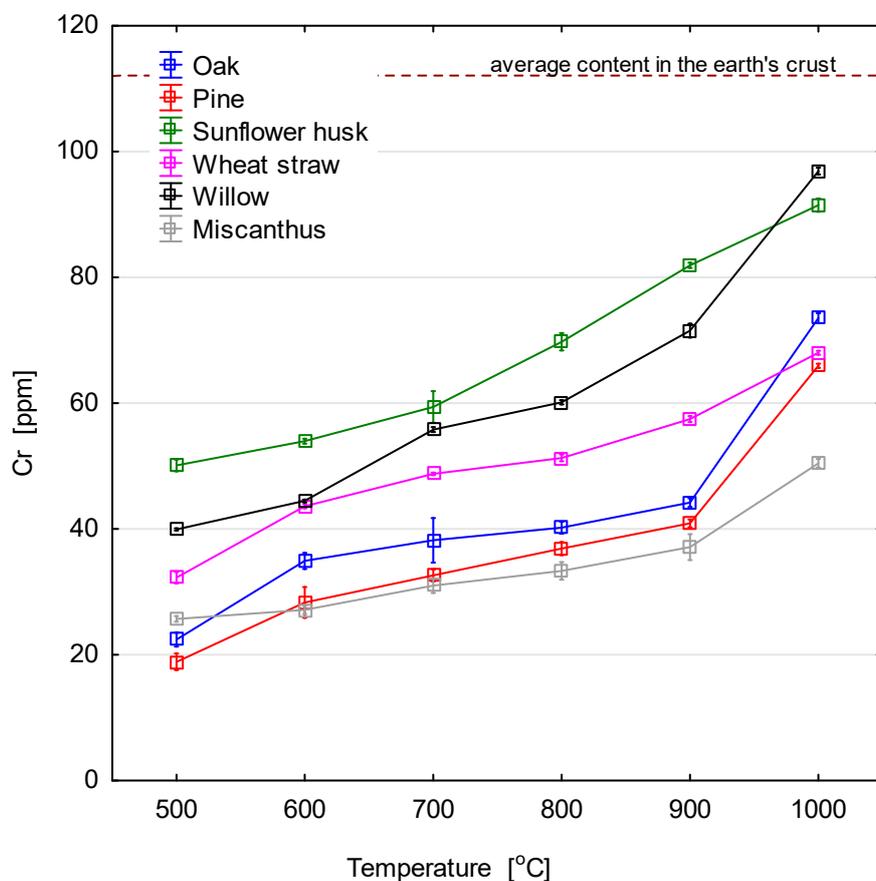


Figure 2. Changes in Cr content in the examined biomass depending on ash-forming temperature.

Considering that the average content of Cr in the Earth’s crust is 112 ppm, the content of this element was not high. Cr is a metal that in combustion (oxidation) technologies remains in condensed (solid) phases, regardless of the oxygen potential of the system and the presence of sulfur and chlorine. Both in the pyrolysis and gasification processes under Cr reducing conditions, it takes the form of Cr<sub>2</sub>O<sub>3</sub> oxide up to 1067 °C. According to Szczepaniak [20], regardless of the form in which Cr is in the original material, this element should ultimately remain in solid post-process residue and in insoluble form. The above was confirmed by the obtained test results.

The highest Zn content was found in willow ash, an average of 601.4 ppm, and the lowest in oak ashes, an average of 114.9 ppm. As ash-forming temperature increased, the content of this element in the ashes decreased, a similar dynamics of Zn changes was observed for willow and miscanthus (Figure 3).

The determined Zn content in the examined ash differed significantly from the average content in the Earth’s crust, which is 70 ppm. In oxidation technologies, Zn mainly moves to the gas phase. Zn is a relatively volatile metal (boiling point 907 °C) but quite reactive and showing high affinity to sulfur. At low temperatures, Zn should not move into the gas phase as vapors. At high temperatures (827 °C), Zn, in the conditions of pyrolysis, steam gasification, or initial phases of gasification with air, is reduced to metal vapors and in this form it can be discharged from the reaction zone with the gas phase [20]. This pattern of Zn’s behavior is consistent with the obtained test results. Nevertheless, the behavior of zinc in thermal processes can be significantly different, depending on the type of process, temperature and composition of the biomass used.

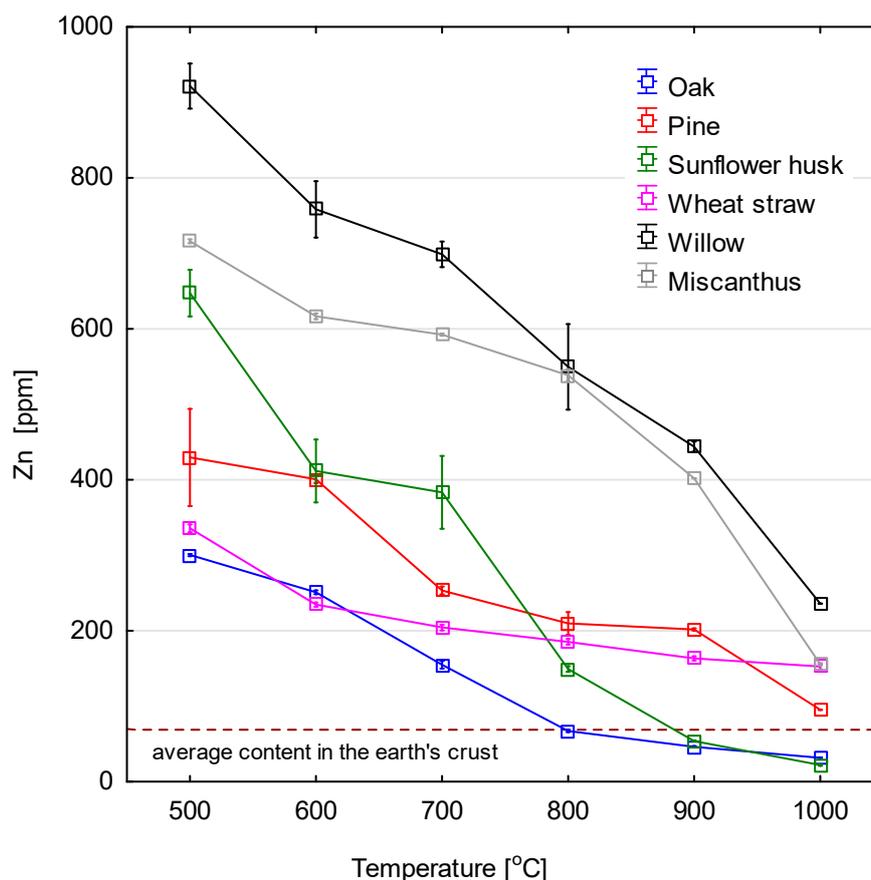
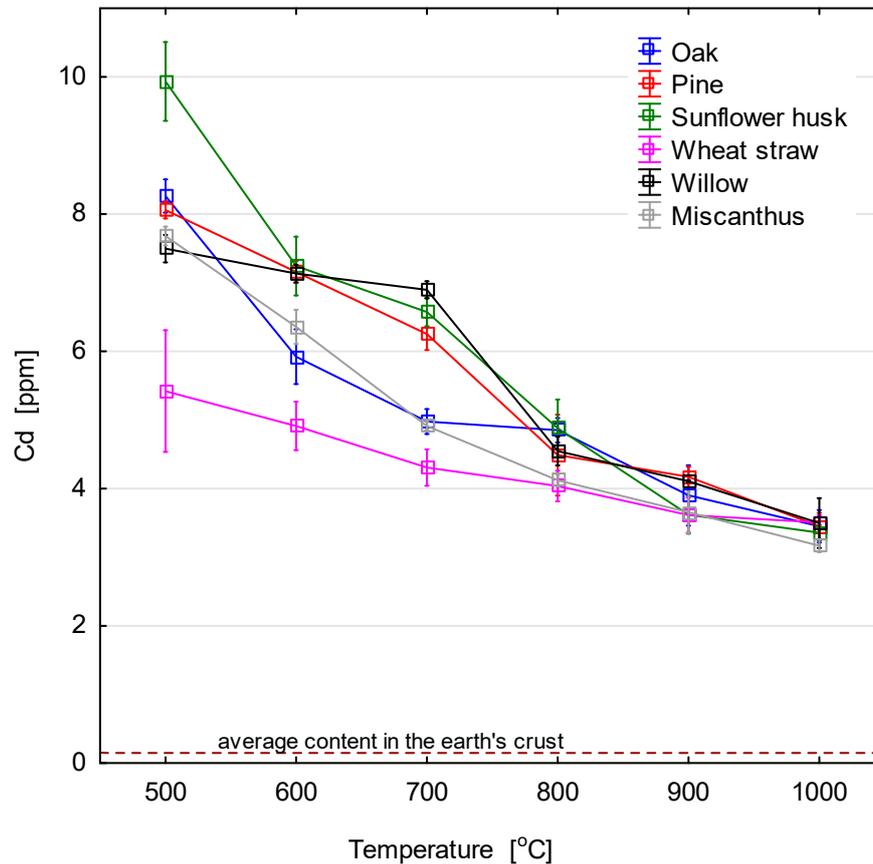


Figure 3. Changes in Zn content in the examined biomass depending on ash-forming temperature.

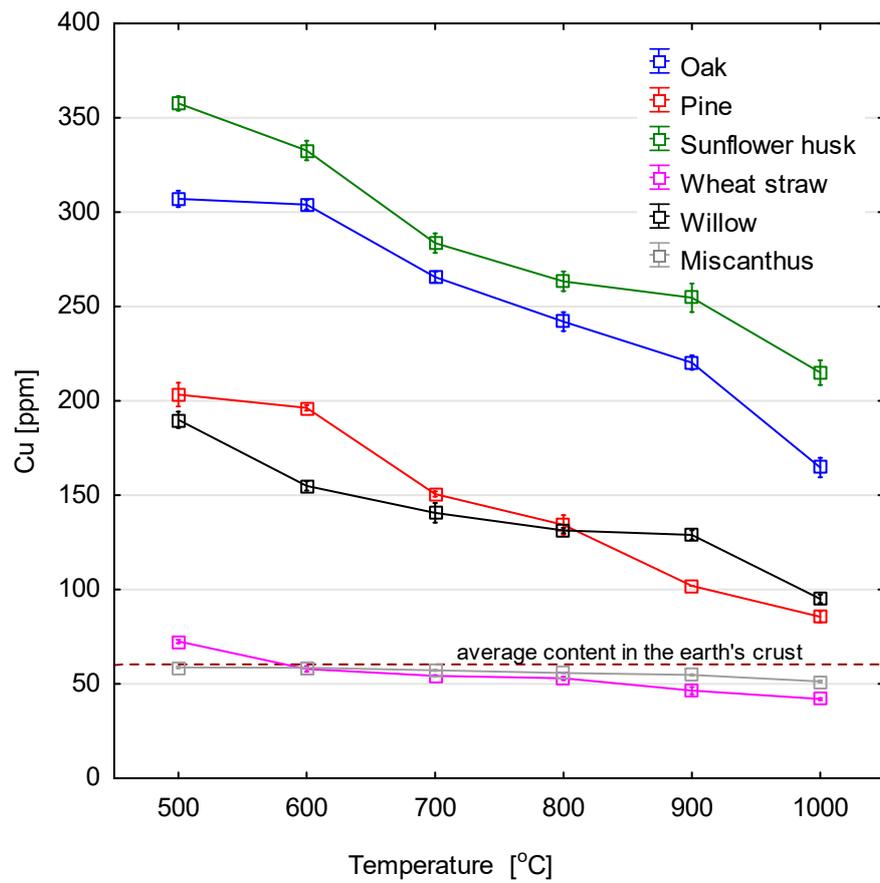
The highest Cd content was found in sunflower husk ash, on average 5.9 ppm, and the lowest in wheat straw, on average 4.3 ppm (Figure 4). In all cases, a decrease in the Cd content in ashes was observed as ash-forming temperature increased. A similar dynamics of changes in sunflower husk and miscanthus was observed.

The determined Cd contents in the ashes were significant (maximum 10.2 ppm), the average Cd content in the Earth’s crust is 0.15 ppm. In the range of low oxygen potentials, cadmium is present in the form of solid sulfide up to the temperature of approximately 427 °C and then moves to the gas phase as elemental cadmium. The total passage of cadmium to the gas phase occurs at temperatures exceeding 527 °C. Above the mentioned temperature range, i.e., 427–527 °C, cadmium moves to the gas phase regardless of the oxygen potential of the system [20].



**Figure 4.** Changes in Cd content in the examined biomass depending on ash-forming temperature.

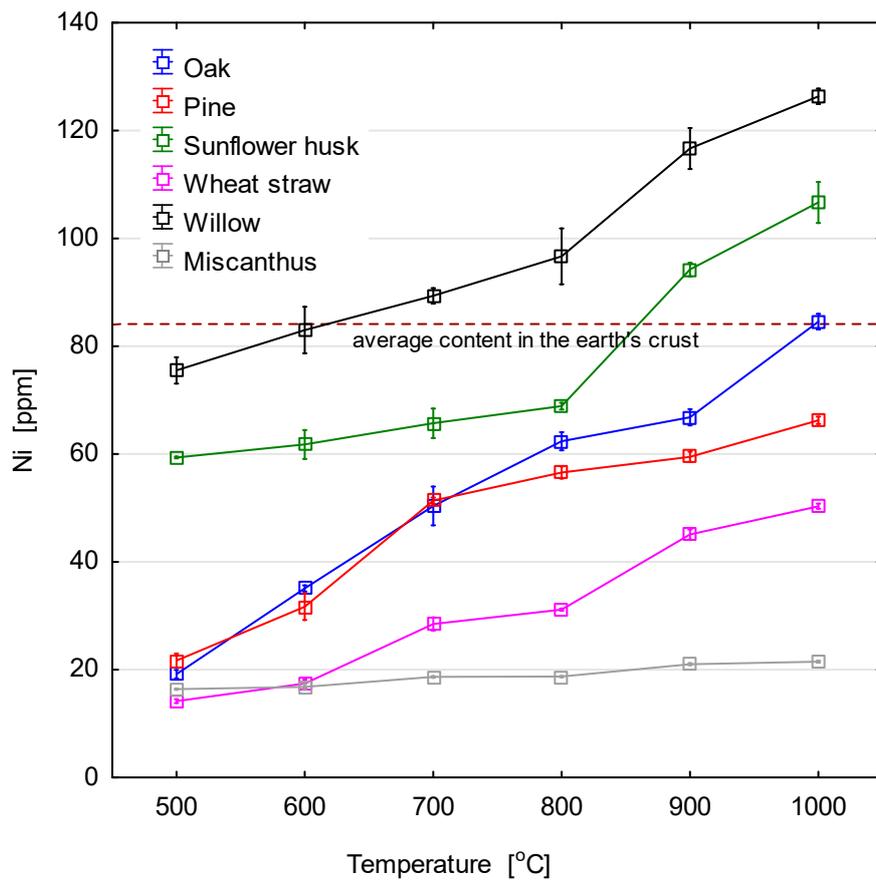
The highest Cu content was found in sunflower husk ash, an average of 284.5 ppm, and the lowest in miscant and wheat straw ashes, on average 56.1 and 54.4 ppm, respectively. As ash-forming temperature increased, Cu content decreased in the examined ash (Figure 5). Apparently, this tendency was visible for sunflower husk and oak ashes, where the changes proceeded with similar dynamics; however, in the case of miscant and wheat straw, it was almost imperceptible. The marked content of Cu in the ashes of sunflower, oak, pine and willow husks is higher than the average content in the Earth’s crust, which is 60 ppm.



**Figure 5.** Changes in Cu content in the examined biomass depending on ash-forming temperature.

Copper, considered to be a precious metal, is easily reduced in favorable conditions to free metal. In combustion technologies, Cu is first retained in slag phases. However, it is characterized by a clear affinity to sulfur, which is why, in the presence of this element, in the reducing conditions, a stable combination is copper sulfide  $\text{Cu}_2\text{S}$ . When oxygen potential is changed, oxidizing copper sulfide is oxidized to sulfate at lower temperatures ( $427\text{ °C}$ ) or to copper oxide  $\text{CuO}$  at higher temperatures ( $827\text{ °C}$ ). Under reducing conditions, when copper is bound to sulfide, small amounts of copper can pass to the gas phase in the form of  $\text{CuCl}$ , especially at temperatures higher than  $827\text{ °C}$ . After changing the oxygen potential, the amount and differentiation of the oxide forms of copper in the gas phase clearly increases, which means that this metal is completely discharged into the gas phase [20]. The obtained test results show that the decrease in Cu content in ashes along with the increase in the ash-forming temperature was related to the transition of this element to the gas phase, but not to the same extent for all the biomass types tested.

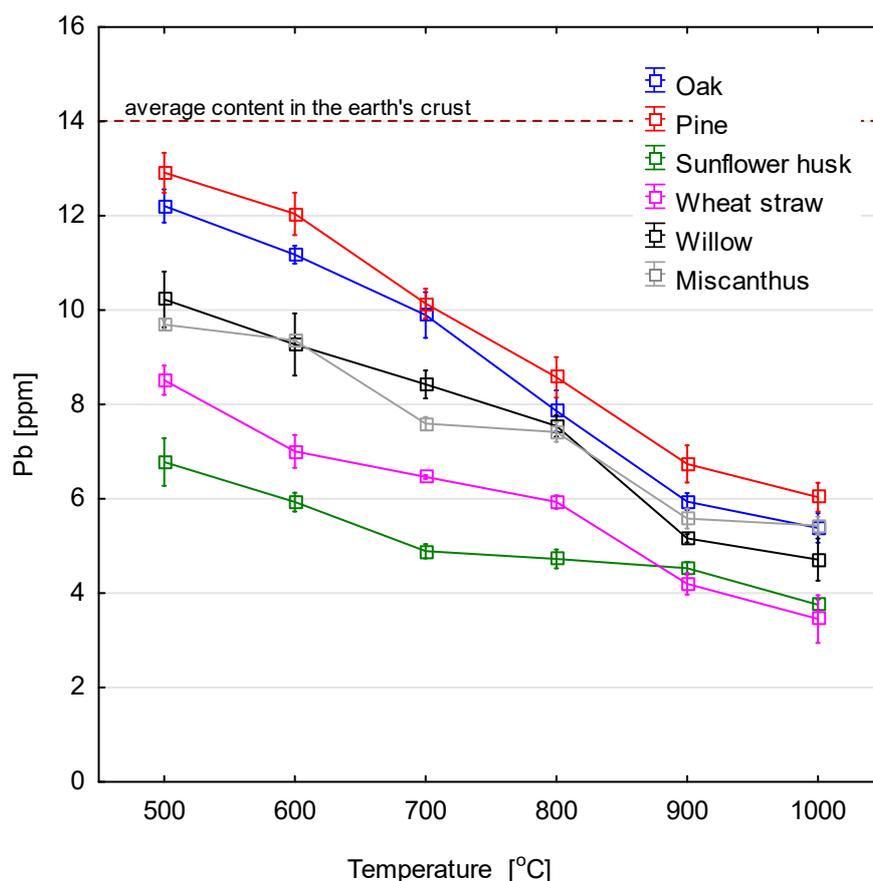
The highest Ni content was found in willow ash, on average  $97.9\text{ ppm}$ , and the lowest in miscanthus ash, on average  $18.9\text{ ppm}$ . This content was very different and it varied in many ways as ash-forming temperature increased. In general, the Ni content increased with the increase of ash-forming temperature with similar dynamics as for willow and sunflower husk. Only for miscanthus this trend was very poorly visible (Figure 6).



**Figure 6.** Changes in Ni content in the examined biomass depending on ash-forming temperature.

Considering that the average Ni content in the Earth’s crust amounts to 84 ppm, it was assumed that the content determined in the examined ash was not excessive (maximum 127 ppm). In combustion processes, Ni remains primarily in the slag. A characteristic feature of the behavior of nickel in the conditions of pyrolysis and gasification is the ability of this metal to form a sulfide phase and its transformation during oxidation, depending on the temperature, into the sulfate (at lower temperature) or oxide (at higher temperature). During pyrolysis without external gases, nickel sulfide  $Ni_3S_2$  is transformed at 757 °C into elemental nickel. At lower temperatures (427 °C), nickel is in the form of sulfides and at higher temperatures (827 °C) in the form of metallic sulfide.

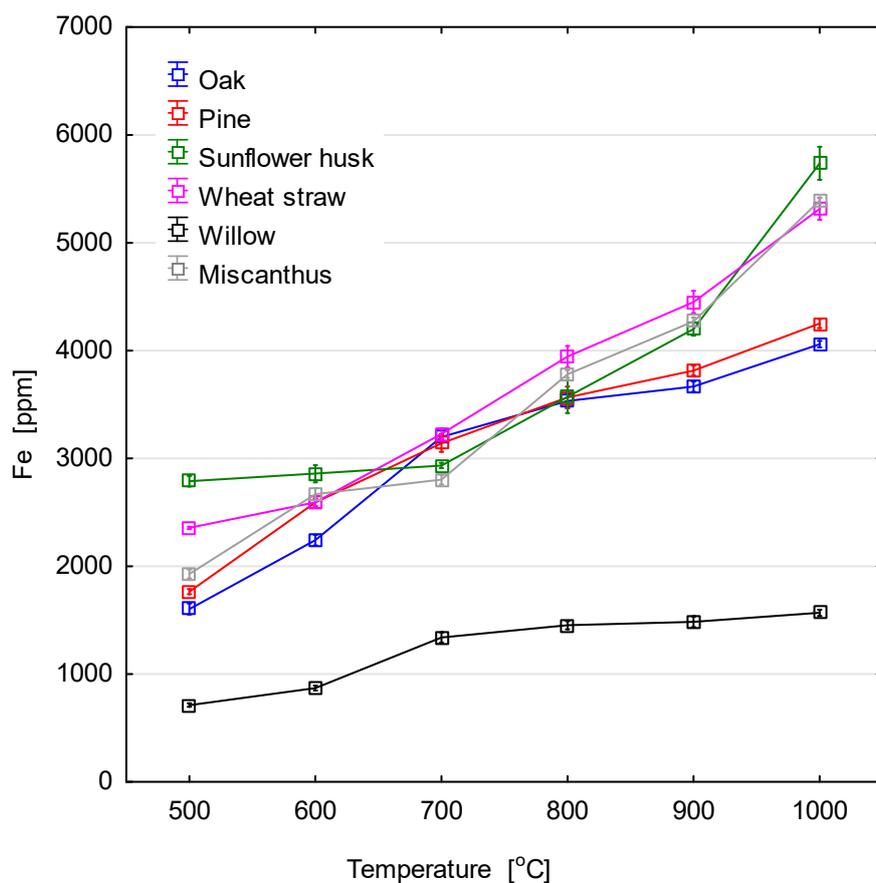
The highest Pb content was determined in pine ash, an average of 9.4 ppm, and the lowest in sunflower husk 5.1 ppm. It was clearly observed that the Pb content decreased with the increase of ash-forming temperature for all the types of biomass studied (Figure 7).



**Figure 7.** Changes in Pb content in the examined biomass depending on ash-forming temperature.

The content of this element was not excessive (maximum 13.1 ppm), while the average Pb content in the Earth’s crust is 14 ppm. Pb in combustion processes goes mainly to volatile dust. As described in [20], in the case of simple pyrolysis, the dominant form at lower temperatures (up to about 527 °C) is solid lead sulfide (PbS). At slightly higher temperatures, this form of sulfide disappears, and in its place appears a gas form of PbS, which is accompanied by vapors of metallic lead. The significance of elemental lead in the gaseous form in relation to the gaseous sulfide form increases with increasing temperature and from about 827 °C the metallic lead vapor prevails over the sulfide vapors. At higher temperatures in the initial period, lead is roughly divided between the two gaseous forms of sulfide and elemental lead. After changing the potential of the system to oxidation (at 827 °C), a complex sequence of transformations to lead sulfate follows, which is accompanied by lead oxide PbO in the form of vapors. At an even higher temperature of 1227 °C, only PbO is present in the system. After changing the potential for oxidation, the basic form of lead is PbCl<sub>2</sub>. After the temperature rises to about 1227 °C, the main form in the reduction zone is elemental lead in the form of vapors. In the oxidizing area, lead oxide in the form of vapors predominates, supplemented by two chloride forms, PbCl and PbCl<sub>2</sub>.

The highest Fe content was found in sunflower husk ash (on average 3681 ppm), the lowest in willow (on average 1238 ppm) and the content in this type of biomass was significantly different from the content in the other materials tested (Figure 8). Fe content increased with increasing ash-forming temperature with different dynamics depending on the raw materials.



**Figure 8.** Changes in Fe content in the examined biomass depending on ash-forming temperature.

The Fe content in the examined ash was not excessive (maximum 5797 ppm), in the Earth's crust this element occurs on average in the amount of 5.63%. Iron is usually not treated as a nuisance, let alone a dangerous element, but sometimes in conditions of its high concentration in the material subjected to thermal processes this element can potentially compete with other metals in chemical equilibria and create characteristic phases. Up to the temperature of 647 °C, iron oxides ( $\text{Fe}_3\text{O}_4$  and later  $\text{FeO}$ ) will be present in the system, which should be accompanied by  $\text{FeS}$ , binding most of the sulfur contained in the starting material. Since, after the oxidation of metallic iron, the amount of sulfide phase is systematically mixed in a short time and it is also depleted and only the form of  $\text{Fe}_3\text{O}_4$  remains in the system, after the oxygen potential's jump, this form oxidizes to  $\text{Fe}_2\text{O}_3$  [20].

In combustion processes, 90–97% Fe is retained in the slag. This image is completely consistent with the results obtained; the metal remained in condensed phases and did not move to the gas phase.

Thermodynamic calculations suggest that Cd and Pb are preferentially converted during combustion into  $\text{CdCl}_2/\text{PbCl}_2$ . In addition, not only metal, but also hydrochlorides and limited metal oxides may evaporate [21]. Zn is relatively less volatile than Pb and Cd but  $\text{ZnCl}_2$  and Zn metal residuals were volatilized. However, conversion to  $\text{ZnCl}_2$  is limited because a significant amount of Zn is present in the form of a stable oxide. Other volatile metals, including Ar and Sb, show similar behavior and their ash content is generally very low. Hg almost completely passes into the exhaust gas due to the high vapor pressure, but the Hg content in the unprocessed biofuels is very low (0.01–1 ppm) [22,23]. Litophilic metals, such as Fe, Cu, Cr and Al, go to coarse volatile ash in large quantities not only because of their low volatility, but also because they are in oxide form and are very stable [24].

In the literature, little research concerns the emissions of heavy metals during the small-scale combustion of various solid biofuels. Scientific reports show that, as ash-forming temperature increases,

the ash content decreases, which is also confirmed by the results obtained. The temperature of biomass incineration also has some influence on the migration of elements. Its increase promotes further degradation of minerals. According to Wang et al. [25], Fe shows an upward trend due to its low volatility, while other metals show slight fluctuations. The work in [26] distinguishes, depending on the temperature range and biomass examined, elements of high volatility (Hg and Se), varied volatility (Cd and Pb), average volatility (Cu, Zn, Ni, and Cr) and low volatility (Mn, Ba, Co, and As). A similar division was made in [27], where trace elements are ranked according to their average retention in combustion ash. The most volatile are Hg and Se, followed by Cd, Tl, Pb and As. Partial retention is observed in Zn, Sb, Cr, V, Cu, Sr, Mo, Mn and Ba ashes. The highest retention of elements in the ash is recorded for Be, Co and Ni. The above was confirmed in most cases by the research results obtained here. Among the analyzed elements, the content of Zn, Cd, Cu, and Pb decreased with increasing temperature, while the content of Ni, Cr, and Fe increased. Thus, the exceptions were Ni Cr and Fe, whose ash content clearly increased with increasing ash-forming temperature.

According to Vamvuka [28], olive oil ash was enriched with Cr, Cu, Ni and Mn, while the content of toxic elements Se and Pb was below 9 ppm. The highest Cr content at 2000 ppm was attributed to the type of fuel.

The biomass biofuels examined by the authors of [29], relative to coal and peat, produced higher Zn emissions, but lower or similar emissions of the sum of other metals. In addition, Zn and Pb were the two heavy metals with the highest content in the volatile fraction. The above was reflected in the obtained test results; Zn and Pb content decreased with increasing temperature, which indicates their transition to the gas phase.

The increase in temperature during pyrolysis of sewage sludge leads to the transformation of less stable heavy metals to more stable forms in the biocarbon. The degree of conversion and trends are individual for each metal and for particular materials tested [30].

Jiménez et al. [31] determined the content of trace elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As and Pb) in aerosols generated during biomass combustion, under defined realistic combustion conditions, which included temperature changes and concentrations of O<sub>2</sub> and SO<sub>2</sub> in flue gas. Two different trends were observed: when O<sub>2</sub> was increased in the flue gas, the content of Cr, Ni and Mn increased, and the reverse effect was observed for the remaining elements. Changes in SO<sub>2</sub> concentration had little effect on the results, with the notable exception of Fe, the amount of which decreased with the increase of SO<sub>2</sub> in the flue gas. In samples taken at two different temperatures (566 °C and 900 °C), at higher temperatures Pb and Cu in the gas phase were found, while Cr, Mn, Fe, Ni and Zn were condensed earlier. Pb was condensed between 560 °C and 900 °C, while part of Cu was not condensed and was still present as a lower temperature vapor.

According to the authors of [30], among the operation factors (temperature, heating rate, reaction time, etc.), temperature is the main factor in the redistribution of heavy metals. Moisture and Cl content are important, especially in high temperature thermal processes (combustion and gasification), because the authors found that the moisture content reduces the volatility of heavy metals, while the content of Cl causes them to volatilize. Thermally stable metals (Cr, Mn and Ni) are less volatile under typical conditions in the temperature range of 200–1100 °C during thermal processes and they are contained in residues. On the contrary, heavy metals with lower thermal stability (Hg, Cd, As and Pb) are susceptible to volatility.

The content of heavy metals in biomass ash presented in [32] was generally below the limits for fertilizers or soils. However, the significant variability in mineral and chemical composition of ash indicates that a comprehensive examination of ash samples is necessary to determine the possible scope of its application.

To investigate the effect of biomass and combustion temperature on the content of each of the analyzed elements in the ash samples, a two-way analysis of variance (two-way ANOVA) was carried out. The test results are summarized in Table 1.

**Table 1.** Results of two-factor analysis of variance (two-way ANOVA) for biomass (B), temperature (T) and biomass and temperature interaction (BxT).

Source of Variation	Df	Element							
		Cd		Cr		Cu		Fe	
		F	p-Value	F	p-Value	F	p-Value	F	p-Value
B	5	397.99	<0.001	14,612.49	<0.001	82,647.67	<0.001	22,833.15	<0.001
T	5	3323.72	<0.001	17,895.24	<0.001	9560.88	<0.001	22,962.55	<0.001
BxT	25	88.62	<0.001	340.49	<0.001	808.88	<0.001	791.78	<0.001

Source of Variation	Df	Ni		Pb		Zn	
		F	p-Value	F	p-Value	F	p-Value
		B	5	24735.82	<0.001	2778.71	<0.001
T	5	7187.77	<0.001	4464.35	<0.001	6640.38	<0.001
BxT	25	360.09	<0.001	95.06	<0.001	326.44	<0.001

Df is the number of degrees of freedom, F is the value of statistics F (statistics F of Fisher).

Based on the obtained results (Table 1), a significant impact of biomass, temperature and biomass and temperature interaction on the content of individual metals in ash was found (all *p*-values < 0.001).

The Tukey test examined detailed differences between means and determined homogeneous groups of average contents of individual trace elements in the biomass under study (Table 2). The average content of Cr, Cu, Fe, Ni and Zn for the raw materials tested differed significantly at the significance level of 0.05 (Table 2). For Cd, no significant differences were found between pine and willow. There was no significant difference in mean Pb content for miscant and willow.

As to temperature comparisons (Table 3), the Tukey test found significant differences for all the means comparisons at the significance level of 0.05.

**Table 2.** Results of detailed comparisons of average content of individual trace elements in the tested biomass with the Tukey test at the significance level of 0.05.

Biomass	Cd	Cr	Cu	Fe	Ni	Pb	Zn
	ppm						
Miscant	4.98	34.12	56.07	3474	18.86	7.51 <sup>a</sup>	503.50
Oak	5.23	42.24	250.61	3050	53.06	8.75	141.93
Pine	5.60 <sup>a</sup>	37.25	145.38	3188	47.84	9.41	265.05
Sunflower husk	5.93	67.76	284.50	3681	76.11	5.10	277.96
Wheat straw	4.30	50.23	54.36	3647	31.11	5.93	212.67
Willow	5.61 <sup>a</sup>	61.46	140.18	1238	97.92	7.56 <sup>a</sup>	601.39

The means marked with the same letter (in the column) do not differ significantly.

**Table 3.** Means for the determined temperatures.

Temperature	Cd	Cr	Cu	Fe	Ni	Pb	Zn
°C	ppm						
500	7.81	31.54	198.22	4386	34.38	10.06	558.44
600	6.45	38.73	184.08	3647	40.96	9.13	445.50
700	5.65	44.29	158.69	3308	50.65	7.90	381.17
800	4.49	48.60	146.64	2773	55.73	7.01	283.27
900	3.84	55.51	134.54	2304	67.22	5.36	218.54
1000	3.40	74.38	108.94	1858	75.94	4.80	115.58

The detailed differences between the means were also examined when considering the combination of biomass and temperature (Table 4). In the columns corresponding to the examined elements, the means that did not differ significantly are marked with the same letters. Different groups of

homogeneous (not significantly different) means were obtained for various elements. The key results presented in Table 4 are discussed below.

Comparing the average Cd content, a division into groups of means that did not significantly differ in similar or the same temperatures was obtained, e.g., the means obtained at the temperature of 1000 °C for different materials (marked a). These are the smallest means. Another homogeneous group are the means (marked with the letter b) corresponding to miscant and temperature 900 °C, oak and temperature 1000 °C, pine and temperature 1000 °C, sunflower husk incinerated at temperatures 900 and 1000 °C, wheat straw at temperatures 900 and 1000 °C as well as willow and temperature 1000 °C. Sunflower husk at 500 °C and wheat straw at 500 °C were significantly different from the other means (there are no letters denoting homogeneous groups).

In the Cr content, no significant differences were found between the means obtained for miscant and temperatures of 500 and 600 °C (letter a). The most similar in terms of Cr content were miscant and pine (letters b, d, and e); the most differences were found for sunflower husk, willow and oak (there are no letters denoting homogeneous groups).

Comparing Cu content, the most similarities were observed for wheat straw and miscant (letters a–d), and the most significant differences were found for sunflower husk, pine and oak.

There were no significant differences in the mean Fe contents in the samples of willow at lower temperatures (letters a and b). Fe contents in the samples were similar to pine and oak at 800 °C (letter g), pine and sunflower husk at 700 °C (letter i), and pine, wheat straw, and miscant at 900 °C (letter d). The most differences were found for willow, oak and wheat straw.

As to Ni comparison, there were no significant differences either for miscant and wheat straw (letters a–c) miscant and oak (letters c–e) or pine and oak (letters e, g, and j). The most differences concerned willow.

There were no significant differences for Pb content in wheat straw and sunflower husk samples burned at temperatures 1000 °C (letter a) and 900 °C (letter b) or in other temperatures (letters f, g, i, and j) and in willow, miscant and oak (letters e and m).

In terms of Zn content in sunflower husk and oak samples at temperatures 900 and 1000 °C (letters a–c), wheat straw and pine (letters f–h), no significant differences were obtained. The most significant differences were found for willow.

**Table 4.** Results of detailed comparisons of mean combinations of biomass and temperature with the Tukey test at the significance level of 0.05.

Biomass	Temperature	Cd	Cr	Cu	Fe	Ni	Pb	Zn
	°C							
Miscant	500	7.68 <sup>prs</sup>	25.70 <sup>a</sup>	58.77 <sup>d</sup>	5390 <sup>l</sup>	16.40 <sup>ab</sup>	9.69 <sup>op</sup>	716.00 <sup>o</sup>
	600	6.36 <sup>m</sup>	27.14 <sup>ab</sup>	58.55 <sup>d</sup>	4271 <sup>k</sup>	16.82 <sup>bc</sup>	9.36 <sup>o</sup>	616.67 <sup>n</sup>
	700	4.91 <sup>jk</sup>	30.99 <sup>c</sup>	57.24 <sup>cd</sup>	3781 <sup>j</sup>	18.67 <sup>bcd</sup>	7.60 <sup>lm</sup>	592.33 <sup>n</sup>
	800	4.12 <sup>efg</sup>	33.33 <sup>d</sup>	55.83 <sup>bcd</sup>	2803 <sup>e</sup>	18.73 <sup>bcd</sup>	7.42 <sup>kl</sup>	538.33 <sup>m</sup>
	900	3.65 <sup>bcd</sup>	37.11 <sup>e</sup>	54.74 <sup>bcd</sup>	2669 <sup>d</sup>	21.03 <sup>de</sup>	5.58 <sup>ef</sup>	402.00 <sup>ij</sup>
	1000	3.17 <sup>a</sup>	50.43 <sup>i</sup>	51.27 <sup>b</sup>	1928	21.49 <sup>e</sup>	5.43 <sup>e</sup>	155.67 <sup>d</sup>
Oak	500	8.26 <sup>t</sup>	22.41	307.00 <sup>i</sup>	4059	19.17 <sup>cde</sup>	12.21 <sup>s</sup>	300.33
	600	5.92 <sup>l</sup>	34.92	304.00 <sup>i</sup>	3665	35.08	11.18	251.00 <sup>h</sup>
	700	4.98 <sup>k</sup>	38.19 <sup>e</sup>	265.67 <sup>h</sup>	3534	50.37 <sup>g</sup>	9.90 <sup>pr</sup>	155.00 <sup>d</sup>
	800	4.85 <sup>ijk</sup>	40.20 <sup>f</sup>	242.00	3199 <sup>gh</sup>	62.38 <sup>i</sup>	7.86 <sup>m</sup>	67.26 <sup>c</sup>
	900	3.90 <sup>cde</sup>	44.18 <sup>g</sup>	220.33	2242	66.83 <sup>jk</sup>	5.94 <sup>fg</sup>	46.29 <sup>abc</sup>
	1000	3.45 <sup>ab</sup>	73.52	164.67	1603 <sup>c</sup>	84.56 <sup>l</sup>	5.38 <sup>e</sup>	31.69 <sup>ab</sup>
Pine	500	8.06 <sup>st</sup>	18.87	203.33	4250 <sup>k</sup>	21.69 <sup>e</sup>	12.91	429.67 <sup>kl</sup>
	600	7.16 <sup>op</sup>	28.30 <sup>b</sup>	196.33	3814 <sup>j</sup>	31.67 <sup>f</sup>	12.04 <sup>s</sup>	400.67 <sup>ij</sup>
	700	6.25 <sup>lm</sup>	32.61 <sup>d</sup>	150.67 <sup>g</sup>	3566 <sup>i</sup>	51.34 <sup>g</sup>	10.14 <sup>r</sup>	253.33 <sup>h</sup>
	800	4.49 <sup>ghi</sup>	36.88 <sup>e</sup>	134.33 <sup>f</sup>	3141 <sup>g</sup>	56.58	8.58 <sup>n</sup>	209.67 <sup>fg</sup>
	900	4.17 <sup>efgh</sup>	40.88 <sup>f</sup>	102.00	2591 <sup>d</sup>	59.49 <sup>h</sup>	6.74 <sup>ij</sup>	201.67 <sup>f</sup>
	1000	3.45 <sup>ab</sup>	65.95	85.63	1764	66.26 <sup>j</sup>	6.04 <sup>gh</sup>	95.30

Table 4. Cont.

Biomass	Temperature	Cd	Cr	Cu	Fe	Ni	Pb	Zn
	°C							
Sunflower husk	500	9.93	50.09 <sup>hi</sup>	357.67	5736	59.37 <sup>h</sup>	6.78 <sup>ij</sup>	647.33
	600	7.24 <sup>op</sup>	53.95	332.67	4200 <sup>k</sup>	61.77 <sup>hi</sup>	5.93 <sup>fg</sup>	411.67 <sup>jk</sup>
	700	6.57 <sup>mn</sup>	59.39 <sup>j</sup>	283.67	3572 <sup>i</sup>	65.71 <sup>j</sup>	4.89 <sup>cd</sup>	383.33 <sup>i</sup>
	800	4.88 <sup>ijk</sup>	69.76	263.33 <sup>h</sup>	2934 <sup>f</sup>	68.90 <sup>k</sup>	4.73 <sup>c</sup>	149.33 <sup>d</sup>
	900	3.62 <sup>bc</sup>	81.92	254.67	2859 <sup>ef</sup>	94.23 <sup>m</sup>	4.53 <sup>bc</sup>	53.97 <sup>bc</sup>
	1000	3.36 <sup>ab</sup>	91.47	215.00	2788 <sup>e</sup>	106.67	3.76 <sup>a</sup>	22.13 <sup>a</sup>
Wheat straw	500	5.42	32.25 <sup>cd</sup>	72.54	5315 <sup>l</sup>	14.17 <sup>a</sup>	8.52 <sup>n</sup>	335.67
	600	4.91 <sup>jk</sup>	43.60 <sup>g</sup>	57.94 <sup>d</sup>	4450	17.44 <sup>bc</sup>	7.01 <sup>jk</sup>	234.67 <sup>gh</sup>
	700	4.31 <sup>fgh</sup>	48.75 <sup>h</sup>	54.24 <sup>bcd</sup>	3944	28.49	6.46 <sup>hi</sup>	204.33 <sup>f</sup>
	800	4.04 <sup>def</sup>	51.29 <sup>i</sup>	53.03 <sup>bc</sup>	3226 <sup>h</sup>	31.13 <sup>f</sup>	5.93 <sup>fg</sup>	185.33 <sup>ef</sup>
	900	3.61 <sup>bc</sup>	57.46	46.48 <sup>a</sup>	2593 <sup>d</sup>	45.08	4.20 <sup>b</sup>	163.33 <sup>de</sup>
	1000	3.51 <sup>abc</sup>	68.02	41.96 <sup>a</sup>	2356	50.32 <sup>g</sup>	3.45 <sup>a</sup>	152.67 <sup>d</sup>
Willow	500	7.50 <sup>pr</sup>	39.93 <sup>f</sup>	190.00	1568 <sup>bc</sup>	75.51	10.23 <sup>r</sup>	921.67
	600	7.13 <sup>op</sup>	44.45 <sup>g</sup>	155.00 <sup>g</sup>	1485 <sup>ab</sup>	83.00 <sup>l</sup>	9.27 <sup>o</sup>	758.33
	700	6.90 <sup>no</sup>	55.80	140.67	1452 <sup>a</sup>	89.33	8.43 <sup>n</sup>	698.67 <sup>o</sup>
	800	4.55 <sup>hij</sup>	60.14 <sup>j</sup>	131.33 <sup>ef</sup>	1338	96.67 <sup>m</sup>	7.55 <sup>lm</sup>	549.67 <sup>m</sup>
	900	4.11 <sup>efg</sup>	71.53	129.00 <sup>e</sup>	871.00	116.67	5.16 <sup>de</sup>	444.00 <sup>l</sup>
	1000	3.50 <sup>abc</sup>	96.90	95.10	712.67	126.33	4.71 <sup>c</sup>	236.00 <sup>gh</sup>

The means marked with the same letter within the column do not differ significantly.

#### 4. Conclusions

The use of ash from biomass combustion for fertilizing purposes may be subject to restrictions due to the presence of heavy metals and other inorganic compounds that arise as a result of thermal-chemical reactions. A big problem is the variability of heavy metal concentrations in the ash resulting from differences in the properties of the biomass itself, which makes it impossible to indicate the only effective method of biomass conversion. It is therefore necessary to carry out effective monitoring of the heavy metals content in biomass ash to ensure that its use does not pose a threat to the environment.

The content of ash in the examined biomass was relatively low and typical for a given raw material regardless of the ash-forming temperature. With its increase, the density of the ash formed decreased, and for wood biomass this change was significant and exceeded 70–80%.

The content of heavy metal elements in the examined ash was not excessive and cannot be considered as potentially dangerous. As the ash-forming temperature increased, the content of Zn, Cd, Cu and Pb decreased, hence it can be inferred that at higher temperatures they went into the gas phase. Cr, Ni and Fe are thermally stable and less volatile metals, thus the ashes were enriched with them at increased ash-forming temperature.

The results can be used as a reference to environmental assessment and optimization of biomass combustion technology in low power boilers.

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