Study of potential availability of heavy metals to phytoremediation to use of fly ash from biomass combustion

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Abstract Fly ashes, formed as a result of burning biomass are a new class of by-products of combustion and due to the large variety of these materials their chemical composition has not been fully determined. Their use is limited, despite the fact that their production is increased.

The this work presents results of studies on the possibility of limiting the potential availability of Cu, Mn, Pb and Zn for plants by use of inorganic stabilizer - fly ash from biomass combustion. In this study was evaluated usefulness of fly ash from biomass to binding mobile fractions of heavy metals (Cu, Mn, Pb and Zn). The investigations executed using three extraction tests in which the use the following extraction solutions: 1 M HNO_3 – acid soluble forms (As), 0.05 M EDTA – bioavailability forms (Bio), 2.5% CH_3COOH – exchangeable forms (Ex). The values of following parameters such as: Mobility Index (MI), Contamination Factor (CF), Pollution Load Index (PLI), Geo – accumulation Index (I_{geo}) and Ecological Risk Index (RI) were definite and determined suitability test soil stabilizer. Furthermore, the multivariate statistical analysis was carried out.

It was found, that phytoremediation process using tested fly ash from biomass combustion can be applied to contaminated soil by heavy metals.

Keywords: biomass ash, heavy metals, FAAS

1. Introduction

Ecotoxicological condition of soil in the world is one of the most serious environmental problems, especially in relation to heavily urbanized and industrialized areas. According to a report on the environment condition prepared by the European Environment Agency in 2015, in Europe there were about 3 million areas which were a potential sources of emission of pollutants, especially heavy metals and mineral oils. In Poland, soil contamination occurs locally and applies primarily to industrial areas [Kabata-Pendias, 2011]. Nevertheless, it was found that in the vicinity of former and current sources of emissions an exceeding of established values for heavy metals, defined in the relevant legal acts, for example, Regulation of the Minister of Environment (Poland) or US EPA Standards (USA), takes place. The high toxicity of heavy metals, ability to accumulation and ease of penetration through biological membranes cause, that the heavy metals have a negative influence on various physiological processes occurring in microorganisms, plants, animals and humans [Kabata-Pendias, 2011]. To reduce the toxic effects of metals on living organisms, it is necessary to lower the bioavailability or reduce the contents of these elements in soil. This can be achieved by implementing physicochemical or biological methods. There is a wide range of physicochemical methods enabling reduction of bioavailability or removal of heavy metals from the soil. The most commonly described are: solidification [Aboulroos *et al.*, 2006; Chen *et al.*, 2009; Gollmann *et al.*, 2010; Voglar and Leŝtan, 2010], vitrification [Chou *et al.*, 2011; Kuo *et al.*, 2009], thermal extraction [Mulligan *et al.*, 2001a, b], chemical extraction of metals [Moon *et al.*, 2016], electrokinetic and electrochemical removal [Korolev, 2008; Mulligan *et al.*, 2001b; Suér *et al.*, 2003], lessivage or removal of topsoil [Kos and Leŝtan, 2004a, b; Zhang *et al.*, 2010]. They are relatively expensive, can lead to a greater toxic influence of heavy metals on living organisms, moreover, their use may cause changes in the structure and nutrients of soil.

In the remediation process of soils contaminated with heavy metals, noteworthy are minimally invasive remediation solutions (GRO - "gentle" remediation options) [Cundy *et al.*, 2013]. These include the phytoremediation methods, among others, phytoextraction and aided phytostabilization which seem to be the most promising strategies for remediation of areas contaminated with heavy metals [Koptsik, 2014; Lee *et al.*, 2014; Pavel *et al.*, 2014;]. Aided phytostabilization is a combination of phytostabilization with chemical immobilization of heavy metals with the use of various organic and inorganic materials called stabilizers, which are administered into the soil. They have a high sorption capacity, which enables them to bind the mobile fraction of heavy metals, and thus lower their bioavailability and toxicity. Examples of stabilizers used in the aided phytostabilisation process include: alkaline compounds – they are administered into the soil in the form of various calcium compounds, for example, $CaCO_3$, CaO, $Ca(OH)_2$, $CaMg(CO)_3$ [Lombi *et al.*, 2002; Paulose *et al.*, 2007; Verdugo *et al.* 2011]; their addition is not recommended for soils contaminated with Cr and Mn due to the high mobility of these elements [Koptsik, 2014]; phosphorus compounds e.g., hydroxyapatite [Guo *et al*., 2006; Kumpienie, 2010] or phosphates(V) calcium, ammonium, potassium and sodium [Nzihou and Sharrock, 2010] - their usage is recommended for the immobilization of Pb; hydrated iron oxides - for example, goethyt reduces the toxicity of arsenic in the soil [Hartley and Lepp, 2008], amorphous iron(III) oxide [Warren *et al*., 2003], hydrated manganese oxides, especially synthetic, i.e., cryptomelane and birnessite - for immobilizing lead [Sonmez and Pierzynski, 2005]; aluminosilicates, including in particular, clays [Hale and Küchnel, 1997] and zeolites [Shi *et al*., 2009], for example, clinoptilolite is one of the most effective molecular sieve capable of sorption of Cd, Pb, Zn, Cu and Pd. Its effectiveness supports the addition of calcium compounds [Sun *et al*., 2016]. Fly ash from the combustion of coal is an additive stabilizing heavy metals in the soil [Gatima *et al*., 2006; Gupta *et al*., 2002; Ram and Masto, 2014]. The best stabilizing effect, after the application of fly ash from the coal combustion of coal into the soil occurs in the case of contamination by heavy metals in the form of Cu, Pb, Zn and Ni cations [Ram and Masto, 2014].

In this paper, ash from the combustion of biomass was used as a stabilizer of heavy metals (Cu, Mn, Pb and Zn). It is a by-product (waste) received during the combustion of biomass, which is currently more widely used in the commercial power industry [CSOP Report]. The evaluation of usefulness of this stabilizer was based on defining its role in binding of the mobile fraction of heavy metals in soil under laboratory conditions. On this basis, the efficacy of aided phytoremediation in remediation of soil contaminated with Cu, Mn, Pb and Zn was evaluated.

2. Experimental

2.1. Materials

Analyzes were carried out with the use of ash from the combustion of biomass from CHP Arłamów (Poland). The experiment was performed under laboratory conditions on the experimental soil sampled from the surface layer (0 - 30 cm) in the area of Rzeszow University of Technology (Poland). The primary ash and soil samples for chemical analysis were dried at room temperature until to get air-dry state and then prepared for the analysis according to the procedure described in Polish Standard PN-77/G-04528-00.

2.2. Determination of total concentration of investigated metals

For the determination of the total content of investigated metals were prepared laboratory samples, respectively for soil and ash, then were mineralized in mixtures of concentrated acids (HF and $HClO_4$ for soil, HF and HCl for ash). Detailed description of mineralization procedures contained in works [Kalembkiewicz *et al*., 2008]. Determination of the concentrations of Cu, Mn, Pb, and Zn in solutions after mineralization were performed by flame atomic absorption spectrometer (PERKIN-ELMER 3100 Model (Shelton Instruments, CT USA) in conditions placed in Table 1.

2.3. Determination of mobile form of investigated metals

In order to determine the degree of mobility of Cu, Mn, Pb and Zn in the soil and ash from the combustion of biomass, 3 procedures of individual extraction with the use of the following extraction solution were applied: 0.05 M EDTA - bioavailability forms (Bio); 2.5% CH_3COOH - exchangeable forms (Ex); 1 M HNO_3 - determined forms soluble in acids (As). The procedure was identical, namely, into the weighed out, air-dry samples of ash or soil with mass 1.0000 (± 0.0001) g, 5 cm^3 of proper extraction solution was added and shaken on a laboratory shaker (Vibramax 100, Heidolph of Instruments, Germany) at speed v = 900 rpm for 24 hours. Then, by centrifugation and/or filtration through a filter paper for quantitative analyzes MN 616 (Macherey - Nagle, Germany), phasing was performed. Determination of the concentrations of Cu, Mn, Pb, and Zn in solutions from extraction were performed by flame atomic absorption spectrometer PERKIN-ELMER 3100 Model (Shelton Instruments, CT USA) in conditions placed in Table 1.

2.4. Research of the possibility of limiting the availability of the metals by the use of biomass ash

Analyzes of the possibility of limiting the availability of investigated metals were carried out by adding, into the soil, biomass ash in an amount of 5% of weight in relation to the initial weight of the soil sample. After mixing the samples were left for 3 weeks at room temperature in order to stabilize their properties. Then the soil with ash was subjected to extraction procedure in order to determine the mobile forms of Cu, Mn, Pb and Zn. Conditions and extraction process were described in detail in point 2.3.

Table 1. The conditions of determination of selected metals by FAAS method

Parametr	Cu	Mn	Pb	Zn
Wavelength [nm]	324.8	279.5	217.0	213.9
Sensivity [mg/dm^3]	0.45	0.052	0.19	0.084
Spectral width slit [nm]	0.7	0.2	0.7	0.7
Concentration of standard solutions [mg/cm^3]	2.0, 4.0, 5.0	2.0, 2.5, 6.0, 12.0	9.0, 20.0	1.0, 3.0, 5.0, 6.0
Flow rate of gas [dm^3/min]	0.8 – 1.0			

2.5. Analysis of results

On the basis of results, the values of the following parameters were calculated:

Mobility Index (MI) - is defined as the percentage of the mobile forms of element in different environmental objects [Kumar *et al*., 2009]. This degree was calculated from the following relationship:

$$MI_{(Me)} = \frac{[Me]}{[Me]_{experim.}} \cdot 100\%$$

where: $MI_{(Me)}$ – degree of mobility of particular element, %; [Me] – concentration of metal in mobile forms, mg/kg; $[Me]_{experim.}$ – total concentration of metal, mg/kg.

Contamination Factor (CF) – is defined as the quotient of the concentrations of the different metals in the soil with addition of stabilizer and concentrations of these metals in the soil experimental [Ghannem *et al*., 2016]. Contamination factor was calculated from following formula:

$$CF_{(Me)} = \frac{[Me]_{stab.}}{[Me]_{experim.}}$$

where: $CF_{(Me)}$ – contamination factor for particular element; $[Me]_{stab.}$ – concentration of metal in soil with addition of stabilizer, mg/kg; $[Me]_{experim.}$ – total concentration of metal in experimental soil, mg/kg.

The values of the contamination factor (CF) were interpreted as follows:

- if CF < 1 – there is low level of impurities,
- if 1 < CF < 3 – there is moderate level of impurities,
- if 3 < CF < 6 – there is high level of impurities
- if CF > 6 – there is very high level of impurities

[Ghannem *et al*., 2016].

Pollution Load Index (PLI) - is defined as the square root of n-the degree of the pollution factor for individual environmental objects or heavy metal [Ghannem *et al*., 2016]. This index is calculated from the following relationship:

$$PLI = \sqrt[n]{CF_1 \cdot CF_2} \cdot ... \cdot CF_n$$

where: PLI – pollution load index; CF_n – pollution factor for individual environmental object.

If PLI > 1 - this means that there is contamination by heavy metals in individual object, whereas if PLI <1 - there is no contamination of heavy metal [Ghannem *et al*., 2016].

Geo – accumulation Index (I_{geo}), were calculated from following equation:

$$I_{geo} = \log_2\left(\frac{[Me]_{stab.}}{1,5 \cdot [Me]_{experim.}}\right)$$

where: I_{geo} – geo – accumulation index; $[Me]_{stab.}$ – concentration of metal in soil with addition of stabilizer, mg/kg; $[Me]_{experim.}$ – total concentration of metal in experimental soil, mg/kg [Ghannem *et al*., 2016].

Geo – accumulation index includes seven classes described below [Ghannem *et al*., 2016]:

- class 0 – no contamination: $I_{geo} \leq 0$,
- class 1 – low contamination: $0 < I_{geo} < 1$,
- class 2 – moderate contamination: $1 < I_{geo} < 2$,
- class 3 – moderate to high contamination: $2 < I_{geo} < 3$,
- class 4 – high contamination: $3 < I_{geo} < 4$,
- class 5 – high to very high contaminatio: $4 < I_{geo} < 5$,
- class 6 – very high contamination: $I_{geo} > 5$.

Ecological Risk (Index, RI) - is the sum of the factors involved in the potential threat environmental objects by heavy metals [Hu *et al*., 2013; Chai *et al*. 2016]. Ecological Risk is calculated from formula:

$$RI = \Sigma E_{(Me)}$$

where: $E_{(Me)}$ – single risk factor for the metal defined by the equation below as:

$$E_{(Me)} = T_{(Me)} \cdot CF_{(Me)}$$

where: $T_{(Me)}$ – toxic agent response for the metal, the value for Cu, Mn, Pb and Zn are successively: 5, 1, 5, and 1; $CF_{(Me)}$ – contamination factor for metal [Hu *et al*., 2013; Chai *et al*. 2016].

2.6. Statistical analysis

The statistical analysis of the obtained results was performed based on the Pearson linear correlation coefficient and hierarchical cluster analysis. For this Statistica 12.5 program was used.

3. Results

3.1. Determination of total concentration of investigated metals

The presence of heavy metals in the soil is generated by two essential sources, natural and anthropogenic. In assessing the degree of contamination of the soil by particular metal we should take account of its natural content in the bedrock, and the content related to human activity. Execution of mineralization allowed the determination of the total content of the investigated metals in the soil and biomass ash. The results are presented in Table 2.

3.2. Determination of mobile form of investigated metals

The obtained results of determination of the different mobile forms, including bioavailability (Bio), exchangeable (Ex) and acid soluble (As) forms of Cu, Mn, Pb and Zn in investigated samples, i.e. experimental soil, biomass ash and soil with addition of ash are presented in Table 3.

Table 2. Total concentration of investigated metals in soil and biomass ash (n = 5, p = 95%)

Metal	Content of metal [mg/kg]	
	Experimental soil	Biomass ash
Cu	29.99 (± 0.0)	37.67 (± 1.88)
Mn	375.18 (± 35.85)	3600.0 (± 100.0)
Pb	96.85 (± 5.03)	90.23 (± 4.51)
Zn	113.29 (± 39.86)	73.8 (± 3.69)

Table 3. The content of mobile form of investigated metals in soil, biomass ash and in soil with addition of ash (n = 5, p = 95%)

Metal	Content of metal [mg/kg]		
	Experimental soil	Biomass ash	Soil with addition of ash
Cu (Bio)	4.99 (± 0.01)	< l. d.	10.35 (± 3.85)
Cu (Ex)	5.0 (± 0.01)	< l. d.	15.75 (± 3.25)
Cu (As)	9.99 (± 0.01)	25.11 (± 0.01)	51.25 (± 0.85)
Mn (Bio)	< l. d.	< l. d	12.76 (± 1.98)
Mn (Ex)	< l. d.	< l. d	30.75 (± 2.54)
Mn (As)	317.83 (± 30.9)	239.88 (± 33.86)	61.49 (± 2.97)
Pb (Bio)	19.19 (± 15.18)	< l. d	1.17 (± 0.85)
Pb (Ex)	45.98 (± 6.8)	< l. d	15.0 (± 0.75)
Pb (As)	27.48 (± 7.96)	59.37 (± 2.97)	103.58 (± 5.18)
Zn (Bio)	< l. d.	16.92 (± 0.85)	23.38 (± 6.88)
Zn (Ex)	< l. d.	22.28 (± 1.14)	35.43 (± 3.87)
Zn (As)	15.99 (± 6.8)	23.59 (± 1.18)	43.53 (± 5.12)

l. d. – limit of detection

4. Disccusion

4.1. Analysis of results

Adding of additives into the soil during the aided phytostabilization process aims at transforming ionic forms and readily soluble metal compounds into sparingly or high sparingly soluble forms. This is occur by the following processes: sorption of metals, metal precipitation from solution, change in oxidation state of metals, humification, formation of secondary minerals containing metals. As a result, there is a reduction in leaching of metals and their absorption by plants, microorganisms, invertebrates and vertebrates [Chaney *et al*., 2010]. In addition, an inorganic stabilizer, which is used in the aided phytostabilization process, should meet the following criteria: 1) should effectively immobilize metals; 2) should be cheap and easy to obtain or produce; 3) should be non-toxic to plants and even stimulate their growth; 4) should be devoid of any negative influence on any environmental components subjected to phytostabilization [Berti and Cunningham, 2000]. Taking into account the above criteria and the results values of the following parameters were calculated: Mobility Index (MI), Contamination Factor (CF), Pollution Load Index (PLI), Geo – accumulation Index (I_{geo}) and Ecological Risk Index (RI). They are presented in Table 4 and Figure 1 and 2. On the basis of values of degrees of mobility of the individual elements, it was estimated that the degree of mobility of Mn (84.71%) and Pb (96.49%) in the experimental soil, significantly decreases after application of biomass ash and amounts to 6.66 and 65.8%, respectively. However, the mobility of Zn for soil containing ash (85.08%) increases in comparison to the soil without the addition of this stabilizer (14.11%). In turn, the degree of mobility of Mn, in all investigated samples, is maintained at the same level, i.e., approximately 67.6% (Fig. 1). By analyzing the results presented in Table 4, it was found that the concentration of Mn, which contaminates soil with addition of ash from the combustion of biomass is at a high level. Degree of contamination of Cu, Pb, Zn can be described as equable. The value of geoaccumulation index for Mn indicates a fluctuation from moderate to high contamination of soil with the addition of ash. I_{geo} values obtained for Cu, Pb and Zn confirm low levels of contamination for soil with the addition of ash from the combustion of biomass. The obtained value of Pollution Load Index (PLI) for soil with the addition of ash informs about the presence of contamination with Cu, Mn, Pb and Zn in the analyzed sample. Analysis of results (Fig. 2) indicates that the highest concentration among the investigated metals in the experimental soil containing ash from the combustion of biomass, in relation to the potential ecological threat to the surface layer of soil, has Cu (34.04%), Mn (31.93%), Pb (29.07%), and Zn (4.97%). The total value of the.

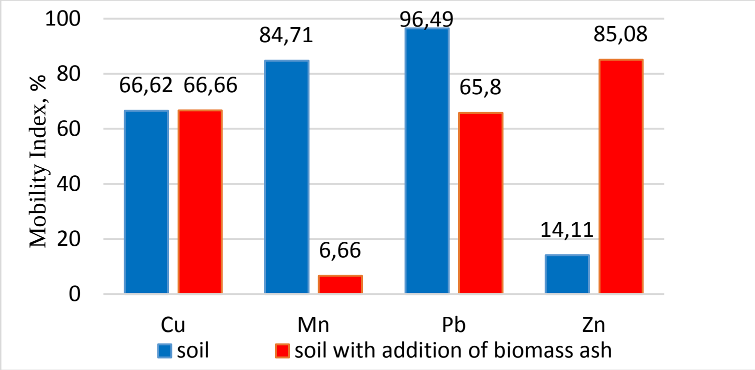

Figure 1. The degree of mobility [%] investigated heavy metals in the soil and experimental soil and in soil with addition biomass ash

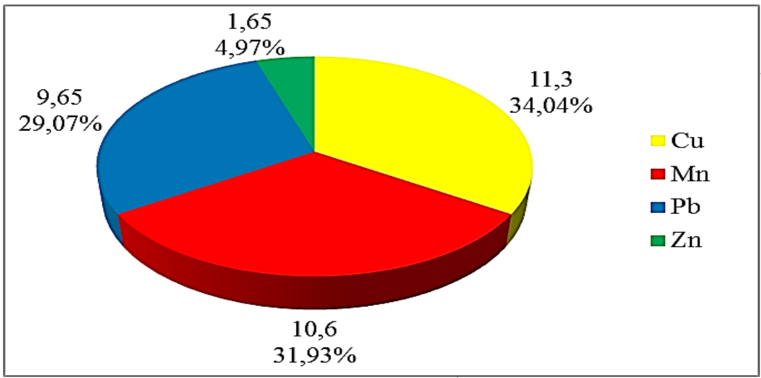

Figure 2. The share of the investigated metals in the soil with addition of ash in relation to the potential environmental risk of the surface layer of soil

Table 4. The summary of the designated parameters for soil with the addition of biomass ash

Metal	MI [%]	CF	Degree of contamination	PLI	I_{geo}	Geo – accumulation Index
Cu	66.66	2.26	moderate	2.96	0.58	low contamination
Mn	6.66	10.6	very high		2.82	moderate to high
Pb	65.8	1.93	moderate		0.37	low contamination
Zn	85.08	1.65	moderate		0.14	low contamination

ecological risk index for soil with the addition of biomass ash is 33.2

4.1. Statistical analysis

A hierarchical cluster analysis was performed in order to analyze the chemical affinity between the analyzed metals in the biomass ash. This resulted in obtaining an dendrogram presented in Fig. 3. On its basis, the presence of two groups was noticed. First group included copper and zinc – which are closely linked, and the second group included manganese and lead.

In order to determine the correlation between analyzed metals in the experimental soil, with the addition of biomass ash, a correlation matrix was prepared (Table 5). On the basis of Pearson's correlation coefficients, in the investigated sample, a significant correlation between the content of Mn and Pb (R = 0.997), Mn and Zn (R = 0.998), Pb and Zn (R = 0.988) was noticed. This means that the increase of Mn content in the soil containing ash entails an increase of the Pb and Zn content, while the increase of Pb content is related to the increase of Zn content.

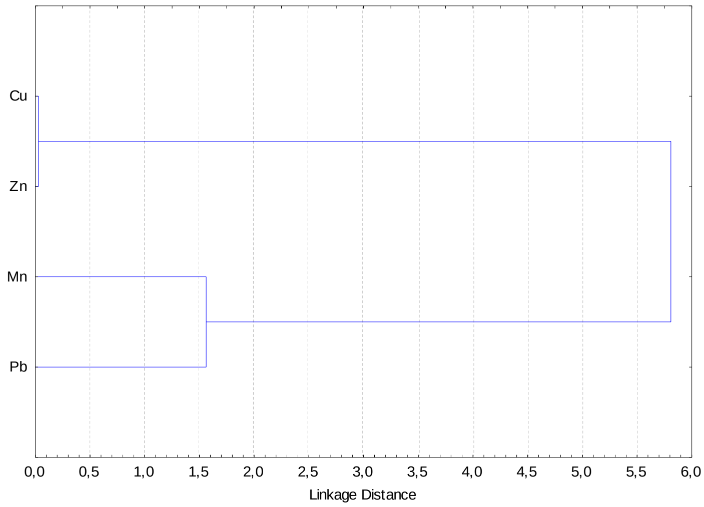

Figure 3. Dendrogram representing the cluster analysis investigated metals in the biomass ash

Table 5. The summary of Pearson correlation coefficients for the tested metals in the soil with the addition of biomass ash

	Cu	**Mn**	**Pb**	**Zn**
Cu	1			
Mn	-0.581	1		
Pb	-0.647	0.997*	1	
Zn	-0.524	0.998*	0.988*	1

* - significance level $\alpha = 0.05$

5. Conclusion

Ash from the combustion of biomass is a cheap and easy to produce material. It has immobilizing properties in relation to the manganese and lead. Immobilization of metal occurs within alkalization of soil, precipitation of insoluble phases and sorption of metals after complexation processes. Influence of biomass ash on soil is detrimental, nevertheless it depends mainly on the analyzed metal. Implementation of fly ash from the combustion of biomass in the process of aided phytostabilisation is a cheap and effective method of phytoremediation with respect to the manganese and lead. However, further analyzes are crucial in order to determine the influence of this stabilizer on the growth and development of tested plants. Their results will help explicitly evaluate the suitability of fly ash from the combustion of biomass in the aided phytostabilization process.

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