

# Ameliorative effect of phyto-ash and biogas digestate improvers on soil contaminated with heavy metals

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**Keywords:** soil, heavy metals, remediation, phyto-ash, biogas digestate, improvers.

**Abstract:** Nine phyto-ashes from the biomass combustion of birch (*Betula*), oak (*Quercus*), red oak (*Quercus rubra*), horbeam (*Carpinus*), pine (*Pinus sylvestris*), poplar (*Populus*), maple (*Acer*), oilseed rape straw (*Brassica napus*) and wheat straw (*Triticum aestivum*) were blended with a biogas digestate at 1:1 mass ratio to give nine organic-mineral soil improvers. The concept of the research was to outline an eco-friendly and low cost soil improver for remediating degraded lands. These (i.e. phyto-ashes, improvers and the biogas digestate) were applied (0, 5, 10, 20, 40 t·ha<sup>-1</sup>) to a soil metallurgically contaminated with Cu, Zn, Pb and Cd. Of several tested parameters, pH changes revealed that organic-mineral soil improvers may efficiently replace (linear R<sup>2</sup>>0.90\*\*\*\*, P<0.001) phyto-ashes in soil remedial goals. Buffering properties expressed by the cation exchange capacity (CEC) improved progressively: 29, 52, 71, 100% (phyto-ash treatments) and: 18, 37, 44, 73% (improvers treatments) for the rates 5, 10, 20, 40 t·ha<sup>-1</sup>, respectively as referred to the control CEC. The Dynamic Remediation Efficiency (DRE) indices for Cu, Zn, Pb, Cd revealed metal-specific geochemical reactions initiated by phyto-ashes, improvers and biogas digestate. The rates 5.0–10.0 t·ha<sup>-1</sup> for phyto-ashes and about 20 t·ha<sup>-1</sup> for improvers [1:1, i.e. Phyto-ash:Biogas digestate] are recommended. For biogas digestate, the rates 10–20 t·ha<sup>-1</sup> were found more efficient.

## Introduction

The incineration of plant biomass generates residues, namely phyto-ashes, which are probably the earliest ever known mineral fertilizers in the human history. With respect to plant species and the industrial process with temperature fluctuating generally within the range of 600–900°C (Diatta and Kowalski 2017, Kowalczyk-Juśko 2009), the physical and chemical composition of phyto-ashes may differ significantly (Xiao et al. 2011). These factors decide about the quality and usefulness for further application of phyto-ashes (Pitman 2006, Stankowski and Maciorowski 2011).

In the USA, phyto-ashes originate from the electrical power plants and paper industry, where 90% are directed to landfilling. However, in the North-East states, 80% are recycled into soils and 5% subjected to composting with sewage sludge. The remaining 15% are disposed off at landfill sites. These practices have led to reducing by 66% the costs generated by landfilling in the states like Maine and New Hampshire (Campbell 1990, Vance 1996).

Industrial phyto-ash in Poland (designated by the code 10 01 03 for recycling according to the R10 process) is closely related to the availability of plant biomass as reported in the “Energetic Politics of Poland” by 2030 (Fijałkowska and Styszko 2011, Stolarski et al. 2013). The Ordinance of the Minister of Environment (December 20<sup>th</sup>, 2005) for the emission standards from installations (Dz.U. No 260 pos.

2181), defines the biomass as a product consisting entirely or partly of plant substances. They originate from forestry and agriculture, and are combusted for energy recovery.

The application of phyto-ashes for alleviating soil acidity and simultaneously fertilizing soils was being progressively desisted as a result of emerging of aglime, potassium salts on the eve of the 20<sup>th</sup> century (Maltas and Sinaj 2014). The systematic reduction of non-renewable mining sources, for instance phosphate and potassium reserves, is the driving force for re-exploring back the remediative potential of phyto-ashes. Their use for agriculture, silviculture and degraded soils may be possible only after proper recycling and should be strictly supervised (Ciesielczuk et al. 2011, Vassilev et al. 2013).

The alkalinity (reactivity based pH) of phyto-ashes is one of the most critical parameters, which deserves attention. Its acid neutralizing capacity (ANC) is referred to calcium carbonate (CaCO<sub>3</sub>) equivalent (fixed for 100%). According to Hébert and Breton (2008), pure phyto-ashes recorded ANC of 115% (as compared to CaCO<sub>3</sub>), but the addition of tree bark slowed it to 64%. Therefore, this practice may shape and slow down the high ash alkalinity to eco-friendly less reactive components (soil improvers). The net progress in waste management (Circular Economy Package 2018) as well as the Ordinance of the Polish Minister of Environment (January 23<sup>th</sup>, 2015) on the R10 recycling process in force should initiate such opportunity, where recycled products are expected to be profitable to agriculture and improve the environment as well.

Recycling concerns also biogas digestates resulting from anaerobic digestion of plant biomass as well as biowastes such as animal manures (Sandars et al. 2003, Voca et al. 2005). They are generally rich in plant nutrients, hence their application back on lands for crop growth. This practice is intended to improve soil fertility and simultaneously reduce the use of mineral fertilizers, resulting further in the protection of agricultural and water ecosystems from excess of nitrogen and phosphorus (Commission of the European Communities 1991, Wiśniewski et al. 2015).

One of the tasks is to optimize the recycling of phyto-ashes and anaerobic digestates, as both residues contain different amounts of plant nutrients. Opportunities should be given to this process, where the driving force sounds as “Dilution is the solution”, (Diatta and Kowalski 2017). Therefore, the recycled components (organic-mineral, basically) used as soil improvers may offer a promising win-win opportunity in crop production and preventing adverse environmental impacts of waste disposal (Garg et al. 2005) and also act as remediative agent for degraded or marginal soils (Diatta and Chudzińska 2009).

The mobility, bioavailability and toxicity of heavy metals depend strongly on their chemical speciation and soil properties (Gupta et al. 1996). By raising the pH and simultaneously improving soil capacity, most of metals are immobilized (Basta and McGowen 2004, Bradshaw 2000, Ciesielczuk et al. 2014). The efficiency of this process is based on interactions between soil and additives (for instance organic-mineral components, as in the case of the current study), which lead to the emergence of specific equilibria controlled by sorption, precipitation and complexation reactions (Madejón et al. 2006). Ameliorative effects of phyto-ashes and biogas digestates on soil contaminated with heavy metals are thought to proceed similarly.

The paper focuses on the evaluation of nine phyto-ashes from birch (*Betula*), oak (*Quercus*), red oak (*Quercus rubra*), horbeam (*Carpinus*), pine (*Pinus sylvestris*), poplar (*Populus*), maple (*Acer*), oilseed rape straw (*Brassica napus*), wheat straw (*Triticum aestivum*) and a biogas digestate for their remediative potentials on a soil contaminated with Cu, Zn, Pb and Cd. Specifically, phyto-ashes and biogas digestate recycled (blended) components were investigated as organic-mineral soil improvers in inactivating heavy metals in contaminated soils. Recommendations have been formulated.

## Materials and methods

### Experimental design

The composite soil (40.0 kg) was made of 50 single samples mixed thoroughly (10 sampling sites  $\times$  5 single soil samples collected like a five on a dice with 15 m distance from the central point) and consisting of 0.80 kg per sample. They were collected from the area located at the south-eastern side with respect to the Miasteczko Śląskie zinc and lead smelter (N 51°41'03" and E 15°57'12"). The soils at this location were the most impacted by the smelter, since western winds dominate. Soils were sampled at the depth of 0–30 cm (by using a bucket auger) at 500–1500 m away from the smelter. The composite soil was dried at room temperature, next passed through a 2 mm mesh sieve and then stored for further experimental use.

### Physical and chemical analysis of the soil

The composite soil was tested for pH, potentiometrically in an aqueous and 1 mole KCl dm<sup>-3</sup> slurry at the ratio 1:2.5 (Polish Standard 1994). The content of oxidisable organic carbon was assayed according to the method described by Wang et al. (2012), whereas the effective cation exchange capacity (CEC<sub>ef.</sub>) was evaluated first by extracting Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> with 1 mole CH<sub>3</sub>COONH<sub>4</sub> dm<sup>-3</sup> (pH 7.0) and then by summing these ions along with hydrolytic acidity (Hazelton and Murphy 2007). Since heavy metals sorption as well as retention could be expected as a result of the application of phyto-ashes, soil improvers and biogas digestate, therefore the soil used in the current trial was submitted to the determination of the specific surface area (SSA) by using the EGME (Ethylene Glycol Monoethyl Ether) method, (Carter et al. 1986, de Jong 1999). Soil characteristics are listed in Table 1.

### Determination of total copper, zinc, lead and cadmium content in the soil

The total contents of Cu, Zn, Pb and Cd in soils were assayed according to the ISO 11466 procedure (International Standard 1995). Air-dried samples (1.00  $\pm$  0.001 g) were weighed into a glass Erlenmeyer flask and 15 cm<sup>3</sup> of *aqua regia* (concentrated nitric acid to concentrated hydrochloric acid as 1:3 ratio) was added. Next, the mixture was heated on a sand-bath at 140°C for 2 hours under reflux. After cooling, it was filtered through filter paper into 15 cm<sup>3</sup> test tubes and filled up to the mark with bidistilled water.

**Table 1.** Selected physical and chemical parameters of the soil used in the pot trial

Parameter	Unit	Value
Sand	g·kg <sup>-1</sup>	680
Silt		200
Clay		120
C <sub>org.</sub> <sup>1</sup>		11.6
pH <sub>H<sub>2</sub>O</sub>	–	6.8
pH <sub>KCl</sub>		5.7
SSA <sup>2</sup>	m <sup>2</sup> ·g <sup>-1</sup>	13.5
CEC <sub>ef.</sub> <sup>3</sup>	cmol <sub>(+)</sub> kg <sup>-1</sup>	11.2

<sup>1</sup> Organic carbon, <sup>2</sup> Specific surface area, <sup>3</sup> Effective cation exchange capacity

### Reactive forms of Cu, Zn, Pb, Cd

Soil samples (5.00 g) were weighted into 50 cm<sup>3</sup> PE tubes and 20 cm<sup>3</sup> 0.11 mole CH<sub>3</sub>COOH dm<sup>-3</sup>, pH 3.0 were added. The mixture was shaken on a rotative shaker (120 rpm) for one hour and next filtered through a filter paper into 15 cm<sup>3</sup> test tubes. This test represents the first fraction (with modification) of the 4-step BCR fractionation method (Sutherland and Tack 2002). The amounts of metals determined by this test are considered as potentially soluble in the soils, hence expressed as „reactive”.

### Bioavailable forms of Cu, Zn, Pb, Cd

The test used for characterizing the *bioavailable* forms of Cu, Zn, Pb and Cd is 0.10 mole NaNO<sub>3</sub> dm<sup>-3</sup> which was applied at the ratio 1:2 (Gupta and Hani 1989). Therefore, 10.0 grams of the soils were weighted into 50 cm<sup>3</sup> PE tubes and 20 cm<sup>3</sup> of the chemical test were added. The mixture was shaken on a rotative shaker (120 rpm) for one hour, left to equilibrate for one hour and then filtered through a filter paper into 15 cm<sup>3</sup> test tubes.

All extractions were replicated twice. The concentrations of Cu, Zn Pb and Cd were determined by atomic absorption spectrometry (AAS), (Varian 250 Spectra plus). The relative standard deviation (RSD) was calculated from pooled data for applied methods. In the precision test, the average RSD (%) for all metals in particular tests (i.e. total, reactive and bioavailable forms) ranged from 0.90 to 15.6%. The accuracy of the total metal contents was determined using a reference material [Estuarine sediment 277 CRM certified by the Bureau

Community of Reference (BCR), Brussels, Belgium]. Metals extracted by the chemical tests are summarized in Table 2.

### Chemical characteristics of investigated materials

#### Phyto-ashes

In total, nine (9) phyto-ashes have been tested in the current study. The wood with barks as well as the straw of crop plants were incinerated at 600°C for 4 hours in a muffle furnace (Xiao et al. 2011). The recovered ashes are listed below:

- 7 wood ashes, namely: birch (*Betula*), oak (*Quercus*), red oak (*Quercus rubra*), horbeam (*Carpinus*), pine (*Pinus sylvestris*), poplar (*Populus*), maple (*Acer*),
- 2 crop plant ashes: wheat (*Triticum aestivum*), oilseed rape (*Brassica napus*).

The contents of some elements in the relevant ashes are illustrated in Fig. 1 (CaO), and Fig. 2 (SiO<sub>2</sub>). Trace elements i.e., Cu, Zn, Pb and Cd are listed in Table 3.

#### Biogas digestate

The product tested in this study was supplied from a biogas power plant in the form of dry-darkish granules (1.0–1.5 mm). The biogas digestate was produced from maize biomass. The chemical analysis (Table 4) revealed a low N and Ca contents as well as heavy metals (Pb and Cd), too.

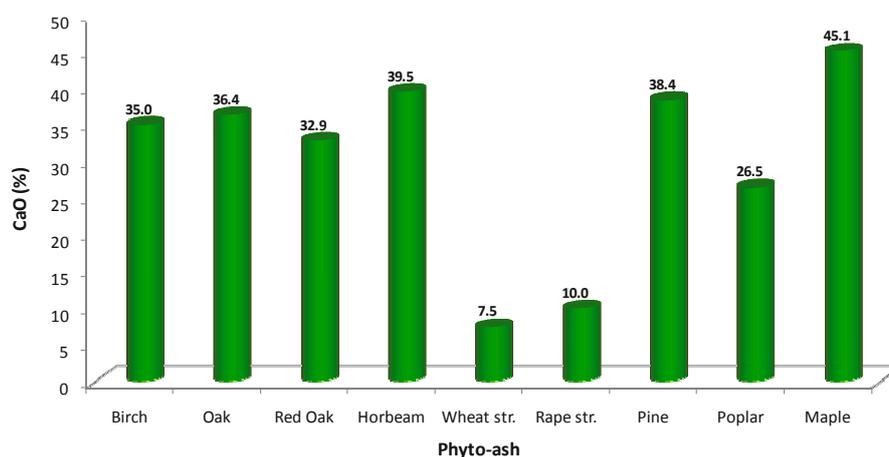
#### Organic-mineral soil improvers and pot trial

The concept of the current paper was verified by elaborating organic-mineral soil improvers on the basis of the particular phyto-ashes and the biogas digestate at the mass ratio 1:1

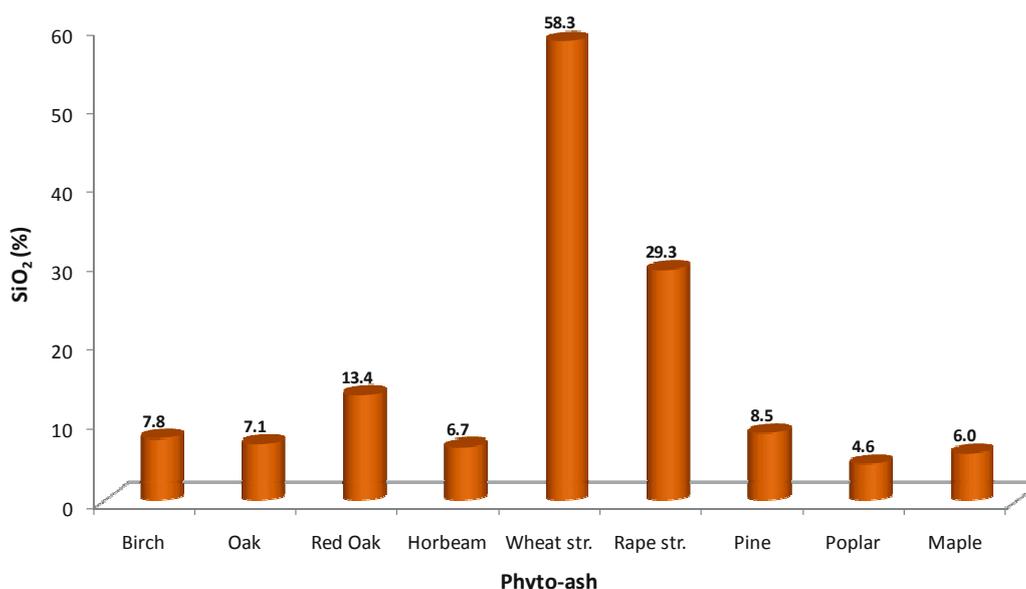
**Table 2.** Total content, reactive and bioavailable forms of heavy metals of the tested soil

Heavy metal	Total content <sup>1</sup> ( <i>Aqua regia</i> )	Reactive forms <sup>2</sup> (0.11 mole CH <sub>3</sub> COOH dm <sup>-3</sup> )	Bioavailable forms <sup>3</sup> (0.10 mole NaNO <sub>3</sub> dm <sup>-3</sup> )
	mg·kg <sup>-1</sup>		
Cu	377.8	25.4	0.95
Zn	936.5	315.3	44.6
Pb	667.2	17.4	0.08
Cd	17.4	5.1	0.60

<sup>1</sup> ISO 11466 procedure (International Standard 1995), <sup>2</sup> Sutherland and Tack (2002), <sup>3</sup> Gupta and Hani (1989).



**Fig. 1.** Content of CaO of the particular phyto-ashes (Wheat str. – wheat straw; Rape str. – oilseed rape straw)



**Fig. 2.** Content of SiO<sub>2</sub> of the particular phyto-ashes (Wheat str. – wheat straw; Rape str. – oilseed rape straw)

**Table 3.** Content of trace elements of tested phyto-ashes and official regulations (Limits)\*

No	Phyto Phyto-ash	Cu	Zn	Pb	Cd
		mg·kg <sup>-1</sup>			
1	Birch ( <i>Betula</i> )	143	2328	50	6.0
2	Oak ( <i>Quercus</i> )	197	255	34	6.0
3	Red Oak ( <i>Quercus rubra</i> )	233	262	63	9.0
4	Horbeam ( <i>Carpinus</i> )	160	158	32	3.0
5	Wheat straw ( <i>Triticum estivum</i> )	33	299	28	2.0
6	Rape straw ( <i>Brassica napus</i> )	19	136	5	1.0
7	Pine ( <i>Pinus sylvestris</i> )	143	604	32	7.0
8	Poplar ( <i>Populus</i> )	61	334	72	4.0
9	Maple ( <i>Acer</i> )	97	173	39	1.0
–	* Ordinance of July 10, 2007 for Fertilizers and Fertilization (Dz.U. Nr 147 poz. 1033)	–	–	140	50

**Table 4.** Chemical composition of the biogas digestate used in the study

pH <sub>H2O</sub>	Dry matter	Total N	CaO	Cu	Zn	Pb	Cd
–	%			mg·kg <sup>-1</sup>			
7.6	75	0.50	0.55	7.3	48.2	3.6	0.27

(Table 5). Before blending both substrates, an acidic (pH = 4.6) biogas effluent (from the digestate used for producing dry-darkish granules), previously filtered, was spray-added to all phyto-ashes for lowering their high reactivity (pH) in order to prevent possible losses of nitrogen. The ratio of the effluent to phyto-ashes was as 20 cm<sup>3</sup> to 50 g of ash, respectively.

The pot trial was carried out in 2016. The composite soil, i.e., 0.80 kg was weighted in triplicate to PE pots and equivalent rates, i.e., 0, 5, 10, 20 and 40 t·ha<sup>-1</sup> of phyto-ashes, biogas digestate and soil improvers were added. The moisture level was kept at 75% FWHC (Field water holding capacity)

and the incubation was run for 150 days at ambient temperature 19–22°C. Soil samples for evaluating the ameliorative and remediative effects of these amendments were collected at the end of the incubation period, dried at room temperature, passed through a 1.0 mm mesh sieve and next stored in PE bags.

#### *Evaluation of the remediation efficiency and Cu, Zn, Pb, Cd inactivation*

The physical and chemical features of amendments (phyto-ashes, biogas digestate, soil improvers) investigated in the current trial differed significantly, hence their reaction in the

**Table 5.** Elaboration of the organic-mineral soil improvers on the basis of phyto-ashes and biogas digestate

No	Phyto-ash from	Biogas digestate	Phyto-ash	Organic-mineral soil improver
	Ratio 1:1		pH <sub>H<sub>2</sub>O</sub>	
1	Birch ( <i>Betula</i> )	Biogas digestate (pH = 7.6)	13.2	9.8
2	Oak ( <i>Quercus</i> )		12.9	8.9
3	Red Oak ( <i>Quercus rubra</i> )		13.4	8.7
4	Horbeam ( <i>Carpinus</i> )		13.2	9.0
5	Wheat straw ( <i>Triticum aestivum</i> )		11.5	7.8
6	Rape straw ( <i>Brassica napus</i> )		12.1	8.4
7	Pine ( <i>Pinus sylvestris</i> )		13.4	9.7
8	Poplar ( <i>Populus</i> )		13.1	9.8
9	Maple ( <i>Acer</i> )		13.6	10.0

soil will result in respective dynamic geochemical alterations and simultaneous amelioration process. Since the soil was contaminated with Cu, Zn, Pb, Cd, therefore the evaluation of metal inactivation efficiency became of prime importance. This process was undertaken by using chemical tests, which extracted the amounts of Cu, Zn, Pb, Cd expressed as reactive (0.11 mole CH<sub>3</sub>COOH dm<sup>-3</sup>, pH 3.0; Sutherland and Tack 2002) and bioavailable (0.10 mole NaNO<sub>3</sub> dm<sup>-3</sup>; Gupta and Hani 1989). The latter ones are in geochemical equilibrium, hence the calculation of the Dynamic Remediation Efficiency (DRE) as reported below (Authors):

$$DRE (\%) = \frac{(Reac_{Cu, Zn, Pb, Cd} - Bio_{Cu, Zn, Pb, Cd}) \cdot 100}{Reac_{Cu, Zn, Pb, Cd}}$$

where,

$Reac_{Cu, Zn, Pb, Cd}$  expresses the amounts of Cu, Zn, Pb and Cd extracted by 0.11 mole CH<sub>3</sub>COOH dm<sup>-3</sup>, pH 3.0, [mg·kg<sup>-1</sup>];

$Bio_{Cu, Zn, Pb, Cd}$  expresses the amounts of Cu, Zn, Pb and Cd extracted by 0.10 mole NaNO<sub>3</sub> dm<sup>-3</sup>, [mg·kg<sup>-1</sup>];

The Statistica 10.0® Package (StatSoft) was used for statistical summary as well as stepwise analysis. Graphs and linear relationships were elaborated by using the Excel® sheet facilities.

## Results and discussion

Soil degradation, either physical or chemical is a process that should be mitigated by applying environmentally friendly measures and ensuring long term sustainability. The latter one is also reflected by soil fertility and biological activity, which are worth using additives for achieving remediation targets. This approach has been initiated in the current study with the use of phyto-ashes, biogas digestate and their blended organic-mineral components designated as soil improvers.

The data reported in Table 1 show that the investigated soil is decidedly sandy, but slightly acidic with pH<sub>KCl</sub> of 5.7 and organic carbon content leveling at 11.6 g·kg<sup>-1</sup>. On the basis of ranges suggested by Sequi and de Nobili (2000) i.e., C<sub>org</sub> <5.8 g·kg<sup>-1</sup> (very low); 5.8–10.4 g·kg<sup>-1</sup> (low), 11.0–14.5 g·kg<sup>-1</sup> (moderate), C<sub>org</sub> >14.5 g·kg<sup>-1</sup> (high), the level of organic carbon should

be classified as moderate. The reported parameters jointly shaped buffering characteristics, with CEC amounting to 11.2 cmol<sub>(+)</sub> kg<sup>-1</sup>. Ratings reported by Hazelton and Murphy (2007), i.e., CEC <6 (Very low); 6 < CEC < 12 (Low); 12 < CEC < 25 (Moderate); 25 < CEC < 40 (High) and CEC > 40 (Very high) point out at a low value. Such a state may strengthen the chemical degradation process induced by Cu, Zn, Pb and Cd concentrations as reported in Table 2. The share of reactive and bioavailable metal fractions in their total content varied significantly in the order 3% (Pb) < 7% (Cu) < 33% (Cd) < 38% (Zn). This pattern shows that the reported soil buffering capacities, even low, were efficient enough for inactivating Pb and Cu, but the process was less pronounced in the case of Cd and Zn. The behavior of these metals should be explained by the magnitude of the affinity expressed by electronegativity values, which follow the order 1.65, 1.69, 1.90 and 2.33 for Zn, Cd, Cu and Pb, respectively (Sanderson 1989). The values decidedly imply that Zn and Cd are weakly retained by soil particles, then are potentially mobile and may be of great environmental threat at high concentrations as compared to Cu and Pb. Therefore, the incorporation of additives, namely soil improvers, particularly organic-mineral for ameliorating soil physical and chemical properties is aimed at increasing Zn and Cd inactivation.

The concept of the study was based on a recycling trial of nine phyto-ashes with relevant chemical composition CaO (Fig. 1), SiO<sub>2</sub> (Fig. 2), heavy metal content (Table 3) and one biogas digestate as reported in Table 4. These characteristics are of prime value in the process of elaborating environmentally friendly organic-mineral blends as soil improvers. Three aspects have been initially taken into consideration: i) organic matter content for raising its level in treated soils, ii) calcium concentrations for extending soil buffering properties, i.e., CEC, iii) pH for regulating geochemical as well as biological soil processes and finally silicon oxides, that may be acting as additional heavy metals inactivators.

The chemical composition of phyto-ashes discriminates three outstanding operational groups on the basis of CaO and SiO<sub>2</sub> contents:

for CaO,

CaO (%) < 15 (wheat straw, rape straw ashes),

15 < CaO (%) < 30 (poplar ash),

CaO (%) > 30 (birch, oak, red oak, hornbeam, pine, maple ashes),

for  $\text{SiO}_2$ ,

$\text{SiO}_2$  (%) < 15 (birch, oak, red oak, hornbeam, pine, poplar, maple ashes),

$15 < \text{SiO}_2$  (%) < 30 (rape straw ash),

$\text{SiO}_2$  (%) > 30 (wheat straw ash).

The distribution pattern exhibited by these ranges points out at a specific rule: the higher the CaO level, the lower the  $\text{SiO}_2$ , except for pine, poplar and maple ashes (Fig. 1 and Fig. 2). Much more striking was the relationship observed for ashes obtained from wheat and rape straws, where  $\text{SiO}_2$  prevailed. Therefore, it should imply that the high  $\text{SiO}_2$  concentration of these ashes may be involved in the process of heavy metal inactivation, then will stimulate a sustainable soil amelioration. Zinc and cadmium are directly concerned.

Phyto-ashes were additionally tested for Cu, Zn, Pb and Cd concentration for evaluating any possible inputs once incorporated into soils along with improvers. Data listed in Table 3 revealed a close dependence of metal concentrations on the type of plant materials, i.e. plant species. For the whole tested ashes, Cu varied within 19–233  $\text{mg}\cdot\text{kg}^{-1}$ , Zn fluctuated in an extremely large range i.e., 136–2328  $\text{mg}\cdot\text{kg}^{-1}$ , with the highest concentration found for birch ash. Of these metals, only Pb and Cd varied relatively less: 5.0–72 and 1.0 to 9.0  $\text{mg}\cdot\text{kg}^{-1}$ , respectively. In Poland, the application of phyto-ashes as liming materials has been regulated in the Ordinance of July 10, 2007 for Fertilizers and Fertilization (Dz.U. No 147 pos. 1033), where the maximally allowable metal concentrations for Pb and Cd are leveled accordingly to 140 and 50  $\text{mg}\cdot\text{kg}^{-1}$ . No quantitative restrictions were set for Cu and Zn, due to their biological role as well as agricultural importance. On this basis, the investigated ashes may be applied for agricultural purposes, then also for soil amelioration goals.

### Soil reaction (pH) – a master index for phyto-ashes and soil improvers

Data listed in Table 4 and Table 5 imply that recycling of both wastes into environmental friendly soil improvers may be a successful task, based first on significantly decreasing

the high reactivity (pH) of phyto-ashes. It varied from 11.5 (wheat straw ash) to 13.6 (maple ash), but leveled at nearby 7.8 (wheat straw ash + biogas digestate) to 10.0 (maple straw ash + biogas digestate). The joint effect of organic acid addition as well as the initial pH of biogas digestate (i.e. 7.6) resulted in obtaining soil improvers characterised by pH lower by about 2 to 3 units as compared to raw phyto-ashes. The incorporation of organic matter may have initiated buffering processes, which dynamically stabilize the pH and the resulting post-reaction by-products (i.e. soluble organic substances) to react and form chelates with heavy metals (Diatta and Chudzińska 2009, Kumpiene 2003, Madejón et al. 2006). The key role of pH in soil ameliorative trials is illustrated by Fig. 3 and a sum up of the specific relationships established for the pairs phyto-ash rates *versus*  $\text{pH}_{\text{H}_2\text{O}}$  and soil improver rates *versus*  $\text{pH}_{\text{H}_2\text{O}}$  is presented in Table 6. The rates of phyto-ashes, biogas digestate and soil improvers were equivalent to 0, 5, 10, 20 and 40  $\text{t}\cdot\text{ha}^{-1}$  and their direct effect to soil properties, pH mainly, implied that phyto-ashes exerted the leading control.

This process may be explained by an instant release of CaO compounds (phyto-ashes), which was gradually moderated by biogas digestate. The coefficients of determination ( $R^2$ ) outcome basically from linear regressions corroborated the geochemical behavior of both phyto-ashes and soil improvers, since they varied in relatively narrow and similar ranges i.e.,  $0.888 < R^2 < 0.962$  and  $0.891 < R^2 < 0.990$ , respectively. The observed patterns are not in line with the values of slopes (Slo) of the equations:  $0.024 < \text{Slo} < 0.047$  (phyto-ash) and  $0.014 < \text{Slo} < 0.026$  (soil improvers).

One of the practical findings of these data is that the values of soil improver slopes are almost half those of the phyto-ashes, but the resulting effect, i.e. changes of soil pH is similar. In other words, 50% of phyto-ash supplemented by 50% of organic matter (biogas digestate, in this case) may be generating and controlling pH at the same level like 100% of the phyto-ash, irrespective of the applied amount. The whole mechanisms resulting from the incorporation of soil improvers lead finally to the occurrence of sustainable conditions

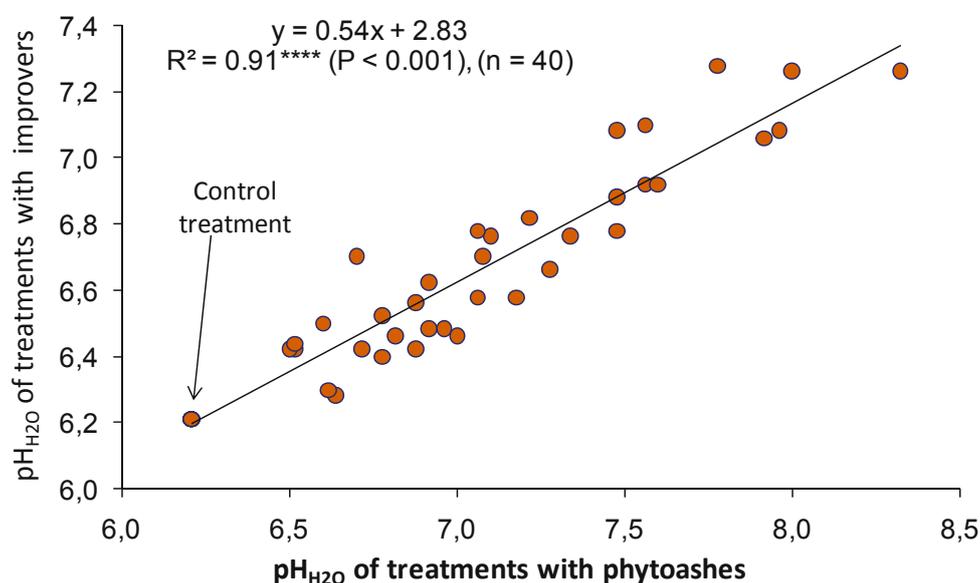


Fig. 3. Relationships between  $\text{pH}_{\text{H}_2\text{O}}$  of treatments with phyto-ashes and  $\text{pH}_{\text{H}_2\text{O}}$  of treatments with soil improvers (all rates included)

efficiently controlled by organic matter (Bolan et al. 2004, Carter 2002).

**Buffering potentials versus geochemical sustainability**

Alterations in the cation exchange capacity (CEC) as induced by the incorporation of phyto-ashes, biogas digestate and soil improvers resulted in the formation of new geochemical standard-state, i.e., buffering properties. The latter ones are directly responsible for more or less active processes involved in sorption and inactivation as well as desorption and mobility of chemicals in soils, heavy metals among others. The application of phyto-ashes and soil improvers shifted CEC values (Table 7) from a low (particularly for the control treatment, CEC = 11.2 cmol<sub>(+)</sub> kg<sup>-1</sup>) to a moderate range i.e., 12 < CEC < 25 cmol<sub>(+)</sub> kg<sup>-1</sup> (Hazelton and Murphy 2007). Mean values calculated for the whole phyto-ash and soil improvers treatments revealed the following patterns:

- % increase of phyto-ash treatments CEC (reference to the control CEC)  
29, 52, 71, 100 for the rates 5, 10, 20, 40 t·ha<sup>-1</sup> respectively,
- % increase of soil improvers treatments CEC (reference to the control CEC)  
18, 37, 44, 73 for the rates 5, 10, 20, 40 t·ha<sup>-1</sup> respectively.

The relatively lower CEC increase as observed for the improvers treatments was strictly related to the high share of biogas digestate (50%), which in turn recorded a very low CaO content. Next, calcium (Ca) was mostly organically bound, and then could not be released promptly in appreciable concentrations, as in the case of phyto-ash. The ratio of CaO (phyto-ash) to CaO (biogas digestate) may therefore be considered as a prognostic index of physical and chemical stability of these organic-mineral soil improvers. The conceptual mechanisms are illustrated in Figure 4.

**Table 6.** Linear regressions established for the pairs phyto-ash and soil improvers rates versus pH<sub>H2O</sub> of the treatments

No	Phyto-ash	Phyto-ash treatments	*R <sup>2</sup>	Soil improver treatments	R <sup>2</sup>
		y = pH <sub>H2O</sub> ; x = rates		y = pH <sub>H2O</sub> ; x = rates	
1	Birch ( <i>Betula</i> )	y = 0.040x + 6.39	0.962	y = 0.021x + 6.22	0.990
2	Oak ( <i>Quercus</i> )	y = 0.031x + 6.39	0.940	y = 0.018x + 6.25	0.957
3	Red Oak ( <i>Quercus rubra</i> )	y = 0.032x + 6.35	0.956	y = 0.021x + 6.28	0.978
4	Horbeam ( <i>Carpinus</i> )	y = 0.040x + 6.52	0.900	y = 0.025x + 6.27	0.989
5	Wheat straw ( <i>Triticum aestivum</i> )	y = 0.030x + 6.34	0.960	y = 0.020x + 6.35	0.891
6	Rape straw ( <i>Brassica napus</i> )	y = 0.024x + 6.33	0.944	y = 0.014x + 6.31	0.918
7	Pine ( <i>Pinus sylvestris</i> )	y = 0.037x + 6.46	0.888	y = 0.026x + 6.28	0.981
8	Poplar ( <i>Populus</i> )	y = 0.047x + 6.54	0.920	y = 0.025x + 6.31	0.960
9	Maple ( <i>Acer</i> )	y = 0.040x + 6.46	0.934	y = 0.021x + 6.26	0.979

\* Coefficient of determination

**Table 7.** Changes in cation exchange capacity (CEC) as a result of phyto-ashes, soil improvers and biogas digestate incorporation

Plant materials	Control	Phyto-ash				Soil improver			
		Rate [t·ha <sup>-1</sup> ]							
		5	10	20	40	5	10	20	40
		CEC [cmol <sub>(+)</sub> kg <sup>-1</sup> ]							
Birch ( <i>Betula</i> )	11.2	14.9	19.1	21.6	25.0	13.0	14.6	15.8	22.1
Oak ( <i>Quercus</i> )		15.5	18.9	20.9	23.5	13.6	16.3	17.4	19.9
Red Oak ( <i>Quercus rubra</i> )		14.2	16.2	18.9	21.7	12.9	14.8	16.2	18.9
Horbeam ( <i>Carpinus</i> )		14.2	16.2	19.3	23.2	13.6	15.2	17.3	19.0
Wheat straw ( <i>Triticum aestivum</i> )		14.5	15.9	17.5	20.6	12.1	14.7	16.0	17.6
Rape straw ( <i>Brassica napus</i> )		13.2	14.3	16.5	19.5	12.8	13.4	14.9	16.0
Pine ( <i>Pinus sylvestris</i> )		15.8	18.5	19.3	23.2	14.7	16.2	16.8	19.8
Poplar ( <i>Populus</i> )		14.2	16.7	18.8	21.9	13.2	16.3	17.7	20.4
Maple ( <i>Acer</i> )		14.4	18.4	20.0	23.8	13.1	16.4	18.6	21.2
Biogas digestate rate [t·ha <sup>-1</sup> ]		-	-	-	-	5	10	20	40
CEC-based digestate application [cmol <sub>(+)</sub> kg <sup>-1</sup> ]		-	-	-	-	11.9	12.7	14.4	15.9

A number of reactions were simultaneously running at the edge of both substrates as well as intra elaborated soil improvers. They deal with the formation of soluble low molecular organic compounds, build up of aggregates with calcium (CaO) and silicates (SiO<sub>2</sub>) acting as aggregating agents, deprotonation of digestate COOH, OH, NH<sub>2</sub> and CH<sub>3</sub> functional groups, the formation of carbonate ions (HCO<sub>3</sub><sup>-</sup>) at the interface CO<sub>2</sub>-functional groups. These mechanisms, complex by essence, proceed mainly at a molecular level (Schulten and Leinweber 2000), hence hardly detectable by physical approach. The emergence of negative charges as a result of HCO<sub>3</sub><sup>-</sup> formation (Davranche et al. 2003) as well as deprotonation process, strongly activates soil buffering characteristics reflected by dynamic sorption and retention of various ions, heavy metals particularly (Düring et al. 2003). All these mechanisms are strictly controlled by changes of pH induced by the presence of phyto-ashes. Such chemical reactions consequently decrease the concentrations of heavy metals, particularly Pb, in the ambient soil solution and simultaneously favor their mitigation (Basta and McGowen 2004).

#### **Metal inactivation – Eco-friendly and integrative amelioration**

The harmful effects of heavy metals in soils depend strictly on the type and the concentrations of their active forms. These may be discriminated by applying chemical tests (extractants), which enable performing a ground evaluation of the environmental fate of the particular metals. This has been the case of the reactive (extractant: 0.11 mole CH<sub>3</sub>COOH dm<sup>-3</sup>, pH 3.0) and bioavailable (extractant: 0.10 mole NaNO<sub>3</sub> dm<sup>-3</sup>) concentrations maintaining a constant geochemical equilibrium. The incorporation of phyto-ashes, biogas digestate and soil improvers strongly altered this equilibrium, but also created appropriate amelioration conditions (pH and CEC increase). Finally, heavy metals were inactivated giving rise to eco-friendly soil environment. Authors have evaluated this process by using the Dynamic Remediation Efficiency (DRE) parameter. Data are illustrated in Fig. 5 for Cu, Zn, Pb, Cd and three amendments, i.e. phyto-ashes, improvers and biogas digestate. Three specific patterns may be observed:

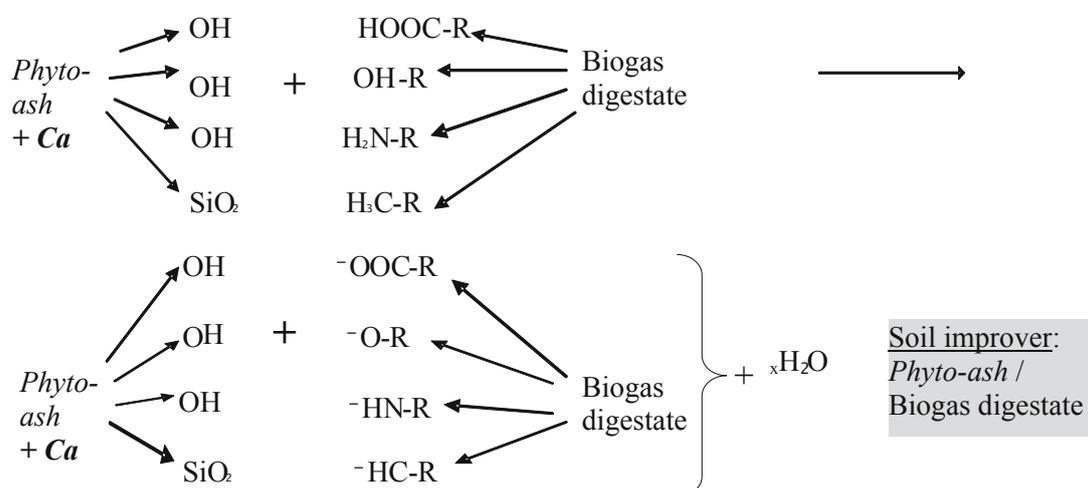
- i) higher DRE for Cu and Pb, whereas relatively lower for Zn and Cd in treatments with soil improvers,
- ii) higher DRE for Zn and Cd, whereas relatively lower for Cu and Pb in treatments with phyto-ashes,
- iii) higher DRE for Cu and Pb, whereas relatively lower for Zn and Cd in treatments with biogas digestate.

The possible explanation of these particularities relies in the chemical composition of the soil additives, with phyto-ash consisting mostly of CaO and OH, whereas soil improvers with CaO, organic matter and OH. Therefore, metals highly susceptible for precipitation (Zn and Cd) reacted mostly with phyto-ashes as compared to those exhibiting high affinity to organic colloids (Cu and Pb), for soil improvers. This rule is confirmed by electronegativity values, which follow the order 1.65, 1.69, 1.90 and 2.33 for Zn, Cd, Cu and Pb, respectively (Sanderson 1989).

Soil contamination with heavy metals results generally from the accumulation of various metals simultaneously. Natural processes occurring in soils act as mitigating factors, where metals are more or less inactivated (Bradshaw 2000, Mulligana and Yong 2004). These mechanisms are highly efficient in soils rich both in organic matter and clay, as compared to sandy ones. The latter ones are much more susceptible to chemical degradation creating environmental concerns. Hence the need for soil improvers, particularly organic-mineral like those tested in the current work, to counteract negative impacts and sustainably ameliorate the soils. It should be an opportunity for recovering degraded lands and allocating them to agricultural as well as recreational purposes.

#### **Conclusions and statements**

The study has revealed that recycling and soil application of phyto-ashes should consider four basic characteristics, i.e. initial aqueous pH as well as CaO, SiO<sub>2</sub> and heavy metal content. Of the nine tested phyto-ashes, two (from wheat and rape seed straws) exhibited the lowest CaO with simultaneously highest SiO<sub>2</sub> contents. The permissible levels of Pb and Cd were not exceeded (Ordinance of July 10, 2007 for Fertilizers and Fertilization Dz.U. No 147 item. 1033), hence their safe application both for agricultural and environmental goals.



**Fig. 4.** Phyto-ash and biogas digestate interactions resulting in the formation of organic-mineral soil improver (Authors' conceptual illustration)

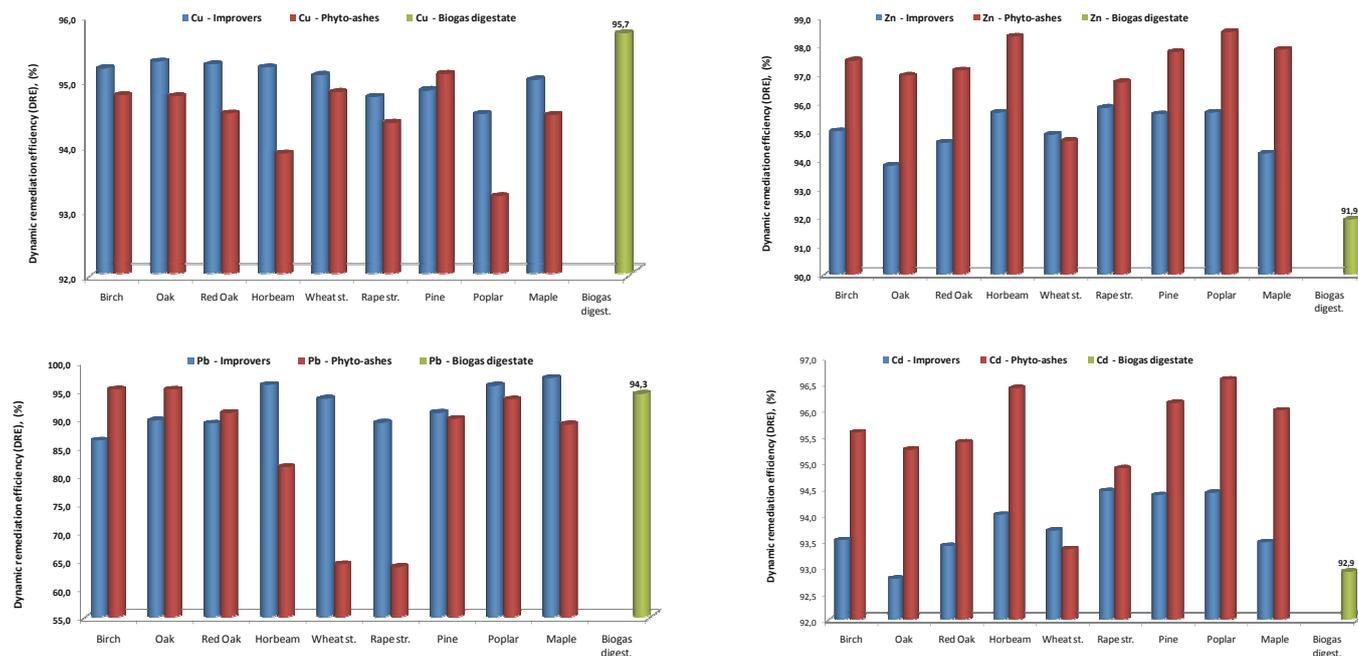


Fig. 5. Dynamic Remediation Efficiency (DRE) of phyto-ashes, soil improvers and biogas digestate towards Cu, Zn, Pb and Cd

Geochemical changes resulting from the application of phyto-ashes and improvers dealt strictly with buffering properties expressed by the cation exchange capacity (CEC). A net increase was achieved by referring to the control CEC: increase (%) of phyto-ash treatments CEC: 29, 52, 71, 100 and of improvers treatments CEC: 18, 37, 44, 73 both for the rates 5, 10, 20, 40 t·ha<sup>-1</sup>, respectively.

Heavy metals inactivation reflected the chemical effect of phyto-ash as well as eco-friendly value of improvers. The Dynamic Remediation Efficiency (DRE) for Cu, Zn, Pb, Cd revealed two specific patterns: i) higher DRE for Cu and Pb, whereas relatively lower for Zn and Cd in treatments with soil improvers; ii) higher DRE for Zn and Cd, with relatively lower for Cu and Pb in treatments with phyto-ashes.

Adequate recycling of phyto-ashes throughout blending with biogas digestates gave rise to organic-mineral soil improvers highly efficient for counteracting negative impacts of heavy metal in soils. It is a growing need and opportunity for recovering degraded lands and allocating them to sustainable agricultural purposes. The rates 5.0–10.0 t·ha<sup>-1</sup> for phyto-ash and about 20 t·ha<sup>-1</sup> for improvers [1:1, i.e. *Phyto-ash:Biogas digestate*] are recommended. For biogas digestate, the rates 10–20 t·ha<sup>-1</sup> were found more efficient.

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## Remediacyjne działanie polepszaczy z popiołu z biomasy roślinnej oraz pofermentu na glebę zanieczyszczoną metalami ciężkimi

**Streszczenie:** W pracy zastosowano 9 popiołów z biomasy roślinnej: brzozy (*Betula*), dębu (*Quercus*), dębu czerwonego (*Quercus rubra*), grabu (*Carpinus*), sosny (*Pinus sylvestris*), topoli (*Populus*), klonu (*Acer*), słomy rzepaku (*Brassica napus*) oraz słomy pszennej (*Triticum aestivum*), które wymieszano z pofermentem w stosunku 1:1. Otrzymano 9 organiczno-mineralnych polepszaczy glebowych. Koncepcja badań polegała na wyodrębnieniu taniego i środowiskowo przyjaznego polepszacza do remediacji gruntów zdegradowanych. Zanieczyszczone Cu, Zn, Pb and Cd próbki gleb pobrano w strefie zlokalizowanej po południowo-wschodniej stronie Huty Zn i Pb w Miasteczku Śląskim. Popioły z biomasy roślinnej, polepszacze oraz poferment zastosowano w dawkach 0, 5, 10, 20, 40 t·ha<sup>-1</sup>. Skuteczność procesu remediacyjnego oceniono przy użyciu testów: 0,11 mola CH<sub>3</sub>COOH dm<sup>-3</sup>, pH 3,0 (Reaktywne formy Cu, Zn, Pb, Cd) oraz 0,10 mola NaNO<sub>3</sub> dm<sup>-3</sup> (formy biodostępne). Spośród wielu

zbadanych parametrów, zmiany pH ujawniły, że polepszacze mineralno-organiczne mogą skutecznie zastępować (liniowe  $R^2 > 0,90^{***}$ ;  $P < 0,001$ ) popioły z biomasy roślinnej w zabiegach remediacyjnych. Właściwości buforowe wyrażone pojemnością wymienną w stosunku do kationów (CEC) poprawiły się progresywnie: 29, 52, 71, 100% (na obiektach z popiołami) oraz: 18, 37, 44, 73% (na obiektach z polepszaczami) odpowiednio dla dawek 5, 10, 20, 40 t·ha<sup>-1</sup>, w porównaniu do CEC na kontroli. Wskaźniki dynamicznej skuteczności remediacyjnej (DRE) dla Cu, Zn, Pb i Cd wskazały na specyficzne reakcje geochemiczne zainicjowane popiołami, polepszaczami oraz pofermentem. Dawki 5,0–10,0 t·ha<sup>-1</sup> dla popiołów roślinnych, ok. 20 t·ha<sup>-1</sup> dla polepszaczy [1:1, tzn. popiół:poferment] oraz 10–20 t·ha<sup>-1</sup> pofermentu są zalecane.