

## A BLEND OF BIOASH AND GYPSUM UTILIZED FOR AGRO-ENVIRONMENTAL PURPOSES IN A SOIL INCUBATION EXPERIMENT

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**Abstract.** Soil improver, nutrient supplier and heavy metal stabilizer effects of ash residue remaining after the process for K recovery was examined in a soil incubation model experiment using two soil types (acid sandy soil and neutral loam soil) at 4 ash residue dose levels (0, 1, 3, 5%). Possible environmental risks posed by its application were also studied by ecotoxicological assays. As the result of ash residue treatment alkalinity of the soils has been raised in all treatments. In the case of acid soil even the use of 1% of ash residue proved to be enough for neutralising the soil pH. Ash residue is principally suitable for K and P supply and mostly in soils with poor nutrient content, where ash residue applied in 1% dose is able to increase the concentration of plant available K and P significantly. According to the results, the ash residue proved to be able to decrease the mobility of Pb and Zn which means that it can be an effective stabilizer in acid and neutral soils. Stabilization has probably occurred via adsorption. Based on the findings of the ecotoxicological assays, the use of 1% ash residue does not present substantial environmental risk.

**Keywords:** *biomass ash, soil amelioration, fertilization, heavy metal stabilization, ecotoxicology*

### Introduction

Increasing importance of biomass combustion has raised problems related to the resulting ash as a by-product. Every year tens of thousands of tonnes of biomass ash (bioash) are produced in biomass power plants and heating plants. Handling and disposal of bioash as waste is costly and presents environmental risks. However, product manufacturing from bioash means an alternative enabling the utilization of this special waste. According to several studies the high CaCO<sub>3</sub> content of bioash makes it suitable for the improvement of acid soils (Ulery et al., 1993; Muse & Mitchell, 1995; Meiwes 1995; Vance, 1996; Zang et al., 2002; Deydier et al., 2005; Vassilev et al., 2013). Because of its high nutrient content (firstly K and P) it can be utilized as a nutrient source (Ohno & Erich, 1993; Fransman & Nihlgard, 1995; Vance, 1996; Demeyer et al., 2001; Bungart et al., 2001; Park et al., 2005; Ahmaruzzaman, 2010; Tan & Lagerkvist, 2011; Huotari et al., 2008) as well. Furthermore, due to their adsorption

capacity combustion products could be applied for soil remediation purposes by decreasing heavy metal mobility in contaminated soils (Feng et al., 2004; Srivastava et al., 2006; Gruiz et al., 2009; Ahmaruzzaman, 2010; Vassilev et al., 2013).

Biomass ash is composed of porous carbon-containing particles and irregularly shaped mineral particles. More than 80% of bioash is below 1 mm in size (Etiegni & Campbell, 1991). Its main component is  $\text{CaCO}_3$ . Density of bioash varies between 0.27 and  $0.51 \text{ g/cm}^3$  (Muse & Mitchell, 1995). Alkalinity, acid neutralizing capacity of bioash is also significant (Demeyer et al., 2001).

Macroelement content of bioash varies over a wide range with the following median values: 0.06% N, 0.42% P, 18% Ca, 0.97% Mg and 2.27% K (Vance, 1996). Still, it is the applicability of bioash to be used as K and P supplier that might be of huge significance in plant production.

Similarly to macroelements, microelement concentration of bioash also shows great variation. According to the analyses of several bioashes with different origins the highest mean concentration among microelements was that of Mn (4370 mg/kg), followed by Zn (443 mg/kg), Cu (75 mg/kg), B (110 mg/kg), and Mo (15 mg/kg). Concentration of As, Ni, Cr and Pb varied between 23 and 65 mg/kg, whereas regarding non-essential trace elements the concentrations of Se and Hg ( $< 0,5 \text{ mg/kg}$ ), as well as Cd and Co ( $< 10 \text{ mg/kg}$ ) proved to be low (Someshwar, 1996).

In spite of being reasonable, application of bioash in plant production should be carried out cautiously due to its composition that might include organic and mineral pollutants. Besides contaminating both soils and groundwaters it can also affect their acidity, chemical composition and biodiversity in a disadvantageous way (Vassilev et al., 2013).

The possibilities of the re-utilisation of biomass ashes have been studied worldwide including industrial and agricultural purposes (Lima et al., 2012; Huang et al., 2011; Huang et al., 1992). One of the latest potential options is to use it as a raw material for K fertilizers. According to the method that is now being improved potassium is extracted from herbaceous biomass ash with  $80\text{-}90^\circ\text{C}$  water, thereafter solution and residue (ash residue) are separated by filtration. Following the addition of sulphuric acid the solution is condensed and potassium-sulphate is gained as the end product. Through processing the residue with gypsum and carbon-dioxide, a soil improver with high Ca and K content is produced. This resulting blend of ash residue and gypsum (hereafter "ash residue") enriched with Ca contains significant amounts of macro- and microelements. Regarding its basic properties, ash residue has similar qualities to that of untreated biomass ash (*Table 1*). It should be noticed that data from literature show great variances. Concentration values of several components of the ash residue analysed in our experiment were found to be of similar order of magnitude to those published before with the exception of Mn and Na for which we obtained lower values.

Blends of ash and gypsum have already been tested as construction materials (Sadique et al., 2013). In present experiment the soil improver, nutrient supplier and heavy metal stabilizer effects of the ash residue described previously were studied in a soil incubation model experiment. Possible environmental risk posed by its application was examined as well, using ecotoxicological methods. According to literature data favourable overall effects of the material could be expected. However, it should be considered that by containing significant amounts of potentially toxic elements, ash residue can cause environmental risk. These negative effects have already been demonstrated on different aquatic test organisms (Barbosa et al., 2013). On the grounds

of these, principal questions to be answered are the following: (i) whether the ash residue is applicable for all of the three aforementioned purposes and (ii) whether its utilization is limited by the potential toxicity caused by its composition. Based on the literature, toxicological knowledge on the application of ash originating from the combustion of herbaceous plants as a soil improver is limited. This work might also provide new findings to this topic.

**Table 1.** pH and element composition (mg/kg) of different biomass ash and ash-residue

Parameter	Wood ash (Etiegni & Campbell 1991)*	Wood ash (Huang et al., 1992)*	Reed canary-grass ash (Paulrud et al., 2001)	Switchgrass ash (Vassilev et al., 2013)	Ash residue
Particle size distribution	80 %: <1 mm				18 %: 2-0.05 mm 82%: 0.05-0.002 mm
Density	0.27 – 0.51 g/cm <sup>3</sup>				0.41 g/cm <sup>3</sup>
pH	9-13.5				9.5
N	600	900			0
P	14000	6900	11800		44050
S	4455	6800			28570
Ca	317400	109400	18200		154600
Mg	22500	16200	7400		37390
K	41300	28600	28300		91510
Na	3400	1600	1800		101
Al	23650	13000	3200		1222
Fe	19500	3300			1563
Mn	6693	3470		872	222
Zn	700	794		103	576
Cu	145	78		66	388
Ba	8	127			64
Pb	130	66			1.2
Ni	47	12		37	42
Cr	86	14		49	6.1
Cd	21	3		9.8	3.6

\*In: Demeyer et al., 2001

## Materials and methods

### Experimental design

Topsoil (0-0.2 m depth) samples were used in order to examine the effects of ash residue on soil properties and on heavy metal mobility. The samples were taken from two soil types, one from an acid sandy soil (Nyírlugos, EOY coordinates: 874919, 265291) and the other from a neutral loam soil (Gyöngyös, EOY coordinates: 716000, 271195). These types were chosen with the purpose of studying the effects of ash residue on two soils that differ from each other basically regarding both their alkalinity

and colloid content. Soils were contaminated artificially except for one case in which it was left in its natural state, as follows:

1. uncontaminated soil sample: acid soil (Nyírlugos) (USS),
2. acid soil (Nyírlugos) contaminated with Pb and Zn salts ( $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZnSO}_4(7\text{H}_2\text{O})$ ) + 400 mg Pb and 800 mg Zn/kg of soil (LZSS),
3. loam soil (Gyöngyös) contaminated with mine refuse (11%) (Gyöngyösoroszi) (MRLS),
4. loam soil (Gyöngyös) contaminated with communal sewage sludge (Gödöllő) (SSLS).

Ash residue was mixed to the soil in the following ratios: control, 1, 3 and 5 m/m%. Each treatment was performed in three replicates. Total element contents of the soil mixtures are summarized in *Table 2*.

**Table 2.** Total (cc.  $\text{HNO}_3$  +  $\text{HCl}$  soluble) element concentrations of the four soils (mg/kg)

Element	USS	LZSS	MRLS	SSLS	limit values*
<b>Ca</b>	576	507	13683	18153	-
<b>K</b>	1543	1513	10644	11713	-
<b>P</b>	383	365	2925	5520	-
<b>Mg</b>	1012	1012	5432	6095	-
<b>S</b>	117	380	1607	1008	-
<b>Zn</b>	17.4	<b>599</b>	<b>235</b>	<b>591</b>	200
<b>Cu</b>	5	5	<b>85</b>	<b>195</b>	75
<b>Ba</b>	32.0	37.1	<b>306</b>	<b>407</b>	250
<b>Ni</b>	7.08	6.85	<b>51.1</b>	<b>46.6</b>	40
<b>Cr</b>	10.2	9.8	<b>75</b>	<b>198</b>	75
<b>As</b>	1.23	0.99	<b>43.2</b>	11.0	15
<b>Cd</b>	0.032	0.042	<b>1.14</b>	<b>3.40</b>	1
<b>Co</b>	3.14	2.98	16.0	13.2	30
<b>Pb</b>	5.12	<b>418</b>	<b>164</b>	48.1	100
<b>Mo</b>	0.127	0.186	2.25	1.13	7
<b>Se</b>	<dl	<dl	<dl	0.953	1

<dl: under detection limit. dl Hg: 0.12 mg/kg; dl Se: 0.6; \*contamination limit values for soils in joint decree No. 6/2009; Bold characters indicate values above limit.

Each pot was filled with 1 kg of soil. In the case of the second soil mixture concentrations of Pb and Zn in the soil were four times higher than the limit values of the Hungarian regulations (Government Joint Decree No. 6/2009. (IV. 14.) KvVM-EüM-FVM on limit values established for the protection of groundwater and the geological medium). The levels of sewage sludge and mine refuse dosage were calculated in a way that the concentrations of some elements in the soil exceed the contamination limit values (according to the Joint Decree No. 6/2009. (IV. 14.) KvVM-EüM-FVM) many times over (*Table 2*). Different contaminants were applied in order to have a better understanding of heavy metal stabilization processes these materials are supposed to take part in.

Element composition and some properties of the ash residue are presented in table 1. It can be seen that it had a pH ( $\text{H}_2\text{O}$ ) value of 9.5, contained 28.3%  $\text{CaCO}_3$  and no nitrogen, whereas its ammonium lactate (AL) soluble  $\text{K}_2\text{O}$  and  $\text{P}_2\text{O}_5$  contents were

10.5% and 3.7%, respectively. Some parameters of the soil mixtures can be found in Table 3.

**Table 3.** Selected properties of the soil samples

Soil	pH (H <sub>2</sub> O)	CaCO <sub>3</sub> %	OM %	Upper limit of plasticity	CEC meq/100g
USS	5.04	0.00	0.92	33	1.76
LZSS	4.19	0.00	0.97	33	1.67
MRLS	7.04	0.26	4.44	45	27.9
SSLS	7.05	0.56	6.05	53	34.1

All contaminants (Pb and Zn solution, mine refuse and sewage sludge) and the different doses of ash residue were added to the soils at the same time. After homogenisation, the mixtures were filled into pots and incubated for 1 month. The mixtures were wetted to 70% of field capacity of the soils.

## Methods

### *Analyses of soil parameters and soil chemical properties*

The soil was analysed according to the following standards: pH(H<sub>2</sub>O) – ISO 10390:2005, humus content – ISO 14235:1998, CaCO<sub>3</sub> content – ISO 10693:1995, cation exchange capacity (CEC) - ISO 11260:1994; aqua regia extract, distilled water 1:10 extract, NH<sub>4</sub>-acetate + EDTA-soluble element fraction – MSZ 21470-50:2006, ammonium acetate buffer extract – MSZE 21420-31;2006, ammonium-lactate soluble element content - MSZ 20135:1999, particle size distribution - MSZ-08-0205:1978.

### *Ecotoxicological tests*

All microbiological and ecotoxicological assays were performed in three replications. The number of aerobic heterotrophic colony forming units was determined in wet soil samples. The soil samples for the *Sinapis alba* root and shoot growth inhibition test were dried, ground and passed through a 2 mm sieve.

*Aerobic heterotrophic colony-forming units.* The soil microbial biomass and the number of viable microorganisms can be used to assess soil quality and are relatively easy to determine using routine methods such as plate count tests (Benedetti & Dilly, 2006). In this experiment different soil dilutions in sterile distilled water were inoculated into an appropriate media ensuring that after the incubation period one colony is formed from one living cell. The method was described by Lorch et al. (1995). The number of aerobic heterotrophic microorganisms was expressed as colony forming units (CFUs) per g of soil.

*Sinapis alba root and shoot growth inhibition test.* In the presence of toxic substances the germination rate and the root and shoot growth of *Sinapis alba* (white mustard) plants are inhibited (OECD, 2006). The test was performed as described by Leitgib et al. (2007). Five grams of soil were measured out into a 10 cm diameter Petri-dish, wetted to its water holding capacity and 20 seeds with over 90% germination ability were placed on the soil surface. The samples were incubated at 23° C in the dark for three days. The length of roots and shoots were measured manually with a ruler. The growth inhibition was expressed as follows:  $I(\%) = (C-L)/C \cdot 100$ , where I means the

inhibition %, C means the length of shoot or root in the control (OECD soil), while L means the length of shoot or root of *Sinapis alba* in the sample. The artificial soil recommended by the OECD Guideline 207, (OECD, 1984) (content: 70% sand, 20% clay, 10% peat) was used as the uncontaminated control.

### Statistical Analysis

The data were analysed for treatment effects using one-way analysis of variance (ANOVA) on the main treatments (time period, different layers). Significant differences between the treatment means were calculated by the LSD (least significant difference) test at  $p < 0.05$ . In the correlation analysis the asterisks, \*, \*\* and \*\*\* indicate significance at  $p < 0.05$ , 0.01 and 0.001, respectively. Statistica v.9 (StatSoft Inc.) software was used for all the statistical evaluations.

## Results

### Soil amelioration and nutrient supply

As presented in *Table 4*, the pH value has increased by more than 3 units in the case of the light-textured acid sandy soil. Correspondingly the application of 3% of ash residue made the sandy soils alkaline, whereas 1% of it (equivalent to 10t/ha  $\text{CaCO}_3$ )

*Table 4. Some soil properties in function of ash residue treatment*

Soil	Ash-residue %	pH (H <sub>2</sub> O)	CaCO <sub>3</sub>	AL-K <sub>2</sub> O	AL-P <sub>2</sub> O <sub>5</sub>	CEC
			w/w%	mg/kg	mg/kg	meq/100g
USS	0	5.00	-	65	138	1.76
	1	7.64	0.09	793	952	3.83
	3	8.48	0.40	2504	2521	4.72
	5	8.69	0.82	3972	3680	5.84
	LSD <sub>5%</sub>	0.1	0.05	198	312	1.29
LZSS	0	4.19	-	70	151	1.67
	1	6.93	-	852	960	3.15
	3	8.43	0.36	2620	2286	4.06
	5	8.70	0.69	4200	3565	4.72
	LSD <sub>5%</sub>	0.08	0.04	438	186	0.96
MRLS	0	7.04	0.26	884	3748	27.9
	1	7.62	0.51	1680	4461	29.7
	3	8.05	0.90	3477	6111	25.6
	5	8.20	1.52	5140	7340	25.5
	LSD <sub>5%</sub>	0.05	0.11	169	373	n.s.
SSLS	0	7.05	0.56	936	7070	34.1
	1	7.50	0.75	1800	7869	35.3
	3	7.94	1.13	3633	8727	33.5
	5	8.13	1.56	5526	9873	30.7
	LSD <sub>5%</sub>	0.06	0.19	221	762	2.9

n.s. = not significant

proved to be enough to neutralize them. It can be stated that regarding the experimental acid sandy soils, the pH value of 6.8 being desired when liming can be reached by using an ash residue dose of 15 t/ha. CaCO<sub>3</sub> contents were also found to increase significantly in both soils and following all treatments. The acid sandy soil had the smallest CEC, while the largest was that of the loam soil contaminated with sewage sludge. Regarding the acid sandy soil, ash residue treatment has increased CEC compared to the control in all of the cases, whereas no significant change was observed for loam soil contaminated with mine refuse. As for the loam soil contaminated with sewage sludge, 5% ash residue treatment has lowered the CEC statistically in comparison with the no ash treatment. This might be originated in the dilution effect (*Table 4*).

In the case of present experiment addition of 1% ash residue resulted in the 12-fold increase of AL-soluble K and the 7-fold increase of P in the acid sandy soil compared to the control (*Table 4*). In the case of the 3% ash residue treatment this surplus was 38-fold for AL soluble K and 18-fold for AL soluble P, while with the addition of 5% ash residue it reached 61-fold and 27-fold AL-K<sub>2</sub>O and AL-P<sub>2</sub>O<sub>5</sub> content of the control soil, respectively. With regards to the neutral loamy soil a 2-fold increase was observed in the case of AL soluble K with the use of 1% ash residue, whereas P was not found to increase considerably compared to the control. By adding 3% of ash residue this surplus proved to be 4-fold regarding AL-K<sub>2</sub>O and about 1.5-fold for AL-P<sub>2</sub>O<sub>5</sub>. The addition of 5% ash residue led to a fold change of 6 in the case of AL-K<sub>2</sub>O content, whereas in the case of AL-P<sub>2</sub>O<sub>5</sub> content the difference was almost two-fold only in the soil contaminated with mine refuse. The changes in K and P concentrations were significant. Based on these results the ash residue may be suitable primarily for K and P supply.

### Heavy metal stabilisation

Outstanding heavy metal stabilization effect was only observed in the Pb and Zn contaminated acid sandy soil (*Table 5*) of what the most probable cause is its low organic matter content and low metal binding capacity. In the uncontaminated sandy soil the plant available Pb and Zn concentrations increased significantly due to the element content of ash residue. However, even in this soil the water soluble concentrations decreased. Regarding the neutral loam soil the decrease in the solubility of Zn was proven statistically in the acetate and water soluble fractions but the ash increased the plant available NH<sub>4</sub>-acetate + EDTA soluble Pb and Zn concentrations.

**Table 5.** Soluble fractions of Pb and Zn extracted by different solvents in an acid sandy soil

Soil	Ash-residue %	NH <sub>4</sub> -acetate + EDTA soluble	NH <sub>4</sub> -acetate soluble	Water soluble	NH <sub>4</sub> -acetate + EDTA soluble	NH <sub>4</sub> -acetate soluble	Water soluble
		Pb mg/kg			Zn mg/kg		
USS	0	1.90	<dl	0.100	1.6	1.84	0.899
	1	2.43	<dl	0.081	5.7	3.53	0.519
	3	2.54	<dl	0.072	14.7	5.94	0.231
	5	2.79	<dl	0.060	21.9	7.09	0.060
	LSD <sub>5%</sub>	0.55		n.s.	1.7	1.31	0.276
	0	323	125	4.35	649	452	287
	1	307	25	2.64	627	413	11

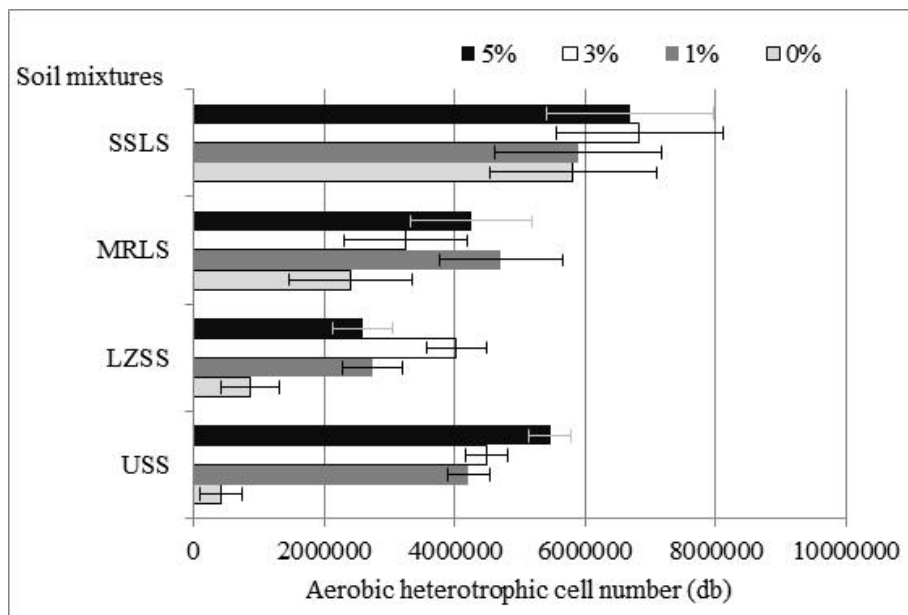
<b>LZSS</b>	<b>3</b>	263	9	1.45	590	386	2
	<b>5</b>	278	6	0.47	580	353	1
	<b>LSD<sub>5%</sub></b>	n.s.	19	0.82	60	34	56
<b>MRLS</b>	<b>0</b>	26.7	<dl	<dl	73	11.8	<dl
	<b>1</b>	27.3	<dl	<dl	85	8.8	<dl
	<b>3</b>	24.1	<dl	<dl	87	7.0	<dl
	<b>5</b>	19.7	<dl	<dl	90	3.8	<dl
	<b>LSD<sub>5%</sub></b>	1.5			7	1.5	
	<b>SSLS</b>	<b>0</b>	19.8	<dl	<dl	314	16.3
<b>1</b>		19.4	<dl	<dl	314	16.7	0.801
<b>3</b>		17.4	<dl	<dl	306	10.9	0.107
<b>5</b>		15.7	<dl	<dl	312	7.7	0.147
<b>LSD<sub>5%</sub></b>		1.7			n.s.	2.3	0.395

n.s. = not significant; <dl = under detection limit

## Toxicology

### *Aerobic heterotrophic colony-forming units (CFU)*

Aerobic heterotrophic cell number proved to be the lowest in the case of the uncontaminated acid sandy soil and it was the highest in the loam soil contaminated with sewage sludge (*Fig. 1*).



**Figure 1.** Aerobic heterotrophic cell number changes of soil mixtures in function of ash residue treatments

It was also found that compared to the soil without ash treatment, cell number has increased significantly as a result of ash residue treatment both in the contaminated and in the uncontaminated acid sandy soils as well as in the neutral loam soil contaminated



with mine refuse. Increase of ash residue dose to 3% and further to 5% was able to raise the aerobic heterotrophic cell number only in some cases.

#### *Sinapis alba* root and shoot growth inhibition test

The results in *Table 6* show that the ash residue had both stimulating and inhibiting effects on the growth of *Sinapis alba* root and shoot growth depending on the soil type and contamination. Mentioned effects were definitely positive only on the lead and zinc contaminated sandy soil where each load level resulted in growth stimulation. Inhibition occurred in the case of other soils on both shoot and root elongation but in most cases only above a load of 1 %.

**Table 6.** Results of the *Sinapis alba* growth inhibition test

Soil	Ash-residue %	Root length (mm)	Root growth inhibition %	Shoot length (mm)	Shoot growth inhibition %
USS	0	24.0	0.0	13.1	0
	1	17.2	28.4	14.5	-10.8
	3	11.7	51.7	10.7	20.1
	5	7.4	68.3	5.9	53.5
	LSD <sub>5%</sub>	5.5	16.4	4.2	25
LZSS	0	4.1	0	4.1	0
	1	13.7	-237	15.4	-276
	3	11.9	-189	10.0	-144
	5	7.1	-74	5.4	-36
	LSD <sub>5%</sub>	2.7	81.1	2.4	46
MRLS	0	12.2	0	12.7	0.0
	1	11.6	3.3	15.0	-18.1
	3	10.2	14.9	14.5	-18.9
	5	7.3	39.4	9.6	26.0
	LSD <sub>5%</sub>	2.4	19.4	4.4	n.s.
SSLS	0	14.2	0.0	16.6	0.0
	1	14.6	-3.5	18.3	-10.2
	3	9.8	30.8	14.3	14.1
	5	9.3	33.9	13.4	18.8
	LSD <sub>5%</sub>	2.3	16.9	4.0	24.5

n.s. = not significant

## Discussion

Based on the results ash residue treatment might be suitable to replace high-dose liming in the case of soils similar to those included in this experiment, in accordance with earlier findings (Ulery et al., 1993; Muse and Mitchell, 1995; Park et al., 2012). Because of the adsorption capacity of bioash, it was important to investigate what effect the ash residue treatment has on the CEC of the soils (Feng et al, 2004; Srivastava et al., 2006; Vassilev & Vassileva, 2007; Umamaheswaran & Batra, 2008). The ash residue treatment increased the adsorption capacity of the sandy soil, thus may improve the

nutrient balance of similar soils. However, the higher (5%) dose levels of ash residue may decrease the CEC of heavier textured soils due to the dilution effect (*Table 4*).

Based on literature data and regarding macroelements, biomass ash contains significant amounts of potassium and also has a relatively high phosphorous content with a mean of almost 0.5% (Vance, 1996; Fransman & Nihlgard, 1995). It contains large concentrations of microelements as well. Contrarily, according to some previous findings, with the addition of bioash to soil the solubility and availability of Fe, Mn, Zn and Cu decreased owing to the increased pH (Clapham & Zibliske, 1992; Krejzl & Scanlon, 1996). The biomass ashes proved to be suitable P and K suppliers for different cultivars (Schiemenz & Eichler-Löbermann, 2010; Kikamägi et al., 2013).

The effect of stabilisation is only presented by the concentration values of Pb and Zn in the four soil mixtures. Outstanding heavy metal stabilisation effect was only observed in the Pb and Zn contaminated acid sandy soil (*Table 5*) which might be explained by its low organic matter content and metal binding capacity. Chemical stabilizers/immobilizers can reduce the mobility of metals through adsorption, the formation of complexes or precipitation (Kumpiene et al., 2008). As shown in table 3, ash residue has increased the CEC of the acid sandy soil.

In the contaminated acid sandy soil the stabilizing effect of ash residue was the most observable on distilled water and ammonium-acetate buffer extractions, the former is representative for the easily mobilisable fraction while the latter for exchangeable cations (Tessier, 1979). The combination of NH<sub>4</sub>-acetate and EDTA is a much stronger extractant than the two mentioned due to the complex forming agent of EDTA which is able to make coordinated metal ions extractable as well (Schnitzer & Khan, 1978; Stevenson, 1982; Ram & Raman, 1984; Peijnenburg et al., 2007). Regarding this extraction stabilization effect of fly ash was not or only very slightly detected, therefore it can be assumed that (owing to the properties of ash residue as well) immobilization occurred via adsorption.

In the case of sewage sludge contaminated loam soil the CEC decreased in function of the amount of ash residue added, thus the observed stabilisation in the case of water and acetate soluble Zn concentration can be traced back to the precipitation of zinc-phosphate due to the P content of ash residue (Crannell et al., 2000; Theodoratos et al., 2002; Diyab et al., 2003).

Based on the above information the ash residue may reduce the element solubility by two ways: increasing the CEC and precipitating the metals into less soluble phosphorus salts. Thus, it is a possible stabilisation agent.

Although microbial count is not a direct measure of activity in soils, it is indicative of soil microbial viability (Bossert & Kosson, 1997) which is in relation with the organic matter and nutrient content of the soils (*Table 2 and Table 3*) (Kanazawa & Filip, 1986; Torsvik & Øvreås, 2002; Maron et al., 2006). Despite that favourable effects of bioash on soil microflora were described previously (Fritze et al., 2000), they were not observable in the soil contaminated with sewage sludge. The positive impacts of ash residue (*Fig. 1*) can be explained by its following features: its capacity to provide good air and moisture supply, the fact that it increases the adsorption surface due to its particle composition, and that it decreases the biological availability of heavy metals by their stabilization (Nielsen et al., 2002; Dombos & Szalkai, 2004; Gillert et al., 2009).

The results of the *Sinapis alba* ecotoxicological test on uncontaminated sandy and contaminated loam soils are partly in accordance with results of similar experiments in literature. Rikala & Jozefek (1990) found that wood ash application in lower rates may

increase the germination but higher doses (over 5 t/ha) have negative effect on it. Similarly, Singh et al. (1997) demonstrated that fly ash application in low rates insignificantly increased the germination of bean (*Vicia faba*) which was inhibited at the rate of 30 % . In our experiment the slightly positive effect was insignificant in contrast to the inhibition on higher ash residue application rates. Thus, the nutrient content of ash residue did not promote the shoot and root growth but in higher doses its potentially toxic element content inhibited these processes. In contrary, on the contaminated sandy soil the ash residue successfully promoted the shoot and root growth due to the stabilisation of Pb and Zn contaminants.

## Conclusions

Due to its alkaline pH and high (nearly 30%) CaCO<sub>3</sub>-content, ash residue as a soil improver has significantly raised the pH of the studied soils. Even 1% dose of ash residue proved to be enough to turn the acid soil into neutral. The ash residue is mainly suitable for nutrient supply, primarily in the soils with poor nutrient content where ash residue applied in 1% dose is able to increase the concentration of plant available K and P significantly. We successfully demonstrated the capacity of ash residue to decrease the solubility of Pb and Zn in both the acid sandy and the neutral loam soils, which means that it is an appropriate stabilizer in the acidic environment. Stabilization has probably occurred via adsorption and precipitation. Based on the findings of the ecotoxicological assays, the use of 1% ash residue does not present substantial environmental risk.

For the establishment of real ways of utilization of ash residue pilot-plant and large-scale field experiments are needed with the application of complex technology evaluation methods (material balance; cost-effectiveness analysis; description of risks).

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