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USING ASH FROM INCINERATION OF MUNICIPAL SEWAGE SLUDGE TO FERTILIZE VIRGINIA FANPETALS

WYKORZYSTANIE POPIOŁÓW ZE SPALANIA KOMUNALNYCH OSADÓW ŚCIEKOWYCH DO NAWOŻENIA ŚLAZOWCA PENSYLWAŃSKIEGO

Abstract: The purpose of this paper was to determine the effect of ash from a sewage sludge incinerating facility on yields and mineral composition of Virginia fanpetals, and on the content of heavy metals in soil. The study was based on a pot experiment in which ash obtained from sewage sludge incineration at the Lyna Wastewater Treatment Plant was used as a substitute of mineral fertilizers. The dominant fertilizing ingredients found in the analyzed ash were phosphorus and calcium. The content of cadmium and lead was lower than the allowable concentrations of these metals in mineral fertilizers. Ash from incinerated sewage sludge did not have any substantial effect on the soil content of the mobile forms of cadmium, copper, lead and chromium. With respect to three metals, namely nickel, zinc and manganese, the medium and high doses of ash raised significantly their concentrations in soil. The rate of ash had no influence on the content of sodium and magnesium in the plants but when the highest dose of ash had been applied, the concentration of calcium in plants rose significantly. Ash modified the content of heavy metals in the plant material only very slightly.

Keywords: ash from incineration of municipal sewage sludge, Virginia fanpetals, phosphorus, heavy metals, soil

Introduction

Diminishing resources of fossil fuels as well as the threat of climate change due to excessive emission of carbon dioxide force people to search for sources of renewable energy. Among the possibilities tested it plant biomass.

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Solid biomass is obtained from waste by-products derived from forestry, agriculture, the timber industry and urban greenery care; some small quantities are also acquired from sorted municipal organic waste. Today, the biomass supply on the energy market can be enriched with biomass produced on field plantations of perennial energy crops [1]. Virginia fanpetals, also known as Virginia mallows (*Sida hermaphrodita*) is such energy crop, grown for its large yields of stems and leaves and known for durable plantations. This plant is also recommended for phytoremediation and rehabilitation of chemically polluted soil because when grown on substrate with an elevated content of heavy metals, it produces quite good yields and accumulates substantial amounts of heavy metals [2].

In 2011, a total of 519. million Mg d.m. of sewage sludge was generated, of which 8 % (41.6 million Mg d.m.) was processed thermally. The waste management plan for 2014 in Poland presumes further reduction of the amount of stored sludge and an increase in the quantity of municipal sewage sludge processed, including high temperature processing (about 30 %), prior to reintroduction to the environment [3]. Also, it is emphasized that the extent of utilization of biogenic substances found in sludge should be maximized, yet the requirements set to ensure sanitary and chemical safety must be met.

Incineration of sewage sludge reduces considerably the volume of such waste. Numerous studies have also implied that ash from combustion of sewage sludge can be used as active ingredient replacing some part of cement, but specific requirements must be met before sewage sludge ash is used in building practice [4–7]. Ash contains high quantities of phosphorus compounds and is therefore valuable raw product for manufacture of fertilizers [8–10] or baked pellets used for wastewater treatment in hydrophyte systems [11]. Two other essential nutrients found in sewage sludge ash are calcium and magnesium, while potassium and sodium are present in smaller amounts. The content of phosphorus in ash from incineration of municipal sewage sludge can be up to 260 $gP_2O_5 \cdot kg^{-1}$ d.m. and is therefore comparable to its concentration in poor quality phosphates [6]. Such ash can also be used for production of technical phosphoric acid [12].

The purpose of this paper has been to evaluate the influence of ash from a sewage sludge incineration facility on yields and mineral composition of Virginia fanpetals and on the soil content of heavy metals.

Material and methods

A two-year of one-factor experiment with four replications was conducted in a greenhouse, at the University of Warmia and Mazury in Olsztyn. Kick-Brauckmann pots were filled with 10 kg of substrate of the grain size distribution of light loamy sand. The substrate was characterized by slightly acid reaction (pH_{KCl} = 5.6), moderate availability of accessible phosphorus (63.2 $mgP \cdot kg^{-1}$), high availability of potassium (125.5 $mgK \cdot kg^{-1}$) and moderate availability of magnesium (62.0 $mgMg \cdot kg^{-1}$). Nitrogen and potassium were applied in the form of mineral fertilizers (ammonium nitrate and potassium chloride), and the source of phosphorus added to soil was ash from incineration of sewage sludge originating from the Lyna WTP in Olsztyn (Table 1). Rates of ash were determined according to its concentrations of phosphorus (Table 2). Virginia fanpetals plant were cultivated from root cuttings. The control treatment was composed of plants grown without fertilization.

Table 1

Design of experiment

Treatment	Fertilization [g per pot]		
	N	P	K
Control	0.0	0.00	0.0
P1	0.5	0.25	0.5
P2	1.0	0.50	1.0
P3	1.5	0.75	1.5

After harvest, plants were weighed and dried. Following digestion in concentrated sulphuric acid(VI) with hydrogen dioxide as oxidizing agent, plant material was submitted to determination of concentrations of the following elements (determination methods in brackets): nitrogen (by colorimetry with the hypochlorite method), phosphorus (by colorimetry with the vanadium-molybdene method), potassium, calcium and sodium (by atomic emission spectrophotometry) and magnesium (by atomic absorption spectrophotometry). The content of heavy metals was determined by the AAS method, having previously mineralized plant material in a mixture of nitric acid(V) and chloric acid(VII) (in a 4:1 ratio) with added hydrochloric acid.

Determinations of the content of mobile forms of heavy metals before the experiment and after the harvest were performed with the AAS method, after extraction in 1 mol HCl dm^{-3}.

Easily soluble forms of heavy metals were extracted from ash in 1 mol HCl $\cdot$ dm^{-3} while hardly soluble ones were hot extracted in concentrated sulphuric acid.

The results of chemical determinations were submitted to statistical analysis aided by Statistica 10 software package. All statistical calculations were performed at the level of significance $p = 0.01$. Fisher's test was applied to verify the significance of differences.

Results and discussion

The results of our examination of the fertilizing properties of ash from the municipal sewage sludge incineration facility at the Lyna Wastewater Treatment Plant in Olsztyn (Table 2) were congruent with relevant data found in literature [6, 11–15] regarding the alkaline nature of ashes, high concentration of phosphorus (62.48 gP $\cdot$ kg^{-1} d.m.) and alkaline metals (44.09 gCa $\cdot$ kg^{-1} d.m. and 12.30 gMg $\cdot$ kg^{-1} d.m.). Same as in the experiments of Bialowiec et al [11] and Ciesielczuk et al [13], other fertilizing elements such as carbon and nitrogen appeared in small quantities.

Table 2

Fertilization properties of ash from incineration of sewage sludge

Dry matter content [%]	pH_{H_2O}	$C_{org.}$ [%]	N	P	Ca	Mg	Na
			[g · kg^{-1} d.m.]				
88.45	8.28 ± 0.07	3.14 ± 0.33	2.19 ± 0.06	62.48 ± 1.27	44.09 ± 4.41	12.30 ± 1.59	14.03 ± 1.28

The X-ray diffraction of ash from sewage sludge burning showed that the high temperature reaction of iron phosphate with the calcium compounds present in sewage sludge generates mixed calcium and iron phosphate ($Ca_9Fe(PO_4)_7$) and hematite [16]. These compounds greatly condition the potential leaching of phosphorus from ash. Owing to their presence, the availability of the forms of phosphorus soluble in citric acid may be as high as 50 % of the total content of this element in ash. Some other research [17] demonstrated that the availability of phosphorus in ash obtained from incineration of a mixture of meat and bone meal (MBM) and sewage sludge (in a 3 to 1 ratio) is as high as 65 % because no presence of hydroxyapatite or tricalcium phosphate ($Ca_3(PO_4)_2$) was detected during the calcination process. These two compounds are most probably decomposed by reacting with iron phosphate present in sewage sludge.

In our examinations, we determined the content of easily soluble (extraction in 1 mol HCl · dm^{-3}) and hardly soluble (extraction in concentrated H_2SO_4) forms of heavy metals (Table 3). Zinc appeared in the highest amount, followed by manganese and copper. The share of the hardly soluble form of heavy metals, with respect to the easily soluble one, ranged from 7 % (chromium) to 62 % (manganese). Latosinska and Gawdzik [18] indicated that heavy metals in sewage sludge ash were dominant in immobile fractions. These metals were bound with alumosilicates, sulfates and permanent organometalic connections. The allowable concentrations of some heavy metals in commercially available mineral fertilizers (arsenic, cadmium, lead and mercury) are defined in The Introduction of Fertilizers on the Commercial Market. Among the metals analyzed in the tested ash, cadmium and lead appeared in the quantities below the allowable limits.

Table 3

Content of heavy metals in ash from incinerated sewage sludge

Specification	Cd*	Cu	Pb**	Ni	Cr	Zn	Mn
	[mg · kg^{-1} d.m.]						
Easily soluble	0.66	396.2	33.16	9.54	10.14	789.0	625.0
Hardly soluble	1.12	870.6	70.09	49.36	128.81	3181.4	1102.4
Share of easily soluble form [%]	50	45	47	19	7	24	62

* Allowable content in mineral fertilizers 50 mgCd · kg^{-1} d.m.; ** allowable content in mineral fertilizers 140 mgPb · kg^{-1} d.m. [19].

Bialowiec et al [11] demonstrated low leachability of contaminants from ash originating from incinerated sewage sludge. Aqueous extracts were characterized by high pH, which may prove high immobilization of heavy metals and translates to their almost negligible leaching.

Fu-Shen Zhang et al [20] demonstrated that alkalinity (calcification effect) of ashes from organic waste corresponds to 10–30 % CaO and is particularly high in ashes from incinerated sewage sludge [13]. The content of plant available phosphorus relative to the total concentration of this element was about 37.6 % (27–44.5 %). The content of calcium in ash was 3- to 12-fold higher than in soil, while that of potassium exceeded the coil concentration by 1.3–6-fold. The concentrations of heavy metals (Ni, Cu, Zn, Cd, Sn, Pb) in ash generated by incinerating sewage sludge was 10- to 200-fold higher than their levels in soils in Japan [20].

Ash from incineration of sewage sludge is a prospective source of phosphorus for making phosphate fertilizers. Due to its high content of heavy metals and a relatively low bioavailability of phosphorus, prior to being used in farming, sewage sludge ash must be detoxicated with thermochemical methods. Increasing the availability of phosphorus to plants through acid processing has been described by several authors [21–23].

Phosphates recovered from sewage sludge ashes produce good fertilizing output without having adverse effects on plants. Considering the fact that agricultural use of raw sewage sludge will most definitely continue to decrease (in Switzerland it is even prohibited), phosphorus recycling will become indispensable. Treatment of ashes from sewage sludge incineration creates a more rational waste management option, as it is both friendly to the environment and focuses on identification and recycling of valuable ingredients [9]. However, due to a relatively high load of heavy metals (especially Cd, Cr, Cu, Ni, Pb and Zn), before being used in farming sewage sludge ash must be treated chemically or physically in order to decrease its content of the above contaminants below the legally binding maximum limits [8].

According to Kalmykova and Karlfeldt Fedje [24], amounts of phosphorus generated every year and arrested in the residues left after incineration of solid municipal waste could cover up to 30 % of the annual demand for phosphorus fertilizers in Sweden. The concentration of phosphorus in ash is slightly higher than in sewage sludge but the substance is not allowed to be applied on arable lands in that country because of its content of heavy metals. However, it would be beneficial to use it as a raw resource for production of fertilizers instead of phosphates.

A study by Ciesielczuk et al [13] revealed high differentiation in the content of heavy metals in ash from incinerated plant biomass. These authors found particularly high amounts of manganese, zinc and copper, which might be a factor justifying the use of ash as a source of supply of these elements to plants. In the light of the current legal regulations, due to the content of lead in excess of the set norm, ash from incineration of pine timber should be excluded from agricultural use.

The soil taken for our experiment was characterized by natural levels of heavy metals (Table 4). Ash applied to fertilize Virginia fanpetals elevated these concentrations but without exceeding the norms set for unpolluted soils. In respect of nickel, zinc and manganese, their concentrations in soil increased in proportion to the rate of ash. The highest ash dose, compared to the control, doubled the soil content of nickel forms soluble in 1 mol dm^{-3} HCl. As for the other heavy metals, the observed changes were much smaller and frequently appeared incidental.

Table 4

Content of heavy metals in soil

Rate of ash	Cd	Cu	Pb	Ni	Cr	Zn	Mn
	[$mg \cdot kg^{-1}$ d.m.]						
	Before the experiment						
	0.05 ± 0.02	1.48 ± 0.14	3.38 ± 0.57	1.76 ± 0.49	0.55 ± 0.13	9.48 ± 0.95	70 ± 19
	After harvest						
Control	0.053a*	2.360a	4.117a	0.806a	0.806a	11.50a	80.10b
P1	0.083a	2.321a	5.685a	1.186ab	0.779a	12.10a	76.49ab
P2	0.029a	2.190a	5.329a	1.265ab	0.757a	14.24b	87.27a
P3	0.044a	2.194a	5.018a	1.604b	0.751a	14.68b	88.89a

* Data designated with same letters do not differ significantly at $P \leq 0.01$.

Bielinska et al [25] did not determine any significant increase in soil concentrations of Zn, Cu or Cd in light soil enriched with fluidized ashes from hard coal in a rate calculated according to their content of CaO and the soil's liming demand. Other authors as well suggested that properly modified fluidized ashes can be used to improve the properties of soil [26]. Fu-Shen Zhang et al [20] concluded that sewage sludge ashes can be used to de-acidify acid soils. However, due to their content of heavy metals and the permissible maximum levels of copper in soil (125 $mgCu \cdot kg^{-1}$), the amount of ash which can be introduced to soil is 40–80 $Mg \cdot ha^{-1}$. The cited researchers emphasize that it would be recommendable to subject ashes to preliminary removal of heavy metals before they are introduced to soil.

Kovacik et al [27] noticed that in response to ashes (in doses from 3 to 150 $Mg \cdot ha^{-1}$) added to soil together with NPK fertilizers, the soil's pH increased and the amounts of plant available calcium, magnesium and potassium as well as the content of total carbon were higher. At the same time, the cation exchange capacity (CEC), total exchangeable bases (TEB) and base saturation (BS) increased whereas the bulk density of soil went down. The disadvantageous effect of the application of ashes was the decreasing content of total nitrogen and higher salinity of soil.

The fertilization level and associated rates of sewage sludge ash had a weak effect on the content of heavy metals in Virginia fanpetals plants, and the observed changes were inconsistent (Table 5). In an experiment by Borkowska and Lipinski [28], intensive nitrogen fertilization significantly decreased the concentration of nickel but a higher dose of phosphorus fertilizer contributed to a decreased amount of nickel in biomass of Virginia fanpetals.

Table 5

Content and uptake of heavy metals by Virginia fanpetals

Rate of ash	Cd	Cu	Ni	Cr	Zn	Mn
	[mg · kg^{-1} d.m]					
Control	0.25a*	2.17a	21.26a	1.62a	19.94a	69.29a
P1	0.40c	2.25a	21.57a	8.03b	28.38a	131.98a
P2	0.21a	2.11a	21.08a	8.81b	19.29a	77.60a
P3	0.35b	2.19a	19.28a	2.10a	22.89a	119.62a
Uptake [mg per pot]						
Control	0.005	0.046	0.455	0.035	0.426	1.482
P1	0.013	0.076	0.726	0.270	0.955	4.440
P2	0.011	0.110	1.099	0.459	1.006	4.046
P3	0.020	0.123	1.081	0.118	1.284	6.710

* Data designated with same letters do not differ significantly at $P \leq 0.01$.

Nitrogen and phosphorus contents in the aboveground mass of Virginia fanpetals increased proportionally to the dose of the ash (Table 6). The plants after the application of the average dose of ash had indeed highest N concentration, while the highest levels of P (2.36 times more than in control plants) was found in plants fertilized with the highest ash dose. The concentration of potassium and magnesium in the control plants was similar to the quantities of these components in Virginia fanpetals fertilized with the highest dose of ash. A significant increase of the calcium content in plant material was found only after the application of the highest dose of ash.

Table 6

Content of macronutrients in Virginia fanpetals

Dose of ash	N	P	K	Na	Mg	Ca
	[g · kg^{-1} d.m.]					
Control	6.15a*	1.65a	37.00b	0.05a	2.24a	27.22a
P1	6.21ab	1.72a	28.75a	0.22b	1.77ab	26.72a
P2	8.50b	1.58a	29.90a	0.25b	1.73b	27.76a
P3	7.47ab	3.89b	34.98b	0.21b	2.39a	33.08b

* Data designated with same letters do not differ significantly at $P \leq 0.01$.

Intensive nitrogen and phosphorus fertilization did not affect significantly the content of macronutrients and chlorine in Virginia fanpetals. Nourishment with potassium in the form of sulphide, compared to chloride, depressed the content of nitrogen, magnesium, calcium and chlorine in Virginia fanpetals [29] No significant changes in the content of crude ash or macronutrients caused by different rates of phosphorus fertilizers were observed [26]. Kalembasa [30] reported that incineration of Virginia fanpetals biomass generates 59.5 kg · Mg^{-1} of crude ash, and the amount of pure ash is 16.0 kg · Mg^{-1}.

The high crude to pure ash ratio (3.72) implicates high concentrations of silicate and carbonates. The dominant elements were calcium (66.3 %) and potassium (11.0 %), while zinc (0.10 %) was the prevailing heavy metal. Antonkiewicz [31] conducted an experiment on use of sewage sludge for rehabilitation of furnace ash disposal sites and found the highest content of Mg, Ca and K in a mix of grasses with white clover nourished with furnace ash alone, while the content of P and Na was the highest in plants fertilized with just sewage sludge.

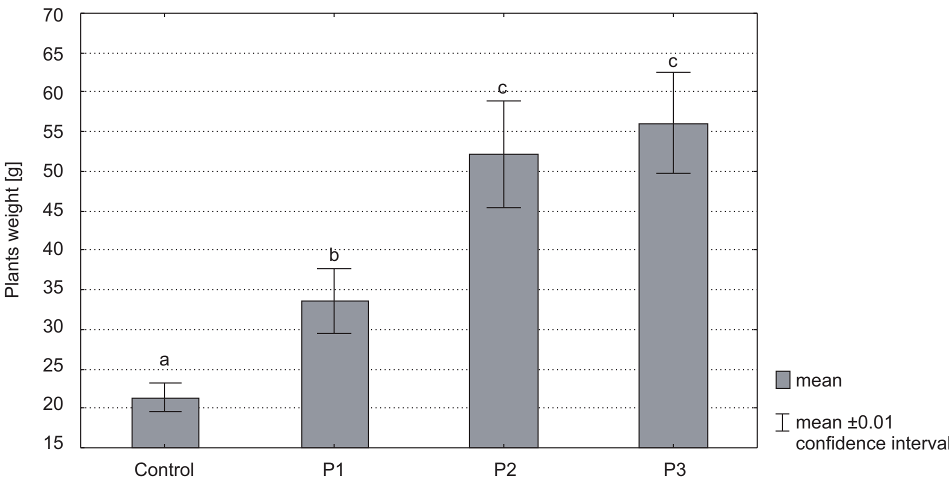

Fig. 1. Plants weight per pot (data destinated with same letters do not differ significantly at $P \leq 0.01$)

The biomass obtained from a single pot increased proportionally to the level of fertilization (Fig. 1). The P1 level fertilization regime raised the yield of Virginia fanpetals by 57 %, while the P2 level increased the yield by 2.5-fold relative to the control. Although the subsequently higher fertilization doses raised the yield of biomass, the increment was not significant. In a study reported by Borkowska et al [32], the level of fertilization with nitrogen (100 and 200 $kg \cdot ha^{-1}$) had no effect on yield of Virginia fanpetals biomass, while the phosphorus fertilization significantly increased biomass yields as the owing to the more intensive branching and increased height of the plants.

Conclusions

Ash originating from the incineration of sewage sludge completed at the Lyna Wastewater Treatment Plant in Olsztyn is characterized by a high mineralization rate and a markedly alkaline reaction. Phosphorus and calcium are dominant fertilizing elements. The content of cadmium and lead is below the permissible levels set for these metals in mineral fertilizers. Ash from incinerated sewage sludge used as a substitute of phosphorus fertilizers did not have any notable effect on the soil content of the mobile forms of cadmium, copper, lead and chromium. With respect to nickel, zinc and manganese, the medium and high rates of fertilizing ash significantly increased the content of these metals in soil. The yield of Virginia fanpetals and its content of nitrogen, phosphorus and potassium increased in proportion to the increasing doses of ash. The rate of ash, however, did not affect the concentration of sodium or magnesium in plants, but after an application of the highest rate of ash the plant content of calcium increased significantly. Ash modified the content of heavy metals in the plant material only very slightly.

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WYKORZYSTANIE POPIOŁÓW ZE SPALANIA KOMUNALNYCH OSADÓW ŚCIEKOWYCH DO NAWOŻENIA ŚLAZOWCA PENSYLWAŃSKIEGO

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Abstrakt: Celem pracy było określenie wpływu popiołu ze spalania osadów ściekowych na plon i skład mineralny ślazowca pensylwański oraz na zawartość metali ciężkich w glebie. Podstawę badań stanowiło doświadczenie wazonowe, w którym popiół ze spalania osadów ściekowych z oczyszczalni „Łyna" w Olsztynie był stosowany jako substytut nawozów mineralnych. W popiele tym dominującymi składnikami nawozowymi były fosfor i wapń. Zawartość kadmu i ołowiu była niższa od dopuszczalnych stężeń tych metali w nawozach mineralnych. Popiół ze spalania osadów ściekowych nie miał istotnego wpływu na zawartość w glebie z mobilnych form kadmu, miedzi, ołowiu i chromu. Średnie i wysokie dawki popiołu znacznie zwiększyły w glebie zawartość cynku, niklu i manganu. Dawki popiołu nie miał wpływu na zawartość sodu i magnezu w roślinach, natomiast największa dawka popiołu istotnie zwiększyła zawartość wapnia w roślinach. Popiół tylko nieznacznie modyfikował zawartości metali ciężkich w materiale roślinnym.

Słowa kluczowe: popiół ze spalania komunalnych osadów ściekowych, ślazowiec pensylwański, fosfor, metale ciężkie, gleba