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ACCUMULATION OF SELECTED HEAVY METALS IN WILLOW SHOOTS (S*alix viminalis* L.) CULTIVATED IN THE NEIGHBOURHOOD OF A COAL ASH AND SLAG LANDFILL

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Abstract

The aim of the study was to evaluate the contents of Cd, Pb, Zn and Cu in shoots of willow (*Salix viminalis L.*) cultivated in the vicinity of a coal ash and slag landfill. The landfill is surrounded by arable lands and meadows. There are two major negative influences of the landfill – dusting and flooding. The result of these interactions is the systematic reduction of agricultural value of the land. A field with an area of 9600 m^2 were chosen. The land is located east to the landfill. A total of 40 samples of biomass was collected. The contents of analysed elements were determined by FAAS using a Unicam Solaar M6 spectrometer. Distance from the landfill affects the contents of Cd, Pb, Zn and Cu in the tested willow shoots. However, there is no single concentration pattern for all the investigated metals. An increase in willow cultivation on the described area can bring a good environmental effect and become an example of proper management of the ash and slag landfill neighbourhood.

Keywords: willow, landfill, bottom ash, heavy metals.

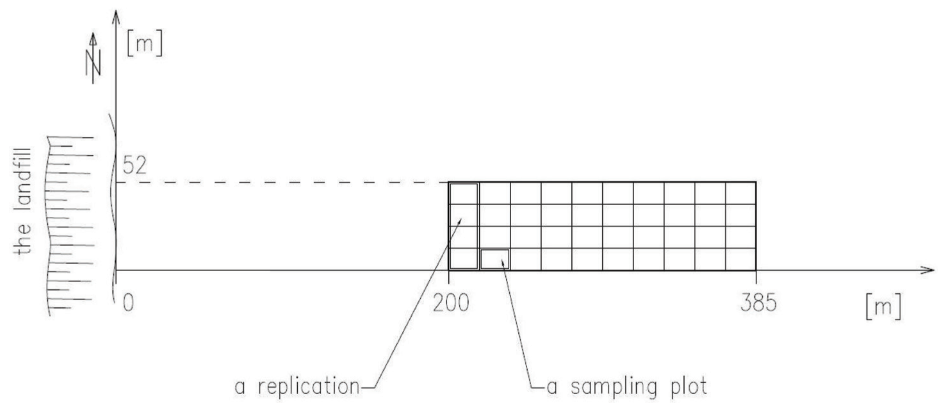
INTRODUCTION

Various solid wastes from energy production: fly ashes, slags or ash and slag mixtures are formed during electric power generation from solid fossils in power stations and combined heat and power stations (Plewa *et al.* 2007). For decades these wastes have been posing a serious environmental problem due to the lack of their rational and effective economic applications, as a result of which considerable amounts of wastes have been landfilled (Galos and Uliasz-Bocheńczyk 2005). Since water is used for hydrotransport of ash-slag mixtures, these objects were frequently located in the vicinity of oxbow lakes, on fertile alluvial soils, in the areas with good agricultural conditions. The landfills biological and technical protection of which was unsatisfactory revealed serious susceptibility to wind and water erosion and became a source of pollution for adjoining areas (Siuta 2005, Franik and Łaptaś 2005, Żygadło and Woźniak 2009). Another negative factor accompanying these landfills could be inundation of adjacent lands as a result of weight effect of huge waste masses stress on groundwater (Kostuch *et al.* 2016). The outcome of the above mentioned impact factors may be progressive agricultural and environmental degradation of the areas bordering the landfills. In order to prevent total agricultural degradation of these areas, they may be used for energy biomass production (Kostuch *et al.* 2016). The energy law obliges electrical energy producers to have a determined amount of "green energy" as a part of their annual offer. A far-reaching objective of the EU climatic and energy policy is to achieve at least 20% of energy generated from renewable sources by 2020. In compliance with the commitments made, the share of renewable energy in the primary energy consumption in Poland is to reach 15% by 2020. In this context it has been estimated that the demand for biomass of energy crops will grow even by 8 million Mg by 2020 (Kabała *et al.* 2010). The paper aims at an evaluation of potential use of willow (*Salix viminalis* L.) cultivated in the vicinity of combustion waste landfills for energy purposes. The detailed aim was to estimate the influence of the distance from the landfill on heavy metal contents in willow.

METHODS

The investigations were conducted in the vicinity of the slag and bottom of former ash landfill CEZ Skawina Power Station SA. The nearby land is under the influence of two negative phenomena: dusting and inundations. The result is a systematic decrease in the agricultural value of these areas. Agricultural production becomes abandoned, the fields are set aside and grasslands fall into disuse. The degradation processes have been the strongest on agricultural lands covering the area of ca. 60 ha situated east of the landfill (Mundała and Szwalec 2016). Here the inundations as well as dusting are most severe, mainly due to the west (50%) and south-west (20%) winds prevailing in this area. The field where willow (*Salix viminalis L.*) had been cultivated for many years was selected to the research. The object was an arable, square-shaped parcel (185 m length and

52 m width). The borders of the parcel were located at a distance of 200 m and 385 m from the landfill base (Fig. 1). The longer side of the parcel was situated parallel to the wind direction. The field was divided into 10 plots located at distances of: 200-218.5 m, 218.5-237 m, 237-255.5 m, 255.5-274 m, 274-292.5 m, 292.5-311 m, 311-329.5 m, 329.5-348 m, 348-366.5 m and 366.5-385 m from the landfill base. Each of these areas was 960 m^2. Each of the demarcated plots was subsequently divided into four other along the direction perpendicular to the line of prevailing winds. In this way, the pairs of plots are each other's replications. One sample of willow shoots was collected from each of the 240 m^2 plots (Fig. 1). One-year-old shoots were sampled and their leaves were removed. Two or three shoots were cut from five randomly chosen bushes from each of forty plots. The sample was about 0.75 kg fresh matter (f.m.). After drying to air-dry matter the shoots were ground in a high-speed grinder. 10 g of air-dry and homogenised plant material was taken for analyses. The samples were weighed with accuracy of 0.0001g. Dry mineralization at 460^{o}C was conducted in a muffle furnace, with dissolving HNO_3 and HCl extraction (Ostrowska *et al.* 1991). Concentrations of cadmium, lead, zinc and copper were determined by FAAS using a Unicam Solaar M6 spectrometer. Spatial distribution of mean contents of the studied heavy metals in willow shoots was analysed on the basis of analysis of variance. All statistical analyses were conducted using Statistica 10.0 programme at the 0,05 significance level. For simplification of the results description in the subsequent chapter, the distance from the plot centre to the landfill basis was assumed, i.e. 209 m, 228 m, 246 m, 265 m, 283 m, 302 m, 320 m, 339 m, 357 m, 376 m (rounded to full metres).



Source: Own elaboration

Figure 1. The field experiment in contents of its localisation to the landfill

RESULTS AND DISCUSSION

Willow (*Salix viminalis* L.) found multiple applications as, among others, wickerwork material and in chemical or furniture industries. In recent years its biomass has been used as power generating raw material which may be burned as chips, briquettes or pellets (Szczukowski *et al.* 2004, Czyż and Dawidowski 2005, Dubas 2006). Srogi (2007) points to the fact that establishing large plantation areas of energy crops, usually located on set-aside and degraded lands, may directly affect heavy metal concentrations and the quality of processed raw material.

Table 1. Contents of Cd, Pb, Zn and Cu in willow shoots (n=40)

Parameter	Cd	Pb	Zn	Cu
	mg*kg^{-1}dry matter (d.m.)			
Min	0.22	1.16	51.65	3.21
Max	0.55	4.20	95.81	9.52
Arithmetic mean	0.396	2.705	68.44	4.38
Geometric mean	0.387	2.616	67.51	4.194
Median	0.39	2.78	68.47	3.75
SD	0.083	0.648	11.47	1.489
V/variability index	%			
	21	24	17	34

Source: Own elaboration

No statistically significant differences were found for cadmium content in willow shoots closest (209 m) and at the furthest distance (376 m) from the landfill. For forty compared pairs of mean contents for this element, only eleven differed statistically significantly between themselves (Table 2). Therefore, finding a rule how the distance influences cadmium content in willow shoots proved impossible. It is different for lead content, as this metal concentrations in shoots are growing with increasing distance from the landfill. The lowest (1.74 mg·kg^{-1}) was noted at the distance of 209 m from the landfill base, higher 2.94 mg·kg^{-1} at the distance of 283 m from the landfill and the highest 3.18 mg·kg^{-1} at the longest distance of 376 m.

Table 2. The significance of differences for each pair of means for cadmium (horizontal) and lead (vertical); n.s.s no statistically significant differences, s.s. statistically significant differences

Cadmium

	209m	228m	246m	256m	283m	302m	320m	339m	357m	376m
209m		n.s.s	s.s	n.s.s	n.s.s	s.s	n.s.s	n.s.s	n.s.s	n.s.s
228m	s.s		n.s.s	n.s.s	s.s	n.s.s	n.s.s	n.s.s	n.s.s	n.s.s
246m	s.s	n.s.s		n.s.s	s.s	n.s.s	n.s.s	n.s.s	n.s.s	n.s.s
265m	n.s.s	s.s	s.s		s.s	n.s.s	s.s	n.s.s	n.s.s	n.s.s
283m	n.s.s	s.s	s.s	n.s.s		s.s	n.s.s	n.s.s	s.s	s.s
302m	s.s	n.s.s	n.s.s	s.s	n.s.s		s.s	s.s	n.s.s	n.s.s
320m	s.s	n.s.s	n.s.s	s.s	n.s.s	n.s.s		n.s.s	n.s.s	n.s.s
339m	s.s	n.s.s	n.s.s	s.s	n.s.s	n.s.s	n.s.s		n.s.s	n.s.s
357m	s.s	n.s.s	n.s.s	s.s	s.s	n.s.s	n.s.s	n.s.s		n.s.s
376m	s.s	n.s.s	n.s.s	s.s	s.s	n.s.s	n.s.s	n.s.s	n.s.s	

Lead

Table 3. Significant differences for each pair of means, copper (horizontal) and zinc (vertical); n.s.s. no statistically significant differences, s.s. statistically significant differences

Copper

	209m	228m	246m	265m	283m	302m	320m	339m	357m	376m
209m		n.s.s	n.s.s	n.s.s	s.s	s.s	s.s	s.s	s.s	s.s
228m	n.s.s		n.s.s	n.s.s	n.s.s	n.s.s	s.s	s.s	n.s.s	n.s.s
246m	n.s.s	n.s.s		n.s.s	n.s.s	n.s.s	n.i	n.s.s	n.s.s	n.s.s
265m	s.s	s.s	s.s		n.s.s	n.s.s	s.s	n.s.s	n.s.s	n.s.s
283m	s.s	s.s	s.s	n.s.s		n.s.s	n.i	n.s.s	n.s.s	n.s.s
302m	s.s	n.s.s	s.s	n.s.s	n.s.s		n.i	n.s.s	n.s.s	n.s.s
320m	s.s	s.s	s.s	n.s.s	n.s.s	n.s.s		n.s.s	n.s.s	n.s.s
339m	s.s	n.s.s	s.s	n.s.s	n.s.s	n.s.s	n.i		n.s.s	n.s.s
357m	n.s.s	n.s.s	n.s.s	s.s	s.s	n.s.s	s.s	n.s.s		n.s.s
376m	n.s.s	n.s.s	n.s.s	s.s	s.s	n.s.s	s.s	n.s.s	n.s.s	

Zinc

No statistically significant differences between zinc values were observed at the extreme investigated distances: 81.27 mg·kg^{-1} (209 m) and 74.15 mg·kg^{-1}

(376 m). Both values are higher and differ significantly from the concentration 57.77 mg·kg^{-1} found in the shoots from the centre of the investigated plot (283 m). Copper concentrations at the distance of 209 m are the highest (6.58 mg·kg^{-1}) and subsequently decrease to 3.85 mg·kg^{-1} (283 m), they differ statistically significantly. Further increase of the distance does not change the copper concentrations (they do not differ statistically) – for 302 m the concentration is 3,59 mg·kg^{-1}, 320 m – 3,36 mg·kg^{-1}, 339 m – 3,50 mg·kg^{-1}, 357 m – 3,90 mg·kg^{-1}, and finally 376 m – 3,69 mg·kg^{-1}. Because the described changes refer to a transect located in accordance with the prevailing wind direction, they may be due to air flow disturbances generated by the 22 m high slag heap and, additionally, by more than a dozen metres high trees growing on the eastern slope of the landfill. The other factors may be metal bearing dust fall from the other sources of emission, such as, among others, a power station situated ca. 2000 m east of the landfill, or carried from the Upper Silesia region by the prevailing wind (Mundała and Szwalec 2016). Since neither mineral fertilizers nor pesticides were used in the described area for several years, their impact on heavy metal contents could be omitted (Mundała and Szwalec 2016). In Poland, various guidelines or branch regulations referring to biomass emphasize such parameters as: moisture content, mechanical strength, calorific value, bulk density and ash content (Wisz and Matwiejew 2005). Lack of clear regulations stating the admissible contents of various pollutants in biomass may open markets to the import of various materials (including wastes) of poor quality, which as a result of their technical processing may pollute the environment. Considering biomass quality assessment in view of trace element concentrations, including cadmium, lead, zinc and copper, PN-EN 14961:2010 standard may be applied. The standards state the reference values and the range within which individual elements occur. For deciduous trees wood (without leaves and bark) the reference value for Zn is 10 mg·kg^{-1} and the most frequent range from 5 to 100 mg·kg^{-1}, the reference value for Cd is 0.1 mg·kg^{-1} and the range 0.05-0.5 mg·kg^{-1}, for lead and copper the values are equal: 2 mg·kg^{-1} and the range 0.5 – 10 mg·kg^{-1}.

In the literature of the subject, the upper limit of the range is treated as the maximum admissible value of a given metal in biomass. Considering cadmium content, 12.5% of the analysed willow shoot samples exceeded the maximum admissible limit. For the other metals, i.e. lead, copper and zinc, all determined values were lower than admissible. However, nearly all determined metal concentrations exceeded the corresponding reference values – for Cd, Pb and Cu in all tested samples, and for Zn in 85% of the samples. Before 2010, when EN 14961:2010 standard had not been in force, biomass was evaluated according to, among others, German standard DIN 51731 (Borkowska and Lipinski 2007), in which among all analysed elements only admissible copper concentration was lower, i.e. below 5 mg·kg^{-1}d.m. If this maximum value is assumed for Cu, in 17.5% of the examined willow shoot samples Cu concentration was exceeded.

A slight exceedance of the admissible cadmium content in the examined willow shoots may be the result of a greater uptake of heavy metals by plants occurring among others in acidified soils (Kabata-Pendias and Pendias 1999, Ociepa *et al*. 2014). Studies conducted in this area prove the presence of slightly acid and acid soils with low humus content (Szwalec *et al*. 2017). The contents of the above mentioned element and all the others may be maintained within the range of values admissible by the quoted PN-EN 14961:2010 standard by, among others, proper fertilization, primarily by organic fertilizers, and maintaining proper soil reaction. Kalembasa *et al.* (2009) evaluated biomass quality cultivated in a many-year field experiment in different fertilization conditions. Values for lead concentrations stated by the authors (1.85 to 5.09 $mg \cdot kg^{-1}$d.m.) were in the range comparable with the tested willow (Table 1). Cadmium (3.87-0.976 $mg \cdot kg^{-1}$d.m.) and copper (7.74-17.23 $mg \cdot kg^{-1}$d.m.) concentrations were higher, whereas zinc content (51.65-95.81 $mg \cdot kg^{-1}$d.m.) was lower. Cuiping *et al.* (2003) characterized the quality of 22 kinds of biomass cultivated in China regarding, among others, their heavy metal content. Mean concentrations of cadmium (0.866 $mg \cdot kg^{-1}$d.m.), lead (10.97 $mg \cdot kg^{-1}$d.m.), copper (76.48 $mg \cdot kg^{-1}$d.m.) and zinc (162.89 $mg \cdot kg^{-1}$d.m.) stated by the authors were between several and over a dozen times higher than determined in the tested willow shoots. Kabała *et al*. (2010) and Stańczyk-Mazanek *et al*. (2014) suggest the use of willow for management of poor quality soils and reclamation of degraded areas. It is of crucial importance for the described area where, as has been mentioned before, each year we observe a systematic decrease in the agricultural value of the arable fields and grasslands situated in this place. Ostrowski *et al*. (2009) point to the fact, that despite a common erroneous opinion about small habitat requirements of willow, the plant grows best in the best soils. Currently it is class IIIa and during intensive growth the plant is greatly sensitive to water deficiency. Considering inundations occurring in this area and additional opportunity to utilize produced biomass by a nearby power station, a considerable extension of willow plantation in this place is recommended.

CONCLUSIONS

1. The distance from the landfill influenced Cd, Pb, Zn and Cu concentrations in tested willow shoots. However, no unanimous concentration pattern was stated for all analysed metals.
2. Investigated willow shoots could be used for power generation.
3. Potential cultivation of willow in the described area may bring good results for the environment and become a right example for the management of the area adjoining a combustion waste landfill situated in the vicinity of oxbow lakes.

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