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ORIGINAL PAPER

STUDY ON THE CONTENT OF HEAVY METALS IN PLANTS WHICH OCCUPY ACTIVE ASH SETTLING PONDS OF THE DOLNA ODRA POWER PLANT*

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Abstract

Ash, a by-product of combustion processes, should be treated as a substance which may replace natural raw materials. However, an unresolved problem is how to tackle ash storage areas, which should be rehabilitated. The purpose of the study was to determine which species of plants are able to colonise active ash settling ponds, and under what conditions these plants can develop. During the plant growing season of 2015, field studies were performed on the surface of two active ash settling ponds of the Dolna Odra Electric Power Station. Special attention was paid to the composition of flora, as well as the chemical composition of ash and plants. The plant coverage of the ash settler surface was found to vary from 1 to 60%, depending on the level of water. The fauna included common pioneer species (*Agrostis stolonifera*, *Atriplex patula*, *Juncus bufonius*, *Phragmites australis*, *Poa pratensis*, *Ranunculus sceleratus*). The conditions of their growth were defined by the content of macro-elements of the ash, which varied from medium to very high, its pH_{KCl} (7.96) and the optimum degree of saturation of the sorption complex with cations (V 98.4%). The factors that modified the plant growth could be high salinity (2.38 mS cm^{-1}) and the content of exchangeable Na (39.5%). The total content of heavy metals in the ash and plants was below the critical one. The species which have been able to colonise the active ash settling ponds belong to the pioneering plants of habitats connected with water. However, the analyzed habitat does not basically affect the morphology of plants, except for common reed.

Keywords: fly ash, flora inhabiting hydrosettlers.

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INTRODUCTION

The appearance of flora spontaneously developing in industrial areas depends on the prevance of stress conditions in the environment. For example, the area affected by industrial contaminations emitted by the Police Chemical Plant is overgrown with the flora consisting mainly of nitrophilous (*Artemisietea vulgaris* class), synantrophic (*Stellarietea mediae* class), felling-site (*Epilobietea angustifolii* class) and meadow species from *Molinio-Arrhenatheretea* class (MELLER et al. 1998). The ability of fly ash deposits to be covered by plants has been investigated in many countries worldwide (BILSKI et al. 2011, PANDEY et al. 2015).

Ash deposited in storage areas causes many hazards and threats to the environmental protection. The leaching of hazardous substances by rainwater filtering through a storage area is particularly dangerous because it may result in the contamination of ground or surface waters over a large area. During hydraulic waste storage, spherical grains of the density lower than that of water create the so-called 'film' on the surface of water, which can be a dozen or even several dozen centimeters thick. These grains dry quickly and are then transported over considerable distances (ŻYGADŁO, WOŹNIAK 2009).

Ash, a by-product of combustion processes, should be treated as a substance which may replace some scarce natural raw materials. Ash can be useful in the construction industry, e.g. added to cements (KHALILA et al. 2014), or to materials for building roads and flood banks (TAKHELMAYUM et al. 2013, STRZAŁKOWSKA 2016). Ash is also used in waste treatment (VISA 2016), rehabilitation of post-industrial sites and in agriculture (KOVÁČIK et al. 2011, KAUR, GOAL 2015, WIERZBOWSKA et al. 2015, ŻOŁNIERZ et al. 2016). However, an unresolved problem is how to tackle ash storage areas, which should be rehabilitated. Such rehabilitation requires considerable know-how and large financial inputs (GILEWSKA 2004). Simultaneously, self-sown plants appear in many sites. This is the flora resistant to the biological conditions of a given area (JASIONKOWSKI et al. 2016).

The purpose of the study has been to determine what species of plants are able to colonise active ash settling ponds, acclimatise to the layer of the microsphere and develop. Another objective was to identify under what conditions these plants developed and how their morphology and chemical composition could be affected.

MATERIAL AND METHODS

Methods of floristic and phytosociological analysis

During the growing season of 2015, field studies were performed over 0.4 hectare of the surface area of two active ash settling ponds (A, B) of the Dolna Odra Electric Power Station in Nowe Czarnowo. Special attention was paid to the composition of the flora. The surface areas of the settling ponds were divided into 18 plots, each measuring 10x10m, where the number of species and specimens of the plants were determined. The study was carried out parallel to subsequent operations of emptying the settling ponds. The floristic studies were performed using the Braun-Blanquet method, which specified the numerical (+-5) coverage of the substrate by plants. 18 phytosociological photos were taken of the two settling pond surfaces, and each photo captured an area of 4 x 4 m of a pond's surface. The identified species were attributed to particular plant communities (Brzeg, Wojterska 2001).

Methods for analysis of habitat

An aggregate sample of the microsphere, referred to as ash, was taken from the material drifting on the water surface of the ash settling ponds (12 plots located every 10 m on the surface of each settling pond). Samples of the aerial plant parts were taken as well. The plant samples were dried to the air-dry condition and ground. Then, the following were determined:

- total content of the elements: carbon (C), nitrogen (N) and sulphur (S), in an elemental analyzer;
- after mineralisation of the samples in a mixture of concentrated acids (HNO_3) and $HClO_4$ (3:1), the total content of P was determined in a colorimeter, Mg, Fe, Zn, Cu, Ni, Pb, Cr, Co – by the ASA method, and Ca, K, Na – by the ESA method.

After drying, a sample of ash was comminuted, and then the following determinations were made: the graining of the sample – by the aerometric method, the sand fractions – by separating them on screens, pH in potassium chloride of the concentration of 1 mol KCl dm^{-3} (pH_{KCl}), salinity – as electrolytic conductivity (the proportion of ash to water 1:5), the content of total Pb, Zn, Cu, Ni and Cd after mineralization in the concentrated acids HNO_3 and $HClO_4$ (1:1), the total content of C, N and S in an elemental analyzer, the assimilable forms of P and K by the Egner-Riehm method and Mg by the Schachtschabel method, the content of Fe, Mn, Zn and Cu forms soluble in 1M HCl, the cations exchangeable: Ca, Mg, K, Na extracted by CH_3COONH_4 of the concentration of 1 mol dm^{-3}, the acidity by the Kappen method, the content of calcium carbonate by the Scheibler method. The density of ash was measured using the pycnometric method on a Quantachrome Instruments Ultrapycnometer (model Ultrapyc 1200 e). Argon of 99.99% purity was applied as the pycnometric gas.

Determination of the content of exchangeable cations and hydrolytic activity allowed us to calculate the sorption complex capacity and the degree of saturation by base cations.

The phytoaccumulation factors (PF) in the plants were calculated according to the formula developed by WIECHUŁA et al. (2013):

$$\mathbf{PF} = \boldsymbol{cr}^{-1}\, cg,$$

cr – content of the element in the plant,

cg – content of the element in the soil.

The PF evaluation

To evaluate the accumulation of heavy metals, after LASKOWSKA and WIECHUŁA (2015) it was assumed that the value of the phytoaccumulation factor (PF) higher than 1 indicates intensive accumulation of metals in a plant, the values from 0.1 to 1 – medium accumulation, whereas from 0.01 - 0.1 – weak accumulation and lower than 0.01 – lack of accumulation.

The coefficients of specific accumulation (CSRA – Coefficient of Specific Relative Accumulation) were calculated from the formula by WIECHUŁA et al. (2013):

$$\mathrm{CSRA} = cr^{-1}\, c,$$

cr – the average amount of the element in the test plant,

c – the average amount of the element in all plants growing in a given area.

RESULTS AND DISCUSSION

Floristic analysis

Spontaneous flora begins to form on ash hydro settling ponds owing to self-sown plants. Six species of plants were found in the area covered by the study: buttercup *Ranunculus sceleratus* L., spear saltbush *Atriplex patula* L., creeping bentgrass *Agrostis stolonifera* L., toad rush *Juncus bufonius* L., common reed *Phragmites australis* (Cav.) Trin. ex Steud and Kentucky bluegrass *Poa pratensis* L. The species of the plants (Table 1) found on the settling ponds belong to common, cosmopolitan plants resistant to stress environmental conditions.

Presence of water in the area occupied by the ash settling ponds of the Dolna Odra Electric Power Station submitted to the study resulted in the dominance of species typical of marshy habitats. DYGUŚ et al. (2014) confirmed the presence of species of the alluvial and even wet habitats in their study. These authors contributed the presence of such species as *Deschampsia caespitosa*, *Symphytum officinale*, *Phragmites australis* to the very high water capacity of furnace waste (mainly fly ash).

Table 1

Ecological features of the identified plant species

Species of plants	Ecological features
Poa pratensis	common species, cosmopolitan, resistant to habitat conditions, creates strong turf, tolerate fairly long pickle, easily develops underground stolons
Agrostis stolonifera	common species, resistant to habitat conditions, easily develops underground stolons, grows on sediments
Phragmites australis	common species, cosmopolitan, resistant to habitat conditions, easily develops underground stolons
Juncus bufonius	common species, cosmopolitan, resistant to habitat conditions, it occurs in sediments
Atriplex patula	common species, cosmopolitan, it occurs in sediments
Ranunculus sceleratus	common species, cosmopolitan, it occurs in sediments

Grasses are characterized by fast reproduction, which means that their population increases manifold in a short time. Three species of grasses were found in the area of the ash settling ponds covered by our study: *Agrostis stolonifera*, *Phragmites australis* and *Poa pratensis*.

Diversification of the flora of the settling ponds

The two ponds differed considerably in terms of the floristic composition and coverage by flora. This was mainly due to the higher water level in settling pond B. The compactness of flora in settling pond A, with the water level of 0.5 m, was 10%, compared to 1% in settling pond B (Table 2). The latter settling pond was covered with clusters of plants in selected locations. (Figure 1). The biggest plant density over the surfaces was in the middle part, just off the shore (from 141 to 153 pieces of plants in settling pond A, and from 101 to 113 specimens of plants in settling pond B). Numerous specimens of *Poa pratensis* with raised green parts (Figure 1) were present along

Table 2

The number of species and specimens of the plants [pcs] in the studied areas of settling ponds A and B

Object A	Experimental plots in the settling pond			Geographic direction ↑ N	Experimental plots in the settling pond			Object B
	4/82	3/49	3/82		3/41	2/31	1/15	
	4/91	2/41	2/97		2/52	1/12	1/10	
	4/153	3/52	2/83		2/113	0/0	1/8	
	3/141	1/69	2/79		2/101	0/0	1/11	
	3/120	1/54	2,65		3/42	0/0	0/0	
	2/88	2/61	2/39		2/5	0/0	0/0	

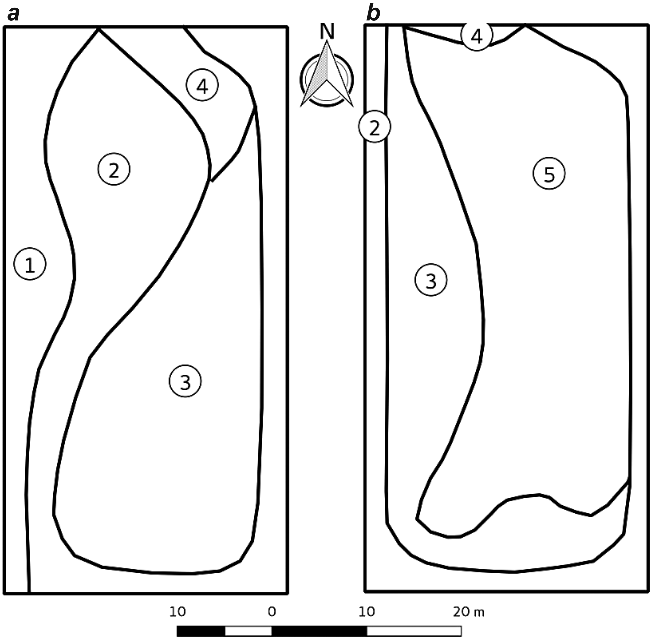

Fig. 1. Border line of dominant species distribution observed on two ash settlers dominant species: 1 – *Poa pratensis*, 2 – *Juncus bufonius*, 3 – *Phragmites australis*, 4 – *Ranunculus sceleratus*, 5 – no plants

the shores of settling pond A. In the least watered places, the compactness of flora reached 60%. Over these areas, meadow grass was accompanied by small specimens of *Agrostis stolonifera* of the wide-spreading form. *Juncus bufonius* considerably overgrown shallow and drier places, located close to the edges of the settling pond, where they co-occurred with single specimens of *Atriplex patula*. Only few specimens of flora were found next to the shoreline of settling pond B. *Phragmites australis* covered the entire surface of settling tank A, whereas the same plant species colonised only a narrow shore belt of settling pond B. *Ranunculus sceleratus* was present next to the filler valves, in the driest places. The higher water level in settling pond B meant that a considerable surface area of this pond was deprived of flora. Similar results were obtained by Jasionkowski et al. (2016). Namely, the plant cover on a fly ash landfill was sparse and most of the substrate surface was bare.

The identified species belonged to three types of the plant habitats: short-lived segetal and rudimentary habitats – the *Stellarietea mediae* class, water and marshy communities – the *Phragmitetea australis* class, and short-lived muddy communities of water body shores and periodically flooded recesses – the *Isoëto-Nanojuncetea* class (Table 3). Four phytocenoses were demonstrated in the studied area (explanations: Cl. – class, O. – order, All. – alliance, Ass. – association, Zb. – community):

Table 3

The phytosociological characteristics of the species dominating and demonstrated in the ash settling ponds

Object	A	B
The number of photos [pcs]	18	18
Relevement I (R) [+-5] stability (S) [I-V]	R S	R S
ChCl. *Phragmitetea*, O. *Phragmitetalia*, All. *Phragmition*		
Phragmites australis	1-4 IV	1-2 II
Agrostis stolonifera	+-1 IV	+ I
ChAll. *Magnocaricion*		
Poa pratensis	3-4 III	.
ChCl. *Isoëto-Nanojuncetea*, O. *Nanocyperetalia*		
Juncus bufonius	2-4 IV	+-1 II
ChAll. *Nanocyperion flavescentis*		
Ranunculus sceleratus	1-4 I	2-3 I
Cl. *Stellarietea mediae*, ChO. *Sisymbrietalia*		
Atriplex patula	+-1 III	+-2 I

Water and marshy communities

Cl. *Phragmitetea australis* (Klika in Klika et Novák 1941) R. Tx. et Preising 1942;

O. *Phragmitetalia australis* W. Koch 1926;

All. *Phragmition communis* W. Koch 1926;

Ass. *Phragmitetum communis* Kaiser 1926;

All. *Magnocaricion elatae* W. Koch 1926;

Zb. *Poa pratensis.*

Short-lived muddy communities of water body shores and periodically flooded recesses

Cl. *Isoëto-Nanojuncetea* Br.-Bl. et R. Tx. 1943 ex Westhoff et al. 1946 nom. illeg;

O. *Cyperetalia fusci* Pietsch 1963;

Zb. *Juncus bufonius*;

ChAll. *Nanocyperion flavescentis* W. Koch. 1926 nom. inval. p. p.;

Zb. *Ranunculus sceleratus.*

The *Phragmitetum* association dominated in the area of the highest water levels, as common reeds settled over the water and marshy areas. In settling pond A, common reed was found over a large surface (1-4 IV), whereas in settling pond B, this plant grew only along the shore (1-2 II). Closer to the shores of the settling ponds, there was a community of plants typical of periodically flooded recesses – *Juncus bufonius* (2-4 IV), which occupied the northern and middle part of settling pond A. A community of these plants was also present in a very narrow strip of the shore of settling pond B (+-1 II). A community of *Poa pratensis* (3-4 III) was present in the least hydrated area. *Poa pratensis* was not present in settling pond B.

Morphology of flora

Except for common reed, all the species of plants were characterised by an appropriate height, colour and ability to bear seeds. Common reed had a faint stem and small saturation of the aerial parts with green. Common reed was unable to reproduce generatively, but created new patches through few but very long rhizomes.

Analysis of the habitat

The material stored in the active ash settling ponds may be classified as the subsoil. The specific density of the ash taken from the settling ponds was lower than the specific density of water (Table 4), with the fraction of sand dominating in the ash. The clay content substantiated the classification of this material to the textural group of sand (PTG 2009).

The pH_{KCl} value of ash (Table 5) matched the alkaline reaction [pH], although higher pH values (Komonweeraket et al. 2015, Kaur, Goal 2015) were found in ash from an electric power station. The electrolytic conductivity (Table 5) it was higher than in the soil of a sulphur mine (Likus-Cieślik et al. 2015). While evaluating the remaining properties shown in Table 5, we should pay attention to the content of calcium carbonate, which indicates considerable resistance of the material to acidification. This finding is all the

Table 4

Ash specific density and percentage content of fractions of a diameter

Specific density (g cm^{-3})	Content of the fraction of a diameter (mm), %								
	skeleton > 2.0	sand						silt	clay
		2.0-1.0	1.0-0.5	0.5-0.25	0.25-0.1	0.1-0.05	Σ	0.05-0.002	<0.002
0.625	0.0	0.0	0.0	0.0	11.2	79.8	91.0	4.0	5.0

Table 5

Selected physicochemical properties of ash

pH_{KCl}	Electrolytic conductivity (mS cm^{-1})	$CaCO_3$	Total content			Available forms		
			C	N	S	Mg	P	K
		(g kg^{-1} soil)				(mg kg^{-1} soil)		
7.96	2.380	20.4	6.86	0.477	2.13	99	160	373

more important because the sulphur content was elevated by anthropogenic sources, as in the forested soil of the sulphur mine (Likus-Cieślik et al. 2015).

The C/N proportion (14.4:1) was similar to that found in agrarian soils (Meller et al. 2013). The content of the macro-elements (Table 5) available to plants was very high, whereas the content of the micro-elements was high.

The capacity of the ash sorption complex (Table 6) was higher than the capacity of natural soils with the graining typical of clays (Meller et al. 2013). The saturation of the sorption complex with alkaline cations (V) was 98.4%, whereas the percentage of sodium was 39.5% (Table 6). The above

Table 6

Hydrolytic acidity, exchange cation content and sorption properties [cmol(+)/kg] as well as base saturation, BS (%), and shares of exchangeable Ca, Mg, K and Na in CSC

HA	Ca_{ex}	Mg_{ex}	K_{ex}	Na_{ex}	BEC	CSC	BS (%)	Share in CSC (%)			
[cmol(+) kg^{-1}]								Ca	Mg	K	Na
0.49	16.2	0.73	1.08	12.1	30.1	30.6	98.4	52.9	2.4	3.5	39.5

justified a conclusion that it was saturated sorptively more than natural soils (Chudecka, Tomaszewicz 2015). Following Ochman and Jezierski (2011), the V value above 80% is very favourable for the growth and development of plants, provided that the percentage of sodium is below 30%. While the first condition (the V value) in the tested ash was fulfilled, the second was not - which should be viewed as harmful for plants. Simultaneously, the share of magnesium in the sorption complex was lower than in natural soils (Zalewska 2007).

As the composition of combustion by-products is conditioned by carbon (Bradło et al. 2014), the evaluation of the content of heavy metals in ash is necessary. Their excessive quantities may affect both plants and the ways in which ash can be used. The content of heavy metals (Table 7) did not exceed

Table 7

Total content of heavy metals in ash and plants

Sample	Zn	Cu	Pb	Cr	Co	Ni
	(mg kg^{-1} soil)					
Ash	53.6	73.3	92.39	32.19	13.31	53.02
Phragmites australis	16.0	4.5	1.612	3.529	0.200	7.567
Poa pratensis	10.1	5.8	1.390	3.255	0.177	6.322
Agrostis stolonifera	24.6	8.0	0.664	4.862	0.815	8.162
Juncus bufonius	28.5	10.8	2.586	4.414	1.175	7.668
Atriplex patula	48.8	16.3	4.836	3.710	0.634	7.616
The average content	18.6	6.5	1.355	3.913	0.606	7.492

the critical values accepted in the *Regulation of the Minister Of Environment* (2016), which refer to the soils of category IV – industrial lands, and soils of category II, agricultural lands, very light mineral soils.

The content of heavy metals in the studied plants was lower than the critical values for organic fertilizers accepted in the *Regulation of the Minister of Agriculture and Rural Development* (2008). This was caused by the alkaline reaction of the ash as well as the high content of cations of calcium, magnesium and sodium, which limited the solubility and bioavailability of metals (JASIEWICZ, ANTONKIEWICZ 2009). In an evaluation of values of the phytoaccumulation ratio, PF (LASKOWSKA, WIECHUŁA 2015) for zinc, chromium and nickel (Table 8), it was found that the degree to whch these elements were

Table 8

The value of the phytoaccumulation coefficient (PF) for heavy metals in plants

Species of plants	Heavy metals					
	Zn	Cu	Cr	Co	Ni	Pb
Phragmites australis	0.299	0.061	0.110	0.015	0.143	0.017
Poa pratensis	0.189	0.079	0.101	0.013	0.119	0.015
Agrostis stolonifera	0.459	0.109	0.151	0.061	0.154	0.007
Juncus bufonius	0.532	0.148	0.137	0.088	0.145	0.028
Atriplex patula	0.304	0.066	0.115	0.048	0.144	0.010

accumulated was medium, irrespective of species of plants. Phytoaccumulation was low for cobalt. Differences in the PF values among the species occurred only in the case of copper and lead. Bentgrass and common rush accumulated copper to a medium degree, whereas the remaining plants absorbed this element to a low degree. The PF values for lead indicated low accumulation, whereas no accumulation of this element was found in bentgrass.

The values of the ratios of specific accumulation of heavy metals (CSRA) show that toad rush had the biggest capacity to accumulate heavy metals.

Table 9

The value of the specific accumulation coefficient (CSRA) factor for heavy metals in different species plants

Species of plants	Heavy metals					
	Zn	Cu	Cr	Co	Ni	Pb
Phragmites australis	0.810	0.617	0.879	0.338	1.018	1.031
Poa pratensis	0.510	0.796	0.811	0.299	0.851	0.889
Agrostis stolonifera	1.241	1.100	1.211	1.377	1.099	0.425
Juncus bufonius	1.439	1.487	1.099	1.986	1.032	1.655
Atriplex patula	0.823	0.664	0.924	1.071	1.025	0.600

Toad rush was surpassed by creeping bentgrass only in the case of chromium accumulation. The plant with the lowest CSRA values for Zn, Cr, Co and Ni was Kentucky bluegrass. Common reed accumulated copper to the lowest degree, whereas creeping bentgrass accumulated lead to the lowest degree (Table 9).

CONCLUSIONS

1. The species which have been able to colonise the active ash settling ponds belong to the pioneering plants of habitats connected with water, i.e.: water and marshy (the *Phragmitetea australis* class), muddy water shores and periodically flooded recesses (the *Isoëto-Nanojuncetea* class) and from the short-lived segetal and rudimentary communities (the *Stellarietea mediae* class).

2. The settling ponds studied differed in the degree of plant cover of the surface areas, and in the location of plant patches.

3. The fly ash which created the top layer in the settling ponds had reaction tolerated by plants and supplied macro- and micro-elements available for the plants.

4. Factors which limit the development of flora could be high salinity and excessive content of sodium in the sorptive complex. However, this basically does not affect the morphological make-up of plants, except for common reed.

5. The content of heavy metals (Zn, Cu, Cr, Cd, Ni, Pb) in ash proved that the ash was moderately contaminated material. However, it did not cause excessive accumulation of the above elements in plants.

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