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Herbaceous plants as heavy metals accumulators in conditions of ash and slag dumps

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Key words: *pollutants, heavy metals, bioaccumulation indexes, vegetation of technogenic ecotopes, phytoremediation.*

Storage of ash and slag waste causes a number of environmental problems, including the transformation of natural geochemical cycles and the change of the natural radioactive background due to the increased concentration of heavy metals and radioactive isotopes in coal combustion products. Plants can provide an effective approach for the analysis and monitoring of heavy metals contamination. Additionally, vegetation plays a significant role in the restoration and remediation of heavy metal-contaminated soils. The application of plants in phytoremediation is a green and sustainable solution for decontaminating polluted sites. Moreover, the key role in the restoration of contaminated sites belongs to native species. Within the presented research, the abilities of native dominant species to accumulate and tolerate heavy metals in conditions of ash and slag dumps were investigated on a limited number of samples. Primary analysis of the bioaccumulation of heavy metals through the bioaccumulation coefficient showed that zinc has the highest accumulation capacity in the studied species. The ability to bioaccumulate the analyzed heavy metals decreases in the following order: Zn > Fe > Cu > Mn > Cd > Ni > Pb. Indexing the biogeochemical activity of the tested species showed higher levels of biochemical activity for *Anthemis arvensis* L. than for *Achillea millefolium* L., however, these data need to be confirmed by statistical analysis. Determination of the translocation index of elements reflected the high mobility of zinc and cadmium with a high rate of transferring to above-ground biomass, but the potential for accumulation requires scaling up the experiment with the involvement of a larger number of samples and performing statistical data processing. Due to their ability to accumulate heavy metals in roots, plant species could be used for phytostabilization. Establishing methods of biomonitoring and the development of green reclamation technologies with native species application need further research with both selected species and other local species. The presented research showed primary results of bioindication and references for phytoremediation of heavy metal contamination of the ash and slag dumps, which is relevant for other similar environmental conditions.

Key words: *pollutants, heavy metals, bioaccumulation indexes, vegetation of technogenic ecotopes, phytoremediation.*

Акумуляція важких металів трав'яними рослинами в умовах зростання на золошлаковідвалах

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Ключові слова: *полютанти, важкі метали, рослинність техногенних екотопів, індекси біоакумуляції, фіторемедіація.*

Накопичення та зберігання золошлаковідвалів викликає низку екологічних проблем, серед яких трансформація природних геохімічних циклів, зміна природного радіоактивного фону через підвищення концентрації важких металів та радіоактивних ізотопів у продуктах спалювання вугілля. Рослинні організми є високоінформативними біоіндикаторами забруднення важкими металами. Крім того, рослинність відіграє пріорітетну роль у відновленні та рекультивації забруднених важкими металами ґрунтів. Використання рослин у фіторемедіації є перспективним, екологічно стійким рішенням для відновлення територій, що зазнали забруднення важкими металами. Слід зазначити, що ключова роль у відновленні таких земель належить саме місцевим аборигенним видам. У представленому дослідженні показано первинне дослідження на обмеженій кількості зразків здатності аборигенних видів рослин до акумуляції важких металів та стійкості до них в умовах золошлаковідвалів. Аналіз накопичення важких металів через коефіцієнт біоакумуляції показав що найвищу акумулюючу здатність у досліджуваних видах виявляє цинк. Здатність аналізованих важких металів до біоакумуляції зменшується у порядку: Zn > Fe > Cu > Mn > Cd > Ni > Pb. Попередня оцінка індексації біогеохімічної активності досліджуваних видів показала дещо вищі рівні біохімічної активності *Anthemis arvensis* L., аніж *Achillea millefolium* L., проте ці дані потребують підтвердження статистичним аналізом Визначення індексу транслокації елементів відобразило високу рухливість цинку та кадмію, що характеризується високою інтенсивністю переходу цих елементів у надземну біомасу. Завдяки здатності накопичувати важкі метали в коренях, досліджувані види рослин можна використовувати для фітостабілізації, однак аналіз потенціалу до акумуляції потребує масштабування експерименту із залученням більшої кількості зразків та проведення статистичної обробки даних Для широкого впровадження методів біомоніторингу та розвитку технологій фіторекультивації із застосуванням місцевих видів необхідні подальші дослідження як із обраними видами, так і з іншими місцевими видами. Представлене дослідження відображає первинні результати біоіндикації з використанням двох видів аборигеннної флори, а також висвітлює перспективи використання досліджуваних видів у фіторемедіації забруднених важкими металами території золошлаковідвалів.

Ключові слова: *полютанти, важкі метали, рослинність техногенних екотопів, індекси біоакумуляції, фіторемедіація.*

Introduction

Thermal power plants are sources of heavy metal contamination as during the process of coal combustion a significant amount of various trace elements, including heavy metals (such as Pb, Cu, Mn, Zn, Ni, Cd etc.) released to the environment[1,2]. It causes numerous environmental problems – contamination of heavy metals is one of the most pressing threats to water and soil resources as well as human health[3,4,5]. Storage of waste from coal combustion (ash and slag) is another factor of environmental risk from thermal energy production[3,6]. Fly ash contains toxic metals like Zn, Cd, Cr, Pb and Ni, which can cause environmental threat[7,8]. These toxic elements leach out from the fly ash dumps and contaminate nearby soil surfaces and groundwater[9]. Henceforth, heavy metals from fly ash during leaching influence on living organisms[10]. Within the influence of the Burshtyn TPP an increase in concentrations of mobile forms of heavy metal compounds in the environment was shown in previous researches[6,10,11]. In addition, soil contamination with radionuclides is observed[11].

Vegetation as a first acceptor in food chains has a key role in the accumulation of heavy metals[12,13]. Due to accumulation ability, plants are the most useful organisms to evaluate metal contamination[14,15,16]. However heavy metal concentrations in plants differed between species indicating their different strategies for metal accumulation[14]. Numerous research dedicated to analyzing heavy metal accumulation by herbaceous species[13,15]. There are several studies about the accumulation of heavy metals in fly ash lagoons and fields around coal-fired power stations which are contaminated with fly ash[17,18,19,20].

The problem of heavy metal contamination requires sustainable and effective solutions. One of the environmentally friendly approaches is the application of plants in phytoremediation[21,22]. Phytoremediation is a green remediation strategy, which is highly efficient for the decontamination of heavy metal-pollutions[21,23]. Comparing the potential environmental influence of phytoremediation with other treatment technologies, such as chemical and engineering treatments, phytoremediation impresses as the sustainable alternative[22]. Nevertheless, there are critical challenges against the potential of phytoremediation prevail: the lengthy time required and what should be done with the metal-including plant material[22] Despite this limitation, environmental benefits prevail: it enhances biodiversity, helps protect soil, diverse sources of energy and has aesthetic benefits[24].

Native dominant plant species are considered keys to the restoration and remediation of heavy metal contaminated soils[25,26]. Local native plants used for the remediation were better adapted to the soil properties, toxicity level and environmental conditions of the contaminated site[27,28]. The dominant plant species found on contaminated sites show clear tolerance and accumulation traits for heavy metals. They have a defence mechanism against high levels of heavy metals through a prolonged process of natural selection, resulting in their ability to withstand these conditions[29]. Phytoremediation proposes could be fit as herbaceous perennials as well as woody species[30], but as herbaceous species are pioneers and appear first, they could be more efficient than shrubs or trees. Herbaceous species usually adapt faster to adverse conditions because of their life cycles[28]. The main demands for phytoremediation species are well-developed roots, large biomass and tolerance to the high metal concentrations[13], which are inherent for herbaceous vegetation. Beneficial of spontaneous vegetation for phytoremediation purposes in examples of mine sites were shown in several researches[26,27].

Plants are particularly useful for analysis and monitoring heavy metals due to their stationary nature, making them ideal *in situ* bioindicators – plants can provide a cost-effective long-term approach for monitoring metal pollution[12,18,19]. At the same time, vegetation covers could be used for reclamation of heavy metals contaminated sites[23,28,29]. For establishing methods of biomonitoring and development of green reclamation technologies, investigation of the abilities to accumulate and tolerate against trace metals plant species is needed. Due to the high level of pollution of ash and slag dumps, the investigation of heavy metals concentration in plants and their ability to decontaminate the pollutants is especially important in the context of sustainable development of the region.

Therefore, the aim of this study is: (1) to measure metal contents in the native dominant plants; (2) to evaluate the migration potentials of these native dominant plants; (3) to estimate species abilities to remediation and their prospects for phytoremediation in the research area. Despite that the study contains limited data, the research results can provide valuable information about native species bioindication ability and their relevance for remediation of heavy metal-contaminated soil in the ash and slag dumps and other similar environmental conditions.

Materials and methods

The study area is the ash and slag dump site №3 of Burshtyn Thermal Power Plant. Burshtyn TPP annually produces more than 20 thousand tons of solid residues of fuel combustion products. The overall storage facility of ash and slag dump site № 3 is 24,674 million m^3, currently filled for 98.5 % of its capacity.

Soil sampling was carried out in July 2021 at previously determined points. The sampling approach was random; generally, there were 9 test plots. The soil samples were collected from the top layer (0–20 cm) of the soil profile after removing the surface cover. One kilo of soil samples from each point was collected and then stored in plastic bags until chemical analysis.

Two of the most common on the study site herbaceous plants (*Achillea millefolium* L. and *Anthemis cotula* L.) were selected for testing of metal accumulation abilities. Plant samples were collected in the area of the soil sampling point and a total of 30 plant samples. Herbaceous plant samples were divided into roots and shoots and washed gently to remove soil particles adhered to the plants. After washing, plant samples were air-dried at room temperature for two weeks. Mixed samples of dried plants (separately above and below ground biomass) and leaves were 100 gr each. In total, there were 9 samples of each species.

Samples of plants, soil were subjected to an anatomic absorption spectrometer with spectrophotometer AAS-3 to be analyzed for metals like Cd, Zn, Ni, Fe, Mn, Cu and Pb[31]. The instrument setting and operational conditions were done in accordance with the manufacturers' specifications and according to the Ukranian national analyzing standards[32,33].

Based on the results of the concentration of heavy metals, the average mean and the standard error of the mean (M±m), minimum (Min) and maximum (Max) of values and the coefficient of variation (CV, %) were calculated.

Since metals exist in different solid-phase forms that can vary greatly in terms of their bioavailability, the determination of total soil metal content is not a good measure[16]. A more useful tool to quantify contamination and potential environmental and human health risks is the assessment of bioavailability. The bioaccumulation factor (BAF) determines the efficiency of the plant accumulating heavy metals from soil and calculated BAF as the ratio between metal concentrations in root to metal concentration in soil outside the root zone[21,34]:

$$BAF=C_{plant} / C_{soil,}$$

C_{plant} – heavy metal concentration in plant tissue, mg/kg dry weight.
C_{soil} – heavy concentration in soil, mg/kg dry weight.

For the quantitative expression of the general ability of a plant species to the concentration of heavy metals, the biogeochemical index of activity (BIA) of the species was used, which is the total value obtained from the composition of the BAF of individual metals[35]:

$$BIA_{species} = \sum BAF.$$

For herbaceous plants we detect the translocation factor (TF) which is calculated to evaluate the ability of plants to translocate heavy metals from roots to shoots[21,34]:

$$TF=C_{plant\ shoot}/C_{plant\ root}$$

$C_{plantshoots}$ – heavy metal concentration in plant shoots, mg/kg dry weight.
$C_{plantsroots}$ – heavy metal concentration in plant roots, mg/kg dry weight.

Plant species with both bioconcentration factor (BCF) and translocation factor (TF) greater than one can potentially be used for heavy metal phytoextraction and/or phytostabilization[21,34]. Plant species with TF > 1 are regarded as good phytotranslocators[16]. This implies that these species effectively accumulated and transferred heavy metals from the soil to the above ground parts[16]. Plants with translocation and bioaccumulation values less than one are excluders and are not suitable for extracting heavy metals from soils[36].

Results

Evaluation of analyzed samples of herbaceous plants reflects the concentration tendency: the highest concentration was detected for Fe, Mn and Zn, the lowest one was for Cd. The concentration of mobile forms of heavy metals in herbaceous plants is shown in Table 1.

Achillea millefolium accumulated metals in the following order: Fe > Mn > Zn > Cu > Ni > Pb > Cd. Maximum accumulated ones were Fe and Mn – 549,02 mg/kg and 58,9 mg/kg respectively, minimum accumulated element was Cd – 0,34 mg/kg.

Anthemis arvensis accumulated metals in the same order, but with differences of concentration of Ni and Pb: Fe > Mn > Zn > Cu > Pb > Ni > Cd. *Anthemis arvensis* to compare with *A. millefolium* accumulated less Ni than Pb. In *A. arvensis* maximum accumulated ones were Fe and Mn – 529,67 mg/kg and 46,7 mg/kg respectively. The minimum accumulated element was Cd – 0,49 mg/kg. In general, *A. arvensis* accumulated higher concentrations of Cu, Zn, Pb, Cd than *A. millefolium*.

The ability to accumulate high concentrations of metals into plants aboveground biomass was estimated

Table 1 – Heavy metals concentration in 9 samples of herbaceous plants

Achillea millefolium							
	Heavy metal						
	Cu	Zn	Pb	Ni	Cd	Mn	Fe
M±m	7,71 ± 0,45	19,36 ± 1,74	2,37 ± 0,19	3,04 ± 0,34	0,34 ± 0,06	58,88 ± 27,8	549,02 ± 268,9
Max	9,9	28,6	3,6	5,5	0,7	279,5	2544
Min	6,2	12,3	1,5	1,8	0,2	17,1	93
CV, %	17,43%	27,05%	24,82%	33,46%	56,43%	141,77%	146,98%
Anthemis arvensis							
	Heavy metal						
	Cu	Zn	Pb	Ni	Cd	Mn	Fe
M±m	9,56 ± 0,77	28,78 ± 3,31	2,83 ± 0,18	2,89 ± 0,64	0,49 ± 0,08	46,66 ± 5,71	529,67 ± 211,82
Max	13,5	51,3	4,1	6,4	0,9	67	1556
Min	6,6	16,9	2,3	1,1	0,2	15,8	77,8
CV, %	24,25%	34,51%	19,09%	66,23%	51,59%	36,75%	119,97%

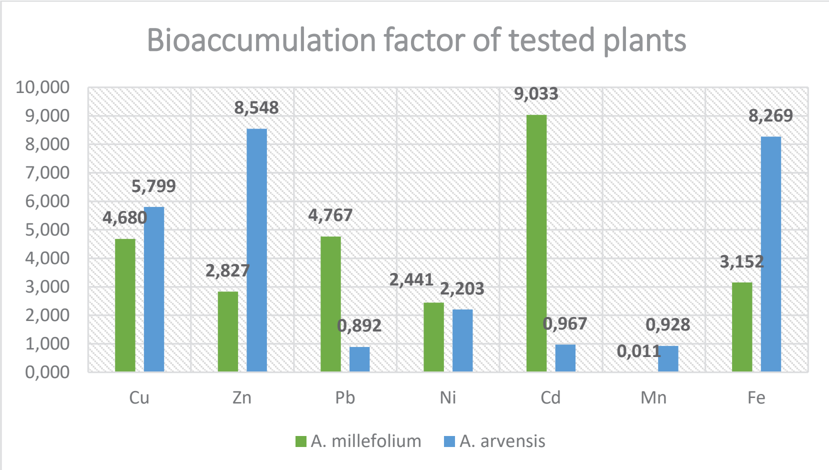

Figure 1. Bioaccumulation factor of tested plants (calculated based on 9 samples of each species and 9 samples of soil)

using the bioaccumulation factor and translocation factor. We calculated the bioaccumulation ability of selected species using the bioaccumulation factor (BAF). Among analyzed plant species, the average value of BAFs of the heavy metals is decreased in the order of: Zn > Fe > Cu > Mn > Cd > Ni > Pb. The highest accumulative ability shows Zn, the lowest – Pb (Fig. 1).

Different species have different potential for heavy metal accumulation. Estimating of species metals accumulation was based on their biogeochemical index of activity (BIA) – a higher BIA coefficient of accumulation was detected for *Anthemis arvensis* (27,606), when *Achillea millefolium* biogeochemical index of activity was 26,910.

Translocation factor (TF) as the ratio between underground and aboveground heavy metal concentration in plant biomass was detected too (Table 2).

The translocation factor for *Achillea millefolium* growing on the study site was found in the order of Zn > Cd > Pb > Cu > Ni > Mn > Fe. The highest value of TF in plants was for Zn with an average value of 1,516, and the lowest one was for Fe with an average value of 0,115.

The translocation factor for *Anthemis arvensis* growing on the study site was found in the order of Zn > Cd > Pb > Cu > Mn > Ni > Fe. The highest value of TF in plants was for Zn with an average value of 1,609, and the lowest one was for Fe with an average value of 0,082.

In the present study TF of all elements lower than one, except Zn in two samples and Cd in one sample. This finding indicates low mobility of Cu, Pb, Ni, Mn and Fe from the roots to the shoots and immobilization of heavy metals in roots.

Table 2 – Translocation factor of selected plants (calculated based on 9 samples of each species and 9 samples of soil)

Heavy metal	*Achillea millefolium*	*Anthemis arvensis*
Cu	0,782	0,685
Zn	1,516*	1,609*
Pb	0,768	0,917
Ni	0,757	0,318
Cd	0,909	1,944*
Mn	0,211	0,635
Fe	0,115	0,082
M±m	0,722 ± 0,18	0,884 ± 0,25
Max	0,115	0,082
Min	1,516	1,944

Comment: * – exceeding of TF above 1

Discussion

Based on our results there was a tendency with the highest concentration of Fe, Mn and Zn in all tested species. Both herbaceous species concentrate high amounts of Mn, Fe and Zn, the lowest was the concentration of Cd. The same trend for metal concentration in naturally growing plants on fly ash dump sites was presented in the results of Pandey et al. 2016 – a high concentration of Zn and Mn was found in *Cynodon dactylon* growing on fly ash dump sites. According to several studies[37,38] Zn is an element with intensive accumulation. Zn inhibits the Cd uptake due to its competitive behaviour with Cd, because both metals are transported by a common carrier at the root plasma membrane, which has more affinity for Zn than Cd[29]. In an example of *Trifolium pratense*[39] were observed accumulation of Cu: copper increases when accumulation of Zn decreases – it's explained as an adaptation to metals contamination[39]. Research of heavy metals accumulation in *Artemisia absinthium*, *Melilotus officinalis* and *Hippophae rhamnoides* growing on ash and slag dump reflects that the highest bioaccumulation factor was for Zn[11].

Previous research of metal accumulation in *Achillea millefolium*[37,38] showed that the species has an ability to Pb accumulation[40], especially in inflorescence. Our research shows low Pb concentration, but the results confirm the low ability to Cd concentration[37,40]. Moreover, there is a seasonic dynamic of heavy metal concentration: in herbaceous species (for example of *Chelidonium majus*), increasing Zn concentration in aboveground biomass during flowering was shown with the highest concentration in root still[41].

To evaluate the ability of plants to translocate heavy metals from roots to shoots we detected a translocation factor (TF)[21,34]. The translocation factor above 1 means that these species effectively accumulated and transferred heavy metals from the soil to the above-ground parts[16]. TF > 1 for such elements like Zn and Cd were shown in the study of metal accumulation on fly ash lagoon[18]– it explains that transferring Zn to the aerial part is beneficial for the survival of the plant, because it’s an important micronutrient[43], but Cd is a nonessential toxic metal. Yoon et al. 2006 showed that Pb and Cu, Zn concentrations were greater in the roots than the shoots – in this case, TF of these elements was below 1[42]. A higher translocation of heavy metals in aerial parts could be a reason for the easy transfer of these pollutants to the food chain[17]. As the index of TF reflects the transfer and redistribution of heavy metals among different parts of plants[13], the TF is below 1, indicating that metals are mainly accumulated in the roots and are rarely transported to the shoots. In our research, metal concentrations for most elements were higher in roots versus in shoots for both species. Higher concentration in roots explained that roots are the preferential metal storage organs[13,44]. Lower metal concentrations in the shoots than those in the roots indicate that the species could be metal excluders[14].

Conclusions

Analysis of bioaccumulation of metals through bioaccumulation coefficients showed that zinc had the highest accumulation capacity in the studied species, and lead had the lowest. The ability to bioaccumulate the analyzed heavy metals decreases in the order: Zn > Fe > Cu > Mn > Cd > Ni > Pb. The study of the biogeochemical activity of the tested species reflected a higher level of biochemical activity for *Anthemis arvensis*. Determination of the translocation index of elements reflected the low mobility of Cu, Pb, Ni, Mn and Fe from roots to shoots and evidenced the accumulation of heavy metals in the roots. Zn and Cd were found to be mobile elements with a high rate of transfer to above-ground biomass. Based on the translocation factor, we can conclude that none of the herbaceous species showed themselves as hyperaccumulators. Due to the ability to accumulate heavy metals in roots, plant species are promising for phytostabilization. However, the presented results are incomplete and require scaling with the involvement of a larger number of cells and statistical analysis.

Consequently, plants on technogenic ecotopes like ash and slag dumps could provide effective analysis and monitoring of heavy metals pollution. Further analysis of the natural vegetation of ash and slag dumps regarding the accumulation of heavy metals will determine their accumulative capacity and tolerance against pollutants and, therefore, their prospects for the use of these plant species in phytoremediation.

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