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ACCUMULATION OF HEAVY METALS IN LEAVES OF TREE SPECIES ON THE ASH AND SLAG DUMPS OF THE BURSHTYN THERMAL POWER PLANT

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Thermal power plant (TPP) facilities are considered as one of the major reasons for environmental pollution. Ash and slag dumps as a special construction for storage of combustion wastes of TPPs are recognized as sources of heavy metals (HMs) contamination for surrounding ecosystems. The present study is the first report of analyzing HMs contamination of the ash and slag dumps of the Burshtyn TPP.

***The aim of the study is** to estimate the content of HMs in the technogenic substrates of ash and slag dumps and investigate soil-plant interactions through analyzing potential of HMs accumulation in the leaves of native dominant woody species.*

***Materials and methods of research.** Soil sampling was carried out in the period of July 2021 at previously determined points. The most common woody species (Populus tremula L., Betula pendula Roth., Salix caprea L.) were selected for testing of HMs accumulation abilities. Samples of plants and soil were subjected to an atomic absorption spectrometer for being analyzed for heavy metals: Cd, Zn, Ni, Cu, Pb, Mn and Fe.*

***Results of research and discussion.** The results showed that the substrates of ash and slag dumps of the Burshtyn TPP were mainly contaminated by lead, copper and cadmium. All tested species concentrated high amounts of magnesium, iron, zinc and low concentration of cadmium. Bioaccumulation factor reflected the highest abilities of accumulation of zinc in all tested species and low level of bioaccumulation of cadmium. The highest index of biochemical activity showed Betula pendula. Salix caprea were found as a promising species for remediation due to intensive accumulation of such elements like cadmium, lead, copper, zinc and nickel.*

***Conclusions and prospects for further research**. We consider plant organisms particularly useful for analyzing HMs accumulation as they can provide a cost-effective and long-term approach for bioindication and monitoring HMs pollution. Moreover, vegetation covers could be used for remediation of HMs contaminated sites*

***Keywords:** devastated lands, heavy metals, HMs accumulation, indices of accumulation, phytoremediation*

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1. Introduction

Particularly difficult task for the sustainable development of Prykarpattya region (Western Ukraine) is the reclamation and remediation of devastated lands in the region. One of the most concerning territories is the ash and slag dumps of the Burshtyn Thermal Power Plant. Ash and slag dumps are special engineering structures for storage of combustion products, which are the source of environmental danger for the whole region as storing of waste materials causes a number of environmental issues, among ecological problems, the HMs contamination is especially dangerous [1, 2]. Weathering and scattering of solid particles of different degrees of dispersion from the surface of the bowls of ash and slag dumps causes HMs pollution of air, water and soil of the surrounding ecosystem. Due to the ingress of ash and slag materials from the bowls of ash dumps into surface and groundwater, there is a change in their chemical parameters, including HMs appearing. The influence of HMs leaching from these waste materials affects the state of the phytobiota on the area of influence of the enterprise [3, 4].

The vegetation coverage plays an important role in the accumulation and transportation of HMs [5, 6]. Therefore, plants are the most available and useful organisms to evaluate metal contamination [7, 8]. But metal uptake abilities and tolerance characteristics are highly variable among plant species [9, 10]. Various metal concentrations in plant tissues differed between species indicating their different strategies for metal tolerance and accumulation [11].

Tendency of accumulation of HMs by tree species was shown in numerous research – the most popular tested species were *Salix* spp. [12, 13], *Populus* spp. [14, 15] and *Betula pendula* Roth. [16]. To estimate abilities of metal accumulation by tree species, it is important to take into account different concentrations in a way of metal translocation – from roots through shoots to leaves, as there is controversial data about mental accumulation in leaves tissues. Some cases [13, 16] showed highest concentration of HMs in a shoot, but depending on elements, they could have the highest concentration in a root, e.g. lead as the most aggressive phytotoxic is mainly concentrated in the root system as a result of an evolutionary and adaptive process of protecting the photosynthetic organs from excessive accumulation of these highly toxic elements [15]. An example of hardwood species, such as red oak [17], has shown that the translocation of metals to leaves is high, another research [15] has shown low accumulation abilities – high metals concentration in soil didn't influence the concentration of *P. pyramidalis* leaves. Important to notice that there is a possibility of HMs accumulation not only from soil horizons, but also from the atmosphere [18]. Therefore, ways of HMs accumulation and their concentration in tissues of different species still have numerous questions and need further research, especially in the context of devastated lands.

The aim of the research: to investigate the content of soil HMs on ash and slag dumps, measure metal contents in the leaves of native dominant woody species and evaluate the accumulation potentials of these native dominant plants. The research results can provide valuable knowledge about woody species prospects in bioindication of HMs contamination of the territory of ash and slag dumps and other similar devastated lands.

2. Materials and methods

The Burshtyn TPP is the largest thermal power plant in the Western Ukraine. The Burshtyn TPP is located in the Halytskyi district, Ivano-Frankivsk region. The capacity is 2400 MW and it annually produces more than 500 thousand tons of solid residues of fuel combustion products [19].

More than 200 ha of land are used for the ash and slag dumps of the Burshtyn TPP, where more than 28 million tons of waste are stored. The ash and slag dumps of the Burshtyn TPP are special hydraulic engineering structures, designed for the storage of solid waste from coal combustion. The study area was the ash and slag dump site No. 3, which is used actively and located 5 km from the Burshtyn TPP, covering in total 91 ha. The overall storage facility of the ash and slag dump site No. 3 is 24,674 million m^3, currently filled for 98.5 % of its capacity [20].

For analyzing HMs accumulation, the soil and plants sampling was carried out in the period of July 2021 at previously determined points. The sampling approach was random, at each sampling location, a plastic spatula was used for sample collection. Generally, there were 9 test plots for soil sampling. The soil samples were collected from the top layer (0–20 cm) of the soil profile after removing the surface cover. One sample consists of 5 point samples, which are selected on a 2×2m site in the four corners of the imaginary envelope and in the middle of it. The mass of the mixed sample was one kilo. One kilo of soil samples from each point was collected, then stored in polyethylene bags until chemical analysis.

Three species (*Populus tremula* L., *Betula pendula* Roth., *Salix caprea* L.) were selected for testing HMs accumulation abilities. Leaves were collected from the tree species at the ends of the growing season. After washing, plant samples were air dried at room temperature for two weeks. Mixed samples of dried plants and leaves were 100 g each.

The laboratory analysis of samples was carried out at the National Scientific Center "Institute of Agriculture of the National Academy of Agrarian Sciences of Ukraine", Kyiv. The samples of plants, soil were subjected to an atomic absorption spectrometer for being analyzed for metals like Cd, Zn, Ni, Fe, Mn, Cu and Pb. The instrument setting and operational conditions were done in accordance with the manufacturers' specifications and according to the Ukrainian national analyzing standards: DSTU 4770-2007, GOST 30178-96 [21, 22].

The bioaccumulation factor (BAF) determined the efficiency of the plant accumulating HMs from soil and calculated BAF as the ratio between metal concentrations in leaves to metal concentration in soil outside the root zone [10]:

$$BAF = C_{plant} / C_{soil}, \quad (1)$$

where C_{plant} = metal concentration in plant tissue (leaves), mg/kg dry weight.

C_{soil} = metal concentration in soil, mg/kg dry weight.

For the quantitative expression of the general ability of a plant species to concentration of HMs, the biogeochemical index of activity (BIA) of the species was used, which was the total value, obtained from the composition of the BAF of individual metals [13]:

$$BIA_{species} = \sum BAF . \quad (2)$$

Since the purpose of the study was to conduct a trial determination of the content of metals both in the soil and in plants to justify the conduct of a future large-scale study, the number of selected samples was insufficient for statistical analysis, and therefore the statistical analysis was not performed. Thus, the results were not statistically significant, however, they are important for assessing the prospects for the selection of plant objects for bioindication of heavy metals contamination of ash and slag pits and technogenic ecotopes.

3. Research results and discussion

Within the influence of the Burshtyn TPP, the concentrations of HMs compounds in the environment are increasing [3, 19]. The high content of zinc, nickel, lead, copper, cobalt, cadmium and iron were found in surrounding ecosystems [23, 24]. The most spread elements in the area, affected by the Burshtyn TPP, are copper, magnesium and zinc [19].

Based on analyzing soil samples, we detected the content of mobile forms of HMs in substrates of the ash and slag dump No. 3. Our results showed different concentrations ranging to compare with the results presented before. In contrast with the previous research where prevalence of zinc, magnesium and nickel was shown [24], the presented here result reflected that soils were mainly contaminated by lead, copper and cadmium.

The average content of mobile forms of metals (mg/kg) in substrates of the ash and slag dump was found in the order: Fe (64.06) > Mn (50.28) > Zn (3.37) > Pb (3.18) > Cu (1.65) > Ni (1.35) > Cd (0.51).

For estimating level of HMs contamination, the permissible limits for HMs in food, water and soil according to international and local standards have been used [25]. Among analyzed elements in the soil samples, collected from the site, exceedance of permissible limits for lead was in four soil samples. Total lead concentrations were variable, ranging from 0.7 to 8.9 mg/kg. There were two samples with exceedance of permissible limits for cadmium. The total cadmium concentration was variable from 0.21 to 0.83 mg/kg. Exceedance of permissible limits was detected for copper in one soil sample. Total copper concentration was ranging from 0.14 to 7.35 mg/kg. Such elements as nickel and zinc weren't exceeding the permissible level and ranging from 1 to 8.4 and from 0.4 to 2.4 respectively. There weren't permissive limits for magnesium and iron. They were ranging from 6 to 148.7 mg/kg and from 9.5 to 124.6 mg/kg respectively.

Heavy metals concentration and behavior in plants vary in different species [4, 16]. To analyze a species potential of HMs accumulation and proposes for phytoremediation, we detected HMs concentration in most common woody species on the study site.

Metal accumulation of the selected species is shown in Table 1. Among analyzed HMs, the highest concentration was detected for iron, magnesium and zinc, the lowest – for cadmium.

Table 1

HMs concentration in leaves samples of the tree species

Metal (mg/kg)	*Populus tremula*	*Betula pendula*	*Salix caprea*
Cu	5.83	5.15	6.575
Zn	108.58	94.4	85.35
Pb	3.25	2.8	3.4
Ni	3.15	3.25	5.975
Cd	0.88	0.475	1.775
Mn	48.98	633.9	204.925
Fe	161.75	200.2	317.4

Populus tremula accumulated metals in the following order: Fe>Zn>Mn>Cu>Pb>Ni>Cd. Maximum accumulated ones were iron and zinc, minimum accumulated one was cadmium.

In *Betula pendula,* the order of metal accumulation was Mn>Fe>Zn>Cu>Ni>Pb>Cd. Maximum accumulated ones were magnesium and iron, cadmium.

Salix caprea accumulated metals in the following order: Fe>Mn>Zn>Cu>Ni>Pb>Cd. Maximum accumulated elements were iron and, minimum accumulated one was cadmium.

In general, all species concentrate high amounts of magnesium, iron and zinc with a low concentration of cadmium. High accumulation of magnesium by tree species was presented before [16, 26]. On the other hand, there was shown that tree leaves accumulated iron and magnesium in low concentration [7, 27]. According to other study [26] at the medium level tree accumulated such elements as copper, zinc, lead.

The evidence that there was no correlation between total metals contents in soil and accumulation of HMs in plants on the ash and slag dumps of the Burshtyn TPP was presented before [24]. It could be explained, that total metal concentrations in soil have been considered poor indicators of metal availability for plants [10]. In the present study, the concentration of metals in plant organisms is higher compared to their associated soils. The same tendency of higher metals concentration in plants biomass was shown for copper mine sites [28].

HMs accumulation is much higher in plants biomass than in soils, suggesting that these plant species can't tolerate HMs [11]. Abilities to accumulate high concentration of metals into their aboveground biomass is named hyperaccumulation [29] and is estimated using the bioaccumulation factor.

We calculated the bioaccumulation ability of the selected species using bioaccumulation factor (BAF). Among the analyzed tree species (Fig. 1), the average value of BAFs of the HMs is decreased in the order of: Zn>Fe>Cu>Mn>Cd>Ni>Pb.

Based on our results, there is a tendency with the highest concentration of iron, magnesium and zinc in all tested species. According to numerous researches on HMs concentration in tree species [16, 26], there was predominantly magnesium concentration in *Betula pendula* leaves and predominance of zinc concentration in *Populus* spp. and *Betula pendula* leaves. High concentration of zinc was detected also in leaves of *Salix viminalis* [13]. Due to Kozlovskyy et al. (2005) and Baranov et al. (2010), *Populus* spp. and *Salix* spp. are species-concentrators of zinc and at the same time cadmium [12, 14]. Despite the ability of cadmium concentration in this species, our results detected cadmium at the lowest level for all tested species.

Conspiciously, *Salix caprea* accumulated slightly high concentrations of copper, lead, nicel, cadmium, iron, but less zinc than other species. In an example of *Salix viminalis* [31, 32], we found evidence that *Salix* spp. can intensively accumulate such elements as cadmium, lead, copper, zinc, nickel and could be proposed as a remediative species.

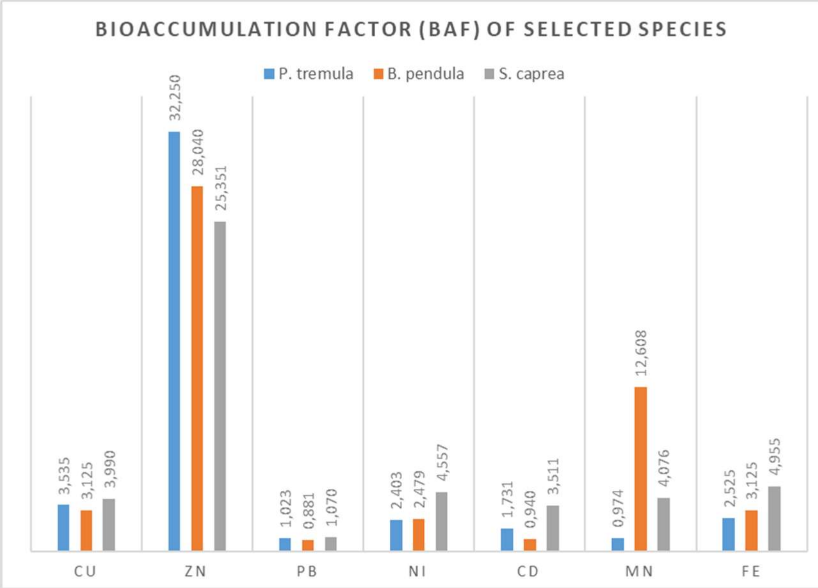

Fig. 1. Value of the bioaccumulation factor (BAF) of the selected speciesDifferent species have different potential of HMs accumulation. Among the selected species, the highest coefficient of accumulation was detected for *Betula pendula*. Abilities to accumulate HMs, uptaken by *Betula pendula* in high concentration, were shown in several researches [26, 30]. The order of species metal accumulation based on their biogeochemical index of activity (BIA) was *Betula pendula* > *Salix caprea* > *Populus tremula* (Table 2).

Table 2

Biogeochemical index of activity (BIA)

Selected species	$BIA_{species}$
Populus tremula	44.440
Betula pendula	51.198
Salix caprea	47.511

Limitations of the study. The study is of a pilot nature, results have the nature of trends, and not statistically proven hypotheses.

Prospects for further research. In future researchs, we plan to expand more samples to have statistically approved results, as well as conduct an analysis taking into account other species and compare accumulation abilities of different species and their prospects for phytoremediation.

4. Conclusions

Based on our results, substrates of the ash and slag dumps of the Burshtyn TPP were HMs concentration and behavior in different species, we detected HMs concentration and accumulation in the tree woodyspecies. There were similar trends for all tested species with the highest concentration of magnesium and iron and the lowest concentration of cadmium. There weren't similar trends between total metals contents in soil and accumulation of HMs in plants on the ash and slag dumps of the Burshtyn TPP.

Bioaccumulation factor reflected that the highest abilities of accumulation by plants was shown for zinc, and the lowest level of bioaccumulation was shown for cadmium. The highest level of species biochemical activity was detected for *Betula pendula* (51,198), the lowest level – for *Populus tremula* (44,440).

As the most promising species for remediation *Salix caprea* was considered. Despite this species having shown the lowest integral index of biochemical activity, it accumulated toxic elements as cadmium, lead and nickel in higher concentration than other species, which were tested.

Insights and findings of the presented research gave the primary results of HMs contamination of the ash and slag dumps. For future establishing methods of biomonitoring and development of green remediation technologies, investigation of the plant species‘ abilities to accumulate and tolerate against trace metals needs further research.

Conflict of Interest

The authors declare that they have no conflict of in-terest regarding this research, including financial, personal, authorship or any other kind of conflict that could influ-ence the research and its results, presented in this article.

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Data availability

Data will be made available on reasonable request.

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