# STUDIES ON THE HEAVY METAL BIOREMEDIATION ABILITY OF MULTIPLE SPECIES – A CASE STUDY ON BAIA MARE SITES

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#### Abstract

Bioremediation is a sustainable method for restoring the quality of soil in urban areas affected by heavy metal contamination. Plant samples were analyzed using portable X-ray fluorescence spectrometry (pXRF) to determine the concentrations of heavy metals accumulated in the studied species. Analysis of the accumulation capacity of heavy metals in various sites revealed significant differences between the plant species investigated. Species such as Lavandula angustifolia, Salix viminalis, Salix alba and Agrostis capillaris showed high levels of bioaccumulation for certain metals, highlighting a specific and differentiated potential for application in phytoremediation processes. These results highlight the need for a rigorous selection of plant species used in phytoremediation, correlated with the predominant type of heavy metal, in order to optimize the efficiency of ecological remediation processes.

**Keywords:** polluted soils, heavy metals, phytoextraction, bioremediation, Agrostis capillaris

### INTRODUCTION

Heavy metals are a type of pollutant commonly encountered, and due to their high toxicity, soil contamination with these substances can represent a significant risk to soil organisms, including microbial communities (Zhao et al., 2019).

Soil pollutants mainly originate from human activities and include biological, domestic and industrial residues, improperly stored waste or manure, all of which have a negative impact on soil metabolism. Industrial metal mining and processing activities constitute a significant source of heavy metal

contamination of agricultural soils (Navarro et al., 2008).

In the context of increasing soil degradation caused by heavy metal pollution resulting from anthropogenic activities, researchers' interest in soil microbial imbalances is growing. Soil acts as an important reservoir for numerous contaminants (Sandu et al., 2018).

Soil is a complex environment, consisting of a solid, a liquid and a gaseous phase, the components of which undergo significant variations. The interaction between this soil system and the plants that grow in it forms

what is known as the soil-plant ecosystem (Chen et al., 2010; Corcoz et al., 2022; Păcurar et al., 2020; Sângeorzan et al., 2024; Wu et al., 2011).

Soil degradation means the reduction or loss of its functions and uses. Soil performs three ecological functions: produces it biomass (food, feed, raw materials), filters and transforms substances between the atmosphere, water vegetation, and provides biological habitat (Sandor et al., 2016; Stoian et al., 2022; Vidican and Sandor, 2015). At the same time, it has technical. industrial and sociofunctions. economic serving support for constructions, a source of resources and an element of heritage that protects archaeological and natural values (Blum et al., 1998; Gaga et al, 2022; Onica et al., 2017; Rotar et al., 2020; Vaida et al., 2021).

When heavy metals reach the they undergo soil, transformations into various geochemical forms because physical, chemical and biological processes, such as adsorption, dissolution. complexation and absorption by organisms (Liu et al., 2013).

The toxicity and bioavailability of heavy metals in soil are influenced not only by their total concentration, but also by the form in which they are found. For example, water-soluble forms and those associated with carbonate are considered the most readily

available to organisms; reducible forms, bound to Fe/Mn oxides, and oxidizable forms, associated with organic matter, can become bioavailable under certain conditions. while the residual fraction, fixed in the soil matrix, is not accessible to plants (Delgado si colab., 2011; Rodríguez și colab., 2009). In this context. understanding the concentration of labile fractions of heavy metals is particularly important (Liu wt al., 2013).

The chemical forms in which heavy metals are found in soil significantly influence their mobility. Cadmium (Cd), zinc (Zn) and molybdenum (Mo) are among the most mobile elements, while chromium (Cr), nickel (Ni) and lead (Pb) have considerably lower mobility. (Fijałkowski et al., 2012).

Given the current need for green spaces in urban landscapes, the value of brownfields as potential recreational space is increasingly widely recognized (Merwin et al., 2022).

Regarding the remediation of soils contaminated with heavy metals (HM), several methods are currently available. Among them, phytoremediation is considered the most environmentally friendly and cost-effective technology. emerging method is based on the ability of certain green plants to extract heavy metals from contaminated soils (Angelova et al., 2015; Carabulea et al., 2022).

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Phytoremediation the by which plants process are introduced into the environment to promote the assimilation contaminants in their roots and leaves. Although this process has been recognized and demonstrated by humans for more than 300 years. scientific studies phytoremediation only began after the 1980s (Lasat, 2000).

Phytostabilization consists of reducing the mobility and bioavailability of soil contaminants, physical through or chemical mechanisms, with the aim of preventing their spread environment. (Vidican et al., 2023). Phytodegradation, method a applicable especially to organic compounds, involves the decomposition or transformation of contaminants into less toxic forms, through the release of enzymes at the root level or through metabolic activities carried out inside plant tissues. (Vidican et al., 2023).

In phytovolatilization, contaminants are absorbed by plant

through the foliar system, through the process of evapotranspiration (Laghlim et al., 2015).

Phytoextraction refers to the accumulation of contaminants in the aboveground (harvestable) biomass of plants either through a

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accumulation of contaminants in the aboveground (harvestable) biomass of plants, either through continuous natural process using hyperaccumulator plants or through an induced process using chelating agents. Hyperaccumulator plants are adapted to soils with naturally high metal content and have the ability to efficiently accumulate various metals in their tissues (Vâtcă et al., 2022; Vidican et al., 2023).

The main aim of this research is to assess the level of heavy metal pollution in relation to a set of plants, from the Baia Mare area, a region known for its industrial and mining activities, which have had a significant impact on soil quality.

#### MATERIAL AND METHOD

The research methodology, including the techniques collecting, processing and analyzing field data, is consistent with the objectives. established In Baia proposed to Mare. we use phytoextraction as the first method, phytostabilization secondary method, given that the

plants were selected based on their phytoextraction potential.

In accordance with the established objectives, based on the favorability and soil indices, the species identified with phytoremediation potential in Baia Mare, according to SPIRE-UIA-138, are the following: *Agrostic capillaris, Calamagrostis epigeos*,

Myschantus giganteus, Reynoutria japonica, Salix alba-existent, Salix alba nou, Salix viminalis, Fraximus excelsor,Iris germanica, Lavandula angustifolia, Pinus nigra, Robinia pseudoacacia, Betula pendula – Parthenocissus existent. quinquefolia, Salix viminalis nou, Acer platanoides, *Amorpha* fructicosa, Sorbus aucuparia, Catalpa bignonioides globose, Equisetum arvense, Juniperus spp., laurocerasus. Prunus Sorbus aucuparia.

These species were selected based on preference criteria for ecological zoning, considering their phytoremediation capacity and other uses. The natural distribution area was assessed to verify whether these species exist in the spontaneous flora, either as species or varieties, whether they meet edaphic thermal necessary and conditions throughout the experimental vegetation cycle (including the sum of temperature

## RESULTS AND DISCUSSIONS

The way in which heavy metals can accumulate in plant and animal organisms, including humans, as well as the pathology they cause, justify the interest given to these pollutants. The lack of monitoring and control of heavy metals in soils, air and water can represent a major danger to the environment and, in particular, to human health.

degrees). The average amount of precipitation was also taken into account to ensure their adaptability to the local environment.

Samples were taken from 5 sites, namely: Craica, different Colonia Topitorilor, RombPlumb, Ferneziu and Urbis in the city of Baia Mare (47°39′ N, 23°34′ E), located in northwestern Romania, on a total area of 7.3 hectares of brown soils. These locations present different levels of heavy metal contamination, mainly originating from anthropogenic activities such as mining, metallurgy and urban expansion. After taking samples from the five experimental sites, they were dried under ambient conditions, then ground using a Grindomix Retsch GM 200 knife mill. Finally, the samples were by portable analyzed X-ray fluorescence spectrometry (pXRF) to determine the heavy metals accumulated in the analyzed plant species.

Metals, natural components of soil, are classified according to physiological role essential heavy metals (such as Fe, Mn, Cu, Zn and Ni), which act as indispensable micronutrients for the physiological and biochemical processes of plants. These are taken up from the soil solution and included in the structure of enzymes and proteins, and non-essential metals (such as Cd, Pb, As, Hg and Cr). which have no known biological role, but regardless of their type, high concentrations of heavy metals can inhibit plant growth and induce symptoms of toxicity, however, certain plant species can survive and even develop in contaminated soils, such as those in the vicinity of mining operations (Laghlini et al., 2015).

Following the analysis of from plant species the contaminated with heavy metals, it was found that certain species have a superior capacity to extract heavy metals, while others have a reduced capacity, and for some species the concentrations of heavy metals were below the detection limit. These results vary depending on the plant species present five on the experimental sites.

The study aimed to identify and analyze the potential for ecological rehabilitation of contaminated soils by applying the phytoremediation technique – a process that involves the use of plants capable of absorbing,

accumulating or stabilizing heavy metals in the soil. In this regard, several plant species from the affected lands were analyzed. The species were chosen based on their tolerance and efficiency extracting or immobilizing metals, and the efficiency of each species will be monitored and compared to determine the most promising solutions for ecological remediation of these degraded soils.

The chosen species must demonstrate the ability to extract heavy metals from the soil through the root system and the foliar apparatus, while it must be able to be subsequently exploited.

Plant species from the Craica site varied significantly in their capacity to accumulate heavy metals (table 1). Agrostis capillaris proved to be the most efficient species for Pb extraction, followed by Myschantus giganteus and Salix alba new. Salix alba – extant had the lowest extraction value.

 $Table\ 1$  Plant species and their capacity to extract heavy metals from the Craica site

Species	Pb	Cu	Cd	Zn
Agrostis capillaris	82.25	66.63	11.13	464.50
Calamagrostis epigeos	4.75	43.25	4.50	98.00
Myschantus giganteus	65.06	42.75	23.31	141.69
Reynoutria japonica	35.63	43.00	17.25	328.00
Salix alba- present	2.50	49.25	20.13	524.88
Salix alba new	60.00	54.13	23.13	830.13
Salix viminalis	36.63	22.63	8.13	131.25

For copper (Cu) extraction, Agrostis capillaris had the highest value (66.63 mg/kg), followed by Salix alba new and Salix alba present. Salix viminalis recorded the lowest value (22.63 mg/kg). In the case of cadmium (Cd), Myschantus giganteus (23.31 mg/kg) and Salix alba new (23.13 mg/kg) were the most efficient, followed by Salix alba – present, and Calamagrostis epigeos had the lowest extraction capacity (4.50 mg/kg). Salix alba exceptional new has an accumulation capacity (830.13 mg/kg), followed by Salix alba present and Agrostis capillaris.

Calamagrostis epigeos had the lowest value (98.00 mg/kg).

After analyzing the extraction capacity of heavy metals in the Colonia Topitorilor site (table 2), it was highlighted that the plant species Agrostis capillaris had the highest value in lead extraction (84.00 mg/kg). Robinia pseudoacacia recorded the highest values for copper extraction (51.88 mg/kg), and Fraxinus excelsior stood out for its highest cadmium extraction capacity (21.08 mg/kg). Salix viminalis showed a very high phytoextraction capacity of Zn (792.50 mg/kg) in this site.

 $Table\ 2$  Plant species and their capacity to extract heavy metals from the Colonia Topitorilor site

Species	Pb	Cu	Cd	Zn
Agrostis capillaris	84		2.75	38
Fraxinus excelsior		25.33	21.08	61.04
Iris germanica	14.75	38.00	16.00	69
Lavandula angustifolia		47.63	18.50	83.63
Pinus nigra		47		104.50
Robinia pseudoacacia	4.25	51.88	20.70	79.88
Reynoutria japonica		42.67	17.33	214.58
Salix alba - new	11.33	50.29	19.50	564.42
Salix viminalis	11.50	36.50	18.00	792.50

In the analysis of the capacity of plant species to extract heavy metals in the Ferneziu site (table 3), it is observed that *Salix alba* (both existing and new) stands out as the most efficient species for the accumulation of lead (Pb), copper (Cu), cadmium (Cd) and zinc (Zn), especially the existing

Salix alba, which accumulated exceptional amounts of zinc. Also, Reynoutria japonica proves efficient in extracting Pb and Cu, while Salix viminalis is well-placed for the accumulation of Cu and Zn. Species from the genera Betula pendula and Parthenocissus quinquefolia are less efficient, with

low values for most metals, especially for cadmium and zinc.

In the Romplumb site (table 4), Sorbus aucuparia is the most species efficient for lead accumulation (23.50 mg/kg), while Agrostis capillaris has the lowest extraction (4.25)mg/kg). Regarding copper, Salix alba - new shows an exceptional accumulation (60.88)mg/kg), and capacity Agrostis capillaris records the lowest value (15.50 mg/kg). For cadmium extraction, Salix alba new is the most efficient species (23.50)mg/kg), compared Reynoutria japonica, which accumulates only 14.75 mg/kg. There is a significant difference regarding zinc accumulation, Betula pendula which has a very high accumulation capacity (1057.75 mg/kg), and Agrostis capillaris which accumulates only 33.25 mg/kg.

Table 3 Plant species and their capacity to extract heavy metals from the Ferneziu site

Species	Pb	Cu	Cd	Zn
Agrostis capillaris	20.75	37.50	16.75	647.50
Betula pendula -existent	15.75	46.75	23.25	272.25
Betula pendula -nou	34.75	46.79	14.38	337.04
Myschanthus giganteus		43.13	14.92	88.54
Parthenocissus quinquefolia	7.08	39.75	20.04	111.75
Reynoutria japonica	36.30	54.93	19.43	330.93
Salix alba - present		55.25	28.50	1963.75
Salix alba - new	57.75	64.00	22.25	839.63
Salix viminalis nou	14.83	54.25	21.91	817.25

 $Table \ 4$  Plant species and their capacity to extract heavy metals from the Romplumb site

Species	Pb	Cu	Cd	Zn
Acer platanoides -nou	13.88	44.50	20.38	101.50
Agrostis capillaris	4.25	15.50		33.25
Amorpha fructicosa			10.50	72.25
Betula pendula	15.50	45.63	22.95	1057.75
Reynoutria japonica	13.75	47.875	14.75	568.38
Robinia pseudoacacia	11.63	44.75	17.63	99.88
Salix alba - present	7.00	34.13	20.13	898.75
Salix alba - new	11.75	60.88	23.50	897.13
Salix viminlis nou	15.38	33.00	19.88	624
Sorbus aucuparia	23.50	47.58	13.08	115.50

In the Urbis site (table 5), Lavandula angustifolia presents the

highest lead accumulation capacity (127.88 mg/kg), followed by

Equisetum arvense (28.25mg/kg). significantly This exceeds values of Juniperus spp., Sorbus aucuparea and Salix viminalis which species represent low accumulations 8 mg/kg. < Lavandula angustifolia differs by a significantly higher concentration of Cu (90.75), almost double that of Juniperus spp. (54.46). Agrostis capillaris records the lowest value, of 19.50. Salix species, such as Salix alba and Salix viminalis, are located in the area of average values, between 31.19 and 40.17.

The highest Cd value was recorded in *Salix viminalis* (43.83), followed by *Juniperus spp.* (20.13) and Equisetum arvense (19.63),

these being the species with the highest capacity to accumulate this metal. In contrast, the lowest values were observed in *Agrostis capillaris* (7.00), *Lavandula angustifolia* (15.13) and *Catalpa bignonioides* globosa (16.13), indicating a lower capacity to accumulate cadmium.

Salix viminalis presented the highest extraction of Zn (498.83), followed by Salix alba (381.06), Equisetum arvense (352.88) and Reynoutria japonica (292.75). The lowest values were recorded in Juniperus spp. (65.21), Prunus laurocerasus (70.13) and Catalpa bignonioides globosa (111.63), which present a significantly lower capacity to absorb zinc.

Table 5 Plant species and their capacity to extract heavy metals from the Urbis site

Species	Pb	Cu	Cd	Zn
Agrostis capillaris		19.50	7.00	125.25
Catalpa bignonioides globosa		45.25	16.13	111.63
Equisetum arvense	28.25	51.63	19.63	352.88
Juniperus spp.	7.46	54.46	20.13	65.21
Lavandula angustifolia	127.88	90.75	15.13	270.50
Prunus laurocerasus		29.25	15.25	70.13
Reynoutria japonica		26.58	17.42	292.75
Salix viminalis	2.75	40.17	43.83	498.83
Salix alba - present		31.19	17.19	381.06
Salix alba new		37.83	19.17	162.17
Sorbus aucuparia	4.00	44.25	15.50	109.25

The analysis of the bioaccumulation capacity of heavy metals in different sites revealed significant variations among the plant species studied. Species such as Lavandula angustifolia, Salix viminalis, Salix alba and Agrostis capillaris were highlighted by high accumulations for specific metals,

indicating a differentiated and selective potential in phytoremediation. These differences suggest the need for an adapted selection of species depending on the type of contaminant present, in order to optimize the efficiency of phytoremediation processes.

Identifying the most suitable candidate plant species represents an essential challenge in the application of phytoremediation, given the risk that hazardous heavy metals (HM) enter human and animal organisms through food chains (Gupta et al., 2013).

Phytoextraction is based on the use of natural hyperaccumulator plants, which have an exceptional capacity to accumulate metals. Hyperaccumulators are plant species capable of accumulating metals at levels up to 100 times higher than those obtained by common non-accumulating plants.

## **CONCLUSIONS**

In the Craica site, the most efficient species in bioaccumulating heavy metals were *Salix alba*, *Agrostis capillaris* and *Myschantus giganteus*, which presented consistently high values for two or more of the analyzed contaminants.

In the Colonia Topitorilor site, *Agrostis capillaris* accumulated the most Pb, *Robinia pseudoacacia* – Cu, *Fraxinus excelsior* – Cd, and *Salix viminalis* presented the highest phytoextraction capacity of Zn, highlighting the selective potential of the species for phytoremediation.

In the Ferneziu site, *Salix alba* (existing and new) proved to be the most efficient species in accumulating Pb, Cu, Cd and Zn, especially the existing variant for

zinc. Reynoutria japonica was efficient in extracting Pb and Cu, and Salix viminalis significantly accumulated Cu and Zn.

At the Romplumb site, *Sorbus aucuparia* stood out as the most efficient species for lead accumulation, and *Salix alba* presented the highest values for copper and cadmium.

At the Urbis site, Lavandula angustifolia stood out for its exceptional capacity for lead and copper accumulation, significantly surpassing other species. Salix viminalis accumulated the highest levels of cadmium and zinc, along with Salix alba and Equisetum arvense.

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