Phytostabilization Potential of *Salix alba* as Biomonitor of Heavy Metals in Soil Pollution near the Erzeni Riverbank

Enkelejda Kucaj*, Marilda Osmani, Anira Gjoni, Azem Bardhi, and Besim Kucaj

Abstract—The great sources of water pollution in Albania in the last decade are urban discharges which indicate in other sistems. The aim of this study was to evaluate the concentration of heavy metals in the soil and plant of *Salix alba*. Samples was collected from the Erzen riverbed. The objectives are based on assessment of the concentrations of physico-chemical characteristics heavy metals obtained from the sediment and willow (*Salix alba*) in Erzeni river. The presence of organic matter in soil - the willow plant - was also analyzed. The use of plants in the recuperation of contaminated soil is low cost, sustainable, and environmentally sound. Heavy metals concentration in soil range as follows: Ni (42.2–98.4 mg/kg); Cr (18.9–34.5 mg/kg), and Pb (53.2–98.4 mg/kg). Some statistically significant differences were observed in the data on the amounts of metals accumulated in the soil, significantly more than in the data on the metal concentrations achieved in the tissues of the *Salix alba* plant. Heavy metal concentration in plants reach values Ni (0.9–3.54 mg/kg); Cr (0.57 - 0.89 mg/kg), and Pb (0.06 -0.19 mg/kg). Average concentrations in heavy metal plant samples were listed in the order Ni> Cr> Pb. The results of nickel, chromium, and lead clearly show higher concentrations in samples 0-25 cm across the range of extractors. The use of diversified plant materials is essential and optimal for the phytoremediation process. These species offer different opportunities through their metallic tolerance and accumulation of underground biomass metals for the permanent removal of these metals from the terrestrial substrate.

Index Terms—Environmental pollution, heavy metal, phytoremediation, *Salix alba*, soil contaminated.

I. INTRODUCTION

Urban development in recent years more and more, the Erzeni River has been invaded and continues to be captured by a rampant human invasion. It has happened due to human activities for indiscriminate use of aggregates for economic purposes. It includes delicate habitats that are very important in terms of their values and has been a lot damaged by human interventions [1]. Utilization of riverbed and shore inert without any criteria is closely related to significant damage to the environment directly influencing the growth of erosion and damage to vegetation [2].

Heavy metal pollution has been a problem due to the discharge and distribution of waste materials into the ecosystem. Uncontrolled discharge of sewage into the river causes the process of eutrophication as well as higher flowering of algae. Lack of dissolved oxygen in surface waters leads to the killing of fish and other oxygen-seeking organisms [3].

Emissions from the production of cement, leather, ceramics, textiles, mining, extraction, and processing of oil and gas, and wood processing plants [4] remain a concern for the industry. Partially treated and untreated waste is discharged into the river. Human activity in rivers and their catchment area can affect water quality and the biodiversity of the aquatic ecosystem. Erzen River and its floodplains are springs with large reserves of sand and gravel, which can be exploited, conveniently and economically, for various uses.

Changing the riverbed, because of the use of aggregates, can severely damage public infrastructure (bridges, pipelines, roads, etc.) and create a loss of biodiversity, the recreational potential of watercourses, and agricultural lands along the river, and other assets. Real estate. Above the “Ura e Peshkatarit” where the use of inert materials is not allowed until the estuary, the activity of inert use is present, where the damages to the agricultural and non-agricultural land are very visible [5]. Based on previous studies, high concentrations of Pb, Ni, and Zn in water are found [6]. In polluted sites, organic and inorganic pollutants are often combined in the same locality [7]. Soil contaminated with heavy metals can impede the successful germination of seeds and seedlings [8].

Phytoremediation is a complementary or alternative, cost-effective, environmentally friendly technology, that utilizes suitable plant species to remove or degrade organic and inorganic pollutants [9]. The genus Salix alba (willow) has a specific capacity to catch heavy metals from soil pollution. [10] has distinguished three types of plants, that are accumulators, excluders, and indicators. The genus Salix (Willow) belongs to the plant family Salicaceae. There are four hundred willow species and more than two hundred hybrids listed [11].

The concentration of heavy metals in the soil is not the only factor to be studied, toxicity and mobility of metals are also affected by their shape and physio-chemical association with soil components, or specification. Heavy metals in soils are often concentrated in surface horizons because of this atmospheric deposition, as well as through vegetation and adsorption by organic matter [12]. Vegetation serves as a buffer between the water and underlying soil. Sediments act as “suffocation” for pollutants, and can remain in the aquatic environment for decades, allowing these pollutants to enter the food chain, and thus into fish tissues [13].

These metals can be transported, dispersed, and accumulated in plants and then passed through the food chain to human beings as the final consumer [14]. However, such remediation technique strategies as immobilization or

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extraction by physic-chemical techniques are too expensive and generally impractical [15]. The aim of this study was to evaluate the concentration of heavy metals in the sediment and plant samples of *Salix alba* collected from the pollution of the Erzen riverbed.

However, metal concentrations in willows depend on species, growth performance, root density, distribution within the soil profile, and sampling period [16]. Moreover, willow has been recently recognized as a good accumulator of heavy metals [17].

II. MATERIALS AND METHODS

This study was based on the assessment of the concentration of heavy metals in plants (*Salix alba*) and sediments in the Erzen River. Sampling for both solutions was performed in the period June 2020.

A. Study Area

Erzen River originates in the south-east of the region, from the pit mountain, behind the Dajti mountain range, cutting the mountainous and hilly areas of Šëngjergji and Qaf-Molla and forming deep valleys, especially in the upper parts of its flow [18].

Erzeni River during its flow takes with it a series of streams that flow in its bed starting from the Shengjergji area of Qaf Molla, and continuing north of Krabra, in Mullet, Farka, Fortuzaj, Arban, continuing towards Peza e Vogël, Ndroqit e Shijakut, crosses the Erzeni Lowland north of the city of Durrës and flows into the Adriatic Sea in the bay of Lalzi [18].

The catchment area of this river is about 759 km² while the annual volume of its discharge is about 1,439 million m³, with a specific discharge of about 31 L/sec*km². Water quality is poor as the river flows through one of the most developed urban areas of central Albania. Efforts to avoid the negative effects of heavy metals on human health and ecological hazards are increasing [4].

![Fig. 1. Erzen River Basin [19] and collected samples of soil and plants.](image-url)

B. Soil Samples and Plant Samples (*Salix alba*)

The concentration of heavy metals has an important role in the dynamics of water, backing material and plant. Industrial effluents and sewage/household waste are dumped into these rivers without prior treatment, thus increasing the concentration of pollutants, including heavy metals in the river water, sediment, and plant. Based on the procedures and methodology according to the geological, morphological, and pedological conditions, five sampling sites were selected in Ndroq, Albania (Fig. 1). Samples of sediments and plants (*Salix alba*) were taken in this area which was analyzed for the concentration of heavy metals in the period of summer 2020.

Soil samples were collected in the root zone of the plant about 0-30 cm deep at each station, using the metal probe and then this material was placed in polyethylene boxes. Each soil and plant sample were representative of 5 sub-samples collected in each sector about 20 m apart, a total of 25 soil and plant samples collected. Samples were transported to the laboratory within the same day. The sediment samples were dried in a thermostat at a temperature of 105 °C for 24 hours. Each sediment sample was ground in a grinding mill used for soils and then passed through a 2 mm sieve.

Samples were digested using nitric acid or aqua regia, HCl: HNO₃ (2:1). The filtered samples were left to rest for a few minutes, and then their measurement was done in the Spectrophotometric Atomic Absorber.

- Determination of trace elements S SH EN 14084:2003
- Determination of lead, cadmium, zinc, copper, and iron by atomic absorption spectrometry (AAS) after microwave dissolution. Estimation of heavy metal sediment pollution has been made possible based on the standard limits of [19]-[21]. The textural class of the soil is determined by the percentage of sand, mud, and clay [22]. The soils of these stations consist of clay, silt, and sand with different % respectively.

The plant samples were first washed and dried in a thermostat at a temperature of 70 °C to constant weight. Drying the materials protects the plant materials from...
microbial decomposition and provides a constant value (Aksoy et al., 1999). The plant samples were passed through the grinding mill, digested using nitric acid or aqua regia, HCl: HNO₃ (2:1). One gram of sediment was then weighed and dissolved with 12 ml of the mixture. After it was diluted with 20 ml of nitric acid and filtered with filter paper in a flask, we put the concentration of the solution in distilled water. The filtered samples were left to stand for a few minutes and then the measurement of heavy metals was done in the Spectrophotometric Atomic Absorber.

C. Assessment of Metal Contamination in Soil

To evaluate the degree of contamination in the sediments, we used five parameters: enrichment factor (EF), geo-accumulation index (I), contamination factor (CF), contamination degree (Cd), and pollution load index (PLI).

- **Enrichment Factor (EF)**

  In our study, enrichment factor (EF) according to [23] was used to assess the level of pollution and potential anthropogenic impacts on river sediments and to identify metallic concentrations. Enrichment factor classification according to [24], EF = Cn in samples taken / C in soil crust

- **Geo-accumulation Index (Igeo)**

  Enrichment of metal concentration above baseline concentrations was calculated using the method proposed by [25] termed the geo-accumulation index (Igeo), which is expressed as follows: I-geo = log₂(Cn / 1.5 Bn)

- **Contamination Factor (CF)**

  The pollution factor and the contamination degree were used to determine the contamination in the sediments at the time of the study. The value of the pollution factor has been suggested by [26] and is calculated: CF = Cm of metal / Cm background, Background and crustal values are obtained according [27].

- **Pollution Load Index (PLI)**

  Pollution and its variations across stations are determined using the pollution load index. [28] explained that the application of PLI provides a simple way to assess pollution in sediment quality [29].

  \[ PLI = n \sqrt{ (CF1 \times CF2 \times CF3 \cdots \times CFn) } \]

  where n is the number of heavy metals studied and CF = are the pollution factors described above.

- **Contamination Degree (Cd)**

  The degree of contamination Cd = ΣCF [30] is defined as the sum of all contamination factors depending on each metal in all analyzed sediment samples 2.3.

- **Bioconcentration Factor, BCF**

  BCF provides an index of the plant's ability to accumulate or accumulate metals that are concentrated in the substrate. BCF is calculated using the equation: BCF = [Metal] plant / [Metal] sediment. A ratio of BCF > 1 indicates the best phyto accumulative capacity of metals in plants [31].

III. Results and Discussion

There is a fundamental concern about the concentration of heavy metals in the environment in soil and plant „Salix alba“ and their threat to human health. The study area is widely affected by progressive discharges of urban, agricultural, and industrial liquid waste without any prior treatment are the main source of water pollution in the Erzen River.

Soil samples were taken in the area below the willow root system. The concentrations of heavy metals obtained from the plant samples show a steady trend of nitrogen, phosphorus, and potassium shown in Table I. The accumulation of nutrients in plants reflects their nutrient requirements, depending on several factors, such as level of production, species, cultivar, soil fertility and/or fertilization, climate, and crop treatments [32].

In general, crops have nutritional needs that represent the number of macronutrients and micronutrients that plants receive from the soil to meet all stages of development [32].

Table II are presented the obtained values of physicochemical characteristics of the soil taken in the bed of the Erzen River, Ndroq. It is noticed that the properties of the soil have a strong influence on the effect of plant growth on the concentrations of heavy metals in the soil substrate as well as nutrients.

Table III is the result of total heavy metal content in soil and plant samples. It is noticed that the results are higher in soil samples than in plant samples.

Based on size test analyses that sediments have the following composition: Clay (9.2%) - Silt (28.7%) - Sand (62.1%) and Gravel (0.0%). Soils were classified as sandy because the percentage of silt was twice the percentage less and clay is less than 30%.

All results from soil and plant samples in Erzen River flow were expressed based on dry mass mg/kg. The average values of heavy metals in the ground in Erzen River, Ndroq. It is noticed that the properties of the soil have a strong influence on the effect of plant growth on the concentrations of heavy metals in the soil substrate as well as nutrients.

<table>
<thead>
<tr>
<th>TABLE I: NUTRIENT OF SALIX ALBA PLANT IN SOIL AT ERZEN RIVER BANK, NDROQ, ALBANIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Determination of nitrogen NH₄⁺ (%)</td>
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<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>S1 3.36</td>
</tr>
<tr>
<td>S2 3.024</td>
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<tr>
<td>S3 3.12</td>
</tr>
<tr>
<td>S4 2.95</td>
</tr>
<tr>
<td>S5 3.47</td>
</tr>
</tbody>
</table>

<p>| TABLE II: PHYSICOCHEMICAL CHARACTERISTICS IN SOIL, AT ERZEN RIVER BANK, NDROQ, ALBANIA |
|-----------------------------------------------|----------------------------|------------------------|</p>
<table>
<thead>
<tr>
<th>Large sand particles (%)</th>
<th>Small sand particles (%)</th>
<th>Powder (%)</th>
<th>Clay (%)</th>
<th>CE ms/cm</th>
<th>pH</th>
<th>CaCO₃ (%)</th>
<th>Potassium K₂O mg/100g</th>
<th>Humus (%)</th>
<th>Nitrogen (%)</th>
<th>Organic matter M.O (%)</th>
<th>Humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>62.1%</td>
<td>28.7%</td>
<td>9.2%</td>
<td>0.2</td>
<td>8.26</td>
<td>16.72</td>
<td>3.53</td>
<td>0.93</td>
<td>6.128</td>
<td>2.84</td>
<td>25.02</td>
</tr>
</tbody>
</table>

The concentration of heavy metals in the soil depends on many factors, but they occur naturally at low concentrations in the soil or are considered soil pollutants at high concentrations due to their acute and chronic toxicity [33].

The concentration of heavy metals in the soil depends on many factors, but they occur naturally at low concentrations in the soil or are considered soil pollutants at high concentrations due to their acute and chronic toxicity [33].
Nickel concentration is another toxic and harmful element, which is a moderate concern due to its potential carcinogenicity in humans; it also has various harmful effects on aquatic life. It is toxic to plant life, too and is a danger to fish. Nickel toxicity is generally a result of wastewater discharges. This chemical element has the property to be easily and quickly absorbed by plants [34]. Nickel concentrations in all soil samples were above the permissible values (35 mg/kg), ranging from 42.2 mg/kg dry mass to 98.4 mg/kg dry mass. The average value achieved for nickel in the study area was 68.9 mg/kg dry mass.

The lead content in the sediments of the Erzen River resulted in an average value of 76.38 mg/kg dry mass resulting in higher values compared to the norm. Chromium is toxic, the element is considered carcinogenic (in high concentrations) and can act as an irritant to the skin if it is passed on to human health. The achieved values for lead were (53.2 mg/kg up to 97.1 mg/kg dry mass), the source of which in the environment can come mainly from anthropogenic sources (mines, plants, etc.). The mean value of all samples was 76.38 mg/kg dry mass, which resulted above the set norm.

Chromium concentrations in soil samples were below the limit values (25 mg / kg), ranging from 18.9 mg / kg dry mass to 34.5 mg / kg dry mass. The average value of this chemical element was 28.18 mg/kg, which was considered above the allowed values, which can show negative effects on biological processes in soil, plants, animals, and humans.

The results for the willow plant samples in the Erzen riverbed are presented in Table III. Nickel concentrations ranged from 0.57 mg / kg dry mass to 0.89 mg / kg dry mass. The mean value for Cr in the Salix alba plant samples obtained was 0.71 mg/kg dry weight which was within the limits allowed by FAO. The chromium content in plants is mainly controlled by its soluble content in the soil. Plants absorb heavy metals from the soil through some of these processes, such as redox reactions, ion exchange, dissolution of precipitation, etc.

The transfer of metals from soil to plant tissues has been studied using evaluation indices and relevant parameters of the accumulation of heavy metals from soil to plants. BCF provides an index of the plants ability to accumulate metals that are concentrated in the substrate. BCF is calculated using the equation: BCF = [Metal] plants / [Metal] sediments

A ratio BCF > 1 indicates the best phytoaccumulative capacity of metals in plants [31]. Table III presents the results of the Bioconcentration Factor for the Plant (BCF) of the average values of the two plant and sediment study periods around the riverbed and the ability of metals to pass from sediment to plant.

In average values these factors represent the ascending order Ni> Cr> Pb, the ratio of metals in plants/sediment is <1, a fact that indicates a phytoaccumulative ability of metals from poor sediment. The research proved a weak link between the concentration of metals in sediments and in plants. The mobility of metals in plants, from roots to leaves is higher than from sediments in plants [35].

A. Assessment of Metal Contamination in Soil

The enrichment factor (EF) is a convenient measure of geochemical trends and is used to make comparisons between areas [36]. The EF values of heavy metals in the Erzen river sediments are listed in Table IV and presented in Fig. 2, calculated as the concentration of heavy metals in the study area. The average value of the EF enrichment factor for Pb in the Erzen River sediments was 3.819 in the range 2 ≤ EF <5, these sites are classified as moderate enrichment (Table IV).
The average value of Igeo for Pb in the sediments of the Erzen River was 1.639, classified in the degree of pollution (1 <Igeo <2). According to the Muller classification, the Igeo values for Pb indicate that the Erzen River sediments are moderately polluted for most sampling sites. According to the sediment quality guidelines, the Erzen River sediments were not highly polluted for the Ni and Cr elements (Table IV).

A contamination factor (CF) was used to determine the contamination status of the Erzen River sediments. The CF calculated for various heavy metals in the Erzen River sediments is shown in Table V.

The average CF value for Pb in the Erzen River sediments was 4.78. This result presented in Table V, shows that most sampling sites have CF classified in the range 3 ≤ CF <6, with Considerable contamination, according to the [26] classification. While for heavy metal Ni the value of the pollution factor marks 1 ≤ CF <3, indicating average pollution. Significant values of the pollution factor at all stations for Cr marking an average value of 0.41, (CF <1 low pollution).

The maximum value of the degree of Cd contamination is set for Pb metal, 12 ≤Cd <24 significant degrees of contamination. The concentration of nickel metal in the sediments of the Erzeni River is rated at 6 ≤Cd <12, the average degree of contamination. While for Cr metal it marked a low degree of pollution, with Cd <6 low degrees of contamination (Table V).

From these indices, the study area is considered to have high pollution with lead, nickel, and chromium. This is due to the impact of external sources such as industrial activities, agricultural waste, etc.

Pollution load index (PLI) and its variations across stations are determined using the pollution load index. [28] explained that the application of PLI provides a simple way to assess contaminated and non-contaminated sediments. For PLI> 1 contamination in sediment quality is demonstrated [29].

From the obtained results we have that almost all the stations taken in the study, in the Erzen River can be classified as places polluted with heavy metals of Pb, Ni, and Cr.

The use of plants in the extraction of metals from contaminated sediments is subject to the category of
Deficiency to minimal enrichment.

The following graph presents the ratio of the concentration of nickel (Ni), Chromium (Cr), and Lead (Pb) metals in the samples taken for study in soil and Salix alba plants in the Erzen riverbed, in the period July 2020. Heavy metals such as Ni, Cr, and Pb were studied because they are usually more disturbing and have the highest concentration in wastewater sludge [35]. The concern for Pb and Cr arises from its possible entry into the food chain.

The results obtained in these experiments suggest that Cr and Ni were highly absorbed by the plant. The concentration of Pb is higher in the soil solution than absorbed by the plant. Heavy metals such as Ni, Cr, and Pb were studied because they are usually more disturbing and have the highest concentration in wastewater sludge [36]. The concern for Pb and Cr arises from its possible entry into the food chain.

The results obtained in these experiments suggest that Cr and Ni were highly absorbed by the plant. The concentration of Pb is higher in the soil solution than absorbed by the plant.

IV. CONCLUSIONS

In this research, the main purpose was the analysis of heavy metals in the samples of sediments and willow plants in the area of Ndroq, in the Erzen River.

Based on size test analyzes that sediments have the following composition: Clay (9.2 %) - Silt (28.7 %) - Sand (62.1 %) and Gravel (0.0%). Soils were classified as sandy because the percentage of silt was twice the percentage less and clay is less than 30%.

According to the results of heavy metals in plant Salix alba and soil it is determined that the content of these contaminants in the study area varies between elements and samples, and those values indicate a potential threat from the industrial sector to the environment. Based on the data obtained we say that the concentration of heavy metals in sediments is higher than in plants.

Concentrations of chromium, nickel, and lead metals in sediments resulted above standard values. Total concentrations in heavy metal sediment samples are ranked in the order Ni > Pb > Cr. The content of heavy metals in the plant samples was within the permitted limits set by the FAO and are presented in ascending order Ni > Cr > Pb.

The use of plants in the extraction of metals from contaminated soils is subject to restrictions on the concentrations of heavy metals achieved in above-ground biomass, as well as the amount of biomass produced by the phytoextraction plant. These soil changes can also serve to fertilize the plant, thus increasing its biomass production. The biocenocentration factor in plants/sediment is <1, indicating that the concentration of metals accumulated in plants is not evenly distributed, but that they aim for their bioaccumulation.

Hyperaccumulation capabilities and pollution prevention characteristics would be essential next step in optimizing phytoremediation and extraction of heavy metals from soil.

The current study shows that effective precautions should be taken by responsible parties to prevent and mitigate not only the situation but also to significantly protect the well-being of residents along the Erzen River.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors are involved in sampling, analysis, and site inspection. All authors wrote the manuscript and read and approved the final version of the manuscript.

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