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Heavy Metals and Ni Phytoextractionin in the Metallurgical Area Soils in Elbasan

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Abstract

The metallurgical complex of Elbasan represents a potential source of the heavy metal pollution, due to the industrial activity conducted before years 1990s. The study focuses in the metallurgical area "Ish-Uzina 12", which today is used as agricultural land.

The aim of this study was to determine the degree of soil contamination by Ni, Co, Pb, Cr and Zn, and to evaluate the phytoextraction potential of nickel hyperaccumulator *Alyssum murale.* The phytoextraction potential of *A. murale* is studied through its cultivation in different conditions. The experimental area is divided into three plots; the first in natural conditions, the second with chemical fertilizer Diammonium phosphate and the third with manure.

This work showed that the concentrations of heavy metals in plots were respectively: in the first plot, the concentration of Ni was 610 mg/kg, Co 75 mg/kg, Cr 370 mg/kg and Zn 80 mg/kg; in the second Ni was 440 mg/kg, Co 120 mg/kg, Pb 165 mg/kg, Cr 310 mg/kg and Zn 75 mg/kg and in the third Ni was 410 mg/kg, Co 115 mg/kg, Pb 10 mg/kg, Cr 380 mg/kg and Zn 90 mg/kg.

Phytoextracted Ni in total harvest reached respectively 1280.9 mg/kg on the first plot, 513.4 mg/kg on the second and 69.1 mg/kg on the third.

Based on the results obtained it can be concluded that the soils of this area are contaminated by Nickel and *A. murale* is a candidate for phytoextraction.

Keywords: heavy metals, phytoextraction, *Alyssum murale*, contaminated soil.

1. Introduction

Heavy metals are part of the soil, but their high levels are considered toxic. Sources of the heavy metal pollution are industrial activities such as mining, metal smelting, production of different oils, fertilization, pesticide use, house waste, etc.[15]. The presence of metals in groundwater and soils can pose a significant threat to human health and ecological systems. The chemical form of the contaminant metal influences its solubility, mobility, and toxicity in ground-water systems. The chemical form of metals depends on the source of the metal waste and the soil and ground water chemistry at the site. A detailed site characterization must be performed in order to assess the type and level of metals present and to allow the evaluation of remedial alternatives [12].

Elbasan is one of the largest cities in Albania, which had the biggest metallurgical complex of the country (155 hectares) from 1970 to 1990. At the same time, it was the main source of soil and groundwater contamination with heavy metals [21, 22]. The population growth and the migration from villages towards cities, after the '90s, have transformed a part of this industrial area in residential area, which now is called Ish-Uzina 12. This is the place with the highest risk of pollution and toxins, and where at least 11 hectares of soil is spotted by the ferrochrome wastes. From 1991, this metallurgical plant released 44.8 tons of toxic dust/year. The pollution emitted from this complex has affected the Shkumbin River (the main watershed in this region), has caused many problems to the microenvironment and adversely affected human health, especially pregnant and lactating

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mothers. These issues have been caused by the presence of toxic gases, vapors, and dust [20].

Hyperaccumulation is a mechanism that is believed to allow plans to survive on serpentine soil [7]. A few number of plant species actively hyperaccumulate Ni and Zn at concentrations up to 2% of their shoot dry weight (DW) without any symptoms of toxicity [1]. Hyperaccumulator plants grow in soils with high concentrations of metals, and therefore they can be used to determine their potential in the management of polluted soils and especially in metal extraction [22]. Previous studies clearly evidenced a great variability in phytoextraction potential in different Albanian populations of *A. murale* depending on the site of collection [2,3,4,8,18,22]. Phytoextraction is a technology, that uses plants to clean contaminated soil by heavy metals. These species have the genetic potential to remove and metabolize contaminants [17]. The main goal of this study is:

- The assessment of the heavy metal concentration (Ni, Co, Pb, Cr and Zn) in soil at one of the ex-factories (Ish-Uzina 12) of Metallurgical plant in Elbasan
- The evaluation of the nickel phytoextraction potential from the hyperaccumulator plant *Alyssum murale.*

2. Material and Methods

The study area was Ish-Uzina 12, which is located roughly 4 km far from the Elbasan city and 0.5 km from the Shkumbini River. The experiment was conducted in agricultural soil. The phytoextraction potential of *A. murale* was studied through its cultivation in different conditions. The experimental area was divided into three 2m^2 plots. In the first plot, the soil was in natural conditions, in the second one the soil was treated with chemical fertilizer Diammonium phosphate (DAP), and in the third plot the soil was treated with cow manure. DAP is used as a fertilizer, which is an excellent source of phosphorous (P) and nitrogen (N) for plant nutrition. It is highly soluble and thus dissolves quickly in soil to release plant-available phosphate and ammonium. The typical formulation is 18-46-0 (18% N, 46% P_2O_5, 0% K_2O) [13]. Manure is organic matter, mostly derived from animal feces, which contribute to the fertility of the soil by adding organic matter and nutrients. Its composition depends on the animal diet. However, 1 kg manure contains an equivalent of 0.64% nitrogen (N), 0.58% phosphate (P_20_5) and 0.81% potassium (K_20) [14]. The soil was planted with *A. murale* seedlings in March 2013 and plants were harvested in July 2013. The soil was watered every day. After the harvest, the plants from each parcel were weighed to determine the wet biomass and after they have been dried in natural conditions, they were weighed again. Sub samples of each soil were air dried and ground to pass through a 2-mm stainless-steel sieve.

Samples were mineralized with a microwave digester (Ethos One Pro-24), where 0.3 gr of soil or plants sample was digested by adding 8 ml HNO_3 69% and 2 ml H_2O_2. Solutions were filtered and adjusted to 50 ml with distilled water. Heavy metals were determined spectrochemically using Atomic absorption spectrophotometer (nov AA-350).

3. Results and Discussion

3.1 Heavy metals in the soil

Based on the results obtained, it is observed that the order of heavy metal concentration in the first plot, in natural condition, is Ni>Cr>Zn>Co>Pb. In the second plot, treated with chemical fertilizer Diammonium phosphate, the order of concentration is Ni>Cr>Pb>Co>Zn. In the third, treated with manure, the order is Ni>Cr>Co>Zn>Pb. The concentrations of Ni and Cr are the highest in each plot. While the concentrations of Co and Zn change depending on the type of fertilization. In the first plot, the concentration of Pb was zero and in the second plot, it is higher when compared with the third one.

Table 1. The concentration of heavy metals in Ish-Uzina 12 soil (mg/kg)

	Plot 1	Plot 2	Plot 3	Average	STDEV
pH	8.88	8.85	8.96	8.9	±0.1
Ni	610	440	410	486.7	±107.9
Co	75	120	115	103.3	±24.7
Pb	-	165	10	87.5	±109.6
Cr	370	310	380	353.3	±37.9
Zn	80	75	90	81.7	±7.6

This study shows that the concentration of Ni was the highest (610 mg/kg) in the first plot and the lowest (410 mg/kg) in the third one. The concentration of Cr was the highest (380 mg/kg) in the third plot and the lowest (310 mg/kg) in the second one. The concentration of Pb was the highest (165 mg/kg) in the second plot and the lowest in the first one. The concentration of Co was the highest (120 mg/kg) in the second plot and the lowest (75 mg/kg) in the first one. Finally, the concentration of Zn was the highest (90 mg/kg) in the third plot and the lowest (75 mg/kg) in the second plot.

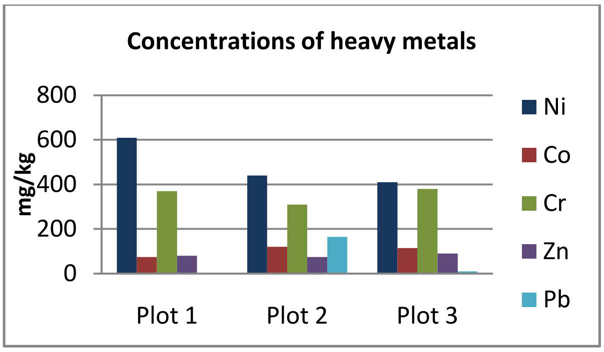

Figure 1. The concentration of heavy metals in Ish-Uzina 12 soil

The nickel content in plots varies from 410 to 610 mg/kg, its average concentration is 486.7 mg/kg. The target value for Nickel is 35 mg/kg (refer to table 2), while the intervention value is 210 mg/ kg according to Denneman and Robberse [11] and Ministry of Housing, Netherland [19] (table 2**).** Cobalt concentrations in plots vary from 75 to 120 mg/kg, and its average concentration is 103.3 mg/kg. Cobalt is a natural component of the Earth’s crust, with an average concentration of 25 mg/kg. In basalt, Co concentrations are in the range 40-50 mg/kg, while much lower concentrations, between 1 and 10 mg/kg are found in granite [5]. Therefore, Co content in all samples was greater than the permissible limits. The chromium content in plots varies from 310 to 370 mg/kg, and its average concentration is 353.3 mg/kg. The permissible limit for Cr according the Dutch standards [19] is 100 mg/kg (Table 2). Cr content in all samples was greater than the permissible limits (see table 1). Sources of chromium (Cr) contamination include releases from electroplating processes and disposal of chromium (Cr) containing waste. Since cobalt naturally occurs in nickel bearing laterites and nickel-copper sulphide deposits, it is most often extracted as a by-product of nickel and copper. According to the Cobalt Development Institute [16], about 48% of cobalt production originates from nickel ores. Nickel contaminations in the soil are metal plating industries, combustion of fossil fuels, nickel mining, and electroplating [6].

Table 2. Permissible limits of heavy metals in soil and plants

Serial No	Elements	*Target Values of soil (mg/kg)	**Intervation Values of soil (mg/kg)	***Permissible Value of plants (mg/kg)
1	Cd (Cadmium)	0.8	12	0.02
2	Cr (Chromium)	100	360	1.3
3	Cu (Coper)	36	190	10
4	Pb (Lead)	85	530	2
5	Ni (Nickel)	35	210	10

*Target values are specified to indicate desirable maximum levels of elements in unpolluted soils.
**Intervention when remedial action is necessary; Source: Denneman and Robberse 1990 and Ministry of Housing, Netherland 1994.
*****Source: WHO (1996).

Zinc concentrations in plots vary from 75-90 mg/kg, its average concentration is 81.7 mg/kg. The maximum intervention limit for Zn in soil is 150-300 mg/kg [10]. The concentration of lead varies from not detectable (-) to 165 mg/kg, its average concentration was 58.3 mg/kg. The permissible limit for lead (Pb) according to the Dutch Standards [19] is 85 mg/kg (Table 2). Only the lead on the second plot exceeds the Standard value (Table 1).

3.2 Nickel phytoextraction

The biomass was weighed in each plot in order to calculate the nickel phytoextraction potential, as the product of plant biomass with the concentration of nickel in the cultivated plants. In the second plot, which was treated with chemical fertilizer Diammonium phosphate, the amount of biomass was the highest, and in the third which was treated with manure the biomass was the lowest. The potassium presence is an inhibiting factor for the plant growth, and therefore the large amount of nitrogen and phosphorous had a positive effect on the growth in our case. However, in the first plot the nickel phytoextraction potential was higher (1173 mg Ni/plot), while in the third was lower (61.6 mg Ni/plot) compared with the other plots, because the amount of nickel in the soil is higher in the first plot then in the others.

Table 3. Biomass production and phytoextraction yield of *A. murale* in Ish-Uzina 12 soil

Plots	Biomass (g)	Ni (mg/kg)	mg Ni/Plot
Plot 1	429	2818	1280.9
Plot 2	558	920	513.4
Plot 3	102	677	69.1

Fertilization has increased the plant biomass. Based on the above results, it can be concluded that fertilization does not affect the concentration of Ni in plant tissues.

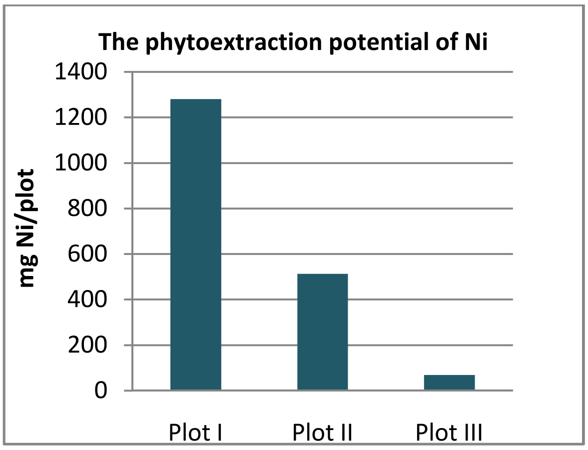

Figure 2. The phytoextraction potential of Nickel in plans

The nickel content in plants varies from 670 to 2800 mg/kg, its average is 621.1 mg/kg. It is rather high compared to the values generally observed in plants and is considered as toxic according to WHO [23], when the permissible recommended limit of Nickel in plants is 10 mg/kg (see table 2). When comparing the biomass production and the phytoextraction yield of *A. murale* in plants, it can be noted that biomass production was proportional with the soil fertilization. Moreover, the phytoextraction potential of nickel was high by this order of plots 1>2>3, and it shows that where the presence of nickel in the soil is greater, its concentration positively affects on the plant growth. Therefore, the first plot has the phytoextraction potential of Nickel higher than the other plots, because here the nickel concentration was the highest (see table 1).

4. Conclusions

The data presented indicate that the soils around the Metallurgical plant of Elbasan are highly polluted with Ni, Zn, Pb and Cr, excluding Co. The high level of heavy metals such as nickel and chromium show that the cause of soils pollution is the processing of mafic materials in Ish-Uzina 12, coming from the southeastern serpentine areas of the country. In addition, the total metal content of soil is also the result of industrial activities. The nickel concentration in the hyperaccumulative plants is lower in those plots where biomass production is higher; therefore, there is a dilution of metals in plants. The increase of biomass quantity under the influence of fertilization shows that Nickel plays a strong role in plant growth. The ability of hyperaccumulative plants to keep the hyperaccumulation ability also in the non-mineralized contaminated soil shows the basic tolerance and adapter priority for the ability of hyperaccumulator. Considering the above results, it can be concluded that *A. murale* could be a useful candidate for phytoextraction technologies in - situ not only on serpentine soils, but also in naturally contaminated soils in our country.

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