PHYTOEXTRATION OF NICKEL FROM INDUSTRIAL AND MING WASTE: A REVIEW

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ABSTRACT

Mining, metallurgy, food processing, textiles, lumber, and cement were among the leading industries in Albania under the previous regime, when heavy industry was a priority and some factories were capable of exporting. After 1989, the sector declined due to the lack of new technology and financing and the dilapidated condition of the factories. Anthropogenic pollution results from daily human activities such asindustrial, mining, agricultural and domestic make exposure to heavy metal release possible. Exposure to heavy metals release poses a threat to human health. Consequently, the removal of heavy metals from soil is unavoidable. There is a range of physical, chemical and biological techniques used to remove heavy metals and metalloids from soils, but the phytoextraction method appears to bean effective and economical technique. Phytoextraction is the removal of metals from soil using plants and relies on the ability of a plant crop to remove and concentrate heavy metals from either naturally metalliferous or contaminated soils. This paper aims to evaluate the concentration of total major (Ca, Mg, and Fe) and trace elements (Ni, Co, Cr, Zn, Pb) in industrial polluted and mining soils and the Ni phytoextraction or phytomining potential of the hyperaccumulator *A. murale* Waldst. & Kit in soil. Given the phytoextraction benefits and the capacity of *Alyssum murale* to accumulate nickel in soil, it could be concluded that *Alyssum murale* could bea candidate for phytoremediationof contaminated soilsatex-industrial sites and industrial and mining waste sites.

Keywords: phytoextraction, phytomining, hyperaccumulator plants, heavy metal, ex-industrial site, mining sites

1. INTRODUCTION

Accumulation of heavy metals in soil, water and air is one of the major environmental concerns worldwide, which mainly occurs due to anthropogenic activities such as industrialization, urbanization and mining. With the increment of urbanization and industrialization, the cases of soil contaminated by heavy metals have increased rapidly and become a threat to food safety, ecological environment, and sustainable development of the agriculture sector (Yao *et al*., 2012). Conventional remediation strategies involving physical or chemical techniques are not cost-effective and/or eco-friendly, emphasizing the need for novel approaches. Phytoextraction is a developing technology that uses plant species to accumulate elements from contaminated or mineralized soils and transport them to their shoots, which may then be harvested as a crop to remove them from the land (Chaney *et al*., 2007). It is a type of phytoremediation, while the term phytomining has been applied to the latter case in which the economic value of the recovered metal is the primary objective. Effective phytoextraxtion requires both plant genetic ability and the development of optimal agronomic management practices. These species have the genetic potential to remove and metabolize contaminants (Li *et al.,* 2000). Many studiesprovide information about the great variability in phytoextraction potential in different Albanian populations of *A. murale*depending on collection site (Shallari *et al*., 1998; Bani *et al*., 2009; Bani *et al*., 2010; Bani *et al*., 2013; Osmani *et al*., 2015; Osmani *et al*. 2018a).

Brooks *et al*., (1977) first used the term hyperaccumulators to describe plants containing >1000 μg/g (0.1%) nickel in their dried tissues. Hyperaccumulators are species capable of accumulating metals at levels 100 fold greater than those typically measured in shoots of the common non accumulator plants. The largest number of Ni-hyperaccumulators is found in the Brassicaceae family in temperate climates, especially Mediterranean Europe and Turkey (Reeves and Adigüzel, 2008). The genus Alyssum (Brassicaceae) contains the greatest number of reported Ni hyperaccumulators, many of which can achieve 30 g kg^{-1} Ni in dry leaf biomass (Baker and Brooks 1989). The Balkans has the highest diversity in Ni hyperaccumulator plants in Europe and is home to the widespread plant *A. murale*, one of the most studied species worldwide for phytomining (Nkrumah *et al*., 2016). The Albanian flora contains a wide range of Balkan endemic taxa, including some serpentine-obligate (Stevanovi´c *et al*., 2003) among which, the most efficient Ni-accumulator individuals of the species *A. murale* (Bani *et al*., 2009; 2010). *A. murale* occurs widely on these ultramafic Vertisols (Bani *et. al*., 2009) and is a spontaneous weed to other crops. The use of nickel hyperaccumulator plant species for nickel phytominig in Albanian ultramafic soil is a reality. Bani*et al*., (2015b; 2019) showed that the phytoextraction potential of *A. murale* (syn. *Odontarrhena chalcidica*) under different agronomic practices in Albanian vertisol can be 112 – 145 kg Ni ha^{-1}. *A. murale* Waldst. & Kit is the most efficient Ni hyperaccumulator plants in Albania (Bani *et al*., 2013; 2015a).

Thepresent paper evaluatesthe concentration of total major (Ca, Mg, and Fe) and trace elements (Co, Cr, Ni, Zn, Pb) in soil in ex-industrial polluted areas, in industrial and mining wastes sites and the Ni phytoextraction or phytomining potential of the hyperaccumulator *A. murale*Waldst. & Kit in soils.

2. MATERIALS AND METHODS

In addition to the Përrenjas dumpsite (41°4’0, 99”N, 20°32’20, 72”E), the present investigation was carried out in the metallurgical plant (ex-industrial site) and dumpsite, located in Elbasan (41°4’58, 54”N, 20°1’24, 51”E) as well. The metallurgic plant in Elbasani is the largest one in the country (4 km far from the city), with a surface of 155 hectares and a treatment capacity of 800 thousand tons/year of iron-nickel and produced an estimated 44.8 tons of toxic dust. The main plants, which have been operating (1967- 1990), are nickel-cobalt plant (Ish-Uzina12), metallurgy electrolysis plant and ferro-chrome plant (Shehu, 2009). This is the most polluted region in the country and produces a considerable amount of toxins, as at least 11 hectares of soil is polluted by the ferrochrome wastes. Industrial activity is the main source of heavy metals contamination in the region (Shallari *et al*., 1998; Sallaku *et al*., 1999; Osmani *et al*., 2015; Osmani and Bani 2017; Osmani *et al*., 2018 a,c). In Përrenjas, the biggest iron, nickel and cobalt mine is located 500 m far from the city center. A considerable amount of ferro-nickel mineral was extracted (500 thousand tons/year). 350 thousand tons was processed in the metallurgical complex of Elbasan and 150 thousand tons was exported to Europe. The metallurgical complex of Elbasani is the main source of soil contamination with heavy metals (Osmani *et al*., 2017; Osmani *et al*., 2018b).

Soil analysis

Soil samples were collected from a overlaying deposit, up to 30 cm when possible. Once collected, they were air-dried and laboratory investigated. The microwave digester was involved for the mineralization process as a means to address the determination of trace metals. Conditions for mineralization were as following: 6 ml HCl, 2 ml HNO3, and 3 ml H_2O_2, per 0.5 g soil. Total major (Ca, Mg, and Fe) and trace elements (Co, Cr, Ni, Zn, Pb) in digestion solutions were measured via atomic absorption spectrophotometry (AAS).

A DTPA–TEA extractant (0.005 M diethylenetriaminepentaacetic acid (DTPA) with 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA)) at pH 7.3 was employed for the availability of Ni. A ratio of 1 g soil: 10 ml DTPA-TEA solution was shaken for 2 h, and then the suspension was centrifuged for 20 min. Once centrifuged, it was filtered through a 0.2 μm pore size cellulose nitrate filter (Echevarria*et al*., 1998). Ni concentrations in the soil extracts were determined spectrochemically using the atomic absorption spectrophotometer (Nov AA-350).

Plant analysis

All plant samples were washed, dried and ground to a fine powder. Nickel concentrations in plants were determined by plasma emission (ICP) spectrometry after microwave digestion of plant samples. A 0.25gdry matter plant aliquot was digested by adding 8 ml of 69% HNO_3 and 2 ml of H_2O_2. The final solution was filtered and made up to 25 ml with deionized water. The atomic absorption spectrophotometry (AAS) was used to measure the nickel concentrationdigestion solutions.

Nickel phytoextraction

The efficiency of phytoextraction depends on the level of soil contamination and the amount of metals accumulated by plants. Metal phytoextraction is determined by biomass production and heavy metals bio concentration degree found at high levels (Mc Grath and Zhao, 2003). The biomass (dried) was weighed in each plot to calculate the nickel phyto-extraction yield (η) as the product of plant biomass (B) with the concentration of nickel in the cultivated hyperaccumulator plant (C_P) (mg kg^{-1}).

$$\eta = B \times C_P$$

3. RESULTS

Concentrations of chemical elements in the soil

Table 1 reports the results for pH and the concentration of the total major (Ca, Mg, and Fe) and trace elements (Ni, Co, Cr, Zn, Pb). Both dumpsites have a similar pH, ranging from 8.4 to 8.6, which shows a similarity to the mineralogical composition. Results obtained show that the dumpsites soils recorded higher metal concentrations than soil in ex-industrial site, where the pH is lower (7.9).

The Përrenjas dumpsite has higher levels of magnesium concentration (25267 mg kg^{-1}) than the Elbasan dumpsite (9941 mg kg^{-1}), which corresponds to the serpentine soil materials and ultramafic originated residues. The ferromagnetic minerals are very rich in Mg (Shallari *et al*., 1998; Bani *et al*., 2014). Accordingly Mg:Ca ratio varied 2.7 in Elbasan Dumpsite soil and 5.8 in Përrenjas dumpsite soil, a range that is reported in ultramafic materials (Proctor, 1971; Shallari *et al*., 1998; Bani *et al*., 2014). The plant species growing on this ex mining area must be physiologically adapted to cope with the high Mg/Ca ratio and Ca deficiency.

Table 1. The pH and the concentration of elements in study soils (mg kg^{-1})

Soil type	pH	Ca	Mg	Fe	Ni	Co	Cr	Pb	Zn
Ex-industrial	7.9	13957	10916	23242	700	112	525	103	142
Përrenjas Dumsite	8.4	4286	25267	36715	6859	286	5458	25.8	117
Elbasan Dumpsite	8.6	3710	9941	34853	1842	245	7185	42.2	135

Iron, nickel and cobalt concentrations are higher in Përrenjas dumpsite (36715, 6859 and 286 mg kg^{-1}) than in Elbasan dumpsite (34853,1842 and 245 mg kg^{-1}) and soil in ex-industrial site (23242,700 and 112 mg kg^{-1}). As a result of the industrial activity, iron-nickel plant and other plants around in Elbasan and the iron, nickel and cobalt mining in Përrenjas, this metal concentrations are higher in all type of soils. 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. Kapusta (2007) said that based on the Cobalt Development Institute about 48% of cobalt production originates from nickel ores. Even though the minerals of ultramafic rocks are the source of soils pollution in theex-industrial sites, the total Ca:Mg ratio was higher than 1 (1.3), differently from that in ultramafic soils.

The Dutch standards define the permissible limit for chrome as 100 mg kg^{-1}. Chrome content in all samples was greater than the permissible limits (Ministry of Housing, Netherland, 1994). Sources of chromium contamination include releases from electroplating processes and disposal of chromium containing waste.

Lead and zinc concentrations in soil were within the permissible limits. The maximum intervention limit in soil for Pb is 50-300 mg kg^{-1}, and for Zn is 150-300 mg kg^{-1}as defined in(86/278/EEC). Anthropogenic activites might be the source of higher Zn concentration (142 and 135 mg kg^{-1}) in the ex-industrial and Elbasan dumpsite soils, than in Përrenjas dumpsite (117 mg kg^{-1}). However, Bani*et al*., (2009) stated that this element could be sometimes found at a high concentration in serpentine soil

Biomass, Ni concentration in plant, Ni yields and DTPA extractable Nickel

The biomass production of metal hyperaccumulators depends on productivity of the soil, harvesting time, climatic conditions. Plant biomass is higher in the soils in ex-industrial site (660 g), than in both dumpsite soils, because this soil is used for agricultural purposes and it is fertilizer with organic and chemical fertilizer. The biomass is negatively correlated with Ni concentration in *A. murale*. In fertilized soils the biomass is higher, while the nickel concentration is lower (Osmani and Bani, 2017; Osmani *et al*., 2018a). Fertilizers increase the biomass and dilution the Ni concentration in plant tissues. Nickel concentrations in plants (Table 2) were higher in Përrenjasi dumpsite soil (2189 mg kg^{-1}) than in Elbasan dumpsite (735 mg kg^{-1}) and soils inex-industrial sites (452mg kg^{-1}), due to chemical availability of Ni in soil (Figure 1).

As it has been already reported, *A. murale* can hyperaccumulate up to 1% of nickel. In the present investigation, *A. murale* could not hyperaccumulatenickel more than 2000 mg kg^{-1} nickel since the available nickel content in soil is very low, and the Caamount in the soils in the soil of ex industrial sites is high. These data are in line with (Bani *et al*., 2010) showing that in *A. murale*, there appears at leastan inverse relationship between the Ni uptake and the Ca concentration in the soil.

Table 2. Plant biomass, nickel concentration in plant and Ni phytoextraction

Soil type	**Plant biomass (g)**	**Ni concentration in plants (mg kg^{-1})**	**Nickel phytoextraction**
Ex-industrial site	660	452	289 mg Ni/m^2
Përrenjas Dumsite	4.2	2189	8.77 mg Ni/pot
Elbasan Dumpsite	4.1	735	3.01 mg Ni/pot

Considering the biomass production and Ni accumulation, *A. murale* can be a potential candidate for phytoextraction of Ni in metal contamination sitein ex industrial site.

The Nickel concentration in soils polluted by anthropogenic activities (maily ultramafic minerals) had low concentration of available Ni as previously shown. Massoura *et al*., (2006) said that the soil is poor in smectite, rich in high-Ni goethite and slightly rich in alkaline.

The amount of the available Nickel in the soil, called Ni $_{DTPA}$, significantly decreased with time of *A. murale* cultivation. DTPA-extractable Ni in the soil was lower after the harvest of *A. murale*, mainly in the ex-industrial site, than in both dumpsite soils. It decreased from 3.8 to 3.1 mg kg^{-1} in ex-industrial soil and in Përrenjas and Elbasan dumpsite, from 4.8 to 3.4 mg kg^{-1} and 4.7 to 3.6 mg kg^{-1}, respectively.

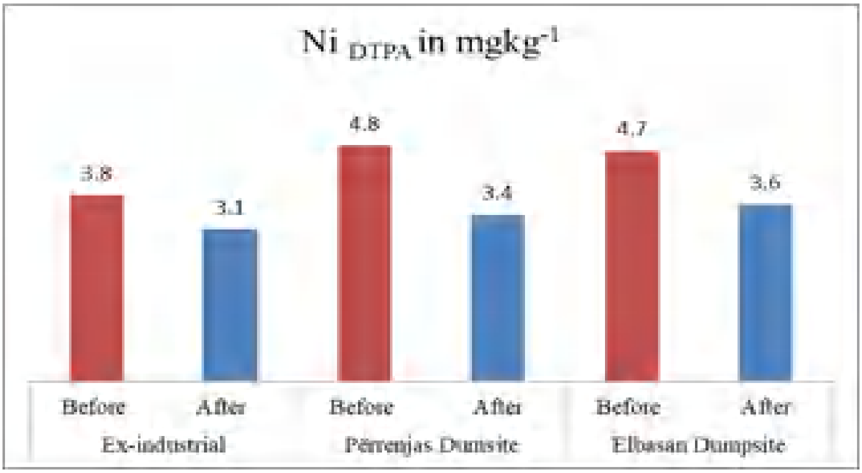

Fig. 1: DTPA extractable Nickel before and after *A. murale* harvest.

The results suggest that *A. murale* takes up Ni from a pool of soil Ni that can be at least partly quantified using DTPA, because the DTPA Ni decreased after the cultivation of *A. murale*. This is confirmed by DTPA previously having shown to extract isotopically-the exchangeable Ni, i.e. Ni from the labile pool (Shallari *et al*., 2001). The contamination potential of the waste resulting from mining materials or metallurgical waste was reduced as the DTPA-extractable pool of Ni in the soil after the successive culture of *A. murale* was reduced.

Ni_{DTPA} here reported is in full accordance with (Shallari *et al*., 2001; Bani *et al*., 2015).

4. CONCLUSION

The data here reported show that industrial activities are the main source of heavy metals pollution. In addition, metal concentrations are higher in the Elbasani dumpsite soil due tothe industrial activity (iron-nickel plant and other plants) and in the Përrenjas dumpsite soil which is rich in iron, nickel, cromium and cobalt mining wastes.

The term “hyperaccumulator” describes a number of plants that belong to distantly related families, but share the ability to grow on metalliferous soils and to accumulate extraordinarily high amounts of heavy metals in the aerial organs, far in excess of the levels found in the majority of species, without suffering phytotoxic effects. 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. The low concentration of available nickel in soil and the high content of calcium compared to the serpentine soils where *A. murale* grows naturally limits the accumulation of nickel. The use of fertilizer has increased nutrients in the soil, which are essentials for plant growth. As a result, we have the growth of plant biomass and Ni phytoextraction. Given the phytoextraction benefits and the capacity of *Alyssum murale* to accumulate nickel in soil, it could be concluded that *Alyssum murale* could be a candidate for phytoremediation in the ex-industrial soils and industrial and mining waste.

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