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HEAVY METALS CONCENTRATION OF DUMPING SITE SOILS AND THEIR ACCUMULATION IN *ALYSSUM MURALE* GROWING IN SELECTED DUMPING SITES IN ALBANIA

RIASSUNTO

Sono più di 26 anni che alcune parti dell'industria pesante in Albania, come la industria mineraria e quella metallurgica, sono chiuse e sono abbandonate. Le zone del cumulo rifiuti nel complesso metallurgico in Elbasan e nella miniera di Prenjas, che occupano grandi superfici, fanno parte della vecchia industria pesante. Come conseguenza, l'inquinamento del suolo in queste zone costituisce una questione importante nei giorni d'oggi. La bonifica del suolo è un metodo per purificare e rivitalizzare il suolo usando piante iperaccumulatori. Questo è il processo di rimozione dei contaminanti per proteggere sia la salute della popolazione che dell'ambiente.

Lo scopo del nostro studio è di studiare il potenziale di *Alyssum murale* per estrarre metalli dai rifiuti di scarico. Due esperimenti sono stati condotti con lo stesso trattamento. Per ciascuna zona di cumulo rifiuti, quella di Prenjas e quella del complesso metallurgico di Elbasan, (i) i campioni di terreno sono trattati con terreno vegetale di Prenjas e terreno di Elbasan, e (ii) con il letame, in percentuali differenti. Per stabilire l'effetto del terreno naturale e del letame sul processo di assorbimento di Ni, la produzione di biomassa e il nichel disponibile, *A. murale* è stato coltivato su questi campioni di rifiuti. Anche il trifoglio rosso (*Trifolium repens*), una pianta non-accumulatore, è stato testato in questo esperimento per la ri-vegetazione delle zone di cumulo rifiuti industriali. La fitoestrazione del Ni ed il fattore accumulativo è stato determinato per tutte e due le specie vegetali.

Entrambe le zone di cumulo rifiuti sono inquinate con metalli pesanti. La concentrazione di Ni (6859 mg kg⁻¹), Fe (36715 mg kg⁻¹), Cd (22.3 mg kg⁻¹) e Co (286 mg kg⁻¹) era più elevata nella miniera di Prenjas, mentre la concentrazione di Cr (7185 mg kg⁻¹), Pb (42.2 mg kg⁻¹) e Zn (135 mg kg⁻¹) era più elevata nel cumulo rifiuti metallurgici di Elbasan. *A. murale* e *T. repens* hanno

presentato una maggiore tolleranza verso Ni. Nell'esperimento in vasi, per il *T. repens* il 1-7% di Ni viene rimosso dal terreno moderatamente contaminato della discarica di Prenjas ed l' 8.7-29% di Ni dalla zona industriale di Elbasan. For *A. murale*, il 17-32% di Ni viene rimosso dal terreno di Prenjas ed il 62% di Ni dalla zona di cumulo rifiuti di Elbasan. Considerando i sopradetti risultati, si puo concludere che *A. murale* potrebbe essere un utile candidato per le tecnologie di fitoestrazione ex situ in terreni contaminati. Inoltre, entrambe le piante, *A. Murale* e *T. repens*, possono essere utilizzate per la rivegetazione delle zone di cumulo rifiuti. L'uso del terreno vegetale è più efficace per migliorare le proprietà dei terreni nelle zone di cumulo rifiuti.

SUMMARY

It is more than 26 years that some parts of the heavy industry in Albania, such as mining and metallurgy, are closed and fell into disuse. The dumpsites of the metallurgical complex in Elbasan and the Dumpsite of the mine in Prenjas, which occupy large areas, are part of the old heavy industry. As a consequence, soil pollution in these areas is an important issue nowadays. Soil remediation is a method of purifying and revitalizing the soil by using hyper-accumulator plants. This is the process of removing contaminants in order to protect both the health of the population and the environment.

The aim of our study is to investigate the potential of *Alyssum murale* to extract metals from the dumpsite waste. Two experiments were carried out with the same treatment. For each dumpsite, Prenjas mine dumpsite and Elbasan metallurgical dumpsite, (i) the soil samples were treated with Prenjas vegetation soil and Elbasan vegetation soil and (ii) with manure, in different percentages. In order to establish the effect of natural soil and manure on Ni uptake, biomass production and the available nickel, *A. murale* was grown on this waste samples. The red clover (*Trifolium repens*) a non-accumulator plant was also tested in this experiment for dumpsite re-vegetation. The nickel phytoextraction and the accumulation factor were determined for both species.

Both dumpsites are polluted with heavy metal. The concentration of Ni (6859 mg kg⁻¹), Fe (36715 mg kg⁻¹), Cd (22.3 mg kg⁻¹) and Co (286 mg kg⁻¹) was higher in Prenjas mine dumpsite, while the concentration of Cr (7185 mg kg⁻¹), Pb (42.2 mg kg⁻¹) and Zn (135 mg kg⁻¹) was higher in Elbasan metallurgical dumpsite. *A. murale* and *T. repens* showed a higher tolerance to Ni. In pot experiment, for *T. repens* 1-7% of DTPA Ni is removed from the contaminated soil of Prenjas dumpsite and 0.8-2.1% of DTPA Ni from Elbasan industrial dumpsite. For *A. murale*, 17-32% of DTPA Ni is removed from Prenjas dumpsite and 8.7-29% of Ni from Elbasan industrial dumpsite. Considering the above results, it can be concluded that *A. murale* could be a use-

ful candidate for ex - situ phytoextraction technologies in contaminated soils. Moreover, both plants, *A. murale* and *T. repens*, could be used for dumping site re-vegetation. The usage of vegetative soil is more effective for improving the properties of dumpsite soils.

INTRODUCTION

Soil contamination, also known as soil pollution is caused by the presence of manmade chemicals in the natural soil environment. Some form of industrial activity, agricultural chemicals or the improper disposal of waste often causes it. A huge amount of heavy metals released every day to the environment from human activities, like fossil fuel combustion, mining, use of fertilizer and pesticides, smelting and sludge amendment, add a toxic compound into the environments, which are organic and inorganic in nature. Some of them are extremely harmful to the environment, even in a very low amount (BIJALWAN and BIJALWAN, 2016). In general, it is very difficult to eliminate metals from the environment. Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soil are contaminated. Treatments can be done in situ (on-site), or ex situ (removed and treated off-site). Both of them are extremely expensive.

Research demonstrates that plants are effective in cleaning up contaminated soil (WENZEL *et al.*, 1999). Phytoremediation, the use of plants to remedy contaminated soils, is an emerging technology requiring a greater understanding of the underlying mechanisms for its optimization (MC GRATH and ZHAO, 2003). Hyper-accumulators are plants commonly grown on metalliferous soils and able to complete their life cycle without any symptoms of metal phytotoxicity (BAKER *et al.*, 2000). These plants can even prosper on contaminated soils and accumulate extremely high contents of trace elements in aboveground biomass (BAKER, 1987). The plant species tolerant to high element contents in soil followed by an intensive uptake of these elements belong in most cases into families Caryophyllaceae, Brassicaceae, Cyperaceae, Poaceae, Fabaceae, and Chenopodiaceae (KABATA-PENDIAS and PENDIAS, 2001).

The intensive research work has resulted in plant-based remediation technologies called phytoremediation (KUMAR *et al.*, 2016). 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). These species have the genetic potential to remove and metabolize contaminants (LI *et al.*, 2000). Previous studies clearly evidenced a great variability in phytoextraction potential in different Albanian populations of *A. murale* depending on the site of collection (SHALLARI *et al.*, 1998; BANI *et al.*, 2009; 2010; 2013; OSMANI *et al.*, 2015).

The objective of this study was to demonstrate the influence of combined factors such as the addition of organic or soil and industrial waste in stimulating the revegetation of this soil. Specifically, the role of *Alyssum murale* in nickel phytoextraction and *Trifolium repens* in soil phytostabilization was investigated. Therefore, the attention was focused on the possibility of using the accumulator plants to prevent pollution and at the same time to remove hazardous pollutants from soils. Similar studies on phytoextraction ability of plants are rare or absent in Albania, because this is one of the first studies in this field in our country.

MATERIAL AND METHODS

The study area

This study was carried in two dumpsites in Bradashesh, Elbasan (41°4'58, 54"N, 20°1'24, 51"E) and in Prrrenjas (41°4'0, 99"N, 20°32'20, 72"E). In Elbasan, the total population is 141,714, in a total area of 872.03 km² and in Prrrenjas is 24,906, in a total area of 322.95 km² (CENSUS, 2011). Elbasan's climate is classified as warm and temperate. The average annual temperature is 14.8 °C in Elbasan. The average rainfall is 1066 mm per year. In Prrrenjas, the climate is mild, and generally warm and temperate. There is a great deal of rainfall in Prrrenjas, even in the driest month. The temperature here averages 12.8 °C. The rainfall here averages 1061 mm per year (KRUTAJ *et al.*, 1991).

Elbasan is one of the largest cities in Albania, which had the biggest metallurgical complex of the country (155 hectares) from 1970 to 1990. It is located roughly 4 km far from the Elbasan city and 0.5 km from the Shkumbin River. At the same time, it is the main source of soil and groundwater contamination with heavy metals (SALLAKU *et al.*, 1999, SHALLARI *et al.*, 1998, OSMANI *et al.*, 2015; 2018). In Prrrenjas, the biggest iron, nickel and cobalt mine is located 500 m far from the city center. Prrrenjas mine extracted 500 thousand tons/year ferro-nickel mineral, where 350 thousand tons was processed in metallurgical complex of Elbasan and 150 thousand tons was exported to Europe.

The soil treatment

The soil selected for the pot experiment was taken from the 0-30 cm layer of a dumpsite soil. It was air-dried and sieved to obtain the fraction ≤ 5 cm. The experiment was carried out using 2-litre plastic pots with 2 kg soil. For each dumpsite, Prrrenjas dumpsite (marked PD) and Elbasan dumpsite (ED), the soil samples were treated with Prrrenjas vegetation soil (PS) and Elbasan vegetation soil (ES) and with manure (M), in different percentages. 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_2O_5) and 0.81% potassium (K_2O) (JERRY, 2013). Eight different substrate treatments have been set up for each dumpsite soils:

Two pots with 100% PD/ED. planted with (A/T)

Two pots with 80% PD/ED + 20% PS/ES planted with (A/T)

Two pots with 50% PD/ED + 50% PS/ES planted with (A/T)

One pot with 80% PD/ED + 20% M planted with (A)

One pot with 50% PD/ED + 50% M planted with (A)

Prior to starting the incubation, the soil was wetted and pre-incubated at greenhouse temperature for 14 days. After this period, each individual pot was planted with four seeds of *Alyssum murale* (A) and *Trifolium repens* (T) in March 2014 and was harvested in July 2014. The pots were watered every day. *T. repens* is was chosen because it grows naturally in ultramafic fields and it is nickel tolerant (BANI *et al.*, 2007). The experiment was conducted in greenhouse.

Sampling methods and sample analyses

After the harvest, the plants from each pot were weighed to determine the wet biomass and after being dried in natural conditions, they were weighed again. Sub samples of each pot were air-dried and they were ground to pass through a 2-mm stainless-steel sieve.

The pH of soil samples were measured with a 1:5 soil-water ratio as follows: The pH meter was first calibrated with standard buffers of pH 7 and 10. Then 10g of 2mm sieved and air-dried soil samples were weighed into plastic containers 100 ml and 50 ml of distilled water added. The mixtures were stirred several times for 60 minutes. Then the soil suspensions were allowed to stand for 60 minutes more undisturbed. The pH meter electrode was then inserted into the settled suspension and the pH of the soil measured.

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

The availability of Ni in dumpsite soils and all treatments were measured using a DTPA-TEA extractant (0.005 M DTPA with 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA) at pH 7.3. A ratio of 1 g soil: 10 ml DTPA-TEA solution was shaken for 2 h, and then the suspension was centrifuged at 5,000 g for 20 min, filtered through a 0.2 μm pore size cellulose nitrate filter (SARTORIUS) (ECHEVARRIA *et al.*, 1998). All extractions were performed in triplicate. Ni concentrations in the soil extracts were determined spectrochemically using Atomic absorption spectrophotometer (Nov AA-350).

Nickel phytoextraction

Nickel is often mobile in plants, and accumulates readily in plant leaves and seeds (WELCH and CARY, 1975) and thus, having a high potential to enter the food chain. Heavy metals uptake by plants, using phytoremediation technology, seems to be a prosperous way to remediate heavy metals contaminated environment (BIEBY *et al.*, 2011). The success of phytoextraction depends especially on the plant's ability (a) to accumulate biomass rapidly, and (b) to store large quantities of the uptake metals in the shoot tissue (BLAYLOCK and HUANG, 2000). In the case of Ni, hyper-accumulation has been defined as the accumulation of at least 1,000 mg kg⁻¹ Ni in the dry biomass of plants grown on a natural substrate (BROOKS *et al.*, 1977). 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 (mg Ni/ pot).

Accumulation factor

Heavy metal concentrations in the shoots and soil extracts were calculated on the dry weight basis. Shoots concentrations are often used for contaminant concentration in plants because soil to plant transfer is one of the major pathways for pollutants to enter the food chain (YOON *et al.*, 2006). As total heavy metal concentration of soils is a poor indicator of metal availability for plant uptake, accumulation factor (AF) was calculated based on metal avail-

$$\eta = B \times C_p$$

ability and its uptake by the plant as follows:

The Accumulation Factor gives an idea of the ability of a plant to accumulate metals absorbed from the soil. In addition, AF quantifies the relative differences in the bioavailability of metals to plants (RADULESCU *et al.*, 2013)

$$AF = \frac{\text{Metal concentration in plant (mgkg}^{-1}\text{)}}{\text{Metal concentration in soil (mgkg}^{-1}\text{)}}$$

RESULTS

pH and heavy metal contents

Below are presented the pH and heavy metals concentration (mg kg⁻¹) for each type of soil sample and plant species, before and after treatment.

Nickel availability

The available Nickel, called Ni_{DTPA}, before and after treatment for Prrenjas mine dumpsite is presented in Fig. 1 and for Elbasan metallurgical dumpsite in Fig. 2.

Effect of treatment in Ni concentration, biomass production and nickel phytoextraction

Results of biomass and nickel concentration in plants (*A. murale* and *T. repens*) depending on the type of treatment are presented in Fig. 3.

The nickel phytoextraction potential, the product of plant biomass with the concentration of nickel in the cultivated plants, is in Fig. 4.

Accumulation factor

The ability of *T. repens* and *A. murale* to accumulate metals absorbed from the both dumpsites soil are given respectively in Tab.1 and Tab. 2.

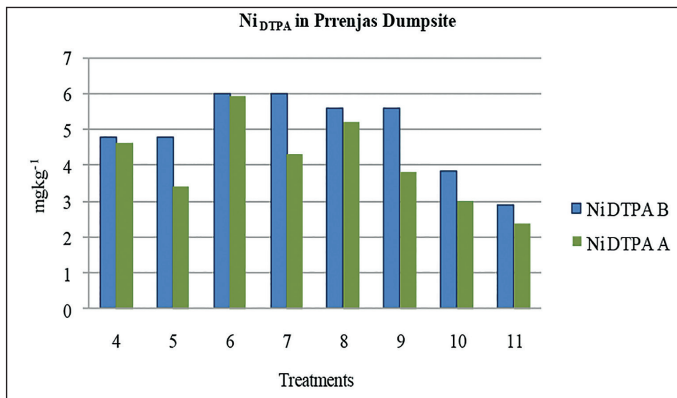


Fig. 1. Ni_{DTPA} in mgkg⁻¹ in Prrenjas Dumpsite before (B) and after (A) treatments (4-11 are the treatment for each plant according Table 1).

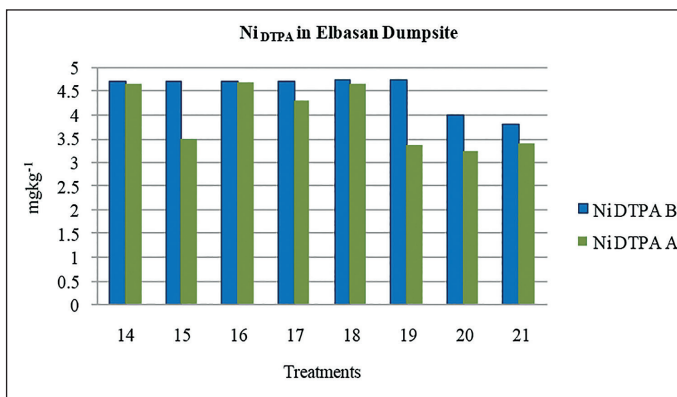


Fig. 2. Ni_{DTPA} in mgkg⁻¹ in Elbasan Dumpsite before (B) and after (A) treatments (14-18 are the treatment for each plant according Table 1).

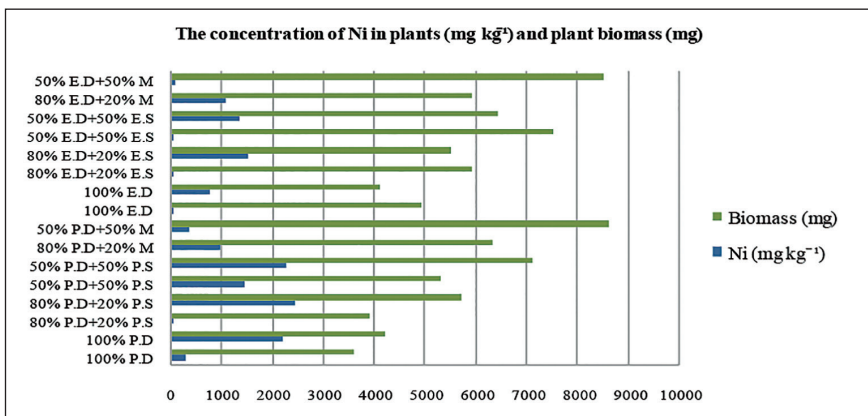


Fig. 3. The concentration of Ni in plants and plant biomass per pot.

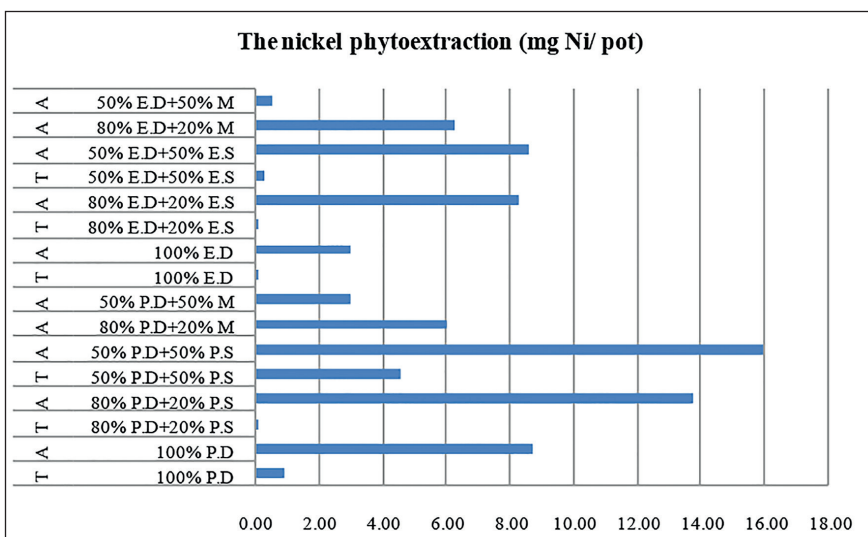


Fig. 4. The nickel phytoextraction in dumpsites after treatment.

No	Period	Species	Soil type	pH	Ni	Cr	Fe	Cd	Pb	Co	Zn
1	Before treatment		Prrenjas Dumsite	8.4	6859	5458	36715	22.3	25.8	286	117
2			Prrenjas vegetation soil	8.7	1235	375	1563	11.6	15.3	107	65
3			Manure	9.2	14.6	28.6	21.0	ND	ND	ND	13.2
4	Afer harvest	<i>T. repens</i>	100% PD	8.4	5948	5326	36494	19.7	23.9	213	85.6
5		<i>A. murale</i>	100% PD	8.4	5752	5100	33834	ND	17.8	211	78.0
6		<i>T. repens</i>	80% PD+20% P.S	8.6	5603	4578	35896	ND	19.7	163	69.5
7		<i>A. murale</i>	80% PD+20% P.S	8.6	5364	4417	33153	ND	21.6	168	76.8
8		<i>T. repens</i>	50% PD+50% P.S	8.8	4243	3895	32570	18.5	28.9	147	72.3
9		<i>A. murale</i>	50% PD+50% P.S	8.6	4000	3881	32047	18.4	31.8	115	71.1
10		<i>A. murale</i>	80% PD+20% M	8.9	5695	4713	34933	10.3	20.4	175	19.0
11		<i>A. murale</i>	50% PD+50% M	9.2	4213	4240	33706	17.5	27.6	133	33.2
12	Before treatment		Elbasan Dumpsite	8.6	1842	7185	34853	21.7	42.2	245	135.3
13			Elbasan vegetation soil	9.1	137	35	19549	13.1	25	72.0	162
14	Afer harvest	<i>T. repens</i>	100% ED	8.6	1571	6910	32817	19.6	37.0	194	118.2
15		<i>A. murale</i>	100% ED	8.7	1506	6184	31970	16.9	30.0	161	112.7
16		<i>T. repens</i>	80% ED+20% E.S	8.9	1451	5853	31874	15.1	34.3	146	114.9
17		<i>A. murale</i>	80% ED+20% E.S	8.7	1136	4709	31642	13.3	32.2	122	114.7
18		<i>T. repens</i>	50% ED+50% E.S	8.8	1762	7176	34245	13.6	29.2	224	122.1
19		<i>A. murale</i>	50% ED+50% E.S	8.6	1112	4170	31856	26.1	29.3	98	125.1
20		<i>A. murale</i>	80% ED+20% M	9.1	1590	5595	31655	17.7	27.8	186	112.1
21		<i>A. murale</i>	50% ED+50% M	9.4	1509	5242	31003	21.1	33.2	191	131.9

Tab. 1. The pH and the concentration of heavy metals (mg kg⁻¹) in two dumpsite soils, before and after treatment.

PD - Prrenjas Dumpsite; ED - Elbasan Dumpsite, M-Manure, PS-Prrenjas vegetation soil, ES-Elbasan vegetation soil.

ND - Not Detected (Ni<1 mg kg⁻¹, Pb<2 mg kg⁻¹, Cd<12 mg kg⁻¹, Co<16 mg kg⁻¹).

Accumulation Factor (AF)						
<i>Trifolium repens</i>						
Metal	100% PD	100% ED	80% PD+20% PS	80% ED+20% ES	50% PD+50% PS	50% ED+50% ES
Ni	0.04	0.02	0.01	0.02	0.34	0.02

Tab. 2. Nickel accumulation factors in *T. repens* plant grown in the industrial and mine dumping site soil.

Accumulation Factor (AF)										
<i>Alyssum murale</i>										
Metal	100% PD	100% ED	80% PD+20% PS	80% ED+20% E.S	50% PD+50% PS	50% ED+50% ES	80% PD+20% M	80% ED+20% M	50% PD+50% M	50% ED+50% M
Ni	0.38	0.49	0.45	1.33	0.56	1.21	0.17	0.67	0.08	0.04

Tab. 3. Nickel accumulation factors in *A. murale* plant grown in the industrial and mine dumping site soil.

DISCUSSION AND CONCLUSIONS

pH and heavy metal contents

Cationic metals are more soluble at lower pH levels (<6.5), so increasing the pH makes them less available to plants and therefore less likely to be incorporated in their tissues and ingested by humans. As shown in Tab.1, soil dumpsites were alkaline with pH average of approximately 8.7. Results obtained show that soils from the dumpsites recorded higher metal concentrations than their corresponding levels at the vegetative soils.

All heavy metals investigated in the dumpsites have significant differences from those obtained in the vegetative soils. Results shows that the samples in both dumpsites are ultramafic material, waste processed in two ex-industrial areas. Regarding the analysis of the heavy metals concentrations in the dumpsite soils, it could be noted that Ni, Co and Fe are higher in Prrenjias Dumpsite, because the wastes are raw, while in Elbasan Dumpsite the concentrations of Cr, Pb and Zn are higher. Ni concentration is lower in Elbasan Dumpsite, because it is processed by the steel plant. The value of Nickel and other metals in vegetation soils, which are used for mixing, are higher in the Prrenjias soils than in those of Elbasan, because the vegetation soil of Prrenjias is serpentine soil and the vegetation soil of Elbasan is agricultural soil. The Nickel concentration in manure is under the limit (< 210 mg kg⁻¹), so it is not contaminated with metal. Before treatment, the concentration of metals is higher in both Dumpsites, and after the harvest, it is reduced depending on the treatment or the plant. In addition, a small portion of the metals is accumulated in plants.

Moreover, the experimental results show that heavy metal concentrations in soils after harvesting the plants is lower where *A. murale* was used in the treatment than in those where *T. repens* were used. This demonstrates the high potential of *A. murale* to accumulate nickel. In general, the levels of Ni, Cr and Co are higher in both Dumpsites showing the ultramafic nature of Dumpsite minerals. These values are higher in the case of reference pots and then reduced because of the influence of vegetative soil or manure.

The intervention value for Nickel when remedial action is necessary is 210 mg kg⁻¹ (DENNEMAN and ROBBERSE, 1990; MINISTRY OF HOUSING, NETHERLAND, 1994). The values measured in the experiment are very high compared to standards. Nickel contaminations sources in the soil are metal plating industries, combustion of fossil fuels, nickel mining, and electroplating (BHAGURE and MIRGANE, 2010). Considering the Ni concentration after treatments and after the harvest, it can be observed that it is influenced more by the soil treatment and less by the plant accumulation. Its value is lower when the dumpsite soils are treated with 50% vegetation soil or manure. The influence of vegetation is observed in the treatment with 50% vegetation soil in both

dumpsites (PD and ED), which are cultivated with *A. murale*, and where the amount of nickel after the harvest is smaller.

The permissible limit for chrome according the Dutch standards is 100 mg kg⁻¹. Chrome content in all samples was greater than the permissible limits (MINISTRY OF HOUSING, NETHERLAND, 1994). Thus, in pots with Prrrenjas dumpsite soils, it was 5458 mg kg⁻¹, while in pots with Elbasan dumpsite soils it was 7185 mg kg⁻¹. The total Cr level is influenced by the addition of different ingredients, such as vegetation soil, but it is less influenced by the plant cultivation mainly *A. murale*.

The typical Iron concentrations in soils range from 0.2% to 55% (20,000 to 550,000 mg kg⁻¹) (BODEK *et al.*, 1988). The iron concentration is higher in pots from Prrrenjas dumpsite (36715 mg kg⁻¹) than in pots from Elbasan dumpsite (34853 mg kg⁻¹). The influence of treatments in its concentration is insignificant.

The limit for Cadmium in soil is 1-3 mg kg⁻¹ according to 86/278/EEC. After the harvest, in pots with Prrrenjas dumpsite soils, it was 22.3 mg kg⁻¹, while in pots with Elbasan dumpsite soils; it was 21.7 mg kg⁻¹.

The limit for Lead in soil is 50-300 mg kg⁻¹ according to 86/278/EEC. After the harvest, it was 25.8 mg kg⁻¹ in pots with Prrrenjas dumpsite soils and 42.2 mg kg⁻¹ in pots with Prrrenjas vegetation soil.

Cobalt is a natural component of the Earth's crust, with an average concentration of 25 mg kg⁻¹. In basalt rocks, Co concentrations are in the range 40-50 mg kg⁻¹, while much lower concentrations, between 1 and 10 mg kg⁻¹ are found in granite (BARCELOUX, 1999). Our values are very high according to natural limits. The Cobalt content, in pots with Elbasan dumpsite soils was 286 mg kg⁻¹ and in Elbasan Dumpsite was 194 mg kg⁻¹. Co concentration is higher in the soil from Prrrenjas than in Elbasan vegetative soil. The cobalt level is influenced by the treatments and by plants cultivation. Its concentration is lower, in the pots with 50%PD+50%PS and in 50% ED+50%E.S planted with *A. murale*. 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 (KAPUSTA, 2007) about 48% of cobalt production originates from nickel ores.

The maximum intervention limit for Zn in soil is 150-300 mg kg⁻¹ (86/278/EEC). In our study, zinc concentration does not exceed this limit. It was measured 147 mg kg⁻¹ in the pots of Prrrenjas Dumpsite, and 135 mg kg⁻¹ in the pots of Elbasan Dumpsite, while in Prrrenjas soil it was 65 mg kg⁻¹ and in Elbasan soil 162 mg kg⁻¹.

Nickel availability

The available Nickel, called Ni_{DTPA} was lower after the harvest, mainly in the pots planted with *A. murale*. After the treatment of dumpsite soils with different portions with vegetative soil and manure, some differences were observed. The amount of DTPA-extractable Ni in the soil significantly decreased with time of cultivation and differed between the two species and treatments. So in pot experiment 0.4-1.8 mg kg⁻¹ Ni was removed in 120 days by *A. murale* grown on the soil of Prrenjas Dumpsite and 0.39-1.24 mg kg⁻¹ Ni from Elbasan dumpsite (Fig. 1 and 2) and for *T. repens* 1-7% of DTPA Ni is removed from the contaminated soil of Prrenjas dumpsite and 0.8-2.1% of Ni_{DTPA} Ni from Elbasan industrial dumpsite. For *A. murale*, 17-32% of Ni_{DTPA} is removed from Prrenjas dumpsite and 8.7-29% of Ni_{DTPA} from Elbasan industrial dumpsite. More effective is the mixing of mineral wastes with vegetative soil for each treatment.

The amount of DTPA-extractable Ni in the soil significantly decreased during cultivation. Since the reduction of DTPA Ni after *A. murale* cultivation occurred, these results suggest that *A. murale* takes up Ni from a pool of soil Ni that can be at least partly quantified using DTPA. This is confirmed by DTPA previously having been shown to extract isotopically-exchangeable Ni, i.e. Ni from the labile pool (SHALLARI *et al.*, 2001). By reducing the DTPA-extractable pool of Ni in the soil after successive culture of *A. murale* it was limited the contamination potential of those waste that came from ultramafic materials or metallurgical waste.

Effect of treatment in Ni concentration, biomass production and nickel phytoextraction

The concentration of Ni in shoots of *A. murale* ranged from 348 to 2416 mg kg⁻¹ in Prrenjas Dumpsite soils and from 64 to 1513mg kg⁻¹ at Elbasan Dumpsite (Fig. 3). The highest Nickel concentration was measured in the treatment 80%PD+20%P.S for Prrenjas dumpsite waste and in 80% ED+20% ES for Elbasan Dumpsite. Consequently, this treatment is more effective for Ni accumulation. This can be explained with the fact that vegetative soil improved physical characteristic of the soil. The higher nickel concentration in *A murale* in Prrenjas can be explained with the fact that the available nickel is higher in Prrenjas dumpsite waste and in Prrenjas vegetative soil (it is a serpentine soil) than in Elbasan industrial dumpsite and Elbasan vegetative soil. Ni in *Alyssum murale* was slightly increased in pots with manure in the case of Elbasan dumpsite, showing the influence of manure in improvement of physical characteristic of the soil. Increasing the amount of vegetative soil and manure has influenced biomass growth.

In both dumpsites, the most effective treatment that increases the biomass is the treatment when we added 50% manure. The nickel concentration in *T.*

repens is lower than *A. murale*. It varies from 1429 mg kg⁻¹ in the treatment 50%PD+50% P.E and 39 mg kg⁻¹ in 50%ED+50%ES. The treatments with 50% Pprenjas and Elbasan vegetation soil are more effective for *T. repens* for Ni uptake. The total cumulative uptake of Ni, by *A. murale* in PD and ED ranged from 3.01 (ED) to 8.77 (PD) mg Ni/pot (dry soil) and showed the effect of available nickel in each dumpsite soil. In the treatments with manure (20%), the total cumulative uptake of Ni, by *A. murale* in PD and ED ranged from 6.07 to 6.29 mg Ni/pot showing the effect of manure on biomass yield. There was a slight increase in comparison with untreated pots, probably due to a very limited positive effect on biomass yield. In Pprenjas Dumpsite, the possibility of nickel phytoextraction is higher in *A. murale* planted in 80%PD+20%PS (13.77 mg Ni/pot) and in 50%PD+50%PS (15.99 mg Ni/pot), where the Nickel concentration and plant biomass are also higher. In addition, in Elbasan Dumpsite the nickel phytoextraction is higher in the treatments with 20% and 50% vegetation soil (respectively 8.32 to 8.61 mg Ni/pot).

In both dumpsites, adding manure increased the plant biomass (Fig. 3), but at the same time, it decreases the nickel concentration in plants, because the concentration of nickel is diluted (BANI *et al.*, 2009). Nickel phytoextraction is more effective in treatment with vegetation soil than with manure. In both dumpsites, the most effective is the treatment with 50% vegetation soil. Nickel yield in *T. repens* is lower in both dumpsites. It varies from 0.1 to 0.9 mg Ni/pot in Pprenjas Dumpsite and 0.1 to 0.3 mg Ni/pot in Elbasan Dumpsite. Therefore, the treatment with 50% vegetation soils is more effective for improving the properties of dumpsite soils.

Considering the above results, it can be concluded that *A. murale* could be a useful candidate for phytoextraction technologies ex - situ not only on serpentine soils, but also in contaminated soils and plants. *A. murale* and *T. repens* could be used for dumping site revegetation. The usage of vegetation soil is effective for improving the properties of dumpsite soils.

Accumulation factor

If the AF > 1 the plants can be accumulators; AF = 1 there is no influence and if the AF < 1 the plant can be an excluder (RADULESCU *et al.*, 2013). The ability of the *Alyssum murale* to accumulate heavy metals is higher. Its ability to accumulated Ni increases in Elbasan dumpsite when the soil is treated with 50% Elbasan vegetation soil (1.21) and decreases when the both dumpsites are treated with 50% manure. The accumulation factors (AF) for Ni in *T. repens* is smaller than one (<1). Its ability to accumulated Ni increases in Pprenjas dumpsite when the soil is treated with 50% Pprenjas vegetation soil (0.34). *A. murale* is an accumulator's plant and *T. repens* is an excluder.

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