THE EFFECT OF ZEOLITES ON THE TRANSFER OF HEAVY METALS FROM SOIL TO MINT

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Abstract. The fundamental objective of this study was to determine the variation over time of the heavy metal content in mint (Mentha Spicata) by the ICP-MS technique. The seeds of the mint plant were grown in the laboratory, each in 2 different pots (a control soil sample polluted with metals and a soil sample contaminated with metals but improved with natural zeolite). At the end of the vegetation period, all parts of the plant (root, leaves, stem, and flowers) were left to dry at room temperature for 2-3 weeks; then, they were finely ground and weighed to determine the metal content. The results show that the studied zeolite can be used as an amendment to reduce the range of heavy metals in the polluted soil, the presence of the zeolite leading to the reduction of the transfer of these metals from the contaminated soil to the plants.

Keywords: zeolites; heavy metals; bioremediation; mint.

INTRODUCTION

The soil is an essential component of the rural and urban environment, being regarded both as a reservoir in which pollutants from the atmosphere accumulate and as an environment that can be assimilated to a complex of sorbents with specific properties. Heavy metals in water, soil, sediment, and vegetation have become a global problem due to increased industrial activity in recent decades. Due to their toxicity, cumulative and non-biodegradable characteristics, heavy metals are potentially dangerous to terrestrial ecosystems and, therefore, to human and animal life [1].

Heavy metals fall into two basic categories: essential and non-essential. Critical metals or micronutrients such as chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), molybdenum (Mo), iron (Fe), selenium (Se), and zinc (Zn) are needed for the optimal functioning of biological and biochemical processes in organisms (including humans) that include redox reactions and the formation of pigments and enzymes. Non-essential metals such as arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) have no known biological function. Essential metals, at high concentrations, can have toxic effects on species and ecosystems. Like most organic pollutants, natural processes do not usually remove heavy metals. [2;3]

Zeolitic volcanic tuffs represent an eco-alternative technological source of the future. That is why it is essential to know and disseminate information regarding the efficiency of using these tuffs in non-conventionalenvironmental depollution technologies. Zeolites have three main properties of great interest for agricultural purposes:

- High cation exchange capacity.
- Increased water retention capacity in free channels.
- High adsorption capacity, which makes them particularly attractive for use as fertilizers. [4]

MATERIALS AND METHODS

The Natural zeolites: Following the studies and experiments within the ICIA with a view to the complex valorization of the volcanic tuff deposits in Transylvania, we decided to use a volcanic tuff from Barsana, Maramures county, in the research activity.

Table 1

Chemical oxide composition of Barsana zeolite

P.C* %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	K_2O %	Na_2O %	TiO_2 %
11.28	65,03	11,48	0,97	3,78	0,55	1,62	1,56	0,02

* losses on calcination

Samples: The seeds of the mint plant (Mentha spicata) were grown in the laboratory, each in 2 different pots (a control soil sample polluted with metals and a soil sample contaminated with metals but improved with natural zeolite). At the end of the vegetation period, all parts of the plant (root, leaves, stem, and flowers) were left to dry at room temperature for 2-3 weeks. Then they were finely ground and weighed to determine the metal content.

Reagents and standards: Mass spectrometry involves separating ions using electric and magnetic fields based on the mass/charge ratio.

Instrumentation used: Microwave digester Berghoff MWS-3+ (Eningen, Germany) •ICP-MS ELAN DRC II Perkin-Elmer; • Grindomix GM 200 knife mill

Reagents and materials used: •HNO_3 65% (Merck, Germany); •H_2O_2 30% of analytical purity (Merck, Germany); Multi-element stock solution 1000 mg/l (Merck, Darmstadt, Germany); •Ultrapure water, Milli-Q (Millipore, Bedford, MA, USA).

Procedure: Three replicates of 0.5 g sample (dried at 40 °C, ground, and homogenized) were subjected to microwave digestion with 8 ml HNO_3 65% and 3 ml H_2O_2 30%. After cooling to room temperature, the sample was diluted to 25 ml with ultrapure water, then filtered through a 0.45 μm cellulose membrane filter. Analogously, the blank samples were prepared. Trace element concentrations in the mineralized solutions were determined using ICP-MS. For the quantitative determination of the desired elements, the external calibration method was used, with the help of which, by interpolation, the concentrations of the analytes in the unknown samples were determined. For this, calibrations were carried out with multi-element standard solutions at different concentration levels, and the calibration curves were plotted. To verify the performance of the proposed method, the sensitivity of the process was studied by determining and calculating the detection and quantification limits.

RESULTS AND DISCUSSION

The concentration of metals in the soil before and after the vegetation period. The metal content of the polluted soil samples and the zeolite-amended soil samples was determined before mint cultivation (April) and after harvest (July) (Table 2). The concentrations of Cd, Co, Cu, Pb, and Zn were not significantly different in the April and July control soil samples. In contrast, Cr and Ni concentrations were approximately two times lower at the beginning of the study than in July.

Table 2

Analyzes of soil samples

Type of analysis	U.M.	Recorded values					Test method
		contaminated soil April	contaminated soil July	contaminated soil July	Soil improved with zeolite April	Alert threshold (Order 756/97)	
pH	Ph unit	5,9	6,8	8,2	7.9	-	2005 SR EN ISO 10523: 2012 ISO 10390:2005
Cadmium	mg/kg	7,28	5,78	2,76	1,88	3	SR ISO 11466: 1999 SR EN ISO11885:2009
Chromium total	mg/kg	42,20	22,70	21,60	9,70	100	SR ISO 11466: 1999 SR EN ISO11885:2009
Copper	mg/kg	75,30	45,40	42,10	45,50	100	SR ISO 11466: 1999 SR EN ISO11885:2009
Nickel	mg/kg	65,70	28,10	32,40	17,30	75	SR ISO 11466: 1999 SR EN ISO11885:2009
Lead	mg/kg	370,50	280,70	44,20	48,70	50	SR ISO 11466: 1999 SR EN ISO11885:2009
Zinc	mg/kg	260,80	190,30	80,30	68,30	300	SR ISO 11466: 1999 SR EN ISO11885:2009

The concentration of metals in different parts of the plant

The analysis of different parts of the plant is essential when evaluating the degree of absorption of the metal and the mobility of the elements in the plant. The metal concentration significantly influences the uptake and accumulation of metals in different plant parts in the soil.

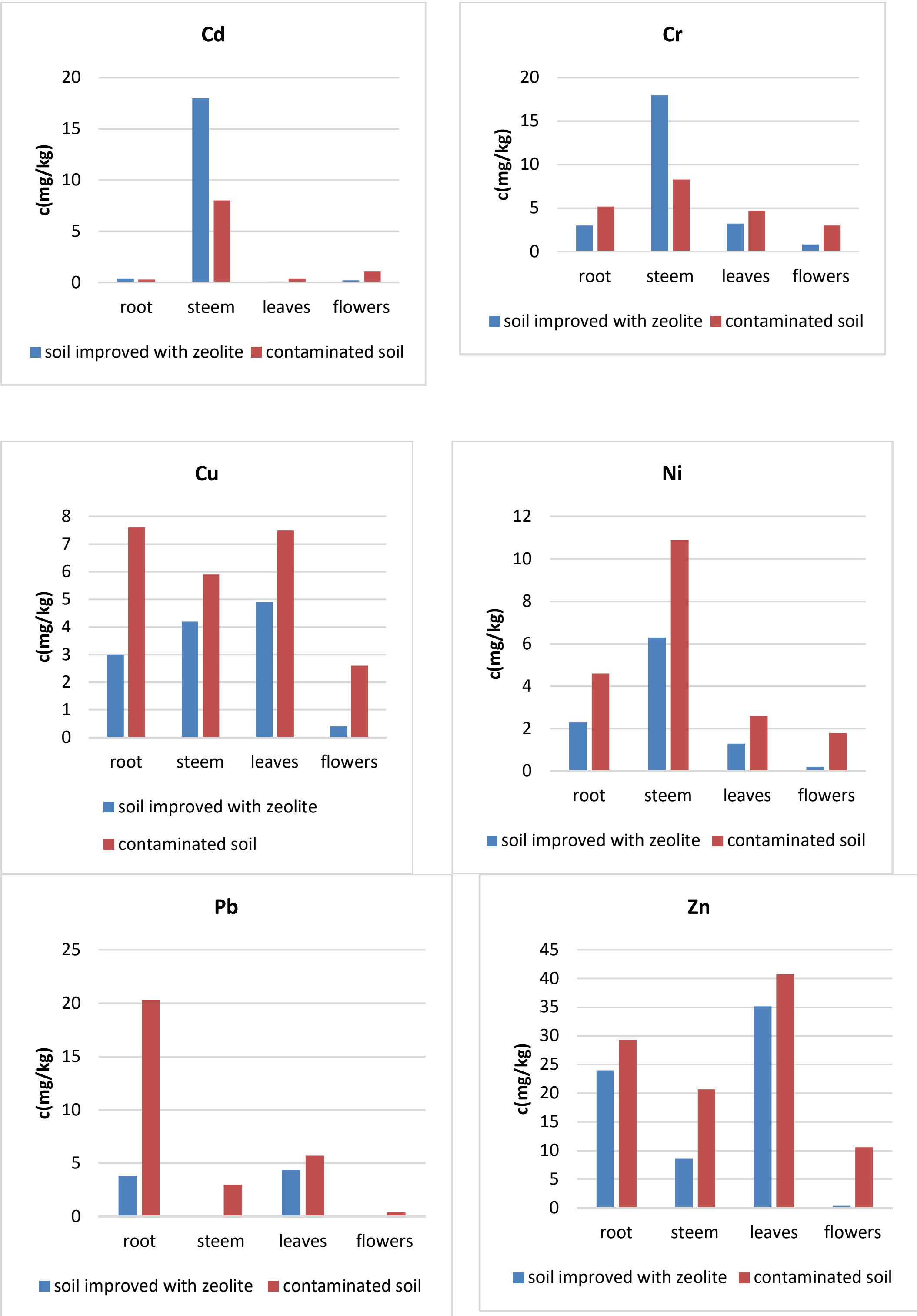

Figure 1. Concentration of metals in different parts of mint from soil samples

CONCLUSIONS

The analysis of transport processes through the prism of transfer phenomena and associated unit operations, as well as the parameters that control the mobility of heavy metals in soils contaminated with heavy metals, as well as in uncontaminated ones, the evaluation of their migration potential and the impact on the ground, are essential aspects that must be taken into account in the study of the effects that the presence of heavy metals induce in the environment.

Plant biomonitoring is an accessible and valuable tool for studying the effect of different pollutants, such as heavy metals. Thus, the simulation, in a laboratory experiment, of the growth of mint on contaminated soil and the soil improved with natural zeolite showed that the accumulation of metals in the vegetative organs of the plants was different: Cu and Pb were accumulated in the roots; Cd, Cr, and Ni in the stem; Zn in leaves. In the root, Cu and Pb values exceed toxic levels in soil polluted with heavy metals. Significant development of the plants grown on the soil improved with natural zeolite compared to the plants grown on the polluted soil was observed, the plants flowering faster, having larger and dark green leaves compared to those raised on the contaminated soil, which had a color of yellow, and green leaves. The studied zeolite can be used as an amendment to reduce the content of heavy metals in the polluted soil, the presence of the zeolite leading to the reduction of the transfer of these metals from the contaminated soil to the plants.

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REFERENCES

1. Biljana D., Buljovčić M., Antić I., Comprehensive assessment of heavy elements and evaluation of potential human health risk in the urban environment: a case study from Novi Sad, Serbia, Environmental Science and Pollution Research volume 29, pages38551–38566 (2022).

2. Sur M.I., Micle V., Polyak T.E., Gabor T., Assessment of Soil Quality Status and the Ecological Risk in the Baia Mare, Romania Area, Sustainability 2022, 14(7), 3739; https://doi.org/10.3390/su14073739

3. Bora F.D., Calugar A., Bunea C., Rozsa S., Bunea A., Assessment of Physicochemical, Macro- and Microelements, Heavy Metals, and Related Human Health Risk from Organically, Conventionally, and Homemade Romanian Wines, Horticulturae 2022, 8(5), 382; https://doi.org/10.3390/horticulturae8050382

4. Senila M., Neag E., Cadar O., Kovacs D., Aschilean I., Kovacs M., Simultaneous Removal of Heavy Metals (Cu, Cd, Cr, Ni, Zn and Pb) from Aqueous Solutions Using Thermally Treated Romanian Zeolitic Volcanic Tuff, Molecules 2022, 27(12), 3938; https://doi.org/10.3390/molecules27123938

5. *** Ordinul nr. 756 din 3 noiembrie 1997 pentru aprobarea Reglementarii privind evaluarea poluarii mediului

6. ***, European Food Safety Authority. Scientific Opinion of EFSA Panel on Contaminants in the Food Chain (CONTAM), www.efsa.europa.eu, accessed on 03.10.2022