

## ***In situ* immobilisation of heavy metals in soils using natural clay minerals**

SENAD MURTIĆ<sup>1\*</sup>, EMINA SIJAHOVIĆ<sup>2</sup>, HAMDİJA ČIVIĆ<sup>2</sup>, MIRZA TVICA<sup>3</sup>, JOSIP JURKOVIĆ<sup>4</sup>

<sup>1</sup>Department of Plant Physiology, Faculty of Agriculture and Food Sciences, University of Sarajevo, Sarajevo, Bosnia and Herzegovina

<sup>2</sup>Department of Plant Nutrition, Faculty of Agriculture and Food Sciences, University of Sarajevo, Sarajevo, Bosnia and Herzegovina

<sup>3</sup>Department of Soil, Faculty of Agriculture and Food Sciences, University of Sarajevo, Sarajevo, Bosnia and Herzegovina

<sup>4</sup>Department of Chemistry, Faculty of Agriculture and Food Sciences, University of Sarajevo, Sarajevo, Bosnia and Herzegovina

\*Corresponding author: [murticsenad@hotmail.com](mailto:murticsenad@hotmail.com)

**Citation:** Murtić S., Sijahović E., Čivić H., Tvica M., Jurković J. (2020): *In situ* immobilisation of heavy metals in soils using natural clay minerals. *Plant Soil Environ.*, 66: 632–638.

**Abstract:** This study attempted to evaluate the efficiency of zeolite and pyrophyllite ore materials in reducing the mobility of heavy metals in soil near the lignite mining dumps, and consequently in their availability for plants. Extraction of pseudo-total and available forms of heavy metals from soil samples was performed by using *aqua regia* and ethylenediaminetetraacetic acid, respectively. Concentrations of heavy metals in soil and plant samples were determined by atomic absorption spectrophotometry. The results of this study illustrate that application of zeolite and pyrophyllite could be a suitable technique to reduce heavy metals availability in soils. Zeolite treatments have been shown to be significantly effective in reducing cadmium (Cd) mobility, as well as pyrophyllite treatments in reducing lead (Pb) mobility in the studied soil, regardless of applied rates. The accumulation of heavy metals in leaves of maize grown on soil plots treated by zeolite and pyrophyllite, was found to be lower compared to the untreated plots. This finding was to be expected, considering the effects of these treatments on heavy metals mobility in the studied soil.

**Keywords:** contaminated soil; environment; health; remediation; risk elements; *Zea mays* L.

Soils polluted by heavy metals have adverse effects on environment and consequently human health. Among heavy metals, mercury (Hg), cadmium (Cd), chromium (Cr) and lead (Pb) are of major concern, because they are toxic to human even in small amounts (Carolin et al. 2017).

Numerous remediation techniques are used for eliminating or reducing heavy metal toxicity in soils. Reducing heavy metals toxicity in polluted soils by addition of clay minerals is considered to be one of the most effective soil remediation techniques. Clay minerals are effective tools for soil remediation owing to their high cation exchange capacity, high surface area, molecular sieve properties, simplicity of use and low cost. On the other hand, application

of clay minerals is environmentally friendly as it utilises natural ability of clay minerals to adsorb or tightly bind heavy metals present in the soil (Hou and Al-Tabbaa 2014).

Various clay minerals have been widely examined for potential application in the remediation of heavy metal polluted soils. The more commonly used clay minerals include calcite, goethite, montmorillonite, bentonite, zeolite and kaolinite (Ou et al. 2018). The contribution of each of these clay minerals to heavy metal ion immobilisation in soil can vary with the particular heavy metal ion, chemical and physical soil properties as well as the characteristics of the applied clay minerals (Radziemska et al. 2020). One of the least used clay minerals in the soil remediation

<https://doi.org/10.17221/371/2020-PSE>

is pyrophyllite, which is a result of its relatively lower presence in nature, but also insufficient research on its use as a remediation material. Furthermore, natural zeolite from deposits in Slanci near Belgrade (Serbia) has also been rarely studied in terms of its impact on heavy metals immobilisation in soil.

High available levels of heavy metals in soils can negatively affect crop productivity and pose harmful health consequences in all life forms (Jaishankar et al. 2014). Thus, it is crucial to immobilise their available forms in soils to decrease the negative effects on environment. Many scientists agree that zeolite and pyrophyllite are very affordable, reliable and environmentally friendly remediation materials for heavy metal contaminated media (Gu et al. 2019, Jemeljanova et al. 2019).

This study is designed to assess the hypothesis that the heavy metal availability can be reduced by adding zeolites and pyrophyllites, and this could find future use in plant production. Accordingly, the main objective of this study was to evaluate the effect of zeolite and pyrophyllite application in reducing the mobility of heavy metals in polluted soils located near the lignite mining dumps in Gornji Paski (Bosnia and Herzegovina). Most soils near the lignite deposits are polluted, to a greater or lesser extent, with heavy metals (Cipurković et al. 2011, Babajić et al. 2017) and therefore they were chosen as the subjects of this study. An additional objective of this study was to evaluate zeolite and pyrophyllite efficiency in reducing heavy metals accumulation in leaves of maize grown on these soils.

## MATERIAL AND METHODS

**Natural clay minerals.** Natural zeolite ore materials (clinoptilolite) used in this study originated from the deposits in Slanci – Veliko Selo near Belgrade (Serbia) and are characterised by high cation exchange capacity (CEC), more than 1 800 mmol<sub>+</sub>/kg and high pH value of 8.7. Median total contents of zeolite materials were 29.75 % Si, 7.66 % Al, 1.60 % Fe, 3.48 % Ca, 0.53 % Mg, 0.65 % Na, 0.66 % K, 6.2 mg Cu/kg, 3.0 mg Cd/kg, 28.0 mg Co/kg, 5.8 mg Cr/kg, 21.0 mg Ni/kg, 35.0 mg Pb/kg and 42.0 mg Zn/kg. Natural pyrophyllite ore materials used in this study originated from the deposits in Parsovići near Konjic (Bosnia and Herzegovina) and are characterised by lower cation exchange capacity, between 500 and 700 mmol<sub>+</sub>/kg and high pH value of 8.5. Median total content pyrophyllite material were 31.14 % Si, 10.10 % Al,

0.30 % K, 6.65 % Ca, 0.14 % Mg, 1.40 mg Cu/kg, 2.74 mg Ni/kg, 25.68 mg Zn/kg, 0.4 mg Co/kg, 93.14 mg Mn/kg, 7.97 mg Pb/kg and 0.76 Cr/kg. All zeolite and pyrophyllite samples used in this study were milled and sieved to obtain particles size below 0.5 mm.

**Study area.** The study area included three soil plots located near the lignite mining dumps in Gornji Paski (44°29'6"N, 18°39'32"E; Tuzla Canton, Bosnia and Herzegovina). The experimental soil plots (each had 1 000 m<sup>2</sup> in area) were all within close distance of each other. According to the World Reference Base for Soil Resources, all three investigated soil plots were classified as Stagnosol (WRB 2015). Stagnosols (pseudogley soils) mainly occur in humid regions with flat topography. These soils are characterised by mottles in the topsoil and subsoil, accompanied in some cases by concretions and/or bleaching. Low to medium base saturation and pH value < 5.5 are typical chemical characteristics of stagnosols.

**Soil sampling and analysis.** The composite soil sample from each soil plot was collected separately in March 2019, a few weeks before maize sowing, at a depth of 0–30 cm using plastic shovel. Composite soil sample was made by physically mixing five individual soil cores into one homogenous sample. In the laboratory, each soil sample was cleared of plant debris and other impurities, air-dried in a well-ventilated place, and then ground *via* mortar and pestle to achieve homogeneity. One part of each soil sample was sifted through 2-mm sieve for pH and available phosphorus and potassium determination, and the second was sieved through 1-mm sieve for the determination of organic carbon and heavy metals.

Soil pH was measured by the potentiometric method in H<sub>2</sub>O and in 1 mol/L potassium chloride solution (ISO 10390, 2005), available forms of phosphorus (P) and potassium (K) by the Egnér-Riehm method (Egnér et al. 1960), and organic matter by the chromic acid digestion method (ISO 14235, 1998).

Pseudo-total content of heavy metals in soil samples was extracted by *aqua regia* with a volume ratio of 1:3 HNO<sub>3</sub>/HCl as follows: 3 g of air-dried soil (fraction smaller than 1 mm) was placed into 250 mL flat bottom flask and then 28 mL of *aqua regia* was added. The flask covered with a watch glass was allowed to stand 16 h (overnight) in digester and thereafter was heated on hotplate under reflux for 2 h. After cooling down to room temperature, the obtained solution was filtered through quantitative filter paper into 100 mL flask and diluted to the mark with deionised water (ISO 11466, 1995).

Available forms of heavy metals in soil samples were extracted by EDTA solution (0.01 mol/L ethylenediaminetetraacetic acid (EDTA) and 1 mol/L  $(\text{NH}_4)_2\text{CO}_3$ , adjusted to pH 8.6) as follows: 10 g of air-dried soils was placed into 100 mL plastic bottle and then 20 mL EDTA solution was added. The bottle was shaken 30 min at 180 rpm in an orbital shaker, then extract was filtered through quantitative filter paper into 25 mL flask and diluted to the mark with deionised water (Trierweiler and Lindsay 1969).

The concentration of pseudo-total and available forms of heavy metals in the obtained extract was determined by atomic absorption spectrophotometry (ISO 11047, 1998). Soil plot with the highest concentration of heavy metals was selected for conducting the experiment.

**Soil chemical properties at the studied area.** Soil chemical properties at the studied area (soils located near the lignite mining dumps in Gornji Pasci) are presented in Table 1.

All investigated soils were characterised by very low pH (i.e., strongly acidic) and relatively high organic matter content. Furthermore, all soils had a very low supply of available P and medium supply of available K. These results were used to provide recommendations on the fertilisers needed for ideal maize growth and development. Chemical analysis also showed that soil sampled from plot 1 had the highest concentrations of heavy metals and therefore this soil was chosen to evaluate the efficiency of zeolite and pyrophyllite in reducing heavy metals mobility and thus its availability to maize root system (5 × 5).

Table 1. Chemical analysis of three soil plots located near the lignite mining dumps

Parameter	Unit	Soil		
		plot 1	plot 2	plot 2
pH <sub>H<sub>2</sub>O</sub>	–	5.2	5.3	5.2
pH <sub>KCl</sub>	–	3.9	4.1	4.0
Organic carbon	(%)	2.49	2.15	2.26
Available P		5.4	7.1	6.2
Available K		213.0	221.1	212.0
Cu		11.9	11.0	10.8
Zn		34.8	30.1	35.1
Mn	(mg/kg)	247.4	233.1	225.1
Cd		0.1	0.1	0.1
Pb		12.9	10.1	10.1
Ni		34.2	40.2	36.1
Cr		27.6	17.0	18.1

**Experimental design and treatments.** The experimental soil plot was divided into twenty-one equal subplots with 2 m broad untouched area between them. The area and size of each unit subplot were 25 m<sup>2</sup> and 5 × 5 m, respectively. The experiment was set up in a randomised block design with seven treatments in three replications. Experimental treatments were as follows: T1 – soil without soil amendments i.e. control treatment; T2 – soil with zeolite at a rate of 200 kg/ha; T3 – soil with zeolite at a rate of 400 kg/ha; T4 – soil with zeolite at a rate of 600 kg/ha; T5 – soil with pyrophyllite at a rate of 200 kg/ha; T6 – soil with pyrophyllite at a rate of 400 kg/ha, and T7 – soil with pyrophyllite at a rate of 600 kg/ha.

Recommended zeolite and pyrophyllite rates were recalculated based on the experimental plot area (25 m<sup>2</sup>). Zeolite and pyrophyllite materials (fraction below 500 μm) in all experimental subplots were applied fifteen days before maize planting (22 March 2019). All the routine agrotechnical practices needed for successful maize growth in all experimental subplots were identical, suggesting that difference between the studied soil subplots was only in clay minerals treatment. Concentrations of available forms of heavy metals in soil subplots and heavy metal concentrations in leaves of maize were determined at the silking stage. In this stage, silks start to emerge and become visible.

**Plant sampling and analysis.** All leaf samples in the experimental area were collected at the same time (5 June 2019). Three leaf samples from each treatment (30 leaves per sample) were collected, totalling 21 samples. Only fully developed, physiologically active leaves below the ear were sampled. In the laboratory, leaf samples were separately dried at 65 °C for 6 h, ground in a stainless-steel mill, sieved through 1-mm sieve and then stored in paper bags until analysis.

Heavy metals extraction from maize leaves were performed as follows: 1 g of dry leaf sample was placed into the 100 mL Erlenmeyer flask with narrow neck and 10 mL HNO<sub>3</sub> was added. The flask was allowed to stand overnight in digester and then was heated on a hot plate until the solution became clear and semi-dried. After cooling, 10 mL HNO<sub>3</sub> was added again, and the solution was reheated on a hot plate for 1 h. Thereafter, the solution was cooled, filtered through quantitative filter paper into 50 mL flask and diluted to the mark with deionised water (Huang et al. 2004). The heavy metals concentrations in the obtained extract were also determined by atomic absorption spectrophotometry.

<https://doi.org/10.17221/371/2020-PSE>

**Statistical analysis.** All measurements were done in triplicates and the results were presented as average  $\pm$  standard deviation. The collected data were analysed using one-way analysis of variance (ANOVA), and comparisons between averaged values from different treatments were done using the least significant difference test at 0.05 probability significance level ( $P < 0.05$ ).

## RESULTS

**Available forms of heavy metals in the studied soil after natural clay minerals treatment.** The concentrations of available forms of Cu, Zn, Mn, Cd, Pb, Ni and Cr in the studied soil located near the lignite mining dumps in Gornji Pasci after natural clay minerals treatment are presented in Table 2.

Generally, the study revealed that natural pyrophyllite and zeolite have a great potential to significantly reduce heavy metals availability in the studied soil. The study also found a positive effect of zeolite and pyrophyllite treatment to reduce Cr availability in the studied soil, but these findings did not reach statistical significance.

However, the effect of zeolite and pyrophyllite on reducing heavy metals availability in the soil was not the same for all treatments. The addition of zeolite was more effective in decreasing Mn and Cd availability, while the pyrophyllite showed a better effect on reducing Cu, Zn, Pb and Ni availability.

**Heavy metals concentration in leaves of maize grown on the soil treated by natural clay minerals.**

Heavy metals concentrations in leaves of maize depending on clay minerals treatment are presented in Table 3.

As shown in Table 3, the concentrations of heavy metals were lower in leaves of maize grown on soil plots treated by zeolite and pyrophyllite. There were no significant differences in the Cr and Ni concentrations in maize leaves between the experimental treatments. In addition, Pb and Cd concentrations in leaf samples were below the detection limit.

## DISCUSSION

In this research, zeolite and pyrophyllite demonstrated generally high potential to reduce heavy metals mobility in the studied soil. These findings are generally in line with previous studies (Park et al. 2017, Esmaeili et al. 2019, Chalyaraksa and Tumtong 2019).

The addition of zeolite at a rate of 600 kg/ha in the studied soil reduced available forms of Cu by 36.6%, Zn by 36.8%, Mn by 36.2%, Cd by 80.0%, Pb by 20.3% and Ni by 10.5% as compared to control (without clay minerals treatments). The addition of zeolite at application rates of 200 and 400 kg/ha also reduced heavy metals availability in the studied soil, but that reduction was less pronounced.

Several studies revealed a significantly higher zeolite efficiency in immobilising heavy metals in soils, but in these studies a higher zeolite rate was applied (Misaelides 2011, Boros-Lajszner et al. 2017, Belviso 2020). In the present study, however, higher zeolite

Table 2. Concentrations of heavy metals available forms in the studied soil (0–30 cm depth) depending on clay minerals treatment

Treatment	Available forms of heavy metals (mg/kg dry weight)						
	Cu	Zn	Mn	Cd	Pb	Ni	Cr
T <sub>1</sub>	0.71 $\pm$ 0.15 <sup>a</sup>	1.44 $\pm$ 0.21 <sup>ab</sup>	5.97 $\pm$ 0.85 <sup>ab</sup>	0.030 $\pm$ 0.011 <sup>a</sup>	3.15 $\pm$ 0.33 <sup>a</sup>	1.43 $\pm$ 0.31 <sup>a</sup>	0.29 $\pm$ 0.07
T <sub>2</sub>	0.67 $\pm$ 0.21 <sup>ab</sup>	1.46 $\pm$ 0.23 <sup>a</sup>	4.84 $\pm$ 0.76 <sup>c</sup>	0.017 $\pm$ 0.008 <sup>bcd</sup>	2.98 $\pm$ 0.65 <sup>b</sup>	1.39 $\pm$ 0.22 <sup>ab</sup>	0.27 $\pm$ 0.06
T <sub>3</sub>	0.56 $\pm$ 0.19 <sup>cd</sup>	1.39 $\pm$ 0.16 <sup>abc</sup>	4.99 $\pm$ 1.14 <sup>c</sup>	0.007 $\pm$ 0.005 <sup>e</sup>	2.72 $\pm$ 1.02 <sup>cd</sup>	1.39 $\pm$ 0.29 <sup>ab</sup>	0.26 $\pm$ 0.08
T <sub>4</sub>	0.45 $\pm$ 0.23 <sup>e</sup>	0.91 $\pm$ 0.24 <sup>f</sup>	3.81 $\pm$ 1.19 <sup>d</sup>	0.006 $\pm$ 0.005 <sup>e</sup>	2.51 $\pm$ 1.11 <sup>f</sup>	1.28 $\pm$ 0.33 <sup>c</sup>	0.28 $\pm$ 0.04
T <sub>5</sub>	0.57 $\pm$ 0.14 <sup>c</sup>	1.26 $\pm$ 0.21 <sup>d</sup>	6.21 $\pm$ 0.57 <sup>a</sup>	0.019 $\pm$ 0.008 <sup>b</sup>	2.87 $\pm$ 2.3 <sup>bc</sup>	1.20 $\pm$ 0.56 <sup>d</sup>	0.28 $\pm$ 0.05
T <sub>6</sub>	0.51 $\pm$ 0.18 <sup>cde</sup>	1.12 $\pm$ 0.22 <sup>e</sup>	5.55 $\pm$ 1.02 <sup>abc</sup>	0.018 $\pm$ 0.006 <sup>bc</sup>	2.71 $\pm$ 1.1 <sup>cd</sup>	1.06 $\pm$ 0.19 <sup>e</sup>	0.28 $\pm$ 0.04
T <sub>7</sub>	0.43 $\pm$ 0.10 <sup>e</sup>	0.99 $\pm$ 0.26 <sup>f</sup>	4.88 $\pm$ 0.67 <sup>c</sup>	0.013 $\pm$ 0.010 <sup>d</sup>	2.06 $\pm$ 0.96 <sup>e</sup>	1.04 $\pm$ 0.27 <sup>e</sup>	0.27 $\pm$ 0.06
LSD <sub>0.05</sub> <sup>**</sup>	0.085	0.088	0.727	0.004	0.156	0.053	–

T<sub>1</sub> – soil without soil amendments i.e. control treatment; T<sub>2</sub> – soil with zeolite at rate of 200 kg/ha; T<sub>3</sub> – soil with zeolite at rate of 400 kg/ha; T<sub>4</sub> – soil with zeolite at rate of 600 kg/ha; T<sub>5</sub> – soil with pyrophyllite at rate of 200 kg/ha; T<sub>6</sub> – soil with pyrophyllite at rate of 400 kg/ha; T<sub>7</sub> – soil with pyrophyllite at rate of 600 kg/ha. \*\*Averages denoted by the same letter indicate no significant difference ( $P \leq 0.05$ ); LSD – least significant difference

Table 3. Concentrations of heavy metals in maize leaves depending on clay minerals treatment

Treatment	Heavy metals concentrations (mg/kg dry weight)						
	Cu	Zn	Mn	Cd	Pb	Ni	Cr
T <sub>1</sub>	7.57 ± 1.03 <sup>a</sup>	16.78 ± 3.11 <sup>a</sup>	26.67 ± 2.01 <sup>a</sup>	nd <sup>***</sup>	nd	0.88 ± 0.43	0.66 ± 0.23
T <sub>2</sub>	7.40 ± 0.87 <sup>a</sup>	16.53 ± 4.22 <sup>ab</sup>	25.59 ± 1.98 <sup>a</sup>	nd	nd	0.73 ± 0.25	0.52 ± 0.31
T <sub>3</sub>	7.33 ± 1.47 <sup>a</sup>	15.36 ± 2.96 <sup>abc</sup>	25.46 ± 2.44 <sup>a</sup>	nd	nd	0.68 ± 0.41	0.52 ± 0.21
T <sub>4</sub>	6.21 ± 2.10 <sup>b</sup>	12.45 ± 2.87 <sup>ef</sup>	23.89 ± 3.07 <sup>b</sup>	nd	nd	0.63 ± 0.33	0.46 ± 0.26
T <sub>5</sub>	6.41 ± 1.65 <sup>b</sup>	14.15 ± 3.23 <sup>cd</sup>	25.70 ± 2.49 <sup>a</sup>	nd	nd	0.78 ± 0.21	0.46 ± 0.19
T <sub>6</sub>	6.59 ± 3.10 <sup>b</sup>	13.49 ± 2.98 <sup>de</sup>	25.42 ± 1.98 <sup>a</sup>	nd	nd	0.73 ± 0.43	0.47 ± 0.28
T <sub>7</sub>	6.17 ± 1.11 <sup>b</sup>	11.51 ± 2.11 <sup>f</sup>	22.38 ± 3.12 <sup>b</sup>	nd	nd	0.71 ± 0.31	0.50 ± 0.33
LSD <sub>0.05</sub> <sup>**</sup>	0.969	1.438	1.512	–	–	–	–

T<sub>1</sub> – soil without soil amendments i.e. control treatment; T<sub>2</sub> – soil with zeolite at rate of 200 kg/ha; T<sub>3</sub> – soil with zeolite at rate of 400 kg/ha; T<sub>4</sub> – soil with zeolite at rate of 600 kg/ha; T<sub>5</sub> – soil with pyrophyllite at rate of 200 kg/ha; T<sub>6</sub> – soil with pyrophyllite at rate of 400 kg/ha, T<sub>7</sub> – soil with pyrophyllite at rate of 600 kg/ha. \*\*Averages denoted by the same letter indicate no significant difference ( $P \leq 0.05$ ); \*\*\*below the detection limit; LSD – least significant difference

as well as pyrophyllite rates were not used for the remediation purpose due to their potential negative effects on nutrient mobility in the soil, and thus on crop quality and productivity.

Potential of zeolites to reduce heavy metals availability is mainly attributed to the specific structure of zeolite and mechanism of ion-exchange processes. Namely, zeolites are naturally occurring hydrated aluminosilicate minerals characterised by three-dimensional framework structures built of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra linked to each other with oxygen atoms. The aluminosilicate framework is negatively charged and therefore attracts the positive cations such as sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) to compensate the charge imbalance. These cations are exchangeable with certain heavy metal cations in soil solutions making zeolites an excellent adsorbent for the removal of heavy metals from polluted media (Golomeova and Zendelska 2016). Furthermore, the use of zeolites in acidic soils can significantly contribute to increase pH value, thus resulting in lower heavy metals mobility and phytoavailability. Namely, at high soil pH values, the precipitation of insoluble phases with heavy metals as major constituents dominate. Overall, there is currently a strong scientific consensus that the efficiency of natural zeolite in reducing heavy metal mobility mainly depends on both cation exchange capacity and adsorption capacity (Gadepalle et al. 2007, Jiménez-Castañeda and Medina 2017, Brozou et al. 2018). Our results are in line with previous findings.

As shown in Table 3, the addition of zeolite at a rate of 600 kg/ha significantly reduced the concentrations

of Cu, Zn and Mn in the leaves of maize grown on the studied soil, compared to other treatments with or without zeolite. The addition of zeolite at a rate of 200 and 400 kg/ha also reduced Cu, Zn, Mn in the maize leaves, but these effects were not statistically significant. These results were expected since the concentration of available forms of Cu, Zn and Mn were significantly lower in soil plots treated with zeolite at a rate of 600 kg/ha.

An interesting finding of this study was that the addition of zeolite as well as pyrophyllite to studied soil had no significant influence on Ni and Cr accumulation in maize leaves, regardless of applied rates. From the viewpoint of Ni accumulation in the maize leaves, this data were not expected since there was a significant difference in Ni availability in the studied soil between experimental treatments. It is our opinion that the maize accumulates Ni more in the roots than in the above-ground parts, suggesting that plant can activate different mechanisms to prevent or slow down the transport of Ni and other potential toxic elements from roots to other parts. Some of these mechanisms are as follows: binding the heavy metals by root exudates, heavy metal compartmentalisation in different intracellular compartments in root cells, especially in vacuoles, and embedding the heavy metals in the root cell walls. Accordingly, the absence of differences in Ni content of maize leaves between treatments might be caused by low Ni translocation from roots to above-ground parts.

Another interesting finding in this study was represented by the fact that the presence of hazardous heavy metals Pb and Cd was not determined in the

<https://doi.org/10.17221/371/2020-PSE>

leaves of maize, regardless of clay minerals treatment. These results also suggest that some plants, including maize, have evolved different strategies to reduce both uptake and transport of hazardous heavy metals from roots to the above-ground parts of plants. Choice of strategy primarily depends on plant genetic background as well as external environmental factors (DalCorso et al. 2019).

Except zeolite, this study also aims at evaluating the efficiency of pyrophyllite to reduce the mobility of heavy metals in the studied soil and their accumulation in the maize leaves. The addition of pyrophyllite significantly reduced the availability of Cu, Zn, Cd, Pb and Ni in the soil as compared to control, regardless of applied rates. In terms of pyrophyllite effects, the Mn availability in the studied soil was significantly influenced only by 600 kg/ha treatment. Overall, this treatment had the highest efficiency in reducing heavy metals availability in the studied soil. Namely, the addition of pyrophyllite at a rate of 600 kg/ha in the studied soil reduced available forms of Cu by 39.5%, Zn by 31.3%, Mn by 16.1%, Cd by 56.7%, Pb by 34.6% and Ni by 17.3% as compared to the control treatment. A positive effect of pyrophyllite in reducing the availability of heavy metals in soils was also reported by many studies (Caporale and Violante 2016, Singh et al. 2016).

However, although it is known that pyrophyllite has a high potential for adsorption of heavy metals, the mechanisms of these processes are still not fully understood. Panda et al. (2018) reported that pyrophyllite capacity to bind and remove heavy metal ions is mainly attributed to its specific structure based on  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra with vacant sites and numerous channels and cavities, representing potential binding sites for heavy metals. Furthermore, pyrophyllite has the ability to disperse easily in soil solution without clumping, giving it a high surface area. The result is that pyrophyllite has the possibility to contact with various heavy metal ions in soils, resulting in their immobilisation (El Gaidoumi et al. 2019). Furthermore, pyrophyllite addition increases soil pH, and thus reduces heavy metal mobility.

Unfortunately, significant effects of zeolite and pyrophyllite treatments in reducing Cr availability in the studied soil were not demonstrated. This result is inconsistent with previous studies that have generally found that clay minerals, especially zeolite, are effective in removal of Cr ions (Dhal et al. 2013, Keng et al. 2014). Ertani et al. (2017) reported that Cr mobility in soils and consequently their translo-

cation in plants depends primarily on its oxidation state as well as soil properties such as pH, organic matter content, Mn-oxide content and microbial activity in soils.

Considering the fact that Cr mobility decreases in acidic soils with high organic matter content and low oxidation potential (Bogdanović 2007), it can be assumed that the chemical properties of the studied soil, characterised by low pH and high organic content, contributed to low concentration of Cr available forms in all tested soil plots regardless of clay minerals treatment.

Generally, the results of this study have illustrated that zeolite and pyrophyllite application could be a suitable technique for reducing heavy metals availability in soils. Zeolite treatments have been shown to be significantly effective in reducing Cd mobility, as well as pyrophyllite treatments in reducing Pb mobility in the studied soil, regardless of applied rates. The results of this study also showed that the accumulation of heavy metals in leaves of maize grown on soil plots treated by zeolite and pyrophyllite was found to be lower compared to the untreated plots. This finding was to be expected, considering the effects of the treatments on heavy metals mobility in studied soil. However, further studies are needed to confirm this finding as well as other findings presented in this study.

## REFERENCES

- Babajić A., Babajić E., Srećković-Batočanin D., Milovanović D.J. (2017): Petrographic characteristics of mafic extrusive rocks along the southwestern part of Majejica. Archives for Technical Sciences, 16: 1–8.
- Belviso C. (2020): Zeolite for potential toxic metal uptake from contaminated soil: a brief review. Processes, 8: 820.
- Bogdanović D. (2007): Sources of soil pollution by chromium. Annals of Agronomy, 31: 29–35. (In Serbian)
- Boros-Lajszner E., Wyszowska J., Kucharski J. (2017): Use of zeolite to neutralise nickel in a soil environment. Environmental Monitoring and Assessment, 190: 54.
- Brozou E., Ioannou Z., Dimirkou A.T. (2018): Removal of Cr (VI) and Cr (III) from polluted water and soil sown with beet (*Beta vulgaris*) or celery (*Apium graveolens*) after the addition of modified zeolites. International Journal of Waste Resources, 8: 359.
- Caporale A.G., Violante A. (2016): Chemical processes affecting the mobility of heavy metals and metalloids in soil environments. Current Pollution Reports, 2: 15–27.
- Carolin C.E., Kumar P.S., Saravanan A., Joshiba G.J., Naushad M. (2017): Efficient techniques for the removal of toxic heavy metals

<https://doi.org/10.17221/371/2020-PSE>

- from aquatic environment: a review. *Journal of Environmental Chemical Engineering*, 5: 2782–2799.
- Chalyaraksa C., Tumtong M. (2019): Acid soil amendment by zeolite, sepiolite and diatomite. *ScienceAsia*, 45: 253–259.
- Cipurković A., Selimbašić V., Tanjić I., Mičević S., Pelemiš D., Čeliković R. (2011): Heavy metals in sedimentary dust in the industrial city of Lukavac. *European Journal of Scientific Research*, 3: 347–362.
- DalCorso G., Fasani E., Manara A., Visioli G., Furini A. (2019): Heavy metal pollutions: state of the art and innovation in phytoremediation. *International Journal of Molecular Sciences*, 20: 3412.
- Dhal B., Thatoi H.N., Das N.N., Pandey B.D. (2013): Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: a review. *Journal of Hazardous Materials*, 250–251: 272–291.
- Egnér H., Riehm H., Domingo W.R. (1960): Investigations on soil chemical analysis as a basis of the evaluation of plant nutrient status of soils II. Chemical extraction methods for phosphorus and potassium determination. *Kungliga Lantbrukshögskolans Annaler, Sweden*, 26: 199–215. (In German)
- El Gaidoumi A., Doña-Rodríguez J.M., Melián E.P. (2019): Mesoporous pyrophyllite-titania nanocomposites: synthesis and activity in phenol photocatalytic degradation. *Research on Chemical Intermediates*, 45: 333–353.
- Ertani A., Mietto A., Borin M., Nardi S. (2017): Chromium in agricultural soils and crops: a review. *Water, Air, and Soil Pollution*, 228: 190.
- Esmaili A., Mobini M., Eslami H. (2019): Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies. *Applied Water Science*, 9: 97.
- Gadepalle V.P., Ouki S.K., Van Herwijnen R., Hutchings T. (2007): Immobilization of heavy metals in soil using natural and waste materials for vegetation establishment on contaminated sites. *Soil and Sediment Contamination: An International Journal*, 16: 233–251.
- Golomeova M., Zendelska A. (2016): Application of some natural porous raw materials for removal of lead and zinc from aqueous solutions. In: Dariani R.S. (ed.): *Microporous and Mesoporous Materials*. Rijeka, InTech, 21–49. ISBN 978-953-51-2582-2
- Gu S.Q., Kang X.N., Wang L., Lichtfouse E., Wang C.Y. (2019): Clay mineral adsorbents for heavy metal removal from wastewater: a review. *Environmental Chemistry Letters*, 17: 629–654.
- Hou D.Y., Al-Tabbaa A. (2014): Sustainability: a new imperative in contaminated land remediation. *Environmental Science and Policy*, 39: 25–34.
- Huang L., Bell R.W., Dell B., Woodward J. (2004): Rapid nitric acid digestion of plant material with an open-vessel microwave system. *Communications in Soil Science and Plant Analysis*, 35: 427–440.
- IUSS Working Group WRB (2015): World Reference Base for Soil Resources 2014, update 2015. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. World Soils Resources Reports, No. 106. Rome, Food and Agriculture Organisation of the United Nations.
- Jaishankar M., Tseten T., Anbalagan N., Mathew B.B., Beeregowda K.N. (2014): Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7: 60–72.
- Jemeljanova M., Ozola R., Klavins M. (2019): Physical-chemical properties and possible applications of clay minerals and humic acid composite materials. *Agronomy Research*, 17: 1023–1032.
- Jiménez-Castañeda M.E., Medina D.I. (2017): Use of surfactant-modified zeolites and clays for the removal of heavy metals from water. *Water*, 9: 235.
- Keng P.S., Lee S.L., Ha S.T., Hung Y.T., Ong S.T. (2014): Removal of hazardous heavy metals from aqueous environment by low-cost adsorption materials. *Environmental Chemistry Letters*, 12: 15–25.
- Misaelides P. (2011): Application of natural zeolites in environmental remediation: a short review. *Microporous and Mesoporous Materials*, 144: 15–18.
- Ou J.Y., Li H., Yan Z.G., Zhou Y.Y., Bai L.P., Zhang C.Y., Wang X.D., Chen G.K. (2018): *In situ* immobilisation of toxic metals in soil using Maifan stone and illite/smectite clay. *Scientific Reports*, 8: 4618.
- Panda L., Rath S.S., Rao D.S., Nayak B.B., Das B., Misra P.K. (2018): Thorough understanding of the kinetics and mechanism of heavy metal adsorption onto a pyrophyllite mine waste based geopolymer. *Journal of Molecular Liquids*, 263: 428–441.
- Park J.A., Kang J.K., Kim S.B. (2017): Comparative analysis of bacteriophages and bacteria removal in soils and pyrophyllite-amended soils: column experiments. *Water, Air, and Soil Pollution*, 228: 103.
- Radziemska M., Bęś A., Gusiatin Z.M., Majewski G., Mazur Z., Bilgin A., Jaskulska I., Brtnický M. (2020): Immobilization of potentially toxic elements (PTE) by mineral-based amendments: remediation of contaminated soils in post-industrial sites. *Minerals*, 10: 87.
- Singh S., Jena S.K., Das B. (2016): Application of pyrophyllite mine waste for the removal of cadmium and lead ions from aqueous solutions. *Desalination and Water Treatment*, 57: 8952–8966.
- Trierweiler J.F., Lindsay W.L. (1969): EDTA-ammonium carbonate soil test for zinc. *Soil Science Society of America Journal*, 33: 49–54.

Received: July 22, 2020

Accepted: November 4, 2020

Published online: November 25, 2020