

## Use of pyrophyllite to reduce heavy metals mobility in a soil environment

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**Abstract.** This study revealed the effects of pyrophyllite ore materials on heavy metals mobility in soil plots located near the steel mill in Zenica (Bosnia and Herzegovina). The experiment was set up in a randomized block design with four pyrophyllite treatment rates i.e. 0, 200, 400 and 600 kg ha<sup>-1</sup> in three replications. Analyses of the heavy metals (Cu, Zn, Mn, Ni, Cr, Pb, Cd) in soil and plant samples were performed using atomic absorption spectrophotometry. Pyrophyllite addition in soil was found to reduce the availability of all tested heavy metals in the studied soil. The pyrophyllite addition at a rate of 200 kg ha<sup>-1</sup> reduced Mn, Cu and Zn available forms in soil by 11.1, 20.4 and 11.2%, respectively, compared with control. The pyrophyllite addition at higher rates i.e. 400 and 600 kg ha<sup>-1</sup> had an even higher impact on the decrease in Mn and Zn mobility in studied soil in comparison with 200 kg ha<sup>-1</sup>. Additionally, these pyrophyllite rates have the ability to reduce Ni mobility in studied soil. The study also found a positive effect of all pyrophyllite treatments to reduce heavy metals accumulation in the leaves of potato grown on the studied soil. In sum, the results of this study indicate that pyrophyllite treatment could be an effective technique for improving the environmental quality of soils and alleviating the hazards of heavy metals to plants. However, further studies are necessary to confirm or denied this hypothesis.

**Key words:** accumulation, clay minerals, soil-plant system.

### INTRODUCTION

Aluminosilicate clay minerals such as zeolite, pyrophyllite and bentonite have been widely studied regarding their suitability to be used in retention of heavy metal ions and thus for the protection, improvement and also remediation of soils polluted by heavy metals (Chaves et al., 2015; Lee et al., 2019). These minerals, based on a three-

dimensional aluminosilicate framework with numerous channels and cavities, have high retention properties which make them very useful in decreasing bioavailability of heavy metals in soils (Jemeljanova et al., 2019). Most scientists have noted that the ability of aluminosilicate minerals to reduce the mobility and thus availability of heavy metals in soils for plants is the result of their high cation exchange capacity, high surface area, and pore volume enabling the entry and retention of heavy metals in their inter layers (Wang & Li, 2011; Uddin, 2017; Xu et al., 2017).

The use of aluminosilicate minerals as heavy metals retention materials has advantages upon many other remediation techniques in terms of their non-toxic nature, low-cost, and high efficiency (Sharma et al., 2018). Among aluminosilicates, one of the least used materials in the soil remediation is pyrophyllite, which is a result of its relatively lower presence in nature, but also insufficient research on its use as a remediation material.

Pyrophyllite belongs to the class of aluminosilicates with form of the 2:1 layer i.e., the pyrophyllite structure consists of an octahedral Al-O layer sandwiched between two opposing tetrahedral Si-O layers. The bonding between these sandwiches is weak resulting with pyrophyllite's softness (Mohs hardness is between 1 and 1.5). Furthermore, the pyrophyllite has high density (2.7 and 2.9 g cm<sup>-3</sup>), a relatively high cation exchange capacity (between 50 and 70 meq 100 g<sup>-1</sup>) and a pH ranging from neutral to slightly alkaline. It occurs in all shades of colour, particularly white, grey-white, and greenish pink, depending upon the presence of coloured minerals in pyrophyllite ore (Churakov, 2006).

Over the past several decades, the steel industry in Zenica has been associated with emission of large quantities of harmful substances, affecting negatively the air quality, as well as the quality of the soils in the Zenica area, more precisely their use value. Among harmful substances, heavy metals are of great concern due to its adverse effects on human health (Felix-Henningsen et al., 2010; Imeri et al., 2016). However, the presence of heavy metals in soils does not necessarily predict adverse effects on plants and consequently human health if they do not occur in a quantity above permissible limits established by legislation and in forms that is easily absorbed by plants (Kulokas et al., 2019). The normal range of Cu, Zn, Mn, Ni, Cr, Pb and Cd in leaves of plants are 5–20 mg kg<sup>-1</sup>, 20–100 mg kg<sup>-1</sup>, 15–150 mg kg<sup>-1</sup>, 0.02–50 mg kg<sup>-1</sup>, 0.1–1 mg kg<sup>-1</sup>, 0.5–30 mg kg<sup>-1</sup> and 0.1–2.4 mg kg<sup>-1</sup>, respectively (Chaney, 1989; Kastori et al., 1997).

The main objective of this study was to examine the ability of pyrophyllite ore materials from Parsovići – Konjic to decrease the availability of heavy metals in soils located near the steel mill in Zenica. An additional goal of this study was to evaluate pyrophyllite efficiency in reducing heavy metals accumulation in leaves of potato grown on these soils. Potato is food crops that are mostly grown in the study area and therefore is selected as the subject of this study.

## MATERIALS AND METHODS

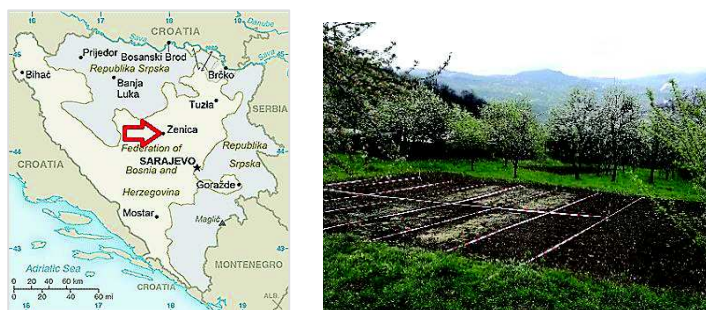
### Materials

The pyrophyllite ore materials from the deposits 'Parsovići–Konjic' (Bosnia and Herzegovina) were used in this study. The particle size of the pyrophyllite materials used in the experiment was smaller than 500 µm.

The median total SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K, Ca, Mg, Cu, Ni, Zn, Co, Mn, Pb and Cr of pyrophyllite ore materials used in this study were 67.6%, 19.1%, 0.3%, 6.7%, 0.1%, 1.4 mg kg<sup>-1</sup>, 2.7 mg kg<sup>-1</sup>, 25.7 mg kg<sup>-1</sup>, 0.4 mg kg<sup>-1</sup>, 93.1 mg kg<sup>-1</sup>, 8.0 mg kg<sup>-1</sup> and 0.8 mg kg<sup>-1</sup>, respectively. The results mentioned above were obtained from the Laboratory at the Faculty of Agriculture and Food Sciences University of Sarajevo.

### Study area

Three agricultural soil plots in Gradište, north-western suburb of Zenica (44°22'5" N, 17°89'85" E) were chosen as a study area (Fig. 1). The area has a temperate oceanic climate (cool summers and cool but not cold winters), with an average annual mean temperature and rainfall of 11.3 °C and 992 mm, respectively. It typically lacks a dry season as rainfall is dispersed evenly throughout the year.



**Figure 1.** Location map of the study site.

The investigated soil plots had approximately 1,000 m<sup>2</sup> in area and were located at a very close distance from each other (up to 500 m). These soils were chosen for investigation because it is located near the steel mill, but also because the populations in this area are fully or partially engaged in agriculture. Accordingly, the results of this study could provide specific data regarding the adverse impacts of heavy metals emission from steel factory on food crops production in the investigated area. All investigated soils were classified as Eutric Cambisol based on the World Reference Base for Soil Resources (FAO, 2014). Slightly acid to neutral reaction, medium texture, good physical properties, moderate organic matter content and base saturation of more than 50% is a typical characteristic of this type of soil.

Soil samples from investigated soil plots were collected once in March 2019 from 0–30 cm depth, using clean steel shovel. Five soil samples from each experimental plot were randomly gathered and mixed properly to obtain a composite soil sample. Thereafter, composite soil samples were placed in plastic bags and brought to the laboratory.

The soil samples were air-dried, crushed and ground using porcelain mortar and pestle, passed through a 2 mm and 1 mm sieve and then stored in paper bags until chemical analysis. Soil with highest concentrations of heavy metals (Cu, Zn, Mn, Ni, Cr, Pb, Cd) was used for conducting the experiment.

### **Experimental design**

The experimental soil area was divided into twelve equal plots. Each plot had area 20 m<sup>2</sup> and the size of each unit plot was 5×4 m. The experiment was set up in a randomized block design with four pyrophyllite treatment in three replications. Distances between two plots were 1 m and the blocks were 2 m apart. Experiment treatments were as follows:

1. T<sub>1</sub> – soil without pyrophyllite i.e. control treatment
2. T<sub>2</sub> – soil with pyrophyllite at rate of 200 kg ha<sup>-1</sup>
3. T<sub>3</sub> – soil with pyrophyllite at rate of 400 kg ha<sup>-1</sup>
4. T<sub>4</sub> – soil with pyrophyllite at rate of 600 kg ha<sup>-1</sup>.

Recommended pyrophyllite ore rate was recalculated based on experimental plot area (20 m<sup>2</sup>). Pyrophyllite ore materials in all experimental plots were applied seven days before planting potato. All other agrotechnical measures needed for optimum potato growth (pest control measures, irrigation) were performed identically on all experimental plots until the time of potato technological maturity.

Concentrations of plant-available forms of heavy metals in soils and heavy metal concentrations in potato leaves were determined at the end of experiment i.e. potato technological maturity stage. All samples of soils and potato leaves in the experiment area were collected at the same time.

### **Soil analysis**

Before performing experiment, the following soil chemical properties were analysed: soil reaction (pH), organic matter (OM), available forms of phosphorus (available P) and potassium (available K), and total forms of heavy metals (Cu, Zn, Mn, Ni, Cr, Pb, Cd). Available forms of heavy metals in soil samples were determined at the end of experiment.

Soil pH was measured in H<sub>2</sub>O and 1 M KCl in a 1:2.5 soil: solution ratio with a Mettler Toledo 320 pH meter. OM was measured by chromic acid digestion method (ISO 14235, 1998) and available forms of phosphorus and potassium by Egnér–Riehm method (Egnér et al., 1960).

Total heavy metals in soil samples were extracted by mineralizing 1 g of dry weight sample with 21 mL aqua regia (HNO<sub>3</sub>: HCl 1:3) for 16 h at ambient temperature. Then, the flask solution was heated on hotplate under reflux for 2 h at 180 °C, cooled down to room temperature, filtered through quantitative filter paper into 100 mL flasks and diluted to the mark with deionized water (ISO 11466, 1995).

Plant-available forms of heavy metals in soil samples were extracted by EDTA solution (0.01 M ethylenediaminetetraacetic acid (EDTA) and 1 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, adjusted to pH 8.6) as follows: 10 g of air-dried soil was transferred into 100 mL plastic bottle, and then 20 mL EDTA solution was added. The bottle solution was shaken for 30 min at 180 rpm in an orbital shaker and thereafter the extract was filtered through quantitative filter paper into 25 mL flask and diluted to the mark with deionized water (Trierweiler & Lindsay, 1969).

Total and available heavy metal concentrations in soil samples were determined by atomic absorption spectrometry (ISO 11047, 1998) and their content expressed as mg per kg dry weight.

### Plant sampling and analysis

Healthy green potato leaves without signs of parasites or disease from each experimental plot were carefully collected at the stage of potato technological maturity in quantity of approximately 200 g. The leaf samples were air-dried and separately powdered with a stainless-steel mill and stored in paper bags until analysis.

Total heavy metals in leaf samples were extracted by mineralizing 1 g of dry weight sample with 14 mL HNO<sub>3</sub> + HClO<sub>4</sub> mixture (2.5:1 v/v) for 4 h at ambient temperature. Thereafter, the flask solution was heated on a hotplate for 30 min, cooled down to room temperature, filtered through quantitative filter paper into 50 mL flasks and diluted to the mark with deionized water (Lisjak et al., 2009). Heavy metal concentrations in leaf samples were also determined by atomic absorption spectrometry (ISO 11047, 1998) and their content expressed as mg per g dry weight.

### Statistical analysis

All measurements were done in triplicates and the results were presented as mean ± standard deviation. The collected data were analysed statistically using Microsoft Excel 2013 software program, and the significant differences between the variants were determined using *Least Significant Differences test* at 0.05 level of probability ( $P \leq 0.05$ ).

## RESULTS

### Basic chemical properties of the studied soils

The results of the soil chemical analysis are presented in Table 1.

Chemical analyses showed that the sampled soils from studied were slight acidic to neutral with moderate levels of organic matter and high content of available forms of phosphorus (P<sub>2</sub>O<sub>5</sub>) and potassium (K<sub>2</sub>O). Soil 1 had highest concentrations of heavy metals (Cu, Zn, Mn, Cr, Pb, Cd) and therefore this soil was selected for conducting the experiment.

**Table 1.** Chemical analysis of soil sample

Parameter	Unit	Soil 1	Soil 2	Soil 3
pH H <sub>2</sub> O	pH unit	7.4	7.3	7.4
pH KCl	pH unit	6.7	6.6	6.8
organic matter	%	2.81	2.23	2.48
P <sub>2</sub> O <sub>5</sub>	mg 100 g <sup>-1</sup>	20.84	8.08	3.22
K <sub>2</sub> O	mg 100 g <sup>-1</sup>	60.9	30.3	34.9
Cu	mg kg <sup>-1</sup>	47.1	41.2	40.2
Zn	mg kg <sup>-1</sup>	53.9	56.7	50.0
Mn	mg kg <sup>-1</sup>	1,411.9	1,322.1	1,400.3
Ni	mg kg <sup>-1</sup>	120.2	160.0	155.9
Cr	mg kg <sup>-1</sup>	31.1	18.0	20.3
Pb	mg kg <sup>-1</sup>	69.5	54.1	55.0
Cd	mg kg <sup>-1</sup>	0.25	0.12	0.13

### Available forms of heavy metals in the soil after pyrophyllite treatment

The concentrations of available forms of Cu, Zn, Mn, Pb, Ni, Cr and Cd in soil plots (mg kg<sup>-1</sup> dry weight), depending on the pyrophyllite treatment, are presented in Table 2 and 3. These results are also presented by a histogram 1 and 2 for easier visualization (Fig. 2).

The presented data illustrates the concentrations of available forms of heavy metals in soil after pyrophyllite treatment. The addition of pyrophyllite reduced the availability of all tested heavy metals in the studied soil compared to control treatments but the magnitude of the effect was not the same for all treatments. However, the statistical

analysis does not confirm the significant effect of added pyrophyllite on the reduction of Cr availability in soils.

**Table 2.** Concentrations of available forms of Cu, Zn, Mn and Pb in the studied soil

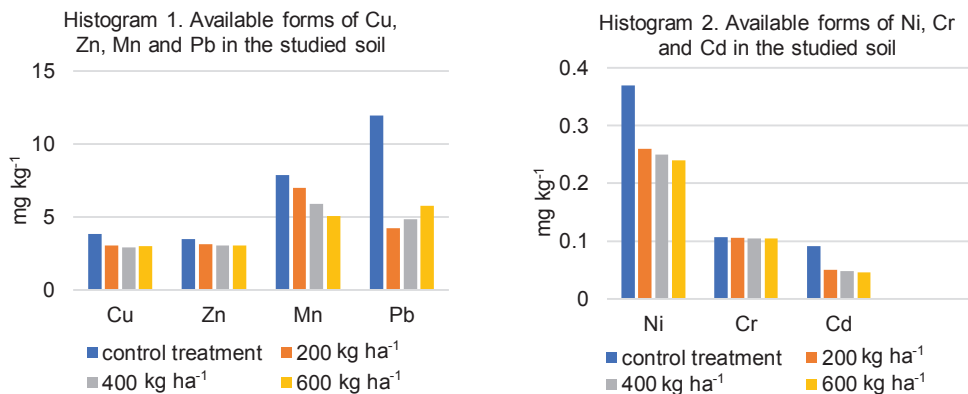
Treatment <sup>1</sup>	Cu	Zn	Mn	Pb
T <sub>1</sub>	3.83 ± 0.24 <sup>a</sup>	3.49 ± 0.15 <sup>a</sup>	7.87 ± 0.25 <sup>a</sup>	11.95 ± 1.61 <sup>a</sup>
T <sub>2</sub>	3.05 ± 0.50 <sup>b</sup>	3.10 ± 0.14 <sup>b</sup>	7.00 ± 0.26 <sup>b</sup>	4.20 ± 0.44 <sup>b</sup>
T <sub>3</sub>	2.89 ± 0.24 <sup>b</sup>	3.02 ± 0.08 <sup>b</sup>	5.89 ± 1.35 <sup>c</sup>	4.85 ± 1.42 <sup>b</sup>
T <sub>4</sub>	3.08 ± 0.36 <sup>b</sup>	3.01 ± 0.40 <sup>b</sup>	5.07 ± 0.78 <sup>d</sup>	5.73 ± 2.91 <sup>b</sup>
Lsd <sub>0.05</sub>	0.451	0.203	0.713	1.851

Values marked with different letters in the same column indicate significantly differences. <sup>1</sup>Experimental treatment: T<sub>1</sub> – control treatment (without pyrophyllite); T<sub>2</sub> – pyrophyllite at rate of 200 kg ha<sup>-1</sup>; T<sub>3</sub> – pyrophyllite at rate of 400 kg ha<sup>-1</sup>; T<sub>4</sub> – pyrophyllite at rate of 600 kg ha<sup>-1</sup>.

**Table 3.** Concentrations of available forms of Ni, Cr and Cd in the studied soil

Treatment <sup>1</sup>	Ni	Cr	Cd
T <sub>1</sub>	0.37 ± 0.03 <sup>a</sup>	0.107 ± 0.02	0.091 ± 0.02 <sup>a</sup>
T <sub>2</sub>	0.26 ± 0.04 <sup>b</sup>	0.106 ± 0.02	0.050 ± 0.01 <sup>b</sup>
T <sub>3</sub>	0.25 ± 0.05 <sup>b</sup>	0.105 ± 0.01	0.048 ± 0.01 <sup>b</sup>
T <sub>4</sub>	0.24 ± 0.03 <sup>b</sup>	0.105 ± 0.03	0.046 ± 0.01 <sup>b</sup>
Lsd <sub>0.05</sub>	0.056	-	0.017

Values marked with different letters in the same column indicate significantly differences. <sup>1</sup>Experimental treatment: T<sub>1</sub> – control treatment (without pyrophyllite); T<sub>2</sub> – pyrophyllite at rate of 200 kg ha<sup>-1</sup>; T<sub>3</sub> – pyrophyllite at rate of 400 kg ha<sup>-1</sup>; T<sub>4</sub> – pyrophyllite at rate of 600 kg ha<sup>-1</sup>.



**Figure 2.** The concentrations of available forms of heavy metals in soil depending on the pyrophyllite treatment.

### Heavy metal concentrations in leaves of potato after pyrophyllite treatment

The heavy metal concentrations (Cu, Zn, Mn, Pb, Ni, Cr and Cd) in potato leaves (mg kg<sup>-1</sup> dry weight), depending on the pyrophyllite treatment, are presented in Table 4 and 5. These results are also presented by a histogram 3 and 4 for easier visualization (Fig. 3).

The presented data have shown that pyrophyllite treatment, regardless of the applied rates, significantly reduced accumulation of heavy metals (Cu, Zn, Mn, Pb, Ni and Cr) in potato leaves as compared to control treatment. The study also found a positive effect of pyrophyllite treatment to reduce Cd accumulation in potato leaves, but these findings did not reach statistical significance.



**Table 4.** Concentrations of Cu, Zn, Mn and Pb in potato leaves

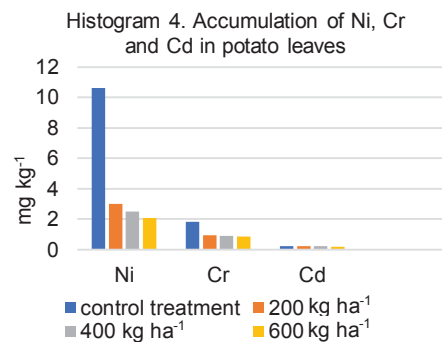
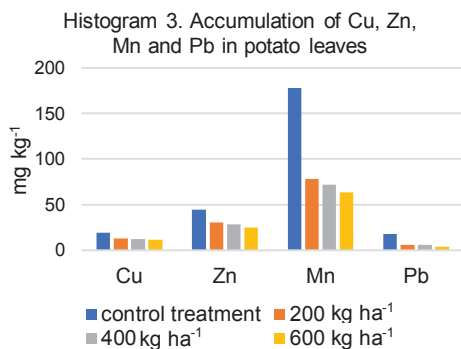
Treatment <sup>1</sup>	Cu	Zn	Mn	Pb
T <sub>1</sub>	19.4 ± 5.6 <sup>a</sup>	44.5 ± 7.2 <sup>a</sup>	177.9 ± 69.2 <sup>a</sup>	18.0 ± 1.7 <sup>a</sup>
T <sub>2</sub>	12.5 ± 1.0 <sup>b</sup>	30.0 ± 4.6 <sup>b</sup>	78.3 ± 26.1 <sup>b</sup>	5.4 ± 2.9 <sup>b</sup>
T <sub>3</sub>	12.0 ± 2.9 <sup>b</sup>	28.1 ± 8.3 <sup>bc</sup>	71.5 ± 10.7 <sup>b</sup>	5.8 ± 1.8 <sup>b</sup>
T <sub>4</sub>	11.2 ± 0.7 <sup>b</sup>	24.6 ± 1.7 <sup>c</sup>	63.7 ± 11.1 <sup>b</sup>	3.8 ± 2.6 <sup>b</sup>
Lsd <sub>0.05</sub>	2.94	5.24	35.34	2.14

Values marked with different letters in the same column indicate significant differences. <sup>1</sup>Experimental treatment: T<sub>1</sub> – control treatment (without pyrophyllite); T<sub>2</sub> – pyrophyllite at rate of 200 kg ha<sup>-1</sup>; T<sub>3</sub> – pyrophyllite at rate of 400 kg ha<sup>-1</sup>; T<sub>4</sub> – pyrophyllite at rate of 600 kg ha<sup>-1</sup>.

**Table 5.** Concentrations of Ni, Cr and Cd in potato leaves

Treatment <sup>1</sup>	Ni	Cr	Cd
T <sub>1</sub>	10.6 ± 4.7 <sup>a</sup>	1.81 ± 0.32 <sup>a</sup>	0.24 ± 0.1
T <sub>2</sub>	3.0 ± 2.1 <sup>b</sup>	0.93 ± 0.36 <sup>b</sup>	0.24 ± 0.1
T <sub>3</sub>	2.5 ± 1.2 <sup>b</sup>	0.91 ± 0.61 <sup>b</sup>	0.23 ± 0.1
T <sub>4</sub>	2.1 ± 1.7 <sup>b</sup>	0.85 ± 0.24 <sup>b</sup>	0.20 ± 0.2
Lsd <sub>0.05</sub>	2.50	0.35	–

Values marked with different letters in the same column indicate significant differences. <sup>1</sup>Experimental treatment: T<sub>1</sub> – control treatment (without pyrophyllite); T<sub>2</sub> – pyrophyllite at rate of 200 kg ha<sup>-1</sup>; T<sub>3</sub> – pyrophyllite at rate of 400 kg ha<sup>-1</sup>; T<sub>4</sub> – pyrophyllite at rate of 600 kg ha<sup>-1</sup>.



**Figure 3.** Accumulation of heavy metals in soil depending on the pyrophyllite treatment.

## DISCUSSION

This paper is an attempt to describe and evaluate the efficiency of pyrophyllite ore material to decrease the mobility of heavy metals in soil and thus their availability for plants. The results of this study demonstrate the high potential of pyrophyllite to immobilize heavy metals in studied soil, regardless of the amount of applied material. These findings are generally in line with previous studies (Kim et al., 2013; Park et al., 2017; Rath et al., 2017).

In the present study, the addition of pyrophyllite was especially successful in reducing Pb and Cd mobility in soil. The addition of pyrophyllite at rate of 600 kg ha<sup>-1</sup> reduced Pb and Cd available forms in soil by 52.1 and 49%, respectively, compared with control treatment. The effect of pyrophyllite at rate of 200 and 400 kg ha<sup>-1</sup> on the decrease Pb and Cd mobility in soil was also highly significant. These results are in agreement with results obtained by Singh et al. (2016).

Considering the soils polluted by Pb and Cd may pose hazards to food crops and consequently human health (Tchounwou et al., 2012; Alle et al., 2016; Borgulat et al.,

2018; Luo et al., 2019), the results mentioned above provide important scientific information in an effort to improve soil protection and quality by applying pyrophyllite. Our opinion is pyrophyllite has the potential to be included in the inventory of efficient soil remediation techniques, especially because the use of pyrophyllite for soil remediation is simple to operate, cost effective and very reliable.

Osacky et al. (2015) reported that the ability of pyrophyllite and other clay minerals to reduce the mobility of heavy metals in soils is the result of their potential to form complexes with heavy metals in their inter layers or on surface areas. The pyrophyllite primarily binds heavy metals in the space between the layers, due to their large pore volume (Ismadji et al., 2015). The efficiency of pyrophyllite to immobilize heavy metals in soil also depends on their dosage, surface area as well as soil physical and chemical properties.

Furthermore, the speciation or chemical form of the element play an important role in in the fixation of heavy metals on the pyrophyllite surface. Namely, heavy metals often have different levels of mobility depending on the specific metal oxidation state (Violante et al., 2010). For example, Cr (III) is, in general, much less toxic and mobile in soils than Cr (VI), and therefore reactions that reduce Cr (VI) to Cr (III) are of great importance for soil remediation.

Although numerous studies confirm that pyrophyllite has high efficiency in removing heavy metals from the soil and water (Prasad & Saxena, 2008; Chawla et al., 2018; Panda et al., 2018), the heavy metal binding mechanisms on pyrophyllite are not completely clear. Scheidegger et al. (1996) have attempted to explain the binding mechanisms between Ni and pyrophyllite surfaces. They reported pH is the primary factor that controls Ni binding on pyrophyllite. The study found that Ni sorption on pyrophyllite, in the lower pH region (i.e.,  $\text{pH} < 7$ ), increased with decreasing ionic strength. Contrary, Ni sorption on pyrophyllite, in the higher pH region ( $\text{pH} > 7$  with high  $\text{Ca}^{2+}$  level), was slower. These results can be explained by the fact that Ni with other ions (primarily  $\text{Ca}^{2+}$ ) compete for the same free sites on the pyrophyllite adsorptive complex. Similar results were reported by Gou et al. (2018).

The results of this study also showed that pyrophyllite addition at a rate of 400 and 600  $\text{kg ha}^{-1}$  in soil has the ability to reduce Ni mobility in studied soil (neutral to weakly basic), indicating the pyrophyllite possesses some mechanisms for Ni retention even in the higher pH region. Zhao et al. (2017) noted the inner-sphere complexes between Ni and pyrophyllite surface areas (with no intervening water molecules) were dominant mechanisms for Ni retention.

In the present study, pyrophyllite also demonstrated the high potential to immobilize Mn, Cu and Zn in studied soil. Namely, the pyrophyllite addition at a rate of 200  $\text{kg ha}^{-1}$  reduced Mn, Cu and Zn available forms in soil by 11.1, 20.4 and 11.2%, respectively, compared with control treatment (without pyrophyllite). The pyrophyllite addition at higher rates i.e. 400 and 600  $\text{kg ha}^{-1}$  had an even higher impact on the decrease in Mn and Zn mobility in studied soil in comparison with 200  $\text{kg ha}^{-1}$  pyrophyllite rate. These findings indicate that pyrophyllite ore material used in this research is potentially useful additive to bind Mn and Zn ions in soils and that their mobility in soil decreases with increasing pyrophyllite rates.

However, a better understanding of the pyrophyllite sorption mechanism could make a significant contribution to improving pyrophyllite efficiency to reduce heavy metals mobility in soils. An interesting data related to pyrophyllite is the fact that



pyrophyllite has the ability to easily disperse in water, enabling a higher area of pyrophyllite exposure in the soil and thus its activity (El Gaidoumi et al., 2019), and finally pyrophyllite could increase soil pH, thus resulting in less heavy metal mobility (Newton & Sposito, 2015). All the above-mentioned scientific data are undoubtedly associated with its sorption mechanism.

As shown in Table 3, all pyrophyllite treatments were also significantly reduced the accumulation of heavy metals (Cu, Zn, Mn, Ni, Cr, Pb and Cr) in the leaves of potato grown on the studied soil. In addition, the pyrophyllite treatments reduced Cd accumulation in potato leaves, but these effects were not statistically significant. The results also showed that 600 kg ha<sup>-1</sup> pyrophyllite rate had the highest effect on the reduction of heavy metals accumulation in potato leaves. This treatment reduced the accumulation of Cu, Zn, Mn, Ni, Cr, Pb and Cr in the potato leaves by 42.1, 44.5, 64.2, 80.0, 52.8, 78.9 and 17.8%, respectively, compared to control treatment. The effect of 200 and 400 kg ha<sup>-1</sup> pyrophyllite rate was also significant but less pronounced.

Generally, the results of this study demonstrated that the addition of pyrophyllite in tested soil reduced heavy metals mobility, thus resulting with low accumulation of heavy metals in potato leaves. One exception to this general rule was the behaviour of Cr in soil- plant system. Namely, the pyrophyllite treatments did not significantly reduce the concentration of Cr available forms in studied soil at the end of experiment, but significantly reduced its accumulation in the leaves of potato grown in the same soil plots. This inconsistent result could be potentially attributed to Cr speciation. As is well known, the Cr mobility in soil can change drastically depending on change in soil pH, redox potential, microbial activity, content of organic matter, content and type of clay minerals etc. Accordingly, changes in Cr chemical forms (speciation) are possible in a relatively short-term, and thus its bioavailability (Huang et al., 2018). We assume that Cr mobility in soil in the initial stages of potato growth were higher, resulting in higher Cr uptake by the potato. However, further studies are necessary to confirm or denied this hypothesis as well as other hypotheses presented in this study.

## CONCLUSIONS

Pyrophyllite addition in soil was found to reduce the availability of tested heavy metals in the studied soil, indicating that pyrophyllite treatment could be an effective technique to stabilize soils polluted by heavy metals. Under experimental conditions of the study, the pyrophyllite addition at a rate of 200 kg ha<sup>-1</sup> reduced Mn, Cu and Zn available forms in soil by 11.1, 20.4 and 11.2%, respectively, compared with control. The pyrophyllite addition at higher rates i.e. 400 and 600 kg ha<sup>-1</sup> had an even higher impact on the decrease in Mn and Zn mobility in studied soil in comparison with 200 kg ha<sup>-1</sup>. Additionally, the accumulation of all tested heavy metals in leaves of potato grown on soil plots treated with pyrophyllite was found to be lower than those in non-treated plots, indicating that pyrophyllite can also alleviate the risk for plants associated with heavy metals.

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