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Effect of clay on the fractions of potentially toxic elements in contaminated soil

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Abstract: The aim of the study was to evaluate the effect of clay as an amendment to decrease the mobility and plant availability of potentially toxic elements (PTEs). Kaolinite and vermiculite were added at a 9% application rate to a contaminated garden soil from Kutná Hora. Half of the original soil was acidified by the addition of HNO₃, to observe the effect of the pH on the adsorption of the PTEs. The samples were analysed four times over an eight-week period to evaluate the effect of the clay additions on the As, Cd, Pb and Zn plant availability and different fractions of the BCR sequential extraction. The results indicate that the PTEs were mainly bound by ion/cation exchange on the edges of the clay minerals and onto the Fe/Mn oxides and organic fractions in the soils. The significance ($P < 0.05$) of the pH was observed for the plant availability of the PTE, especially on the As and Cd. A comparison of the vermiculite in the form of chunks and as powder displayed the most statistically significant results, where the vermiculite powder significantly decreased the plant availability of the As, Cd and Pb, while the opposite effect was observed for the Zn.

Keywords: clay amendment; contamination; plant availability; PTE; soil acidification

During the 13th to 16th century, the mining and smelting industry blossomed and transformed Kutná Hora into one of the largest mining towns in Europe, producing 5–6 tonnes of Ag and 50–100 tonnes of Cu annually (Pauliš & Mikuš 1998). Due to the heavy mining and smelting, the land surrounding the area, including agricultural and garden areas have become subjected to potentially toxic element (PTE) contamination through processes such as leaching, and aeolian or colluvial deposition. This has increased the risks of crop production and water sources becoming contaminated, leading to the consumption of contaminated food and water by people and animals. The consumption of contaminated

foods with As, Cd, Pb and Zn could cause kidney/liver damage, neurological damage, poisoning and certain diseases (e.g., itai-itai disease, in the case of Cd consumption), to name a few (Järup 2003; Kabata-Pendias & Mukherjee 2007; Plum et al. 2010; Science Communication Unit 2013).

Mining took place on quartz enriched with As which was formed from metamorphosed igneous substances (Pauliš & Mikuš 1998). Not only do the quartz veins contain As, but also a wide range of PTEs. The composition and spatial distribution of the contaminants is not completely known despite multiple articles published on Kutná Hora (e.g., Ash et al. 2014; Horák & Hejcman 2016; Tremlová

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et al. 2017). However, the main elements of As, Be, Cd, Co, Cr, Cu, Hg, Pb, V and Zn have been well documented in Kutná Hora soils due to their consistently high concentrations. Elements such as Mo, Ni and Sb were all also found abundantly, but at lower concentrations (Horák & Hejcman 2016).

This paper focuses on evaluating clay as an amendment to immobilise the PTEs in a contaminated garden soil sample from Kutná Hora. There has been growing interest in the remediation and use of amendments to decrease the plant availability of PTEs in contaminated soils. Plenty of research in this field has generated a wide range of literature focused on the amendments and remediation and stabilisation of contaminated soils (e.g., Basta & McGowen 2004; Arcon et al. 2005; Kumpiene et al. 2008; Alloway 2013; Xu et al. 2017; Kypridou & Argyraki 2020). The methods used for amending a contaminated soil depend on the elements present in the soil as well as the binding capacity the amendment possesses.

Two clays, kaolinite and vermiculite, were selected for this experiment due to their different structures, bonding mechanisms, layer charge, particle size and cation exchange capacities (CECs). The paper focuses on the effect of kaolinite and vermiculite on four of the highly concentrated PTEs present in the soil: As, Cd, Pb and Zn. Neumann et al. (2002) discussed that with a larger particle size of a clay there is a decreased available surface area for adsorption, signifying that the influencing factor of the adsorption is the clay particle size. Kaolinite is a 1 : 1 (tetrahedral : octahedral) aluminosilicate that has a low CEC and protonation and deprotonation of hydroxyl groups, which causes the charge of kaolinite to be highly pH-dependant. Two proposed methods of PTE binding to kaolinite were described as an ion exchange and inner-sphere binding (Angove et al. 1997; Miranda-Trevino & Coles 2003; Srivastava et al. 2005; Bhattacharyya & Gupta 2008). Vermiculite is a 2 : 1 (tetrahedral : octahedral) clay that bears a larger CEC. The two mechanisms involved in the PTE binding are through a cation exchange at the planar sites and through the formation of inner-sphere complexes. Like kaolinite, the binding mechanisms of vermiculite are pH dependent (Malandrino et al. 2006; Abollino et al. 2008).

MATERIAL AND METHODS

Soil samples were collected from a productive private vegetable garden in Kutná Hora (Czech

Republic). The samples were suspected to be contaminated due to the vast history of mining and smelting processes that occurred in Kutná Hora; which has been mentioned several times in papers studying PTEs in soils in and around Kutná Hora (Ash et al. 2014; Horák & Hejcman 2016; Tremlová et al. 2016, 2017).

The soil samples were dried, crushed and sieved to < 2 mm. Both the active pH ($\text{pH}_{\text{H}_2\text{O}}$) and exchangeable pH (pH_{KCl}) were determined prior to the experimentation. To test the effect of the pH on the immobilisation of the PTEs, half of the homogenised soil was acidified to reduce the pH of the soil. The soil was mixed with 1.2 litres of water and treated with 60 mL of HNO_3 with a final average pH value of 5.73.

Furthermore, the basic soil characteristics, such as the organic content, soil particle and bulk density, soil porosity, cation exchange capacity (CEC), texture and humus percentage were determined (Pansu & Gautheyrou 2006; Carter & Gregorich 2008). In order to verify that no PTEs were added by the clay to the soil, the content of the four PTEs present in the clays were assessed using XRF (X-Ray Fluorescence) Spectroscopy (Delta Professional, Olympus). The CEC and pH of the clays were also determined prior to the experimentation.

The experiment was set for a duration of eight weeks, with samples being analysed after 2, 4, 6 and 8 weeks. Each analysis consisted of fourteen beakers with seven samples each of 20 g of non-acidified soil and 20 g of acidified soil; each soil type had a control and 3 replicates per clay amendment.

The clays, kaolinite and vermiculite, were obtained from LB Minerals. The clays were applied at a 9% application rate. The 9% application rate was deduced from an experiment conducted by Yin and Zhu (2016) who applied two amendments at application rates of 0%, 2.5%, 5% and 10%. Since 20 g of soil was used per reaction vessel, with a 9% clay application rate, 2 g of each clay was added to the reaction vessels. The kaolinite used in the experiment was in powder form, while the vermiculite was in small 'chunks'. In order to determine if the vermiculite 'chunks' used in the experiment affected its ability to immobilise the PTEs in the soils, the vermiculite was also ground into a fine powder, decreasing the particle size and increasing the surface area, and applied at the same application rate to the non-acidified and acidified soils.

The pseudototal content of the PTEs in each reaction vessel was established after digestion by

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Table 1. The basic soil physiochemical properties

	Min	Median	Max	Mean	SD
pH _{H₂O}	7	7.48	7.52	7.33	0.24
pH _{KCl}	7.26	7.3	7.35	7.30	0.04
pH _{H₂O} (acidified soil)	5.74	5.76	5.79	5.76	0.02
Cox (%)	3.6	3.74	3.91	3.75	0.13
Humus (%)	6.21	6.45	6.74	6.47	0.22
ρ _z (g/cm ³)	2.29	2.34	2.38	2.34	0.04
ρ _d (g/cm ³)	1.04	1.06	1.08	1.06	0.05
CEC (mmol/100g)	21	23	24	22.7	1.25

Cox – oxidisable carbon; ρ_z – particle density; ρ_d – bulk density; CEC – cation exchange capacity; SD – standard deviation; values are means ($n = 3$)

aqua regia. The plant available fraction of the PTEs of all the soil samples was determined by NH₄NO₃ extractions. Determination of the pseudototal and plant available content was determined according to the method by Sabienė et al. (2004). A modified 4-step BCR (Community Bureau of Reference) sequential extraction procedure described by Tokalioglu et al. (2003) was used to determine the exchangeable, reducible, oxidisable and residual fractions of the PTEs in the soil samples. The BCR extraction was determined using 1 g of soil, which was sequentially shaken for 16 h with 4 different solutions. The solutions were applied in the order as follows: 0.11 mol/L of acetic acid to determine the exchangeable fractions, 0.1 mol/L of hydroxylammonium chloride (adjusted to a pH of 2) to determine the Fe and Mn oxide bound fractions, 1.0 mol/L of ammonium acetate for the organic matter and sulphide bound fractions, and lastly, the residual fractions were determined using a mixture of HNO₃ and HCl.

The concentrations of the PTEs were determined by analysis using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Thermo Scientific iCAP 7000) under standard analytical conditions with standard Quality Control/Quality Assurance measures. The effect of the amendments, pH and time was assessed using a multifactor analysis of variance (ANOVA). Data comparing the vermiculite ‘chunks’ and ‘powder’ were analysed using a multifactor analysis of variance (ANOVA) as well as one-way analysis of variance (ANOVA) for each element when compared to the two difference types of vermiculite (chunks and powder) as well as when compared to the pH. All the statistical analyses were performed using Statgraphics (Ver. 16, 2019).

RESULTS AND DISCUSSION

The basic soil properties can be found in Table 1. The soil texture was determined as 84% sand, 2% clay and 14% silt. The concentrations of PTEs present in the kaolinite and vermiculite can be observed in Table 2. The pseudototal and plant available concentrations of the PTEs in the soils before the addition of the clay can be seen in Table 3. The soil guideline values for the pseudototal PTE content in agricultural soils, set by the Ministry of Environment in the Czech Republic are also described in Table 3; the PTE concentrations in the soil sample were 3–4 times higher than the guideline values.

The statistical differences of the amendments on the plant availability of the PTEs are shown in Table 4. The arsenic concentrations displayed a significant difference in the soil pH on the plant availability, with a decreased plant availability in the acidified soils. The increased plant available As concentrations could be due to the As bound by the ion exchange, thus, changes in the pH can easily release As (Bhattacharyya & Gupta 2008). The relationship between the As and pH was clearly depicted by Katsoyiannis and Katsoyiannis (2007), where a positive correlation can be seen between the two factors. The plant available

Table 2. The basic properties of the clays and concentrations in the potentially toxic elements measured using X-ray fluorescence spectroscopy (Delta Professional, Olympus)

	pH	CEC (mmol/100g)	As	Cd	Zn	Pb
			(mg/kg)			
Kaolinite	7.5	3.8	11	1.5	9	60
Vermiculite	9.8	75	3.7	nd	44	8

nd – no data; values are means ($n = 2$)

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Table 3. The pseudototal and plant available concentrations of the potentially toxic elements in the soil before the addition of the clay amendments and the guideline values (Decree No. 153/2016 Coll.) (in mg/kg)

	As		Cd		Pb		Zn	
	PT	PA	PT	PA	PT	PA	PT	PA
Guideline values	20	nd	0.5	nd	60	nd	120	nd
Original Soil	81.3	0.72	2.19	0.004	159	0.107	454	0.74
Acidified Soil	79.8	0.53	2.17	0.015	138	0.237	466	2.17

PT – pseudototal; PA – plant available; nd – no data; values are means ($n = 2$)

Cd concentrations displayed various homogenous groups. In both the non-acidified and acidified soils, the Cd was significantly different from the controls. The different homogenous groups within the non-acidified and acidified soils indicates the significance of the pH on the Cd plant availability. Cadmium is said to be competitively adsorbed by clays until a certain pH threshold value is exceeded. Indicating that above a pH of 7.5, Cd is not mobile in the soils and its solubility is highly dependent on the pH,

which explains the higher plant available concentrations in the acidified soils. Gupta and Bhattacharyya (2006) found an increasing pH led to the increased Cd adsorption by the kaolinite. Angove et al. (1997) found that Cd was bound to kaolinite via the ion exchange and through complexation to the Al and Si groups on the clay edges.

The results of the plant available Pb and Zn concentrations (Table 4) show an overall increased least squares (LS) mean of the elements in the soils, which

Table 4. The statistical differences between the different amendments

	Sample	pH	LS mean	LS sigma	Homogeneous groups
As	control	non-acidified	1.198	0.046	b
	Kaolinite		1.197	0.027	b
	Vermiculite		1.128	0.027	b
	control	acidified	0.681	0.046	a
	Kaolinite		0.694	0.027	a
	Vermiculite		0.698	0.027	a
Cd	control	non-acidified	0.004	0.001	ab
	Kaolinite		0.004	0.001	a
	Vermiculite		0.004	0.001	a
	control	acidified	0.007	0.001	cd
	Kaolinite		0.006	0.001	bc
	Vermiculite		0.009	0.001	d
Pb	control	non-acidified	0.036	0.012	a
	Kaolinite		0.040	0.007	a
	Vermiculite		0.053	0.007	a
	control	acidified	0.039	0.012	a
	Kaolinite		0.045	0.007	a
	Vermiculite		0.048	0.007	a
Zn	control	non-acidified	0.036	0.012	a
	Kaolinite		1.814	0.712	a
	Vermiculite		1.614	0.712	a
	control	acidified	1.995	1.232	a
	Kaolinite		3.456	0.712	a
	Vermiculite		1.983	0.712	a

Control $n = 4$; amendment $n = 12$; all the data are at a 95% confidence level; LS – least squares

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could be explained by the possible heterogeneous distribution of the elements in the soils. However, the overall statistics show no significance of the amendments nor the soil pH on the plant availability of the Pb and Zn. The raw data, however, shows a decreasing concentration of Zn over the 8-week period (data not shown). A possible explanation for the increased Cd and decreasing Zn could be due to the higher Cd mobility in the soils and also due to the strongly bound Zn by clays (Lindsay 1972). The results for the plant available Zn from this experiment are similar (but to a lesser extent) to the results obtained by Alvarez-Ayuso and Garcia-Sanchez (2003a, b), whose results showed a decrease in the exchangeable Zn fraction by 76% in the soil when amended with palygorskite and 99% when amended with sepiolite, proving magnesium silicate clays can efficiently reduce the Zn concentrations. In this experiment, the available Zn fractions showed a decrease ranging from 20–85%. The increasing concentrations for Cd and Pb could be a result of being exchangeably held through the outer-sphere linkages which can be easily displaced by other cations (Alloway 2013). Srivastava et al. (2005) found that Pb had a higher affinity for kaolinite surfaces compared to Cd and Zn, which could explain the decrease in the Pb in weeks 2 and 6, as the kaolinite could have temporarily immobilised the Pb in the soils (data not shown). The experiments conducted by Miranda-Trevino and Coles (2003) indicated that within the first 24-hour contact with kaolinite, Pb is retained to a greater extent than Zn and Cd. Cadmium was the least adsorbed, indicating that Zn and Pb have access to sites unavailable for Cd. Similar results of the affinity for Pb for clays were observed

by Kypridou and Argyraki (2020) when observing the effects of Fe-rich clays on Pb, Zn and Cu.

The increasing concentrations of some PTEs could be due to the isomorphous substitution of PTEs for other cations over time. As clays have a pH-dependent charge from protonation on the clay edges, this can lead to the tetrahedral layer being negatively charged or neutral at most pH values, while the octahedral layer is more likely to develop positive charges at lower pH values. Kaolinite does not follow the process of isomorphous substitution and was found to become more negative with an increasing pH as the protons dissociate from the surface hydroxyls (van der Perk 2006). Kaolinite adsorbs the PTEs via the ion exchange and inner-sphere binding, while vermiculite adsorbs the PTEs via the cation exchange on the planar sites and the formation of the inner-sphere complexes (Bhattacharyya & Gupta 2008; Xu et al. 2017; Manjaiah et al. 2018). As the PTE concentrations vary during certain phases of the experiment, it could be suggested that the elements were mainly bound through exchangeable ion and cation exchange sites on the surfaces of the clays, rather than in the inner-sphere binding.

In Figure 1, the effect of the clay amendments on the soil pH can be found while the original pH of both clays can be found in Table 2. Kaolinite, with a pH of 7.5, and vermiculite, with a pH of 9.8, can be seen to greatly increase the soil pH, especially under acidified conditions (from a pH below 6 to above 7). The increased pH levels of the soils can be the reason behind the decreased concentrations of some of the PTEs (Xu et al. 2017).

The results from the BCR sequential extraction are shown in Figure 2. No drastic changes in the individual

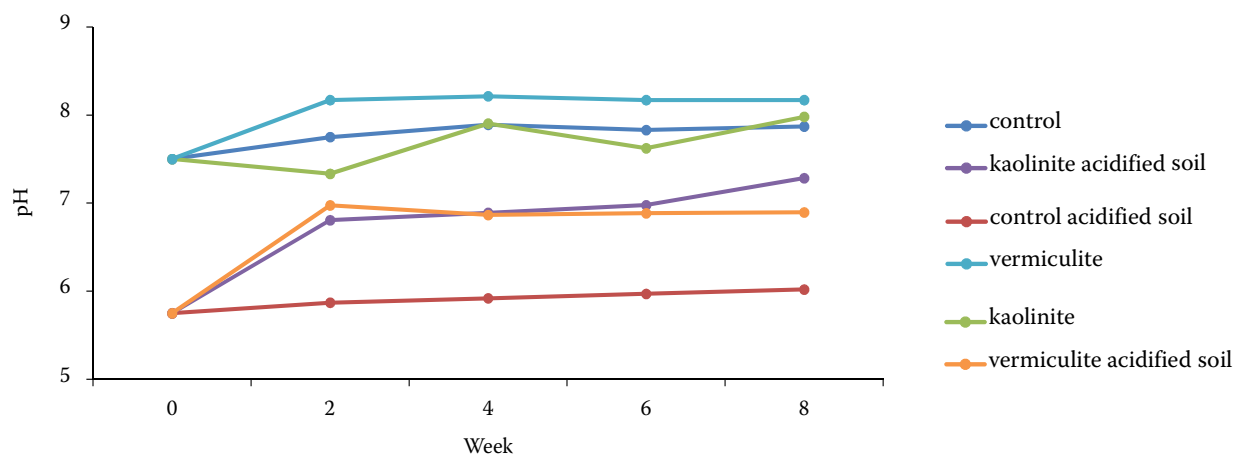


Figure 1. The effect of the clay amendments on the soil pH

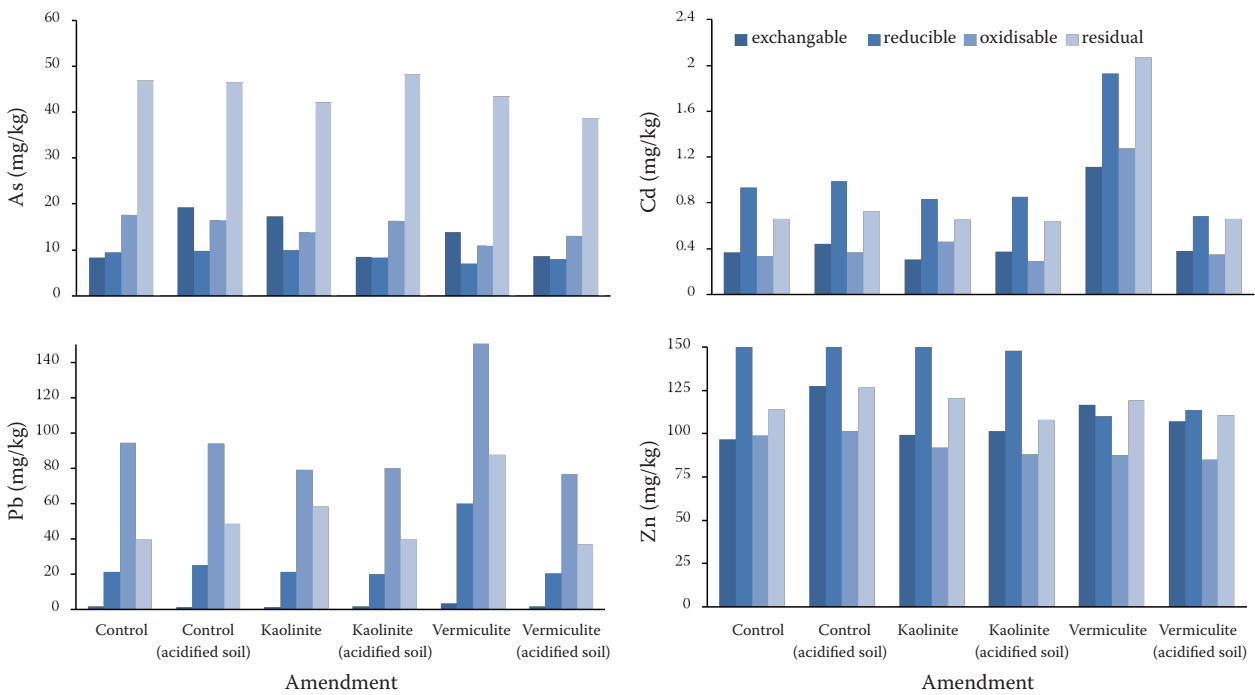


Figure 2. The changes in the different fractions of the potentially toxic elements in the soils after the 8-week treatment with the clays

fractions can be found in PTE concentrations when amended with the clays. Arsenic is found mostly bound in the residual fractions, and under acidified conditions, both clays have decreased exchangeable As fractions.

Cadmium was studied to have an affinity for both organic matter and Fe oxides and is very strongly dependent on the pH (Kabata-Pendias & Pendias 2001; Alloway 2013). The graph in Figure 2 shows a greater Cd affinity

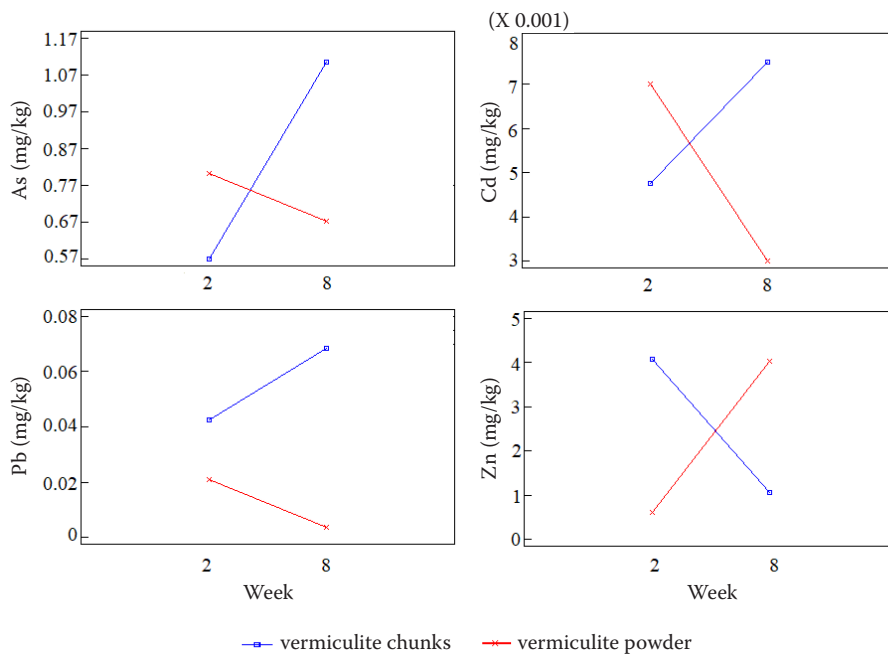


Figure 3. The main effects and interactions between the vermiculite ‘chunks’ and ‘powder’ on the plant available potentially toxic elements ($n = 3$, 95% confidence level)

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Table 5. The multifactor ANOVA of the time, pH and vermiculite and their interactions on the plant availability of the potentially toxic elements concentrations in the soil

	As		Cd		Pb		Zn	
	<i>F</i> test	<i>P</i>	<i>F</i> test	<i>P</i>	<i>F</i> test	<i>P</i>	<i>F</i> test	<i>P</i>
Main effects								
A: week	5.91	0.0379*	1.99	0.1918	0.34	0.5718	10.6	0.0099**
B: vermiculite	1.49	0.2530	6.45	0.0317*	33.8	0.0003****	17.7	0.0023**
C: pH	25.6	0.0007***	42.1	0.0001****	2.33	0.1615	23.0	0.0010**
Interactions								
AB	15.9	0.0032**	58.1	< 0.001***	8.41	0.0176*	2762	< 0.001***
AC	1.41	0.2651	13.5	0.0052**	9.00	0.0149*	2.29	0.1646
BC	0.36	0.5651	3.90	0.0796	1.34	0.2772	23.9	0.0009***

*, **, *** indicate a significance at $P < 0.05, 0.01, 0.001$; *F* tests are based on the residual mean square error; all the data are at a 95% confidence level

for Fe/Mn oxides and residual fractions than organic fractions. Lead is also mainly associated with Fe/Mn oxides and organic matter (Kabata-Pendias & Pendias 2001), and from the graph of Pb concentrations, Pb is mainly bound in the order of organic matter > residual > Fe/Mn oxides > exchangeable fractions. Zinc is known to be associated with organic matter (Kabata-Pendias & Pendias 2001), and as can be seen in Figure 2, that the majority of the Zn is found bound to the organic fractions of the soil. Slight changes can be seen in the reducible As, Cd, Pb and Zn when amended with the clays. The most observable results can be seen in the decreased reducible Zn fractions when amended with vermiculite (by ~30 mg/kg) in both soil pH conditions.

To test if the vermiculite ‘chunks’ affected its abilities to adsorb the PTEs, the vermiculite was crushed into a fine powder. The plant available PTE concentrations can be found in Figure 3. The interaction plots show that from the beginning until the end of the experiment, the plant available concentrations of As, Cd and Pb decreased with the presence of the powdered vermiculite by 0.10, 0.004 and 0.02 mg/kg, respectively. The results of the plant available Zn show the opposite effect where the powdered vermiculite

increased the Zn concentrations by 3.5 mg/kg. This is believed to be due to the other cations present in the soil capable of displacing the Zn as was observed by Gorman et al. (2003) and Cao et al. (2004). As vermiculite in a powdered form has a larger surface area and a smaller particle size, and is not as tightly compact when in chunks, this allows the other cations to displace the Zn more easily (Kabata-Pendias & Pendias 2001). This would explain why the Zn was more effectively retained by the vermiculite chunks rather than by the powdered vermiculite.

To understand the results better, multifactor and one-way ANOVAs were conducted to individually observe the effects of all the factors on the plant available PTEs, the results can be seen in Tables 4–6 and Figures 3 and 4. From Table 5, the multifactor ANOVA results show a statistical significance ($P < 0.05$) in relation to the time (represented as weeks) and pH on the As; the vermiculite type and pH for the Cd; the vermiculite type for the Pb and all 3 factors for the Zn. These results emphasise the significance of the pH on the PTE mobility. However, when observing the effect of the interactions of the factors, the most important factors were a combination of the time and vermiculite, with all the PTEs having

Table 6. The one-way ANOVA comparing the vermiculite ‘chunks’ and ‘powder’ and the pH on the potentially toxic elements levels in the soil

	As		Cd		Pb		Zn	
	<i>F</i> test	<i>P</i>	<i>F</i> test	<i>P</i>	<i>F</i> test	<i>P</i>	<i>F</i> test	<i>P</i>
Vermiculite	0.36	0.559	0.70	0.416	15.6	0.002**	0.09	0.772
pH	10.5	0.006**	6.35	0.025*	0.53	0.480	0.11	0.740

*, ** indicate a statistically significant difference ($P < 0.05, 0.01$) at a 95% confidence level

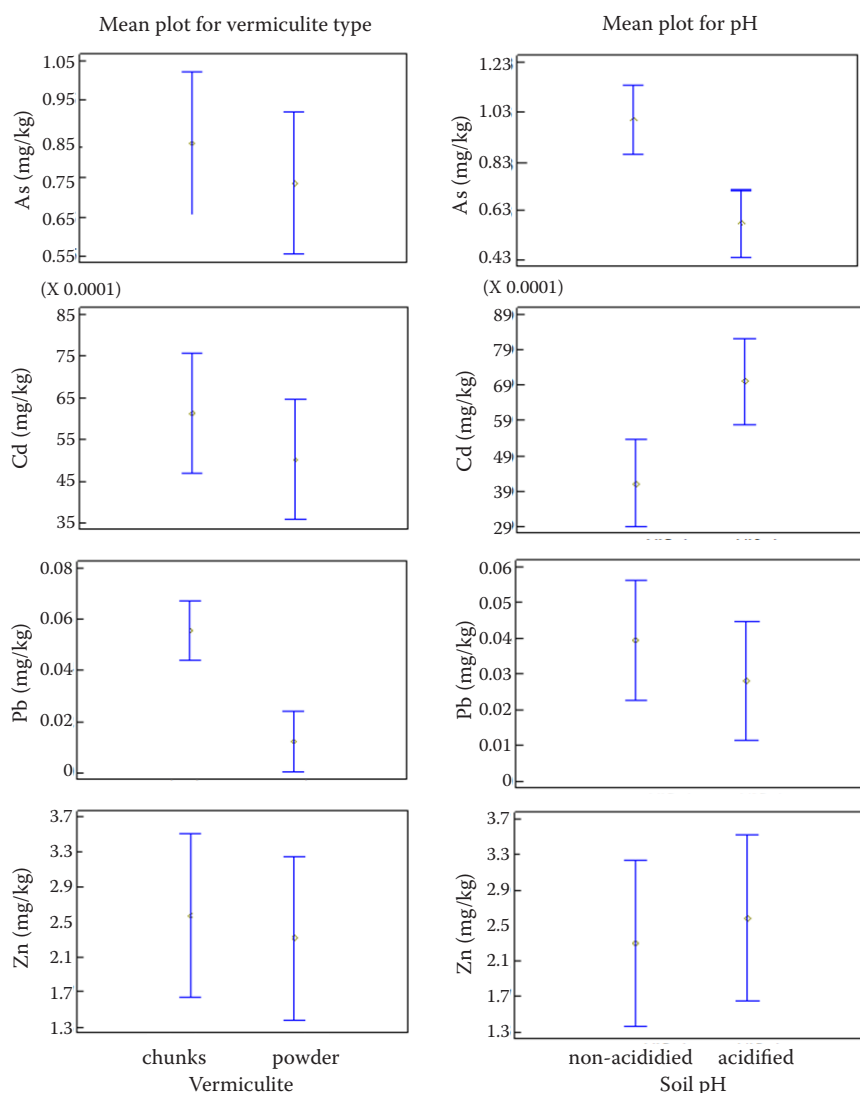


Figure 4. The one-way ANOVA mean plots comparing the vermiculite type and soil pH on the plant available potentially toxic elements with 95% confidence levels

a significance value of $P < 0.05$, followed by a combination of the time and pH. The one-way ANOVA (Table 6) indicates that the effect of the vermiculite type (chunks vs powder) was statistically significant ($P < 0.05$) only on the Pb, while, on the other hand, the one-way ANOVA for the pH was statistically significant ($P < 0.05$) with a 95% confidence level on the As and Cd. The graphical representation (Figure 4) shows a decreased plant available As, Cd and Pb when amended with the powdered vermiculite. The acidified soils decreased the plant available As and Pb concentrations, while the opposite effect was seen from the Cd and Zn. The increased Cd and Zn concentrations in the acidified soils was also seen by Malandrino et al. (2006) and Abollino et al. (2008),

where they found a decreased PTE adsorption with a decreasing pH and found vermiculite to adsorb greater concentrations of Zn and Cd than Pb, further verifying the pH dependence of both the PTEs and the clays.

CONCLUSION

The aim of the experiment was to evaluate the plant available content of the PTEs before and after the acidification and addition of the amendments. As the soil sample was from a productive garden that was used to plant fruits and vegetables, the aims focused more towards reducing the plant available PTEs to prevent contamination of the fruits and vegetables.

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Over the two-month period, the plant available concentrations displayed certain decreases in the PTE concentrations when amended with kaolinite and vermiculite. No obvious differences in the plant available concentrations could be seen between the amendments. The statistical analysis of the data signified the importance of the pH on the plant availability, with a statistical significance ($P < 0.05$) of the pH on the As and Cd plant availability. The vermiculite type (chunks, powder) significantly ($P < 0.05$) influenced the plant availability of the PTE concentrations in the soil. The experiment displayed that vermiculite, as a powder, is a useful and affordable tool for the As, Cd and Pb immobility, indicating the importance of the size, especially of the CECs and particle size of the clays on the PTE immobilisation. The clays were found to increase the pH of the soils, thus, decrease the plant availability of the PTEs.

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