



# EDTA, Water-extractable Lead and Bioavailability of Lead in Soils/Tailings: The Effects of Zeolite and Beringite Amendment

B. A. Osei<sup>1\*</sup>

<sup>1</sup>Department of Soil Science, University of Cape Coast, Cape Coast, Ghana.

## Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

## Article Information

DOI: 10.9734/IJPSS/2017/30837

### Editor(s):

(1) Slawomir Borek, Faculty of Biology, Department of Plant Physiology, Adam Mickiewicz University, Poland.

### Reviewers:

(1) Chen Jiawei, China University of Geosciences, Beijing, China.

(2) K. Narasimhaswamy, Indian Institute of Rice Research, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history/17624>

Original Research Article

Received 2<sup>nd</sup> December 2016

Accepted 9<sup>th</sup> January 2017

Published 26<sup>th</sup> January 2017

## ABSTRACT

A study of the effects of varying rates of zeolite and beringite on water soluble Pb and EDTA-extractable Pb, pH and bioavailability of Pb in non-mined soil/tailings was undertaken. Water-extractable Pb, EDTA-extractable Pb were monitored for 0–12 weeks after amendment and bioavailability of Pb was evaluated by growing lettuce (*Lactuca sativa*) on amended soil/tailings for 4–12 weeks after incubation. Zeolite was more effective amendment in immobilizing Pb in soil/tailings. Application of zeolite led to decrease in the levels of water soluble Pb by 14–32%, 21–44% and 32–51% in the non-mined soil, capped and uncapped tailings respectively at week 12. Similarly, EDTA-extractable Pb decreased by 14–33%, 11–19% and 41–48%. In non-mined soil, the application of zeolite resulted in lower concentration of Pb in lettuce (0.2 mg kg<sup>-1</sup>) while the capped tailings recorded higher Pb (0.33 mg kg<sup>-1</sup>) value than the FAO/WHO limit. The uncapped tailing recorded 0.67 mg kg<sup>-1</sup> Pb.

**Keywords:** Alkalinization; immobilization and stabilization of Pb; phyto accumulation of Pb in lettuce.

## 1. INTRODUCTION

Pollution of soils by heavy metals such as lead (Pb) is of great global concern due to its adverse

effects on the health of man and the environment [1]. Heavy metals, unlike contaminants of organic origin, are generally non-degradable. They also interact with the soil matrix and persist in the soil

\*Corresponding author: E-mail: [bosei@ucc.edu.gh](mailto:bosei@ucc.edu.gh);

for long periods. Heavy metals can therefore be transferred by intake of plants and human health as well as other organisms through the ingestion of both water and food that have been contaminated by the soil [2].

Soil contamination has been identified as one of the main threats to soil quality [3]. Governmental and regional institutions are increasingly giving attention to issues of soil pollution [4]. Subsequently, initiatives have commenced to limit and prevent further soil degradation and to examine applicable remediation measures [5]. There has been extensive reclamation of lands used for mining and the containment of heavy metals at tailings site in Ghana. However, the documentation of these activities is inadequate.

The scientific approach in assessing the effectiveness of the different soil/tailings decontamination methods is lacking. Conventional soil remediation technologies, although suitable for relatively small and heavily contaminated areas, are financially and physically inefficient in extensive and moderately contaminated sites [6]. The new techniques of treating contaminated soils emphasize among others immobilization and stabilisation of potentially toxic elements (PTEs) [7]. The capping of contaminated tailings with lateritic soil does not remove the contaminants from the

soil [8]. This is, however, the main method of remediating heavy metals contained in tailings sites at mining sites in Ghana. Many soil amendments that have been screened for their potential to immobilize heavy metals in soils are alkaline materials such as beringite and zeolite [9,6,10]. The objectives of this study were to assess:

- i. The extent of alkalization of non-mined soil, capped tailings and uncapped tailings through the use of zeolite and beringite.
- ii. The effectiveness of zeolite and beringite on forms of Pb and the bioavailability of Pb after mediation of non-mined soil, capped and uncapped tailings.

## 2. MATERIALS AND METHODS

The soils/tailings were sampled from a mining site in Ghana. The site had non-mined soils, and reclaimed tailings (capped and uncapped). Top soils/tailings samples (0-15 cm) were collected. Forty soil cores were taken from non-mined, capped tailing and uncapped tailing sites, bulked into three composite samples and transported to the laboratory. The samples were prepared by air drying, crushing, discarding of foreign material, crushing and sieving through a 2-mm nylon mesh. Properties of soil/tailings are presented in Table 1.

**Table 1. Properties of soil/tailings at the 0 to 15-cm depth**

Soil property	Site			
	Non- mined soil	Capped tailings I	Capped tailings II	Uncapped tailings
Organic carbon (%)	2.13	0.63	0.55	1.02
Total N (%)	0.19	0.06	0.06	0.10
C: N ratio	11.21	10.50	9.16	10.20
pH (1: 2.5 - soil:water)	5.10	6.79	6.70	7.22
Extractable P - Bray I (mg kg <sup>-1</sup> )	6.58	16.57	4.17	1.53
<b>Exchangeable cations (cmol<sub>c</sub> kg<sup>-1</sup>)</b>				
Ca <sup>2+</sup>	3.47	11.75	10.15	15.39
Mg <sup>2+</sup>	1.60	8.54	3.47	9.61
K <sup>+</sup>	0.21	0.42	0.41	1.40
Na <sup>+</sup>	0.13	0.42	0.38	1.67
<b>Total exchangeable bases (cmol<sub>c</sub> kg<sup>-1</sup>)</b>				
	5.41	21.13	14.41	28.07
Exchangeable acidity (cmol <sub>c</sub> kg <sup>-1</sup> )	0.35	0.10	0.10	0.05
Effective cation exchange capacity (cmol <sub>c</sub> kg <sup>-1</sup> )	5.76	21.23	14.51	28.12
Bulk density (g cm <sup>-3</sup> )	1.26	1.33	1.32	1.39
Total porosity (%)	52.45	49.81	50.19	47.54
Sand (%)	43.65	48.93	73.64	34.62
Silt (%)	46.34	41.06	24.35	61.37
Clay (%)	10.01	10.01	2.01	4.01

## 2.1 Soil Amendment and Incubation Experiment

Five hundred grams (500 g) air dry sample from each of the three sites was placed in 0.5 L plastic containers. The soils/tailings were amended with zeolite and beringite at the rates of 0, 30 and 60 kg ha<sup>-1</sup> (w/w). The soil/tailings samples were mixed thoroughly with the amendments and then moistened to field capacity. There were three replications of the imposed treatments. The completely randomised design was used. The samples were incubated at a room temperature of 25°C in the laboratory and moistened weekly to maintain the soil at field capacity. The soils/tailings were sampled at 0, 4, 8 and 12 weekly intervals, mixing thoroughly before sampling. Five random sub-samples were taken with a spatula and bulked for analysis from each container at these time intervals.

## 2.2 Extraction of EDTA-Pb

Ten (10) grams of air-dried soil was weighed and then pulverized in a clean, nitric acid washed mortar and pestle, for the Ammonium tetrasodium-ethylene-diamine-tetraacetic acid (Na<sub>4</sub>-NH<sub>4</sub>-EDTA) extraction [11,12]. The soil was wrapped in a paper towel before being pulverized with the mortar and pestle to minimize the nitric acid washing necessary for the mortar and pestle. The soil was placed into a 100 ml conical flask and 50 ml of 0.05 M (Na<sub>4</sub>-NH<sub>4</sub>-EDTA) (pH 7) was added. The flask with the soil: Na<sub>4</sub>-NH<sub>4</sub>-EDTA mixture was shaken at room temperature on a mechanical shaker at 125 rpm for 1 hr [11,12]. The slurry was then passed through a filter paper into a sterile 100 ml conical flask. The filtrate was brought to exactly 100 ml with the extraction solution, and the filtrate was analyzed using the Atomic Absorption Spectrophotometer (AAS, Spectr AA 220). The concentrations of Pb were measured at a wavelength of 283.3 nm.

## 2.3 Extraction of Water Soluble Pb

Water soluble Pb was determined by weighing 5 g of soil sample into centrifuge tube, and 50 ml of distilled water was added. The tube was capped and shaken in a mechanical shaker for 30 minutes. After shaking the content of the tube was filtered with Whatman no.42 filter paper. Pb level in extract was determined by AAS at a wavelength of 283.3 nm.

## 2.4 Bioavailability Experiment and Plant Analysis

The bioavailability of Pb in the mediated soils/tailings was subsequently determined after the use of amendments zeolite and beringite. Lettuce (*Lactuca sativa*) was chosen as the plant indicator of the bioavailability of Pb due to its ability to accumulate high amount of heavy metals in the edible leafy aerial parts [13].

The field practices for the cultivation of lettuce as described by [14] were followed. The lettuce seeds were planted in a seedbed that was shaded with oil palm fronds. The seedlings were pricked out three weeks after germination and planted at a spacing of 4 cm x 4 cm. The seedlings were natured for another three weeks and subsequently transplanted into the containers/pots containing the mediated non-mined soil/tailings. The soil/tailings samples were then moistened to field capacity and then moistened weekly to maintain the soil/tailings at field capacity. Fertilizer was incorporated into the soil/tailings samples at the rates of 50 kg N ha<sup>-1</sup>, 45 kg P ha<sup>-1</sup> and 65 kg K ha<sup>-1</sup> at the time of transplanting. At three-weeks after transplanting, 50 kg N ha<sup>-1</sup> was applied as recommended by [14]. The aerial parts of the lettuce plants were harvested and prepared for the analysis of the concentrations of Pb.

A quantity of 1.0 g of the prepared plant material was digested in freshly prepared mixture of HNO<sub>3</sub> – HCl (1:3 v/v) on a digester at 110°C for 3 h to determine the concentrations of Pb [2].

## 2.5 Data Analysis

The Genstat statistical package [15] for the analysis of the data. The analysis of variance (ANOVA) was used to determine the effects of the amendments on pH, water-soluble and EDTA-extractable Pb in the non-mined soil, capped and uncapped tailings. The least significant difference (LSD) was used for the separation of means (95% confidence level). The percentage change in treatment effect on the value of the variable (Pb or pH) was estimated from the relationship:

$$\% \Delta Variable = 100 \left( \frac{V_{x\ Rate} - V_0}{V_0} \right)$$

The percentage change in value of variable at given rate of application of amendment is

represented by  $\% \Delta$  Variable, the value of the variable at a specific rate of application is given by  $V_{X \text{ Rate}}$  and the value of the variable at 0 kg ha<sup>-1</sup> rate of application is represented by  $V_0$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Soil pH and Lead as Influenced by Rate of Application and Type of Amendment at Different Incubation Periods in Soil/Tailings

Table 2 summarises selected properties of soil/tailings before and after amendment at the end of the incubation period. The details of changes in soil /tailings as influenced by incubation period are presented in Tables 3-11.

The effects of different rates of application of the amendments (zeolite and beringite) on the pH of non- mined soil, capped and uncapped tailings are presented in Tables 3- 11.

##### 3.1.1 Effects of amendments on the pH of non-mined soil, capped and uncapped tailing

At 4, 8 and 12 weeks after incubation (WAI), there were significant differences ( $P = 0.05$ ) in soil/tailings pH among the amendments at the different rates of application (Tables 3, 4 and 5). The application of beringite to non-mined soil, from 4 to 12 WAI, yielded the highest percentage change in soil pH of 20.7% at application rate of 60 kg ha<sup>-1</sup>. The addition of 60 kg ha<sup>-1</sup> beringite to uncapped tailings also resulted in a slight but significant increase in pH of 6.9% compared to the un-amended samples between 4 WAI and 12WAI ( $P = 0.05$ ). Generally, the soil/tailings pH of non-mined soil, capped and uncapped tailings after the application of beringite at the rate of 60 kg ha<sup>-1</sup> was significantly greater than the un-amended samples (Tables 3, 4 and 5).

At WAI 12 the application of 60 kg ha<sup>-1</sup> of beringite to non-mined soil, capped and uncapped tailings resulted in significantly higher

soil/tailings pH compared to zeolite and non-amended soil ( $P = 0.05$ ) (Tables 3, 4 and 5).

[16,10] applied at 60 kg ha<sup>-1</sup>. The OH<sup>-</sup> ions of beringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ , that is a constituent of beringite, could have neutralised the H<sup>+</sup> ions on the exchange complex [17]. This possibly led to increased hydroxyl ions (OH<sup>-</sup>) in soil solution and subsequently, increased the pH of beringite-amended soil/tailings. Basic cations such as Mg<sup>2+</sup> and Ca<sup>2+</sup>, derived from MgO and CaO, respectively, are constituents of beringite also contributed to increased alkalinity of beringite-amended soil/tailings. The significantly higher pH of beringite-amended soils could thus be attributed to the high contents of the basic cations, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in beringite [18] within the exchange complex after H<sup>+</sup> ions have been neutralised and Al<sup>3+</sup> and Fe<sup>3+</sup> ions precipitated.

The addition of 60 kg ha<sup>-1</sup> zeolite increased soil/tailings pH values that were significantly greater than those of the control (0 kg ha<sup>-1</sup>) at 4, 8 and 12 WAI ( $P = 0.05$ ) for non-mined soil capped and uncapped tailings (Tables 3, 4 and 5). This could be accounted for not only by the exchange of H<sup>+</sup> ions in soil solution with Na<sup>+</sup> ions of zeolite, which has the general formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ , but also the alkalisation of amended soils by zeolite that has a pH in the range of 7.0 to 9.2 [9,19,20].

Zeolites are alkaline alumino-silicates [21,6] and provide alkalinity to acid polluted soils [22]. This to some extent possibly accounted for the increase in pH of the non-mined soil and uncapped d tailings. Zeolites also have high cation exchange capacity due to the negative charges that are created by the substitution of Si<sup>4+</sup> by Al<sup>3+</sup> in the tetrahedral framework [23]. A substantial exchange of the Na<sup>+</sup> ions of zeolite for H<sup>+</sup> ions in soil solution [9,18,24] might have also contributed to the increase in pH of the different soil/tailings.

**Table 2. Selected soil/tailings properties before and after amendment at week 12**

Before amendment	Non-mined			Capped			Uncapped		
	pH	EDTA -----mg kg <sup>-1</sup> -----	Water	pH	EDTA -----mg kg <sup>-1</sup> -----	Water	pH	EDTA -----mg kg <sup>-1</sup> -----	Water
Zeolite	5.3	2.69	0.023	6.8	9.16	0.045	7.2	8.05	0.014
Beringite	5.3	2.69	0.023	6.8	9.16	0.048	7.2	8.05	0.135
After amendment									
Zeolite	5.6	1.54	0.024	6.6	3.61	0.034	7.3	3.51	0.112
Beringite	5.8	1.54	0.026	6.8	3.75	0.061	7.4	4.78	0.133

**Table 3. Effects of rate of application and type of amendment on the pH of non-mined soil as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
Soil pH				
Zeolite	0	5.3	5.3	5.3
	30	5.5	5.6	5.6
	60	5.8	5.9	5.9
Beringite	0	5.3	5.3	5.3
	30	5.7	5.8	5.8
	60	6.2	6.3	6.4

LSD (0.05) = 0.05

**Table 4. Effects of rate of application and type of amendment on the pH of capped tailings as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
Soil pH				
Zeolite	0	6.5	6.4	6.4
	30	6.6	6.6	6.6
	60	6.7	6.8	6.9
Beringite	0	6.5	6.5	6.5
	30	6.7	6.7	6.7
	60	6.8	6.8	7.1

LSD (0.05) = 0.05

**Table 5. Effects of rate of application and type of amendment on the pH of uncapped tailings as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
Soil pH				
Zeolite	0	7.2	7.2	7.2
	30	7.3	7.3	7.3
	60	7.4	7.5	7.5
Beringite	0	7.2	7.2	7.2
	30	7.4	7.4	7.4
	60	7.5	7.6	7.7

LSD (0.05) = 0.05

At the end of the 12 weeks incubation period, significant differences in pH ( $P = 0.05$ ) were also observed among the amendments applied at the rates of 30 and 60 kg ha<sup>-1</sup> for non-mined soil, capped and uncapped tailings. Subsequently, the magnitude of soil/tailings pH, in decreasing order, was beringite > zeolite for the application of amendments at the rate of 60 kg ha<sup>-1</sup> in non-mined soil, capped and uncapped tailings.

These trends in pH values by the different amendments could have an influence on the

remediation of heavy metals and the subsequent suitability of tailings capping for agricultural purposes. The highest pH value attained through the use of beringite could have significant effects on the immobilisation of heavy metal ions in contaminated soil because of the decreased protons and increased reactivity of existing exchange sites for effective metal binding [6].

**3.1.2 Effects of amendments on EDTA-extractable Pb in non-mined soil, capped and uncapped tailings**

The results of the effects of type and rate of application and type of amendment on the concentration of EDTA-extractable lead (Pb-EDTA) in non-mined soil, capped and uncapped tailings at the different incubation periods are presented in Tables 6, 7 and 8.

**Table 6. Effects of rate of application and type of amendment on EDTA-extractable lead of non-mined soil as affected by incubation period**

	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
EDTA-extractable Pb (mg kg <sup>-1</sup> )				
Zeolite	0	1.707	1.7	1.71
	30	1.557	1.503	1.477
	60	1.297	1.167	1.143
Beringite	0	1.703	1.703	1.7
	30	1.577	1.523	1.5
	60	1.507	1.447	1.397

LSD (0.05) = 0.01

**Table 7. Effects of rate of application and type of amendment on EDTA-extractable lead of capped tailings as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
EDTA-extractable Pb (mg kg <sup>-1</sup> )				
Zeolite	0	3.99	4.01	4.01
	30	3.76	3.63	3.57
	60	3.48	3.33	3.25
Beringite	0	4.01	4.01	4.01
	30	3.87	3.75	3.65
	60	3.72	3.62	3.60

LSD (0.05) = 0.01

The general trend after the application of all the amendments in non-mined soil, capped and uncapped tailings was an initial high percentage change in Pb-EDTA from 0 to 4 WAI (Tables 6, 7

and 8). This was subsequently followed by successively lower decreases in the concentration of Pb-EDTA between 4 and 8 WAI and from 8 WAI to 12 WAI (Tables 6, 7 and 8).

**Table 8. Effects of rate of application and type of amendment on EDTA-extractable lead of uncapped tailings as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
EDTA-extractable Pb (mg kg <sup>-1</sup> )				
Zeolite	0	5.01	4.98	5.00
	30	3.77	3.68	2.93
	60	3.61	3.46	2.60
Beringite	0	4.99	4.99	5.01
	30	4.84	4.80	4.77
	60	4.78	4.69	4.62
LSD (0.05) = 0.01				

In the non-mined soil, the application of 60 kg ha<sup>-1</sup> of zeolite gave significantly lower concentrations of Pb-EDTA than those of un-amended soil and soils amended with beringite at 4, 8 and 12 WAI ( $P = 0.05$ ) (Table 6). However, the application of either 30 kg ha<sup>-1</sup> or 60 kg ha<sup>-1</sup> of zeolite gave the lowest concentrations of Pb-EDTA in capped and uncapped tailings ( $P = 0.05$ ) at from 4 to 12 WAI (Tables 6, 7 and 8). The significantly lower levels of Pb-EDTA of zeolite amended soil/tailings could be partly due to the resistance of zeolite to degradation, chemisorption of Pb in the cavities of the porous zeolite framework and the precipitation as insoluble lead oxides with increased pH [9]. Metal retention and immobilization by zeolite may also be attributed to an increased cation exchange and the formation of stable complexes of cationic metals with the negative charges of the high specific surface area exhibited by zeolite [22,25,19].

At the 30 kg ha<sup>-1</sup> rate of application of zeolite the level of EDTA-Pb was not different from similar rates of application of beringite in non-mined soil at 4, 8 and 12 WAI ( $P = 0.05$ ) (Table 6). However, the same rate of application resulted in significantly lower levels of Pb-EDTA in zeolite- than beringite-amended contaminated capped and uncapped tailings (Tables 7 and 8). [24] Similarly reported of significantly higher concentrations of residual Pb fraction and lower Pb fractions extracted with EDTA in un-polluted acid soil than that recovered from acid contaminated soil amended with zeolite and lime.

Non-mined soil, capped and uncapped tailings amended with either 30 kg ha<sup>-1</sup> or 60 kg ha<sup>-1</sup> beringite produced significantly lower concentrations of Pb-EDTA than un-amended soil/tailings at 4, 8 and 12 WAI ( $P = 0.05$ ) (Tables 6, 7 and 8). Lead minerals are highly insoluble and exhibit low mobility in natural environments [26,27]. The fixation of lead increases and solubility decreases with increasing pH [15,28]. An increase in the pH of beringite amended non-mined, capped and uncapped tailings (Tables 3, 4 and 5) could have resulted in an increased residual Pb fraction and decreased Pb-EDTA concentrations in beringite-amended non-mined soil, capped and uncapped tailings compared to un-amended samples (Tables 6, 7 and 8).

At the 60 kg ha<sup>-1</sup> rate of application of amendments, the concentration of Pb-EDTA in amended non-mined soil, capped and uncapped tailings at 4, 8 and 12 WAI, in increasing order of magnitude, was as follows: Zeolite < beringite. Zeolite is thus more effective amendment for significantly reducing the concentration of lead in soil/tailings.

### **3.1.3 Effects of amendments on water-soluble lead in non-mined soil, capped and uncapped tailings**

Tables 9, 10 and 11 show the data on the levels of water soluble lead (Pb-H<sub>2</sub>O) after the application of different rates of zeolite and beringite in non-mined soil, capped and uncapped tailings.

**Table 9. Effects of rate of application and type of amendment on water soluble lead of non-mined soil as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
Water soluble Pb (mg L <sup>-1</sup> )				
Zeolite	0	0.027	0.027	0.028
	30	0.026	0.025	0.024
	60	0.023	0.022	0.019
Beringite	0	0.028	0.027	0.028
	30	0.026	0.026	0.026
	60	0.042	0.044	0.044
LSD (0.05) = 0.002				

The trend in the concentration of Pb-water of amended soil/tailings showed higher percentage changes between amended and un-amended soil/tailings at 4 WAI. The percentage changes in the levels of Pb-water of amended samples were

lower from 4 WAI to 8 WAI to 12 WAI when compared to that of the control without amendment (Tables 9, 10 and 11). Soil/tailings amended with zeolite at the rate of 60 kg ha<sup>-1</sup> produced significantly lower levels of Pb-water compared to un-amended soil/tailings at 4, 8 and 12 WAI ( $P = 0.05$ ). The application of zeolite at 60 kg ha<sup>-1</sup> also yielded significantly lower concentrations of Pb-water than beringite in non-mined soil, capped and uncapped tailings from 4 WAI to 12 WAI ( $P = 0.05$ ) (Tables 9, 10 and 11).

**Table 10. Effects of rate of application and type of amendment on water soluble lead of capped tailings as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
Water soluble Pb (mg L <sup>-1</sup> )				
Zeolite	0	0.043	0.043	0.043
	30	0.038	0.037	0.34
	60	0.029	0.026	0.024
Beringite	0	0.042	0.043	0.04
	30	0.042	0.038	0.037
	60	0.036	0.035	0.033
LSD (0.05) = 0.002				

**Table 11. Effects of rate of application and type of amendment on water soluble lead of uncapped tailings as affected by incubation period**

Amendment	Rate of application (kg ha <sup>-1</sup> )	Weeks after incubation		
		4	8	12
Water soluble Pb (mg L <sup>-1</sup> )				
Zeolite	0	0.155	1.555	0.155
	30	0.116	0.097	0.105
	60	0.108	0.083	0.076
Beringite	0	0.154	0.154	0.155
	30	0.133	0.141	0.137
	60	0.128	0.115	0.108
LSD (0.05) = 0.002				

Zeolite-amended soil/tailings resulted in increased pH values of 5.5 – 5.9, 6.6 – 6.9 and 7.3-7.5 compared to pH values of 5.3, 6.4 and 7.2 for un-amended non-mined soil, capped and uncapped tailings, respectively (Tables 3, 4 and 5). Generally, an increase in pH results in the reduction of the water soluble fraction of lead [28-30]. The significantly higher pH values ( $P = 0.05$ ) (Tables 3, 4 and 5) and the lower concentrations of the available Pb-EDTA fraction (Tables 7, 8 and 9) of zeolite-amended

soil/tailings ( $P = 0.05$ ) might partly account for the significantly lower levels of water soluble Pb compared to un-amended samples ( $P = 0.05$ ) (Tables 9, 10 and 11).

Furthermore, ion exchange and the sorption of metal ions (chemisorption) occurs within the channels and cavities of the porous lattice structure of zeolite that results in a decrease in the concentration of water soluble and exchangeable fractions in soil solution as observed by [6,31,24]. At 4 WAI, there was no significant difference in Pb-water between the 30 kg ha<sup>-1</sup> and 60 kg ha<sup>-1</sup> ( $P = 0.05$ ) rate of application of beringite. There was also no significant difference between 30 kg ha<sup>-1</sup> beringite amended soils and un-amended soils at all the time-points of the incubation period from 0 WAI to 12 WAI ( $P = 0.05$ ). Increased soil solution pH may have led to reduced mobility of Pb in beringite amended soil [16] and could have accounted for the significantly lower concentrations of water soluble Pb compared to un-amended soil.

The significantly lower levels of Pb-water extracted from zeolite-amended non-mined soil, capped and uncapped tailings compared to un-amended samples ( $P = 0.05$ ) at 4, 8 and 12 WAI application could be also ascribed to the high cation exchange of zeolite [31]. This is supported by [32] who have stated that metal retention by zeolite due to cation exchange takes place irrespective of the value of pH. However, [9] report that the mechanism of action of zeolite in the immobilization and reduction in the water soluble fraction of metal contaminants is due to a combination of the ion exchange properties of zeolite and its ability to increase alkalinity. This explanation is buttressed by [20] and [6] who note that the specific surface area, binding capacity and alkalinity of zeolite results in the immobilisation, precipitation of insoluble phases and reduction in metal levels in soil solution.

Similarly, the application of beringite at the rate of 60 kg ha<sup>-1</sup> to non-mined soil, capped and uncapped tailings resulted in significantly lower concentrations Pb-H<sub>2</sub>O than un-amended samples, at all the time-points of the incubation period ( $P = 0.05$ ) (Tables 9, 10 and 11), possibly due to a pH effect, increased fixation, precipitation or co-precipitation of Pb with Fe, Al and Mn oxides in presence of beringite [16,10]. Subsequently, reduced mobility of Pb could have led to the decreased water soluble fraction in beringite-amended samples.

### 3.2 Bioavailability of Pb in Lettuce Grown on Mediated Soil/Tailings

Figs. 1–3 show the results of the concentration of Pb in lettuce harvested from non-mined soil, capped and uncapped tailings after mediation with beringite, and zeolite.

Lead accumulated in the aerial part of the lettuce plant has been used as an index of bioavailability for the purpose of this study. Generally, the concentrations of Pb in zeolite-amended and beringite-amended soil/tailings were significantly lower than those of un-amended samples ( $P = 0.05$ ) (Figs. 1–3).

The permissible limits of lead in vegetables cultivated for human consumption, cited from different sources are 2.0–2.5 mg kg<sup>-1</sup> [33], 2.0

mg kg<sup>-1</sup> [34] and 0.3 mg kg<sup>-1</sup> [35]. Generally, the concentration of lead in lettuce was within the cited maximum limits. However, the concentration of lead in lettuce harvested from capped and uncapped tailings were 0.03 and 0.1 mg kg<sup>-1</sup>, respectively above the maximum limits set by [36]. The application of 60 kg ha<sup>-1</sup> zeolite resulted in the lowest concentration of Pb in aerial parts of lettuce in non-mined soil, capped and capped tailings (Figs. 1 – 3). Lettuce grown on zeolite- and beringite-amended soil/tailings had significantly lower concentrations of Pb than un-amended samples. This could be partly attributed to the significantly lower concentrations of EDTA-extractable (Tables 6, 7 and 8) and water soluble (Tables 9, 10 and 12) fractions of Pb in zeolite-amended soil/tailings compared to un-amended soil/tailings.

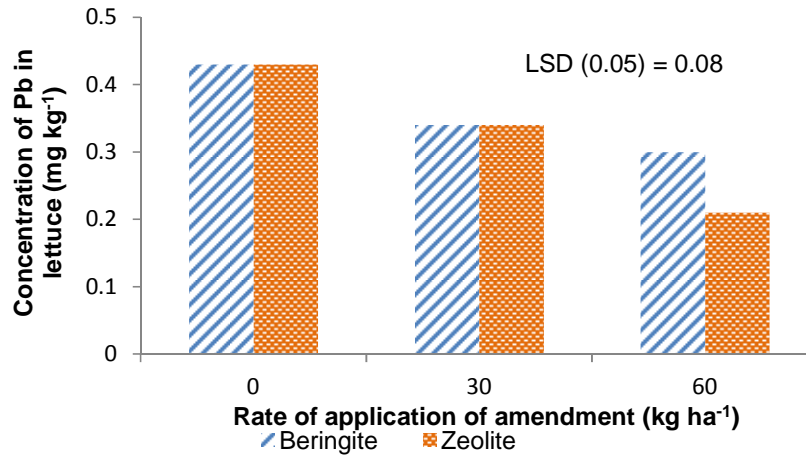


Fig. 1. Bioavailability of Pb in *Lactuca sativa* L. grown on amended non-mined soil

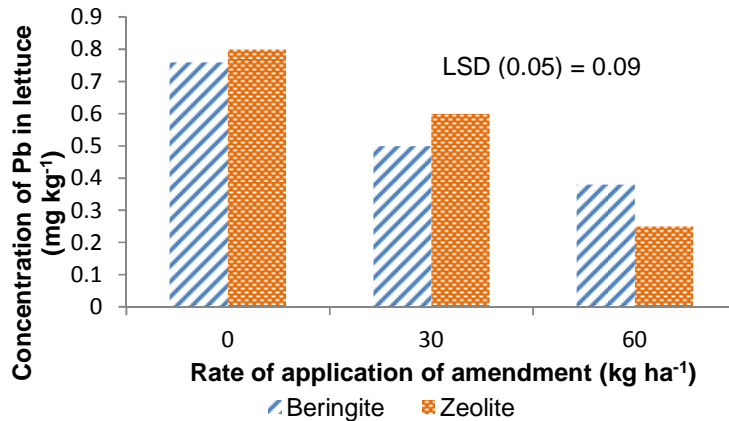
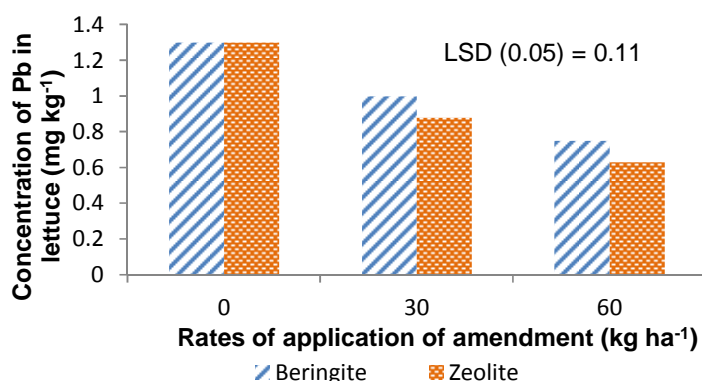


Fig. 2. Bioavailability of Pb in *Lactuca savita* L. grown on amended capped tailings



**Fig. 3. Bioavailability of Pb in *Lactuca sativa* L. grown on amended uncapped tailings**

The non-specific adsorption of Pb through cation exchange of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions that occur within negatively charged zeolite framework, as observed by [36,25], could explain further the reduced mobility of Lead in zeolite-amended soil/tailings. Beringite, on the other hand, exerted its influence on the immobilization and reduced bioavailability of Lead in lettuce through cation exchange and replacement of the high calcium and magnesium constituents of beringite [37,10]. The amendments applied at the rate of  $60 \text{ kg ha}^{-1}$  to soil/tailings could be arranged, in descending order, according to the concentrations of Pb in lettuce as follows: beringite > zeolite.

#### 4. CONCLUSION

The study revealed that beringite-amended non-mined, capped and uncapped tailings resulted in the more significant degree of alkalization. Zeolite was more effective in immobilizing Pb in soil/tailings. An increase in pH with the application of zeolite to soil/tailings resulted in reduced concentrations of EDTA-extractable Pb and water soluble Pb. The least concentration of lead occurred in lettuce harvested from zeolite-amended soil/tailings. Soil/tailings that yielded the least concentrations of Pb after amelioration with beringite and zeolite, respectively also produced the lowest contents of this trace element in lettuce harvested from these soil/tailings.

#### COMPETING INTERESTS

Author has declared that no competing interests exist.

#### REFERENCES

1. Ma LQ, Rao GN. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. *Journal of Environmental Quality*. 1997;26:788-794.
2. Chen ZN, Lee GJ, Lui JC. The effects of chemical remediation of cadmium and lead in contaminated soils. *Chemosphere*. 2000;41:235-242.
3. European Commission. Thematic Strategy for Soil Protection, Communication from the Commission to the Council, the European Parliament, the Economic and Social Committee and the Committee of the Regions. Brussels: European Commission; 2006.
4. European Commission. Impact assessment of the thematic strategy on soil protection. Communication from the Commission to the Council, the European Parliament, the economic and Social Committee and the committee of the regions. Brussels: European Commission; 2006.
5. Poggio L, Vrscaj B, Schulin R, Hepperle E, Marsan FA. Metal pollution and human bioaccessibility of topsoils in grugliasco (Italy). *Environmental Pollution*; 2008. Retrieved June 13 2009. Available:[www.elsevier.com/locate/envpol](http://www.elsevier.com/locate/envpol)
6. Oste LA, Lexmond TM, Van Riemsdijk WH. Metal immobilization in soils using synthetic zeolites. *Journal of Environmental Quality*. 2002;31:813-821.
7. Vangronsveld J, Cunningham SD. Metal contaminated soils. *In Situ* Inactivation and

- Phytoremediation. Georgia TX: RG. Landes Company; 1998.
8. Kertulis-Tartar GM, QML, Tu C, Chirenje T. Phytoremediation of an arsenic-contaminated site using *Pteris Vittata* L.: A two-year study. *International Journal of Phytoremediation*. 2006;8:311-322.
  9. Edwards R, Rebedea I, Lepp NW, Lovell AJ. An investigation into the mechanisms by which synthetic zeolites reduce labile metal concentrations in soils. *Environmental Geochemistry and Health*. 1999;21:157-173.
  10. Mench M, Vangronsveld J, Beckx C, Ruttens A. Progress in assisted natural remediation of an arsenic contaminated agricultural soil. *Environmental Pollution*. 2006;144:51-56.
  11. ADAS. The analysis of agricultural materials. Manual of methods. London: Agricultural Development and Advisory Services; 1986.
  12. Sabiene N, Brazuaskiene DM, Rimmer D. Determination of heavy metal mobile forms by different extraction methods. *Ekologija*. 2004;1:36-41.
  13. Nadia G, Zaghloul AM. Minimizing the human health hazard of lettuce cultivated in some heavy metals affected soils. *Australian Journal of Basic and Applied Sciences*. 2007;1(2):79-86.
  14. Grubben GJ, *Lactuca Sativa* L. In: GH. Grubben GH, editor. *Plant resources of tropical Africa 2. Vegetables*. Wageningen, Netherlands: PROTA Foundation/Backhuys Publishers/CTA. 2004;348-353.
  15. Genstat. *Genstat discovery (3<sup>rd</sup> edition) Genstat Procedure Library Release PL 15.2*. London, VSN International Ltd.
  16. Lombi E, Zhao F, Zhang G, Sun B, Fitz W. et al. *In situ* fixation of metals in soils using bauxite residue: Chemical Assessment. *Environmental Pollution*. 2002;118:435-443.
  17. Vangronsveld J, Ruttens A, Clijsters H. The use of cyclonic ashes of fluidized bed burning of coal mine refuse for long-term immobilization of metals in soils. In: KS. Sajwan KS, Alva AK, Keefer RF. editors. *Biogeochemistry of trace elements in coal and coal combustion by-products*. New York: Academic Publishing. 1999;223-233.
  18. Trgo M, Peric J, Vukojevic-Medvidovic N. Investigations of different kinetic models for zinc ions uptake by natural zeolite Tuff. *Journal of Environmental Management*. 2006;79:298-304.
  19. Van Herwijnen R, Hutchings TR, Al-Tabba A, Moffat AJ, Johns ML, Ouki SK. Remediation of contaminated soil with mineral-amended composts. *Environmental Pollution*. 2007;150:347-354.
  20. Panuccio MR, Sorgona A, Rizzo M, Cacco G. Cadmium Adsorption on vermiculite, zeolite and pumice: Batch experimental studies. *Journal of Environmental Management*. 2009;90(1):364-374.
  21. Glisic PM, Glisic IS, Milosevic NT. The effect of natural zeolites and organic fertilizers on the characteristics of degraded soils and yield of crops grown in Western Serbia. *Land Degradation & Development*. 2009;20:33-40.
  22. Shi WY, Shao HB, Li H, Shao MA, Du S. Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. *Journal of Hazardous Materials*. 2009;170:1-6.
  23. Mohammed MM. Heat capacities, phase transitions and structural properties of cation-exchanged H-mordenite zeolites. *Thermochim. Acta*. 2002;387:121-130.
  24. Garau G, Castaldi P, Santona L, Deiana P, Melis P. Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic populations and enzyme activities in a contaminated soil. *Geoderma*. 2007;142:47-57.
  25. Peric J, Trgo M, Vukojevic-Medvidovic N. Removal of zinc, copper and lead by natural zeolite - A comparison of Adsorption Isotherms. *Water Res*. 2004; 38(7):1893-1899.
  26. Adriano DC. *Trace elements in terrestrial environments: Biogeochemistry, bioavailability and risks of metals (2nd ed.)*. New York, NY: Springer; 2001.
  27. Kabata-Pendias A. *Trace elements in soils and plants (3rd ed.)*. Boca raton, FL.: CRC Press; 2001.
  28. Farrell M, Jones DL. Use of composts in the remediation of heavy metal contaminated soil. *Journal of Hazardous Material*. 2000;175:575-582.
  29. United States Environmental Protection Agency. *Behavior of metals in soils*. McLean JE, Bledsoe BE, editors. EPA Ground Water Issue, EPA/540/S-92/018. 1992;1-25.

30. McBride MB. Environmental soil chemistry. New York: Oxford University Press; 1994.
31. Castaldi P, Santona L, Melis P. Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth. Chemosphere. 2005;6:365-371.
32. Nissen LR, Lepp NW, Edwards R. Synthetic zeolites as amendments for sewage sludge-based compost. Chemosphere. 2000;41:265-269.
33. Samara CP, Misaelides P, Tsalev D, Anousis I, Kouli T, Tzis M. Trace elements distribution in vegetables grown in the industrial area of Thessaloniki, Greece-Frasenius. Environmental Bulletin. 1992;1: 577-582.
34. Malaysian Food Act. Food Act (Act 281) and regulations. Malaysia: The Commissioner of Law Review Revision; 1983.
35. FAO/WHO. Expert Committee on Food Additive, summary and conclusions, 53<sup>rd</sup> Meeting. Rome: FAO; 1999.
36. Stolz J, Yang P, Ambruster T. Cd-exchanged heulandite: Symmetry lowering and site preference. Micropor. Mesopor. Mater. 2000;37(1-2):233-242.
37. Boisson J, Ruttens A, Mench M, Vangronsveld J. Immobilization of trace metals and arsenic by different soil additives: Evaluation by means of chemical extractions. Communication in Soil Science and Plant Analysis. 1999;30:365-387.

© 2017 Osei; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*  
*The peer review history for this paper can be accessed here:*  
<http://sciencedomain.org/review-history/17624>