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Immobilization of lead in a Korean military shooting range soil using eggshell waste: An integrated mechanistic approach

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ABSTRACT

This study evaluated the effectiveness of eggshell and calcined eggshell on lead (Pb) immobilization in a shooting range soil. Destructive and non-destructive analytical techniques were employed to determine the mechanism of Pb immobilization. The 5% additions of eggshell and calcined eggshell significantly decreased the TCLP-Pb concentration by 68.8% due mainly to increasing soil pH. Eggshell and calcined-eggshell amendments decreased the exchangeable Pb fraction to ~1% of the total Pb in the soil, while the carbonate-associated Pb fraction was increased to 40.0–47.1% at >15% application rates. The thermodynamic modeling on Pb speciation in the soil solution predicted the precipitation of Pb-hydroxide [$Pb(OH)_2$] in soils amended with eggshell and calcined eggshell. The SEM-EDS, XAFS and elemental dot mapping revealed that Pb in soil amended with calcined eggshell was associated with Si and Ca, and may be immobilized by entrapping into calcium-silicate-hydrate. Comparatively, in the soil amended with eggshell, Pb was immobilized via formation of Pb-hydroxide or lanarkite [$Pb_2O(SO_4)$]. Applications of amendments increased activities of alkaline phosphatase up to 3.7 times greater than in the control soil. The use of eggshell amendments may have potential as an integrated remediation strategy that enables Pb immobilization and soil biological restoration in shooting range soils.

1. Introduction

Soils contaminated with toxic metals derived from anthropogenic activities are a worldwide problem [1]. Shooting ranges are the second largest source of Pb contamination ranging from 10 to 60,000 tons of annual depositions in different countries [2]. There have been several investigations regarding remediation studies of Pb-contaminated shooting range soil, with the main emphasis being on immobilization technologies. The mechanism of immobilization is based on the formation of inert and highly insoluble species of metals using soil amendments [3]. One of the widely accepted Pb immobilization methods is the phosphate application that relies on the transformation of labile Pb species into more thermodynamically stable species such as chloropyromorphite ($Pb_5(PO_4)_3Cl$). However, limitations to the use of phosphate applications for Pb immobilization have been investigated by a study of Chrysochoou et al. [4]. The reaction of Pb immobilization by phosphorus (P) is pH dependent since the dissolution kinetics of Pb and P in the soil is optimized at pH ≤ 5. Alternatively, acid amendments such as phosphoric acid and phosphate fertilizers have been used to immobilize Pb by P via chloropyromorphite formations [5–7]. Chrysochoou et al. [4] demonstrated that an excessive amount of P up to 3-fold higher than the stoichiometric amount is required for pyromorphite formation in soils. A study of Hashimoto et al. [8] reported that about 70% of Pb species were not immobilized as a form of chloropyromorphite, and the additional supply of P amendment led to only a slight increase in chloropyromorphite formations. Another limitation of Pb immobilization by P is the potential risk of eutrophication associated with the leaching of P in response to high application rates [9]. Considering the practical use of P-containing-amendments for Pb immobilization, the proper amendment selection would be required to reduce a secondary pollution leading to high immobilization efficiency.

Naturally occurring waste materials have been recognized as cost-effective amendments and may be alternatives to the conventional P amendments for immobilizing Pb in the shooting range soils. For soil Pb immobilization, however, only few studies have investigated the use of natural waste materials such as plant residues [10], eggshell and oyster shell [11–14], and poultry litter [8,15]. About 250,000 tons of eggshell waste is generated from the food processing industries worldwide every year [16]. Ok et al. [11] used the eggshell waste as an immobilizing agent and

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demonstrated that the addition of 5% eggshell waste into soils reduced 43.1% Pb concentration extracted by 0.1 M HCl. Because the chemical properties of eggshell waste are similar to those of calcite ($CaCO_3$) [11,17], the mechanisms in Pb immobilization are basically the same. The chemical composition of eggshell waste can be altered to CaO by the calcination that is generally more reactive than non-calcined status [13]. However, the exact mechanisms of Pb immobilization using these waste materials remained unclear [11–13].

This study investigated the effects of eggshell waste on Pb immobilization in the shooting range soils. With the eggshell waste application into those soils, the Pb immobilization was evaluated based on the Pb solubility using the toxicity characteristics leaching procedure (TCLP) and sequential extraction. Thermodynamic equilibrium modeling was used to assess Pb speciation in the aqueous phase. Synchrotoron-based X-ray absorption fine structure (XAFS) spectroscopy was also employed to investigate the Pb speciation in the soil solid phases. The XAFS spectroscopy is known as one of the most powerful tools to elucidate the mechanisms of metal immobilization in soils [18,19]. In addition, the soil enzyme activities were determined to evaluate the biological toxicity of the subjected amendments.

2. Materials and methods

2.1. Soil and amendments

Soil was collected from a shooting range at Icheon located in the southeastern part of Gyeonggi Province, Korea. The soil collected from the backstop was air dried and the bullet fragments were manually removed. The soil was then passed through a 2-mm sieve and characterized for physicochemical properties. The pH and electrical conductivity (EC) were measured at a 1:5 soil/water solution ratio and the soil particle size distribution was measured using the hydrometer method [20]. Soil organic matter (OM) was measured by the Walkley-Black method [21]. Soil subsamples were digested according to the United States Environmental Protection Agency (USEPA) method 3051A and the total contents of Pb, Cu, Sb and Ni were analyzed using an inductively coupled plasma (ICP-OES) spectrometer (Optima 7300 DV, Perkin-Elmer, USA).

Eggshell wastes, used as the soil amendment, were collected from the local restaurants in Gangwon Province, Korea. The eggshells were washed several times with hot water to remove impurities and oven-dried at 105 °C for three days. Completely dried eggshells were ground to pass through a 1-mm sieve according to the method described by Ok et al. [11]. A portion of the eggshell powder was then calcined in a furnace (Carbolite, Sheffield, UK) at 900 °C for 6 h [13]. The eggshell amendments were digested according to the USEPA method 3051A and trace elements were analyzed by ICP-OES. The elemental composition of the eggshells and calcined eggshells was also determined by X-ray fluorescence (XRF) spectrometry (XRF-1700, Shimadzu, Japan) using a scintillation counter and a flow proportional counter to measure heavy and light elements in these amendments, respectively. Additionally, the mineralogical composition of the amendments was determined by X-ray diffraction (XRD) spectrometry (X'pert PRO MPD, PANalytical, Netherlands) using a graphite monochromator and Cu Kα radiation. Powder diffraction file from the International Centre for Diffraction Database (ICDD) was used to identify minerals in each amendment [22].

2.2. Incubation experiment

A soil incubation experiment was conducted to assess the effects of eggshell waste and calcined eggshell waste on Pb immobilization and soil quality. Analytical grade pure $CaCO_3$ and CaO were also applied as soil amendments to compare those potential alternatives of eggshell and calcined eggshell. All treatments were applied to the soil on a weight basis at 0, 2.5, 5, 10, 15, 20, 25 and 30%. Specifically, 100 g of each soil sample was mixed thoroughly with the subjected application rate of each amendment in a high density polyethylene bottle. During incubation, the soil moisture content was maintained at 70% of water holding capacity. Incubation was conducted at room temperature in the dark for 28 days. After incubation, each incubated soil was air-dried for 72 h and stored in air-tight plastic bottles for further analysis. The soil aggregate stability was then measured without disturbing the soil using a wet sieving apparatus (Eijkelkamp, Netherlands).

2.3. Extractions

Immobilization of Pb by the addition of eggshell was evaluated using the TCLP method [23] that is recommended by USEPA and has been widely used for the toxicity characteristics of shooting range soils [24,25]. Lead in soils was extracted with a 1:20 ratio of soil/extraction fluid #1 (pH 4.93) or #2 (pH 2.88). Then, the solution was inverted for 18 h at 30 rpm and filtered through glass fiber filters. The pH and Pb concentration in the TCLP extractant (TCLP-pH and TCLP-Pb) were determined using a pH electrode and ICP-OES, respectively.

For sequential extraction test, the five fractions of Pb, including exchangeable, carbonate bound, Fe/Mn bound, organic bound and residual phases, in the amended and the unamended soils were measured according to the method by Tessier et al. [26]. All extracted solutions at each step were filtered and analyzed using ICP-OES.

2.4. Thermodynamic modeling

Theoretically possible precipitates of Pb in the amended and the unamended soils were predicted in a thermodynamic equilibrium model using Visual MINTEQ ver. 2.6 [27]. To determine the ionic concentrations in solution, 20 mL of 0.01 M $NaNO_3$ was added to 1.0 g of soil and then shaken for 24 h. The filtrate using a 0.45-μm filter paper was analyzed for anions (SO_4, PO_4 and Cl) by ion chromatography (IC) (Metrohm Compact IC-861, Switzerland), and for cations (Pb, Mg, Ca, K, Al and Fe) by ICP-OES. The dissolved organic carbon (DOC) concentrations were also determined using a total organic carbon (TOC) analyzer (5000A, Shimadzu, Japan). The concentrations of these ions and DOC were applied as input components in the visual MINTEQ software at 25 °C and $10^{-3.4}$ atm CO_2 pressure [18]. The model predicted a saturation index (SI) of solid phase Pb based on a database of equilibrium constants and thermodynamic reactions. If the SI value is between −1 and 0 ($-1 < SI < 0$), the solution is saturated with respect to the solid; if $SI < -1$, the solution is undersaturated with respect to the solid; and if $SI > 0$, the solution is supersaturated with respect to the solid.

2.5. Scanning electron microscopy and elemental dot mapping

To investigate the morphological and the elemental changes in soil particles, scanning electron microscopy (SEM) and elemental dot mapping were conducted using a SEM instrument (Hitachi S-4800, Japan) equipped with an ISIS 310 EDX system. The X-ray dot maps are often used to illustrate the distribution of specific elements within a specified area. Air-dried soil samples were placed on double-sided gold coated carbon tape and the images were constructed from a 200-μm area in scanning mode. The distributions of Al, Si, Ca and Pb on the soil surface were mapped according to the method description by Moon et al. [28].

Table 1
Selected physical and chemical properties of soil and amendments.

Soil/amendments	pH[a]	Texture	OM ($g\,kg^{-1}$)[b]	Total Cu ($mg\,kg^{-1}$)	Total Pb ($mg\,kg^{-1}$)	Total Sb ($mg\,kg^{-1}$)	Total Ni ($mg\,kg^{-1}$)
Shooting range	6.66	Sandy loam	10.1	225	4626	23.0	31.1
Eggshell	9.76		23.7	N.D.	N.D.	N.D.	N.D.
Calcined eggshell	12.40		N.D.[c]	0.27	N.D.	N.D.	N.D.

[a] Determined in 1:5 soil:water.
[b] Organic matter.
[c] Not detected.

2.6. X-ray absorption fine structure spectroscopy

For the analysis of soil Pb species, the XAFS spectroscopy was used at beamline BL7C1, the Pohang Accelerator Laboratory (PAL), Korea. Dried samples of the unamended soils and the amended soils with 30% eggshell and 30% calcined eggshell were ground using an agate mortar and pestle and then were passed through a 100-μm sieve. The homogenized samples were packed in a polyethylene bag with a uniform thickness and were sealed with a transparent adhesive tape [28]. The XAFS data were collected in a fluorescence mode at ambient temperature across the Pb L_{III} absorption edge at 13035 eV using a Si(111) double crystal monochromator and a ring current of 120–170 mA. Among our reference library for Pb-XAFS spectra, the selected reference standards were used for the data analysis, including Pb oxide (PbO), cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), Pb-hydroxide ($Pb(OH)_2$), anglesite ($PbSO_4$), Pb-phosphate ($Pb_3(PO_4)_2$), Pb-acetate ($(CH_3COO)_2Pb$), Pb-silicate ($PbSiO_3$), and Pb sorbed to fulvic acid, ferrihydrite, kaolinite and birnessite. These standards were analyzed at beamline BL01B1, SPring-8 in Hyogo, Japan [24]. The Athena software program ver. 0.8.059 was used for the XAFS data analysis [29]. The data were background corrected by fitting a first order polynomial equation to the pre-edge region and then subtracting this equation from the spectral curve. The absorption intensity was subsequently normalized to unity by dividing the magnitude of the spectra from the change of intensity at an absorption edge. A spline function was used to isolate the scattering portion of the spectra yielding the $\chi(k)$ function, which was derived by subtracting the spline function from the experimental spectra. The $\chi(k)$ function was weighted for k^2 and the k-space was used up to 10 $Å^{-1}$ [30].

2.7. Soil enzyme activity

To assess the effects of eggshell and calcined eggshell waste on soil quality, the enzyme activities of alkaline phosphatase, β-glucosidase and dehydrogenase were employed according to the methods described by Tabatabai [31]. The alkaline phosphatase and β-glucosidase activities were determined based on colorimetric estimation of *p*-nitrophenol using a UV spectrophotometer (UV-1800, Shimadzu, Japan) at a wavelength of 410 nm. In addition, the dehydrogenase activity was determined via the colorimetric determination of triphenyl formazan (TPF) produced by the soil microorganisms at a wavelength of 485 nm.

2.8. Statistical analysis

The Statistical Analysis System (SAS) was used for all statistical analysis (SAS ver. 9.1, Cary, NC, USA). Means of four replicates were subjected to one way ANOVA with Tukey's honestly significant difference (HSD) test at a 0.05 significance level. Pearson's correlation coefficients (r) were also computed.

3. Results and discussion

3.1. Soil and amendments characteristics

Table 1 shows the physicochemical properties of the soil and the amendments. The soil was sandy loam with a pH value of 6.66. The total concentration of Pb in the soil was 6.6 times higher than the Korean hazard standard of Pb (<700 $mg\,kg^{-1}$) for military sites [32]. The major element of both eggshell and calcined eggshell was Ca, indicating 47.23 and 93.23% of CaO, respectively (Table 2). The XRD analysis showed the abundance of $CaCO_3$ in the eggshell and CaO in the calcined eggshell (Supplementary data, Fig. S1). The eggshell, which is composed of more than 90% of $CaCO_3$ was gradually dissociated and transformed to a more reactive form of CaO via calcination process [11]. Both eggshell and calcined eggshell amendments were found to be alkaline with pH values of 9.76 and 12.40, respectively (Table 1). The values of pH were similar to those of pure $CaCO_3$ and CaO, indicating the pH values of 9.73 and 12.64, respectively. The OM in the eggshells was 23.7 $g\,kg^{-1}$, while it was not detected in the calcined eggshell. The amendments did not contain toxic elements and were confirmed to be safe for use.

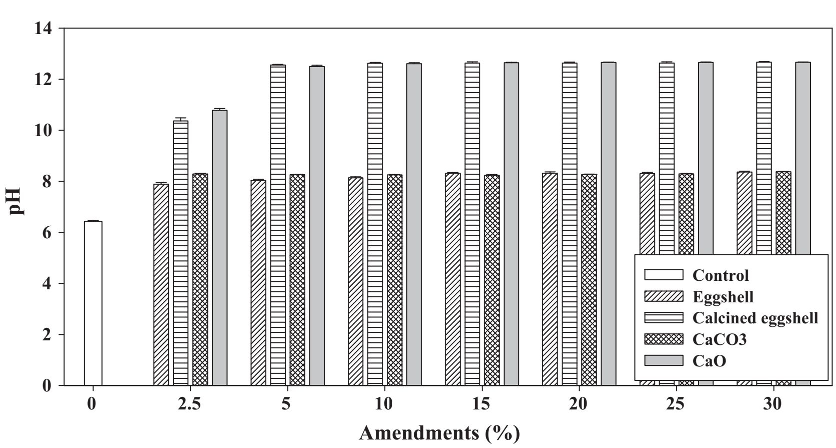

Fig. 1. Changes in soil pH as a function of application rates of different soil amendments including the eggshell, the calcined eggshell, $CaCO_3$ and CaO, along with no addition.

Table 2
Elemental composition (wt%) of eggshell and calcined eggshell.

Amendments	CaO	MgO	P_2O_5	K_2O	SiO_2	Fe_2O_3	Na_2O	TiO_2	MnO	Al_2O_3	LOI[a]
Eggshell	47.23	6.79	0.33	0.07	0.13	0.04	0.51	0.003	0.003	0.14	44.8
Calcined eggshell	93.23	5.07	0.20	0.13	0.16	0.07	0.05	0.03	0.02	0.02	0.62

[a] Loss on ignition.

The amendments led to a significant increase in pH when applied at a 2.5% rate (Fig. 1). The additions of eggshell and calcined eggshell highly increased the soil pH compared to the unamended soil. An increase of soil pH by these amendments was associated with their chemical composition. Calcined eggshells enriched with CaO resulted in a higher pH value than the eggshell that was primarily composed of $CaCO_3$. Pure $CaCO_3$ and CaO also increased the soil pH similar to the eggshell and calcined eggshell amendments, respectively. Increasing the application rate of these amendments greater than 5% did not lead to significant increases in the soil pH due to pH buffering capacity of the soil [33].

3.2. Lead mobility and fractionation

The TCLP-Pb in the unamended soil was 7.9 times higher than the USEPA regulatory level of 5 mg L^{-1} (Fig. 2). The applications of eggshell amendment at higher rates were more effective to reduce the TCLP-Pb concentrations. A sharp decrease of the TCLP-Pb concentration by 68.8% for the unamended soil was observed in response to the application of the eggshell amendment at 5% (Fig. 2a). However, the applications of the eggshell amendment greater than 10% did not further reduce the TCLP-Pb concentration. A similar trend in the TCLP-Pb concentrations was observed in the soil amended with $CaCO_3$ (Fig. 2b). Application of $CaCO_3$ decreased the TCLP-Pb concentration more effectively than that of eggshell, and the TCLP-Pb concentration in the soil amended with 15% $CaCO_3$ reduced below the USEPA regulatory level of 5 mg L^{-1}. Addition of calcined eggshell amendment had a similar reduction in the TCLP-Pb concentration with CaO (Fig. 2c and d). Additionally, the applications of >20% calcined eggshell and >15% CaO reduced the TCLP-Pb concentrations below the USEPA regulatory level of 5 mg L^{-1}. A negative correlation was observed between TCLP-Pb concentrations and TCLP-pH values ($r = -0.948$ at $p < 0.001$ for eggshell; $r = -0.742$ at $p < 0.05$ for calcined eggshell), indicating that the increase in soil pH in response to the amendment additions led to the decrease in solubility of Pb. A similar relationship between TCLP-Pb and TCLP-pH was observed in Hashimoto et al. [24] and Cao et al. [34].

The effects of eggshell and calcined eggshell on Pb immobilization in the shooting range soil were similar to those of $CaCO_3$ and CaO, respectively. The increased soil pH by $CaCO_3$ and CaO additions may be a primary factor of metal immobilization by increasing

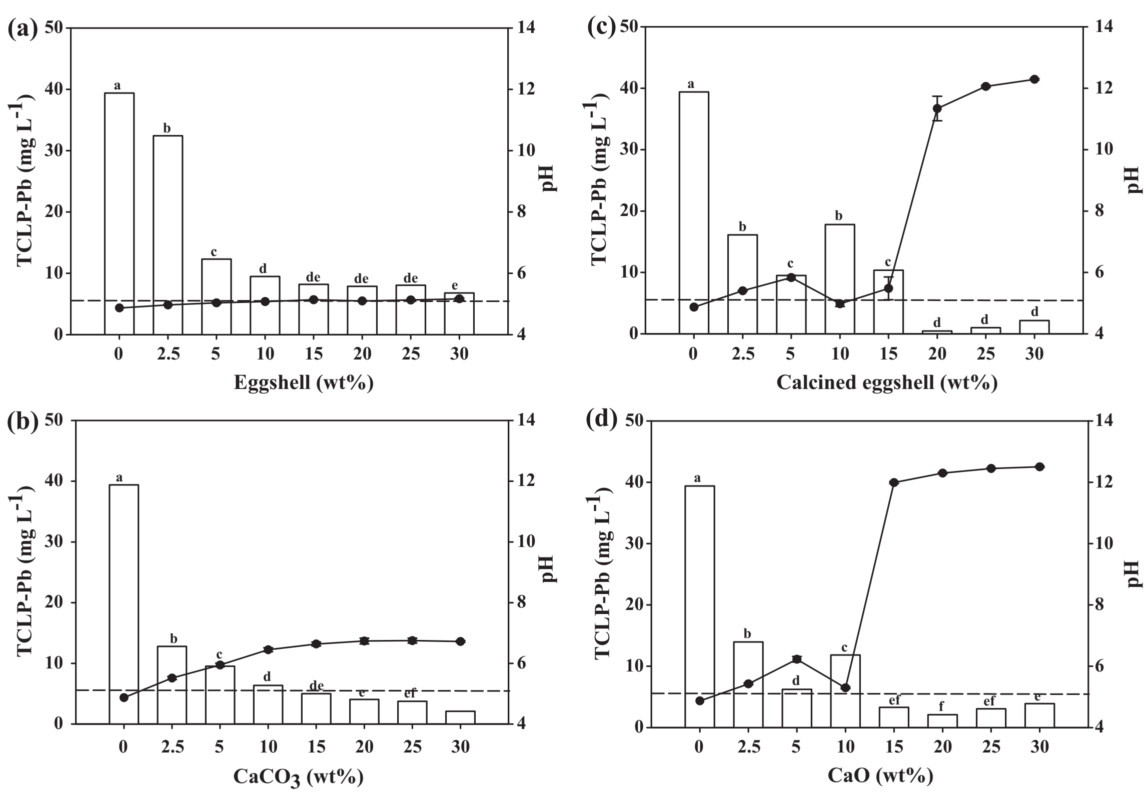

Fig. 2. Toxicity characteristics leaching procedure (TCLP) extracted Pb and pH of leachate in the soils amended with (a) eggshell waste, (b) $CaCO_3$, (c) calcined eggshell waste and (d) CaO. Bars represent the Pb concentration and the closed dots represent the changes of soil pH. The horizontal dashed line shows the Pb regulation of 5 mg L^{-1} from the United States Environment Protection Agency (USEPA). Same letters above each bar indicate no difference at a 0.05 significance level of the Tukey's studentized range test.

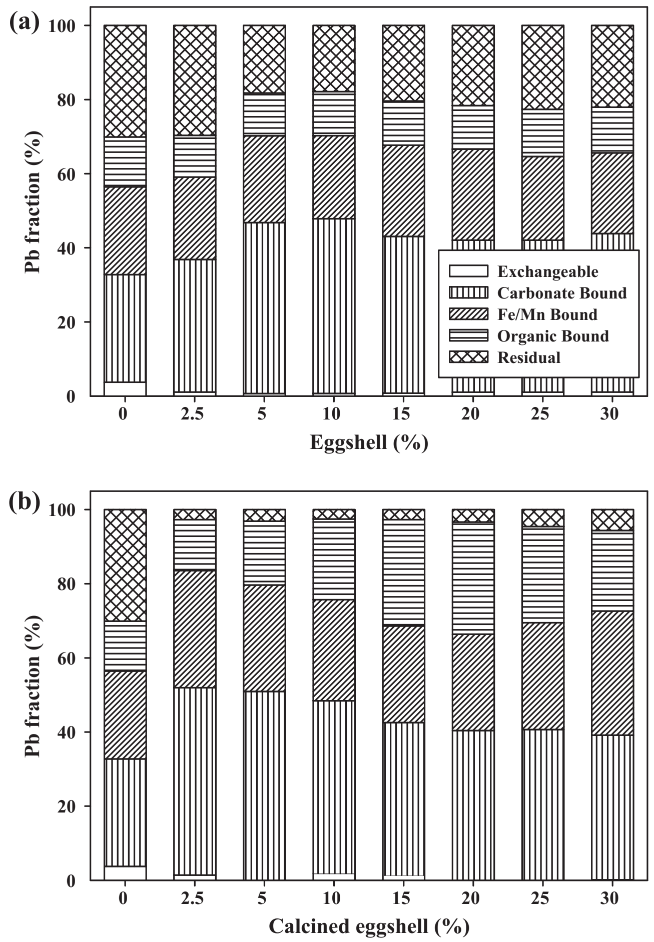

Fig. 3. Lead fractionation in soils amended with (a) eggshell and (b) calcined eggshell as measured by sequential extraction.

negatively charged sites on soil particles, ion exchange, precipitation of metal hydroxides/oxides, and coprecipitation with carbonates and soil minerals [11]. In comparison of eggshell amendment, the efficiency of calcined eggshell amendment for reducing TCLP-Pb concentration was higher due to the increased ion exchange capacity between Pb and Ca (Supplementary data, Table S1). Reactive CaO in the calcined eggshell can be dissociated rapidly into Ca ions, thereby providing more exchangeable sites for Pb than non-calcined eggshell [13]. Moreover, the surface adsorption of Pb with the porous structures of calcined eggshell can be involved in the entire mechanism of Pb immobilization [35].

Pb fractionation of soils amended with the eggshell and the calcined eggshell is shown in Fig. 3. The most predominant Pb fractions were carbonate-associated and residual phases, occupying 29.0% of the total Pb in the unamended soil. The soil contained the Pb fractions associated with Fe/Mn oxides (23.7%), and with organic substances (13.5%) and a minor amount of Pb was present in the exchangeable fraction (3.7%). The distribution of Pb fractions in the soil was notably modified by adding the amendments. Both the amendments of eggshell and calcined eggshell decreased the exchangeable Pb fraction to ~1% of the total Pb in the soil, while the carbonate-associated Pb fraction was increased to 40.0–47.1% at >15% application rates. In contrast to the soil amended with the eggshell, an increase of Pb associated with the oxidizable fraction or with the reducible fraction was found in the soil amended with the calcined eggshell. These changes in Pb fractions were not observed in the soil amended with eggshell and may reside in the difference of chemical and mineralogical properties of amendments. The calcined eggshell amendment with high alkalinity and solubility dissolved the pre-existing Pb in the residual phase, and the redistribution of Pb in humus-associated and Fe/Mn mineral phases was induced. The differences in Pb fractionations between eggshell and calcined eggshell amendments suggested that these amendments decreased the available Pb fractions in soil owing to the different immobilization mechanisms.

3.3. Thermodynamic modeling

Table 3 shows the saturation index (SI) in a 0.01 M $NaNO_3$ aqueous system for the amended and unamended soils using a thermodynamic equilibrium model. All Pb minerals in the unamended soil were undersaturated as indicated by an SI value of <−1. The model predicted the presence of Pb-hydroxide ($Pb(OH)_2$) precipitate in the soils amended with both eggshell and calcined eggshell amendments. Ok et al. [13] also showed that the formation of hardly soluble $Pb(OH)_2$ may be the mechanism of Pb immobilization in a contaminated soil with the lime-based amendments. Greater SI values of $Pb(OH)_2$ in the soils amended with the calcined eggshell than in those amended with the eggshell were due to a pH increase. Lanarkite ($Pb_2O(SO_4)$) was also predicted as possible precipitate in the soil amended with eggshell and indicated SI values of 0.517 and 0.127 for 10 and 30% application rates, respectively. Contrarily, the lanarkite was not predicted in the soil amended with calcined eggshell, likely due to the high soil pH. The lanarkite has been known as a stable mineral at pH values of 8–11 [36,37]; thus, it was only observed in the eggshell amended soil having a pH value of ~8.3. In addition to Pb minerals, the model also predicted gibbsite ($Al(OH)_3$), diaspore ($AlO(OH)$) and ettringite ($Ca_6(Al_2SO_4)_3(OH)_{12}\cdot 26H_2O$) in the soils amended with eggshell and calcined eggshell. These mineral precipitates were not predicted in the unamended soil. Gibbsite and diaspore are well known to adsorb Pb [38,39] and ettringite can encapsulate Pb [34] or replace its Ca with Pb [40], leading to Pb immobilization. The prediction of these Al and Ca precipitates in aqueous phases may possibly provide the Pb immobilization mechanism in the soils amended with eggshell and calcined eggshell.

3.4. SEM/EDS and elemental dot maps

The microstructural changes and the Pb distribution in soils were determined using a SEM with an EDX (Fig. 4). This figure shows the soils amended with eggshell and calcined eggshell at the same application rate of 30%. Results from the EDX data indicated that Si and Al were the major elements on the soil surface amended with eggshell (Fig. 4a). In the soil amended with calcined eggshell, Ca was present as a dominant element along with Si and Al (Fig. 4b). The higher proportion of Ca in soils amended with calcined eggshell may result from the quick release of Ca from CaO compared to soils amended with eggshell (Supplementary data, Table S1). Elemental dot maps indicated Pb associated with Al, Si and Ca in the soil amended with calcined eggshell, whereas the association of Pb with Ca was not observed in the soil amended with eggshell. These findings corresponded to the results of the thermodynamic equilibrium model (Table 3), which predicted the precipitation of ettringite (containing Ca and Al) in the soil amended with calcined eggshell, and gibbsite and diaspore (containing Al) in the soil amended with eggshell. Application of calcined eggshell increased soil pH to 12.6, at which the formation of cementitious hydrates such as calcium-silicate-hydrate (CSH) and calcium-aluminate-hydrate (CAH) occur more favorably than in neutral pH ranges [41]. These hydrate compounds form a hard and relatively impermeable layer in the soil, thus entrapping the metals in soil particles and preventing them from downward leaching. Therefore, Pb stabilization by calcined eggshell applications may be attributable to the incorporation of

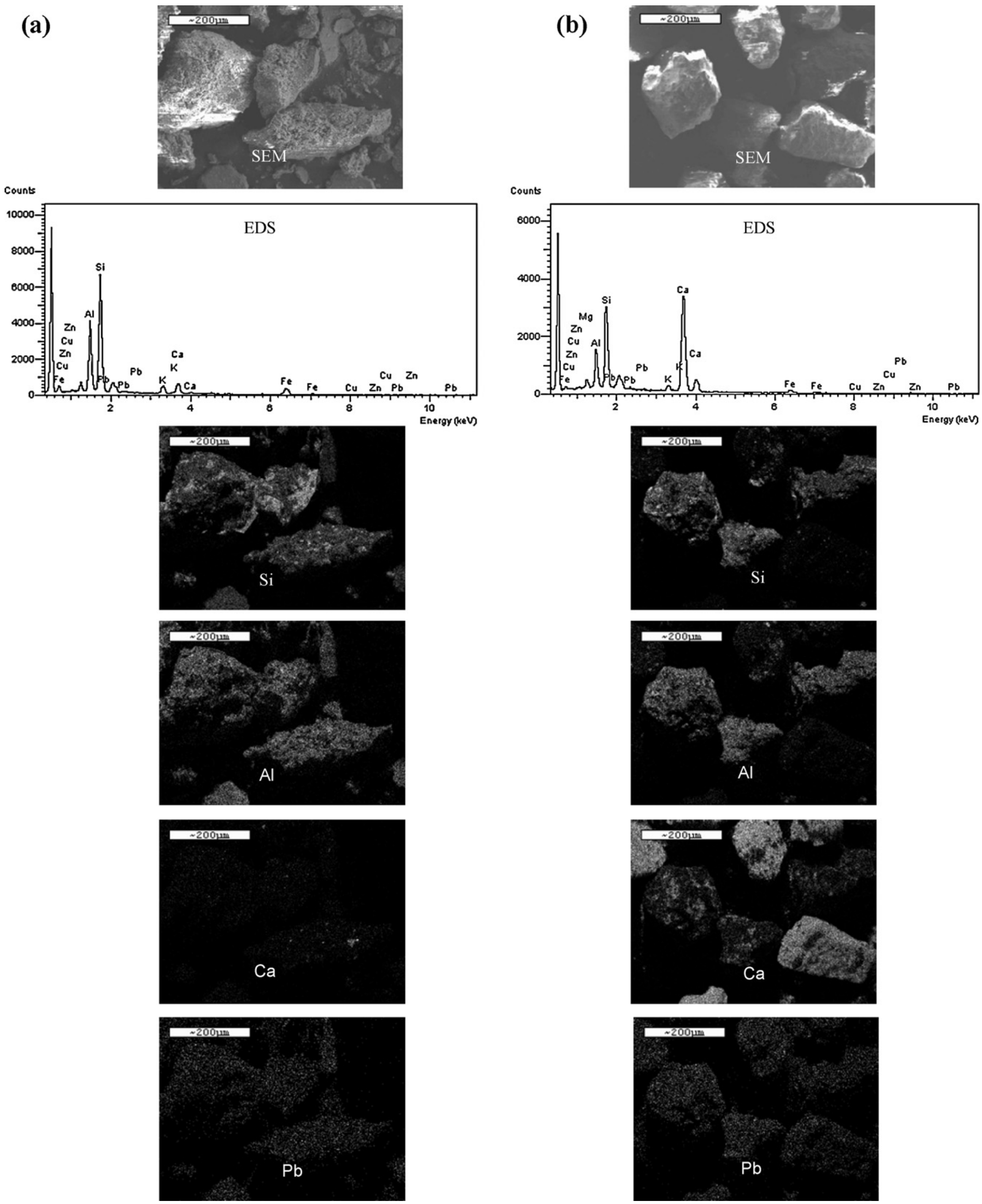

Fig. 4. Scanning electron microscopy (SEM) images, energy dispersive spectra (EDS) and elemental dot maps (Si, Al, Ca and Pb) of soils amended with (a) 30% eggshell and (b) 30% calcined eggshell.

Pb into CSH and CAH phases as supported by elemental dot maps. These results are in agreement with studies of Cao et al. [34] and Badreddine et al. [42] reporting Pb stabilization by the CSH phase determined by X-ray powder diffraction (XRPD) and SEM-EDS analyses.

3.5. Lead L_{III} XAFS spectroscopy

X-ray absorption near edge structure (XANES) spectra of Pb from selected standards and soil samples are shown in Fig. 5. The Pb-XANES spectrum for the soils amended with eggshell and

Table 3
Precipitation of minerals in a 0.01 M $NaNO_3$ aqueous system of unamended and amended soil as predicted by the visual MINTEQ thermodynamic model.

Mineral	Formula	Saturation index (SI)				
		Eggshell			Calcined eggshell	
		0%	10%	30%	10%	30%
Pb-hydroxide	$Pb(OH)_2$	−1.379	1.878	1.886	4.086	4.136
Lanarkite	$Pb_2O(SO_4)$	−2.624	0.517	0.127	−5.028	−4.570
Gibbsite	$Al(OH)_3$	−10.619	2.898	2.855	−0.191	−0.684
Diaspore	AlO(OH)	−9.752	3.765	3.722	0.676	0.183
Ettringite	$Ca_6(Al_2SO_4)_3(OH)_{12}\cdot 26H_2O$	−51.331	−10.523	−9.178	13.086	11.379

calcined eggshell had a similar curvature to that of the unamended soil, but these spectra were visually distinguishable. The difference in XANES spectra indicated that the addition of the amendments altered Pb species in the soils. However, the XANES spectra for standard Pb compounds were featureless and did not allow the determination of possible Pb speciation in the soil.

To elucidate the Pb speciation and its immobilizing mechanism, the EXAFS spectra of the standards and soil Pb were analyzed as shown in Fig. 6. Visual inspection of the Pb-EXAFS spectra of the soil samples suggested the rapid deterioration above 7 Å^{-1}. Previous studies showed that the Pb-EXAFS spectra tend to deteriorate above 7–8 Å^{-1} owing to the highly distorted states of the partially solvated Pb ions and the amplitude reduction effects of self-absorption [43]. A significant deterioration of the Pb-EXAFS spectra occurred in either soils unamended or amended with eggshell and calcined eggshell. A rapid distortion in our EXAFS data hindered the transformation of the spectra to generate radial structure function and induced uncertainty with numerical approaches. For this reason, the spectra were interpreted semi-quantitatively by examining the phase of the electronic wave rather than conducting numerical simulations using the modeled compounds.

The visual differences in fine Pb structures between the soils amended with eggshell and calcined eggshell, determined by the Pb-EXAFS spectra, suggests that the mechanism of Pb

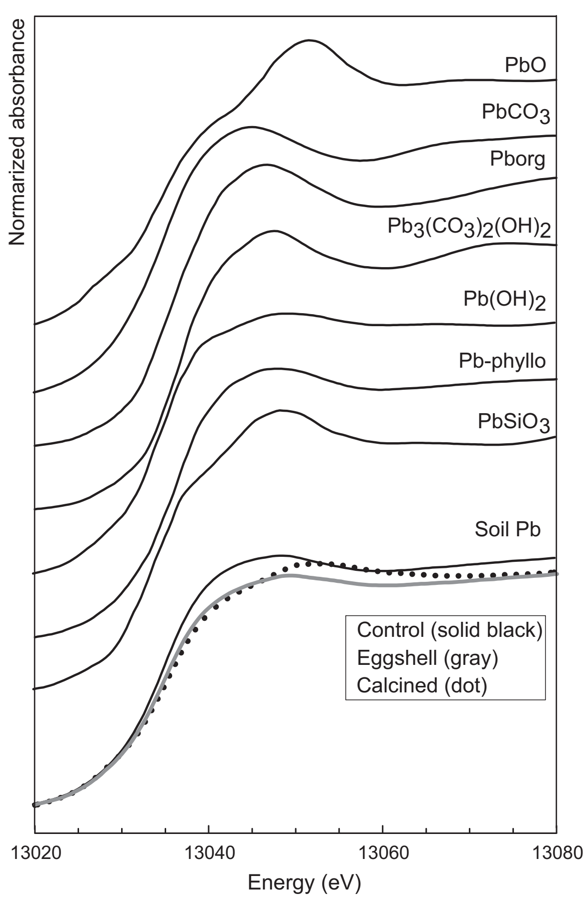

Fig. 5. Normalized Pb-L$_{III}$ edge XANES spectra of reference standards and selected soil samples (control, unamended soil; eggshell, soil amended with eggshell; calcined, soil amended with calcined eggshell; Pborg, Pb sorbed to organic matter; Pb-phyllo, Pb sorbed to phyllosilicates).

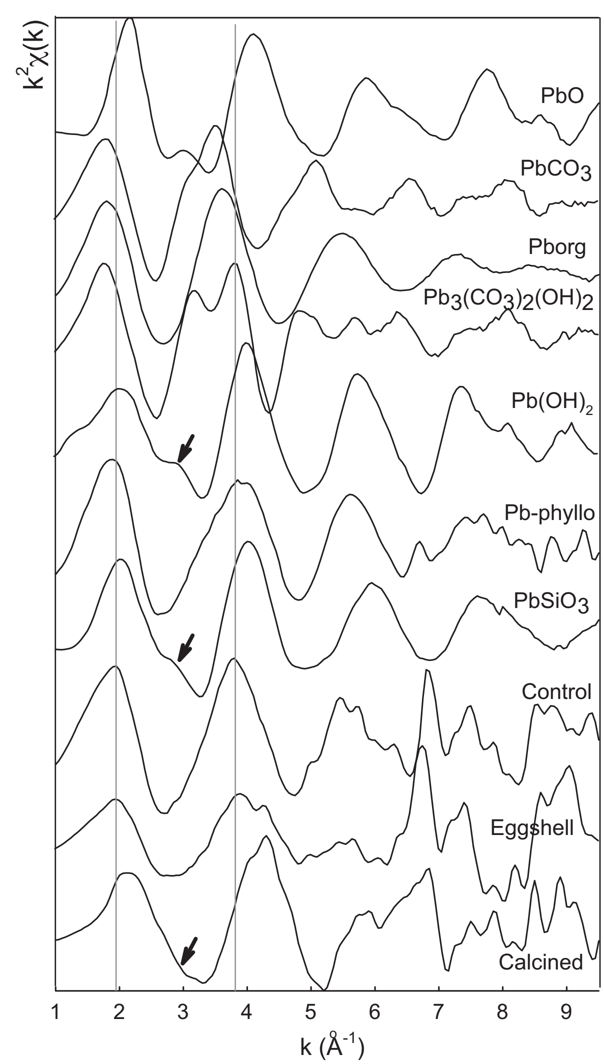

Fig. 6. k^2-weighted EXAFS spectra of selected soil samples and reference Pb standards (control, unamended soil; eggshell, soil amended with eggshell; calcined, soil amended with calcined eggshell; Pborg, Pb sorbed to organic matter; Pb-phyllo, Pb sorbed to phyllosilicates). Arrows indicate the spectral modifications caused by the calcined eggshell amendment corresponding to that in $PbSiO_3$ and Pb-hydroxide.

Table 4
Enzyme activities in soils amended with eggshell and calcined eggshell at different application rates. Means with the same letters are not significantly different using Tukey's studentized range test.

Amendments	Application (%)	Enzyme activities		
		Alkaline phosphatase (mg PNP kg^{-1} h^{-1})	β-glucosidase (mg PNP kg^{-1} h^{-1})	Dehydrogenase (mg TPF kg^{-1} h^{-1})
Eggshell	0	29.50 f	12.60 a	N.D.[a]
	2.5	45.44 ef	10.90 b	N.D.
	5	61.98 de	10.67 b	N.D.
	10	75.46 cd	10.78 b	N.D.
	15	82.07 bcd	11.73 ab	N.D.
	20	94.50 abc	11.51 ab	N.D.
	25	101.69 ab	10.55 b	N.D.
	30	113.29 a	11.70 ab	N.D.
Calcined eggshell	0	29.50 d	12.60 f	N.D.
	2.5	43.48 d	5.98 g	N.D.
	5	72.96 c	2.23 g	6.86 b
	10	94.11 b	20.35 e	8.49 ab
	15	103.38 ab	40.22 d	10.17 a
	20	100.23 ab	52.97 c	9.21 ab
	25	111.69 a	61.93 b	8.16 ab
	30	108.27 ab	79.66 a	8.97 ab

[a] Not detected.

immobilization by these amendments is comparably different (Fig. 6). The Pb-EXAFS spectra for the soils unamended and amended with eggshell had the similar phase as indicated by the correspondence of the first two oscillations. Compared to these data, the Pb-EXAFS spectrum for the soil amended with calcined eggshell shifted to a greater k value and the first two peak positions corresponded to those of $PbSiO_3$ and $Pb(OH)_2$. A notable feature in the fine structure of the $PbSiO_3$ and $Pb(OH)_2$ spectra was observed at the right tail of the first oscillation (~3 $Å^{-1}$), which was also observed in the soil amended with calcined eggshell, but not in the other soils. These findings suggest the formation of $Pb(OH)_2$ and Pb-associated with Si in the soil with calcined-eggshell amendment. The association of Pb with Si was likely derived from dissolution of phyllosilicates under elevated soil pH conditions. The EXAFS spectra reflecting the molecular configuration indicate that the relative contribution of Pb–Si association to the entire Pb speciation was greater in the soil amended with calcined eggshell than in the soil amended with eggshell. The increases in soil pH and Ca concentration in the soil amended with calcined eggshell may enhance the formation of CSH that incorporating with Pb in its structure [34,42]. The association of Pb with Si and Ca are supported by the elemental distribution map illustrating the presence of these elements at the same position of the soil surface (Fig. 4). Taken together, the application of calcined eggshell immobilizes Pb in the soil via cementation by forming CSH, in response to a rapid increase in soil pH.

The Pb-EXAFS spectra of eggshell soil did not show the common features that were found among the spectra of calcined eggshell soil, $PbSiO_3$ and $Pb(OH)_2$ references. This finding however does not completely exclude the possible deduction of $Pb(OH)_2$ or other Pb hydroxide species in the eggshell-amended soil. It is plausible that the alkaline pH condition of eggshell-amended soil was favorable to the formation of $Pb(OH)_2$ and aqueous Pb in the eggshell-amended soil was predicted to be supersaturated with respect to $Pb(OH)_2$ (Table 3). Previous studies reported that pure $CaCO_3$ and the amendment consisting mainly of $CaCO_3$ immobilized soil Pb via formations of $Pb(OH)_2$ or lanarkite, adsorption to Al containing minerals such as gibbsite and diaspore, and co-precipitation of Pb as carbonates [11,13,44].

3.6. Soil enzyme activity

Some soil enzymes quickly respond to soil management practices [45] and can therefore be used as soil biological indicators for determining the immobilization in the highly contaminated soils with organic or inorganic pollutant. In this study, the enzyme activity was investigated quantitatively as shown in Table 4. Alkaline phosphatase, β-glucosidase and dehydrogenase enzymes were selected because of their sensitivity to heavy metals in terms of inhibiting their activities in the soil [31]. Alkaline phosphatase and β-glucosidase can be indicators of soil organic P and C mineralization, respectively, while the dehydrogenase represents the overall microbial activity in the soil [18,31]. The alkaline phosphatase activity in the soils amended with eggshell and calcined eggshell increased up to 3.8 and 3.7 times greater than in the unamended soil, respectively. The β-glucosidase activity in the soil amended with calcined eggshell was also significantly increased by 6 times than the unamended soil; however, that in the soil amended with eggshell was not changed. In addition, the dehydrogenase activity was increased up to 10.17 mg TPF kg^{-1} h^{-1} in the soil amended with calcined eggshell.

Table 5
Correlation coefficients between enzyme activities and soil properties of eggshell and calcined eggshell amendments.

Amendments	Enzymes	Correlation coefficient			
		pH	TCLP-Pb	SOM	Aggregate stability
Eggshell	Alkaline phosphatase	0.813**	−0.891**	−0.960***	0.837**
	β-Glucosidase	−0.617	0.425	0.222	0.060
Calcined eggshell	Alkaline phosphatase	0.871**	−0.830**	0.916***	0.534
	β-Glucosidase	0.461	−0.656	0.906**	0.04
	Dehydrogenase	0.859**	−0.739*	0.847**	0.535

* Significant at 0.05.
** Significant at 0.01.
*** Significant at 0.001.

Correlation test was done to evaluate the enzyme activities vs. various physicochemical parameters in the soils amended with eggshell and calcined eggshell (Table 5). A positive correlation was observed between the alkaline phosphatase activity and the soil pH for both soils amended with eggshell ($r = 0.81$, $p < 0.01$) and calcined eggshell ($r = 0.87$, $p < 0.01$). The direct effect of soil pH on the alkaline phosphatase activity has already been reported [31]. The enzyme activity was also positively correlated with aggregate stability in soils amended with eggshell ($r = 0.837$ at $p < 0.01$) and calcined eggshell ($r = 0.534$). Conversely, the negative correlation between alkaline phosphatase activity and TCLP-Pb concentration in the soils amended with eggshell ($r = -0.89$ at $p < 0.01$) or amended with calcined eggshell ($r = -0.83$ at $p < 0.01$) suggested that these soil amendments improve alkaline phosphatase activity because of decreasing bioavailable Pb fraction. For the soil amended with eggshell, the activity of β-glucosidase decreased as the application rate of eggshell increased. However, the activity of β-glucosidase in the soil amended with calcined eggshell increased at >5% of application rate and had a positive correlation with soil pH ($r = 0.46$). We speculate that an increase of β-glucosidase activity in the soils amended with relatively high rates of calcined eggshell may result from the absorption of evolved CO_2 in a sealed soil container [46].

The dehydrogenase activity is often used as an indicator of metal toxicity in soils. In this study, no dehydrogenase activity was observed in the soils amended with/without eggshell, possibly due to the toxicity of Pb; however, it was observed in the soil amended with calcined eggshell at rates ≥5%. Dehydrogenase activity was also positively correlated with the soil pH ($r = 0.85$, $p < 0.01$) and the OM ($r = 0.84$, $p < 0.01$), and negatively correlated with the TCLP-Pb ($r = -0.73$, $p < 0.05$). These results can be explained by the release of CO_2 from the soil amended with calcined eggshell because the dehydrogenase activity is highly and positively correlated with CO_2 from the soil [31]. Overall, the increase of enzyme activities corresponded to the decrease of TCLP-Pb concentration, suggesting that eggshell and calcined eggshell amendments immobilized Pb and have no detrimental effect on soil quality.

4. Conclusions

Additions of both eggshell and calcined eggshell effectively decreased the TCLP-Pb concentration in the shooting range soil and their performance corresponded to pure $CaCO_3$ and CaO, respectively. Therefore, these amendments can possibly be used as alternatives to $CaCO_3$ and CaO as Pb immobilizing agents. In comparison with eggshell, the calcined eggshell was more effective on the Pb immobilization in the soils because of highly elevating soil pH, and the dissociation of CaO to Ca inducing a rapid decrease of TCLP-Pb concentration. The tested amendments also reduced the exchangeable Pb fractions and transformed them into a carbonate associated Pb fraction at high soil pH conditions. The thermodynamic equilibrium model predicted the precipitation of $Pb(OH)_2$ in the soils amended with eggshell and calcined eggshell. According to SEM-EDX and XAFS investigations, our study clearly illustrated the differences in immobilization mechanisms between eggshell and calcined eggshell amendments in the soil. For the soil amended with calcined eggshell, the Pb was associated with Si and may be immobilized as a form of CSH via cementation reactions, in response to a rapid increase in soil pH. The eggshell amendment would immobilize the soil Pb via formations of $Pb(OH)_2$, lanarkite, adsorption on Al containing minerals such as gibbsite and diaspore, and coprecipitation of Pb as carbonate. However, this study could not exactly determine which Pb species played a primary role in immobilization of soil Pb. For the addition of eggshell amendment, the formation of CSH was less likely involved in the Pb immobilization mechanisms in the soils compared to that of calcined eggshell amendment since the absence of Pb–Ca and Pb–Si associations were found in SEM-EDX and EXAFS studies, respectively.

The amendments induced an increase in enzyme activities indicating improvement in the soil quality. Based on the finding of negative correlations between enzyme activities and TCLP-Pb concentrations, the amendments of eggshell and calcined eggshell reduced the Pb-toxicity in soils, and these amendments would be applicable to Pb immobilization in the highly contaminated shooting range soil.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.047.

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