Environ Earth Sci
DOI 10.1007/s12665-012-1550-1

ORIGINAL ARTICLE

An assessment of the utilization of waste resources for the immobilization of Pb and Cu in the soil from a Korean military shooting range

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Received: 6 December 2010 / Accepted: 12 January 2012

Abstract Military shooting range soils contaminated by heavy metals have been subjected to remediation efforts to alleviate the detrimental effects of exposure on humans and the surrounding environment. Waste materials can be used as cost-effective soil amendments to immobilize heavy metals in contaminated soils. In this study, naturally occurring lime-based waste materials including egg shells, oyster shells, and mussel shells were assessed for their effectiveness toward heavy metal immobilization in military shooting range soil in Korea. Soil was treated in batch leaching experiments with 0, 2.5, 5, 10, and 15% of each lime-based waste material. The results showed that the lime-based waste materials effectively reduced water-soluble Pb at an application rate of 2.5% by weight of the soil. Increase in soil pH from 6.6 to 8.0 was considered to be the main chemistry of Pb immobilization, which was supported by the formation of insoluble Pb species at high pH values as confirmed by the visual MINTEQ thermodynamic model. In contrary, water-soluble Cu was increased in the lime-based waste material-treated soils when compared to the untreated soil. This was likely attributed to the formation of soluble Cu–DOC (dissolved organic carbon) complexes as all lime-based waste materials applied increased DOC contents in the soil. Therefore, care must be taken in selecting the appropriate amendment for immobilizing metals in shooting range soils.

Keywords Small arms firing ranges · Resource recycling · Remediation · Chemical stabilization · Dissolved organic matter · Chemical equilibrium model

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Introduction

Military shooting ranges have become a significant source of soil pollution due to elevated concentrations of metals (Pb, Cu, Sb, Zn, As, Ni, Bi, and Ag) released from used bullets (Dermatas et al. 2006; Moon et al. 2011). Dissolved metals from the bullet and bullet fragments can be released into the soil by chemical processes such as oxidation, carbonation, and hydration (Ma et al. 2007), resulting in elevated soluble metal concentrations in the soil. Recent studies have reported Pb contamination in shooting range soils exceeding total concentrations of 10,000 mg kg^{-1} (Cao et al. 2009; Dermatas et al. 2006; Spuller et al. 2007). These concentrations are 25 times greater than the USEPA screening criteria of 400 mg Pb kg^{-1} (USEPA 1996).

Published online: 26 January 2012

Detrimental aspects in association with contaminated shooting range soils have been evidenced through the investigations of groundwater and surface water contamination levels (Sorvari et al. 2006), effects on the human and other animals (Gulson et al. 2002; Migliorini et al. 2004), reduction in the soil enzyme activities (Lee et al. 2002), and accumulation of heavy metals in plant tissues (Labare et al. 2004). Given these adverse environmental aspects, remedial technology applications to clean up the shooting range soils have become increasingly prevalent. In Korea, many active shooting ranges are being closed due to demilitarization of US army forces from Korea. However, limited information is available for the extent of contamination in those shooting range soils, even though soil and water contamination and noise pollution at these sites have been reported (Green Korea United 2008).

Soil amendments have been widely used to stabilize heavy metals in contaminated soil. These amendments include organic or inorganic materials that stabilize or immobilize metals in soil by converting them into less available forms (Ok et al. 2011a; Yang et al. 2007a). The primary mechanisms involved in the metal immobilization through soil amendments are cation exchange, adsorption, precipitation, or surface complexation (Chen et al. 2009; Ok et al. 2007a). Recently, natural or waste materials have become attractive metal immobilization agents due to their cost-effectiveness (Ok et al. 2011d; Yang et al. 2006; Yang et al. 2007b). For instance, intensive studies have been conducted to remediate Pb-contaminated shooting range soil by the application of phosphorous (P) containing natural materials such as rock phosphate (Cao et al. 2009; Hashimoto et al. 2009; Spuller et al. 2007). However, certain limitations to the use of P containing amendments for Pb immobilization were reported (Chrysochoou et al. 2007; Dermatas et al. 2008), including extremely slow Pb–P reaction kinetics and risk of eutrophication associated with the excessive P leaching from the treated soil. This indicated that the type of contaminant present in the soil as well as any possible side effect of the applied immobilization agent should be taken into account for selection of suitable soil amendment.

Waste materials having liming characteristics can be used as soil amendments because of their cost-effectiveness, which is a key parameter in determining the efficiency of remediation technology. Previously, only a few studies have employed liming materials such as cement and quick lime (Cao et al. 2008), and calcined waste oyster shells (Moon et al. 2010) to immobilize Pb in shooting range soil. Materials such as egg shells, oyster shells, and mussel shells are commonly available as food wastes. According to Statistics of Korea (MIFAFF 2006), 145,000 tons of oyster shells, 87,000 tons of egg shells, and 45,000 tons of mussel shells are being produced each year in Korea. Disposal or possible reuse of these waste materials has become an environmental issue. Likewise, remediation of the shooting range soils contaminated with heavy metals and recycling of waste materials as a resource recovery are challenging environmental issues. Taking these two environmental issues into account, the objective of the study was to assess the feasibility of lime-based waste materials in immobilizing heavy metals in a contaminated military shooting range soil in Korea. Using waste materials as soil amendments, we can simultaneously address the need for soil remediation and waste disposal.

Materials and methods

Soil collection

Soil samples were collected from a military shooting range at Icheon City located in the South Eastern part of Gyeonggi Province, Korea. The shooting practice at the military range mainly consists of small arms using lead bullets. Bullet fragments in the soil were removed, and these took part of 0.13% by weight of the collected soil. The soil was then air-dried and passed through a 2-mm sieve for further physicochemical and mineralogical analysis. Bullet crust was obtained by detaching the soil particles from bullet fragments using an ultra sound sonicator (JAC Ultrasonic 1505, Korea) (Cao et al. 2003).

Preparation of lime-based waste materials

Lime-based waste materials including egg shells, oyster shells, and mussel shells were selected as soil amendments. Waste egg shells and mussel shells were collected from a local restaurant, while waste oyster shells were collected from an oyster farming industry in Tongyeong City, Korea. The lime-based waste materials were processed to powder forms following methods described by Ok et al. (2011b, c). Briefly, the lime-based waste materials were rinsed multiple times using hot water (95°C) to remove impurities and then dried at 105°C for 72 h in a fan forced air-dry oven. The cleaned shells were crushed mechanically, pulverized, and passed through a 1-mm sieve to obtain homogenized powder and stored in airtight containers for further use.

Analysis of soil and lime-based waste materials

Soil texture was determined by the Bouyoucos hydrometer method (Gee and Or 2002). Soil pH and EC were measured electrometrically on 1:5 (weight/volume) distilled water extracts (Yang et al. 2009). Exchangeable cations (Ca, Mg, K, and Na) in soils were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 7300 DV, USA) after extraction with neutral 1 M ammonium acetate (NH_4OAc) and consequent filtration through a 0.45 μm filter (Jung et al. 2011). Cation exchange capacity (CEC) was calculated based on exchangeable cations and hydrogen ion (H^+) concentrations (NIAST 2000). The chlorostannous acid method was adopted to determine available phosphorous (P) in association with an UV spectrophotometer (UV-1800, Shimadzu, Japan) (Kuo 1996). Each subsample was further ground using a ball mill grinder and analyzed for total carbon and nitrogen by a CHNS elemental analyzer (Flash EA 1112, Thermo-electron Corporation, USA). The C/N ratio was calculated from the total C and N contents of the soil sample (Ok et al. 2007b). Soil organic matter (OM) content was calculated from the total carbon content by using a traditional conversion factor of 1.724 (Schumacher 2002). All the measurements were taken in triplicates. Total concentrations of heavy metals in soil and bullet crust were determined by USEPA method 3051A (USEPA 1998). Subsamples were digested using concentrated nitric acid and hydrochloric acid in a microwave digestion unit (MARS-X, HP-500 plus, CEM Corporation), and selected heavy metal concentrations (Cu, Ni, Pb, and Sb) were determined using ICP-OES.

Mineralogical composition of the soil and the lime-based waste materials was determined by X-ray diffraction (XRD) spectrometry (X'pert PRO MPD, PANalytical, the Netherlands) with a graphite monochromator operated at 40 kV and 30 mA to produce Cu Kα radiation at scanning rate of 20 s per step. Minerals were identified by comparing the XRD patterns to the patterns of the International Centre for Diffraction Data (ICDD) database (version 2002). Elemental composition of the prepared lime-based waste materials was determined by X-ray fluorescence spectrometer (XRF-1700, Shimadzu, Japan).

Leaching experiments

Leaching experiments are generally conducted to examine washout of contaminants from soil by contacting to a liquid. There are several test methods for conducting leaching experiments. In this study, the standard batch leaching test described in DIN 38414 S4 guidelines was adopted to assess the efficiency of lime-based waste materials on the immobilization of heavy metals (Spuller et al. 2007). The method is widely used for general assessment of heavy metals stabilization (Al-Tabbaa and Perera 2006). The lime-based waste materials (powdered egg shells, oyster shells, and mussel shells) were mixed with each 10 grams of dried soil at a rate of 0% (untreated), 2.5, 5, 10, and 15%, respectively, based on the weight of soil. 100 mL of de-ionized water (aquaMAX, 18.2 MΩ. cm resistivity) was added to each treatment maintaining a liquid/solid ratio of 10:1. The mixture was trembled for 24 h, and then supernatant was filtered through a 0.45 μm membrane filter (Advantec MFS). The filtrates were analyzed for pH, dissolved organic carbon (DOC) using total organic carbon analyzer (TOC 5000A, Shimadzu, Japan), anions (Cl^{-1}, SO_4^{-2}, PO_4^{-3}, and NO_3^{-1}) using ion chromatograph (Metrohm Compact IC-861, Switzerland), and Pb and Cu using ICP-OES.

Thermodynamic modeling

Thermodynamic modeling is a tool to assess the availability of metals in solid phase. Various thermodynamic models have been used to predict the leaching behavior of heavy metals in soil. We used Visual MINTEQ model (version 2.6) to predict Pb speciation and its possible mineralization (Gustafsson 2008). Input components (Cl^{-1}, SO_4^{-2}, PO_4^{-3}, NO_3^{-1}, Ca^{+2}, and Pb^{+2}) concentrations were collected from batch leaching experiments on untreated soil and each of the treated soils at 15% egg shell powder. The model was run at 25°C using 0.0003 atm CO_2 atmospheric pressure with the fixed pH values that were measured in the corresponding leachate. Equilibrium constants and thermodynamic reactions were used from the model database files. Saturation of specific Pb minerals was calculated from the saturation index (SI) values using following equation:

$$SI = \log IAP - \log K_{sp}$$

where IAP is the ion activity product and K_{sp} is the solubility product constant. SI values >1.0 indicate possible precipitation of mineral (Lindsay 1979).

Statistical analysis

All experimental results were expressed as an average of three replicates with standard deviation. Pearson correlation coefficients between various parameters were calculated using statistical analysis system, SAS package (version 9.1, copy right 2002–2003 by SAS Institute Inc., Cary, NC, USA).

Results

Characterization of soil

Selected properties of the military shooting range soil are presented in Table 1. Soil texture was sandy loam with 56.6% of sand and 14% of clay contents. Soil pH (6.7) was slightly acidic and similar to the typical pH of the cultivated upland soil in Korea (6.0–6.5) (Jo and Koh 2004). Soil organic matter (10.1 g kg^{-1}) and available phosphorous (8.65 mg kg^{-1}) contents were lower compared to optimum values of the upland soil in Korea, i.e., 20–30 g kg^{-1} for

Table 1 Selected physicochemical properties of military shooting range soil and bullet crust

Soil	pH[a]	Sand (%)	Silt	Clay (g kg^{-1})	OM[b]	Available P (mg kg^{-1})	CEC (cmol$_{(+)}$ kg^{-1})	Ca[c]	Mg[c]	Na[c]	K[c]	Total C (%)	Total N	C/N	Total Cu (mg kg^{-1})	Total Pb	Total Sb	Total Ni
Shooting range	6.66	56.6	29.4	14.0	10.1	8.65	5.29	2.74	0.56	0.11	0.79	0.58	0.045	12.9	225	4,626	23	31.1
Bullet crust															2,443	35,076	641	25.1

[a] Determined in 1:5 soil/water ratio

[b] Organic matter

[c] Exchangeable cation

soil organic matter and 300–500 mg kg^{-1} for available phosphorous. Likewise, the exchangeable Ca (2.74 cmol$_{(+)}$ kg^{-1}) and Mg (0.56 cmol$_{(+)}$ kg^{-1}) in the shooting range soil were about 2 to 3 times lower than those of typical values (5.0 and 1.5 cmol$_{(+)}$ kg^{-1}, respectively) observed in Korean upland soil. However, slightly higher exchangeable K (0.79 cmol$_{(+)}$ kg^{-1}) was observed in the shooting range soil compared to the optimum range of exchangeable K (0.50–0.60 cmol$_{(+)}$ kg^{-1}) in the upland soil.

In the shooting range soil, high concentration of Pb (4,626 mg kg^{-1}) was observed, which was 23 times higher than the Korean Standard Warning Level of total Pb (200 mg kg^{-1}) for agricultural lands (MOE 2010). We compared the observed metal concentrations in the shooting range soil with their warning standards for agricultural lands since the study area can be used for cultivation purposes after closure. The Cu contents (225 mg kg^{-1}) in the soil were about 1.5 times greater than warning level (150 mg kg^{-1}). Bullet crust showed higher concentrations of Cu (2,433 mg kg^{-1}), Pb (35,076 mg kg^{-1}), and Sb (641 mg kg^{-1}) as compared to the soil.

Mineralogical composition of shooting range soil and bullet crust is shown in Fig. 1. Mineralogy of both samples was dominated by quartz (SiO_2), albite ($NaAlSi_3O_8$), and muscovite [$KAl_2(AlSi_3)O_{10}(OH,F)_2$] minerals. However, Pb in the form of cerussite ($PbCO_3$) mineral was only observed in bullet crust.

Characterization of lime-based waste materials

The XRF analysis showed that calcium oxide (CaO) appeared to be a dominant composition of the lime-based

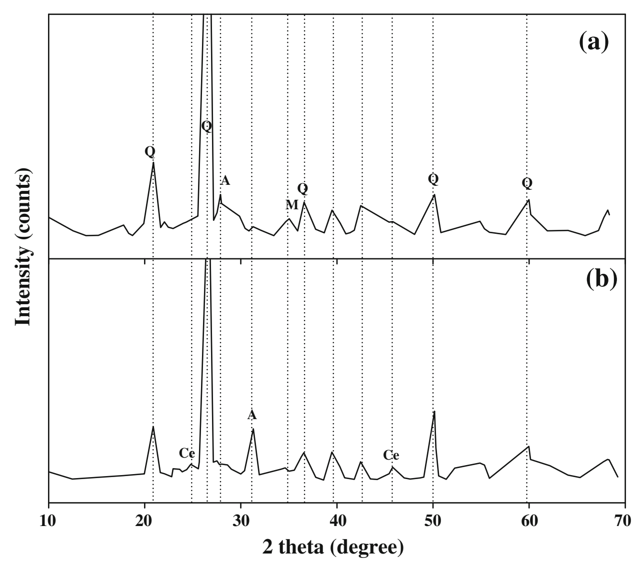

Fig. 1 XRD pattern showing mineralogical composition of **a** shooting range soil and **b** bullet crust. *Q* Quartz, *M* Muscovite, *A* Albite, *Ce* Cerussite

Table 2 Elemental composition of lime-based waste materials

Element	Egg shell (wt%)	Oyster shell (wt%)	Mussel shell (wt%)
Al_2O_3	0.140	0.071	0.008
CaO	47.23	46.39	50.88
Fe_2O_3	0.040	0.053	0.026
K_2O	0.070	0.066	0.017
MgO	6.790	7.590	0.510
MnO	0.003	0.001	0.020
Na_2O	0.510	1.520	0.160
P_2O_5	0.330	0.154	0.062
SiO_2	0.130	0.130	0.044
TiO_2	0.003	0.004	0.011
LOI[a]	44.76	44.04	48.16

[a] Loss on ignition

waste materials at more than 45 wt% (Table 2). The Mg (as MgO) was the second major constituent of egg shell (6.79%) and oyster shell (7.59%). Other studies (Park et al. 2007; Ok et al. 2010, 2011b, c,) have also reported that the main constituent of lime-based wastes is calcite ($CaCO_3$). Mineralogical analysis by XRD also confirmed the presence of calcite as a major component in all three lime-based waste materials (Fig. 2). The main peak was observed at 29° (2 theta) for all lime-based waste materials, which corresponded to calcite ($CaCO_3$) in ICDD database.

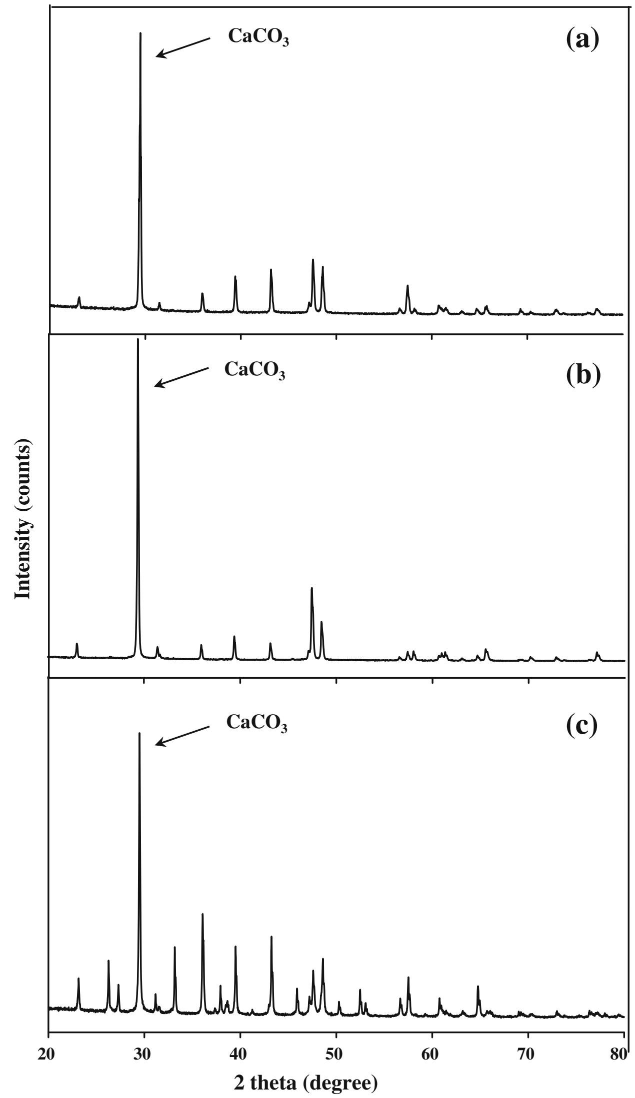

Fig. 2 Mineralogical composition of **a** egg shell powder, **b** oyster shell powder, and **c** mussel shell powder

Leaching experiments

Lime-based waste materials were added to the soil at different application rates, and the solubility of Pb as well as Cu was assessed by conducting batch leaching experiment. The pH of leachate from the untreated soil (0%) was 6.6 and this increased by approximately 1 unit with 2.5% application rate for all amendments (Fig. 3). Additional increase of lime-based waste materials did not increase the soil pH considerably, which may be related to the high buffering capacity of the soil due to the presence of free $CaCO_3$ (Bache 1984). The concentrations of water-soluble Pb in soils were influenced by increased pH following amendment application (Fig. 3). The lime-based waste materials decreased water-soluble Pb contents compared to the untreated soil in the order of egg shell (45% reduction at 2.5% application rate) >oyster shell (38.6% reduction at 2.5% application rate) >mussel shell (22.7% reduction at 10% application rate). In particular, the highest rate of decline of soluble Pb was observed in soil at 2.5% application of lime-based waste materials, which was contributed by significant change in soil pH at the same application rate.

In contrast, water-soluble Cu in the military shooting range soil appeared to be increased with amendment treatments compared to untreated soil (Table 3). The Cu solubility was increased gradually as the application rates increased for all lime-based waste materials with the highest Cu solubility being observed at 15% rate of application. The increased magnitude of Cu solubility was depending on the type of waste materials. Mussel shells and oyster shells increased soluble Cu 9.3 times and 7.9 times in comparison with untreated soil, respectively, while egg shells increased only 3.4 times compared to the untreated soil. The increased solubility of Cu in military shooting range soil by lime-based waste materials was attributed to dissolved organic carbon (DOC). Overall, trends indicate lime-based waste materials increased DOC concentration in the military shooting range soil compared to the untreated soil, and the increase in DOC

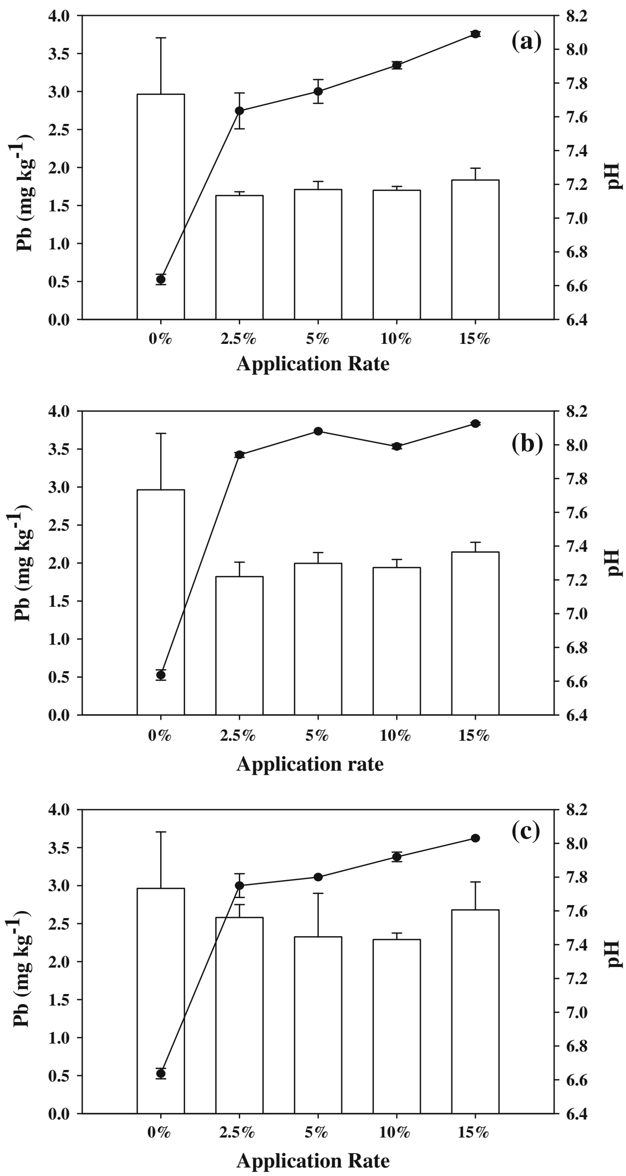

Fig. 3 Effect of pH on Pb immobilization in military shooting range soil by **a** egg shell, **b** oyster shell, and **c** mussel shell. *Bars* showing Pb concentration and *circles* showing pH values

concentration was correlated with the application rate of the materials. Among the amendments, mussel shells and oyster shells induced more increase in DOC concentration compared to the egg shells with almost twice in DOC concentration at 15% treatment rate.

Water-soluble Pb was negatively correlated with pH and DOC of shooting range soil, whereas a positive correlation was observed between water-soluble Cu and both pH and DOC for all three lime-based waste materials (Table 4). Furthermore, oyster shell and mussel shell treatments showed a much stronger correlation ($P < 0.01$) between water-soluble Cu and DOC or pH than egg shell treatment.

Thermodynamic modeling

Visual MINTEQ thermodynamic model predicted that within untreated soil, Pb was predominantly present as organically complexed form (99%). However, in the soil treated at 15% egg shell, organically complexed Pb species was transformed to aqueous $PbCO_3$ and $PbOH^+$. Precipitation of possible Pb minerals in aqueous system of shooting range soil in terms of saturation index is presented in Table 5. Model predicted the saturation indices of 0.31, 1.75, and 0.63 for cerussite, hydrocerussite, and $Pb(OH)_2$, respectively, indicating their theoretical precipitations in the shooting range soil treated with lime-based waste materials.

Discussion

The studied military shooting range soil was an upland soil heavily contaminated with Pb and moderately contaminated with Cu. Greater contents of Pb, Cu, and Sb in the bullet crust collected in the study site implied that the elevated contents of heavy metals in the soil were from the bullet fragments as these metals are the constituents of the bullets (Robinson et al. 2008). Specifically, the presence of cerussite ($PbCO_3$) in bullets crust indicated bullet fragments as a source of Pb contamination. Several studies on shooting range soils have also reported the presence of cerussite as major Pb mineral (Cao et al. 2008; Ma et al. 2007). Calcite ($CaCO_3$) is the main component of waste egg shell, oyster shell, and mussel shell that triggered their use as lime-based soil amendments. Previous studies have clearly demonstrated the use of $CaCO_3$ in immobilizing heavy metals in soil (Hong et al. 2007; Wang et al. 2001).

Leaching experiments were conducted to evaluate the performance of amendments in immobilizing heavy metals in soil (Al-Tabbaa and Perera 2006). Lime-based waste materials effectively reduced water-soluble Pb contents due to the induced increase in soil pH. Soil pH plays a vital role in controlling the solubility and bioavailability of heavy metals in soil (Zhao and Masaihiko 2007). The waste materials used in this study were lime-based and enriched with $CaCO_3$. The dissociation of $CaCO_3$ releases hydroxyl (OH^-) ions into the soil causing deprotonation at the soil surface and an increase in net negative charged surface area on which heavy metal was adsorbed (Grybos et al. 2009). Ok et al. (2010) used natural and calcined oyster shell powders to immobilize Pb and Cd in contaminated soil. They also concluded that the rise in soil pH was responsible for heavy metal immobilization. Visual MINTEQ model predictions supported the Pb immobilization results in terms of theoretical formation of insoluble Pb minerals at high pH. The degree of saturation with respect to specific Pb solid phase is representative of the mineral's SI value

Table 3 Treatment effects of lime-based waste materials on DOC and concentrations of soluble Cu (mean ± SD)

Treatments	Application rate (%)	DOC (mg kg^{-1})	Soluble Cu (mg kg^{-1})
Egg shell	0	52.5 ± 3.19	0.10 ± 0.00
	2.5	49.4 ± 11.4	0.28 ± 0.01
	5	54.9 ± 3.18	0.17 ± 0.06
	10	68.4 ± 31.9	0.23 ± 0.03
	15	71.6 ± 22.1	0.36 ± 0.07
Oyster shell	0	52.5 ± 3.19	0.10 ± 0.00
	2.5	110 ± 23.1	0.66 ± 0.00
	5	114 ± 2.97	0.67 ± 0.05
	10	132 ± 32.4	0.69 ± 0.01
	15	127 ± 8.13	0.82 ± 0.01
Mussel shell	0	52.5 ± 3.19	0.10 ± 0.00
	2.5	104 ± 8.75	0.66 ± 0.03
	5	88.0 ± 2.12	0.70 ± 0.10
	10	108 ± 9.90	0.83 ± 0.12
	15	132 ± 11.8	0.96 ± 0.11

Table 4 Correlation coefficients of water-soluble Pb or Cu related with pH or DOC of military shooting range soil treated by lime-based waste materials

Metals	Egg shell		Oyster shell		Mussel shell	
	pH	DOC	pH	DOC	pH	DOC
Pb	−0.908*	−0.286	−0.932*	−0.892*	−0.751	−0.446
Cu	0.811	0.587	0.985**	0.972**	0.984**	0.953**

* Statistically significant at $P < 0.05$

** Statistically significant at $P < 0.01$

Table 5 Lead minerals precipitation in aqueous system of shooting range soil as predicted by visual MINTEQ thermodynamic model

Mineral	Formula	Saturation Index (SI)	
		Untreated	15% eggshell treatment
Anglesite	$PbSO_4$	−4.66	−3.86
Cerussite	$PbCO_3$	−3.17	0.31
Cotunnite	$PbCl_2$	−12.1	−11.0
Hydrocerrusite	$Pb_3(CO_3)_2(OH)_2$	−8.66	1.75
Laurionite	PbCl(OH)	−6.39	−3.51
Litharge	PbO	−7.38	−3.91
Massicot	PbO	−7.58	−4.11
$Pb(OH)_2$	$Pb(OH)_2$	−2.84	0.63
Phosgenite	$Pb_2(CO_3)Cl_2$	−13.4	−8.87

(Hashimoto et al. 2009). The model predicted that the soil treated with eggshell was saturated with cerussite, hydrocerussite, and $Pb(OH)_2$, whereas untreated soil was under saturated with Pb minerals showing SI values <-1. These predictions indicated that the lime-based waste materials affected the dissolved phases of Pb. At high pH, the solubility of Pb in soil solutions is controlled by the most stable $PbCO_3$ (Lindsay 1979). The results suggested the mechanistic evidence of Pb immobilization by lime-based waste materials. The rise in soil pH by lime-based waste materials led to the precipitation of Pb as $Pb(OH)_2$, $PbCO_3$, and $Pb(CO_3)_2(OH)_2$.

Among the lime-based waste materials examined, egg shell was the most effective in immobilizing Pb in shooting range soil, which may be due to its porous surface structure (Ok et al. 2011b) while oyster shell and mussel shell have fibrous or layered structure (Kwon et al. 2004). Numerous pores in egg shell powder may have increased the surface area and resulted in more adsorption of Pb, which is another possible mechanism of metal immobilization (Chen et al. 2009). In addition to Pb precipitation as Pb-carbonate and Pb-hydroxide, ion exchange could be a further probable mechanism of Pb immobilization, as the lime-based waste materials contain large amounts of Ca and Mg. Pehlivan et al. (2009) indicated that dolomite [$CaMg(CO_3)_2$] can immobilize Pb from aqueous solutions as a result of ion exchange with Ca and Mg.

Increased solubility of Cu was observed in the shooting range soil treated with egg shell, oyster shell, and mussel shell waste materials probably due to the formation of Cu–DOC complexes. Schmidt (2003) reported that the Cu solubility in soil was mainly governed by DOC concentration rather than soil pH, in particular when the soil pH is 6.5–8. Of all divalent cations, Cu forms the strongest complex with dissolved organic carbon, facilitating the transport of Cu in the soil (Nierop et al. 2002). An increase in pH following lime-based waste materials treatment induces increases in the negative charge of organic matter and other solid particles having pH-dependent binding sites (Oste et al. 2002). This mechanism leads to increased repulsion between organic matter molecules resulting in increases in soluble organic matter. Increase in the DOC leaching and subsequent stimulation of the metal migration in the soil by liming has been previously reported (Karlik 1995). In Spuller's study using diammonium phosphate (DAP) to stabilize heavy metals in a shooting range soil, they also observed increased concentration of water-extractable Cu and concluded that this was mainly due to the formation of Cu–DOC complexes (Spuller et al. 2007).

Conclusions

Lime-based waste materials (egg shells, oyster shells, and mussel shells) were recycled as a resource to improve the quality of environment. Highly contaminated shooting range soil with Pb was treated with lime-based waste materials. Pb was effectively immobilized by egg shell, oyster shell, and mussel shell, and several mechanisms could be explained for Pb immobilization by the lime-based waste materials. The rise in soil pH due to the addition of lime-based waste materials resulted in the formation of relatively insoluble Pb-hydroxide. Results from the Visual MINTEQ thermodynamic model predicted the formation of insoluble Pb-hydroxide and Pb-carbonate at high pH in the military shooting range soil treated with egg shell. In addition to Pb precipitation at elevated pH, ion exchange with Ca and Mg could result in increased immobilization of Pb by egg shell and oyster shell compared to mussel shell. However, all lime-based waste materials failed to immobilize Cu. In fact, leaching of Cu from the military shooting range soil with the addition of lime-based waste materials was observed and was attributed to the formation of soluble complexes between Cu and DOC. Since liming can increase the dissolved organic matter in soil, and metals transportation through soil can be facilitated by the formation of organic complexes, care must be taken in selecting the appropriate soil amendment for immobilizing a target metal in the contaminated shooting range soil.

Acknowledgments This study was supported by the National Research Foundation of Korea Grant funded by the Korean Government (Project number: 2009-0071439). Instrumental analysis was supported by a grant from the Institute of Environmental Research and the Central Laboratory of Kangwon National University in Korea.

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