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Mobility Retardation of Cd, Pb and Mn in Acid Soil Using Phosphate Fertilizers

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Abstract

Contamination of heavy metals in soil is a major problem that causes damage to the environments. The aim of this research was to observe the efficiency of phosphate fertilizer, including phosphate rock, di-ammonium phosphate, and monopotassium phosphate in stabilizing lead, cadmium, and manganese in contaminated soil. The sampling soil was an acid sandy clay loam soil from Rayong Province which is one of the most industrialized provinces in Thailand. After applying fertilizers to the soil, the determination was on soil pH, the total concentration of heavy metals, heavy metal forms in soil and potential of heavy metals to enter the biological system. The results showed that phosphate rock, diammonium phosphate, and monopotassium phosphate increased the soil pH from 3.60 to 6.5, 7.0 and 5.2, respectively. Phosphate fertilizers could change an unstable form to a more stable form of heavy metals. Phosphate rock (7.5 g/kg_{soil}) has the highest potential for reducing the mobility of all three metals (about 80% for manganese, 60% for cadmium, and 50% for lead), followed by monopotassium phosphate. The results obtained from the extraction with DTPA and $CaCl_2$ were closely related to the results obtained from the sequential extraction method. Phosphate rock was the best to reduce potentially toxic metals phytoavailability. Soil improvement with phosphate fertilizer was considered a good alternative for stabilizing soils contaminated with cadmium, lead, and manganese.

Keywords: Correlation; Heavy metals; Mobility retardation; Phosphate fertilizer; Soil-amendment

1. Introduction

Contamination of heavy metals in soil is a major problem in Thailand, for example, lead contamination in Klity Creek, Karnchanaburi Province and cadmium contamination in Mae Sot District, Tak Province. Major sources of heavy metal contamination include the use of chemicals in agriculture, smelters, and industrial plants (Sun *et al.*, 2010). The mining industry is another important source. Information from Department of Groundwater Resources (2011) indicated that lead, manganese, and cadmium in the soil around the gold mining area in the district of Tabklao, Pichit Province were 79, 23,707, and 39 mg/kg, respectively. According to the Notification of the National Environment Board No. 25 (2004), the amount of lead, manganese, and cadmium in the soil used for living and agriculture must not exceed

400, 1,800, and 37 mg/kg, respectively. Heavy metals contaminated in the environment harm the health of exposed people. It can enter the human body by breathing, dermal contacting, or ingestion (Mulligan *et al*., 2001). Plants that grow in contaminated sites absorb the metal to accumulate in various parts (Sirichamorn *et al*., 2017). There are several techniques for soil remediation, but each technique has its drawbacks. The electro-kinetic technique requires electricity so it is costly. Vitrification techniques will result in hardening of soils so there will be a problem of cultivation of those soils. Soil washing will leave chemicals contaminated in the soil. Stabilization and fixation of heavy metals in soil is an interesting alternative due to its high performance and low cost. It is an in-situ treatment technique so it is easy to operate (Huang *et al*., 2016). After adding the immobilizing agent, the agriculture activity on the soil can perform normally. Researchers study on applying various immobilizing agents such as limestone, sepiolite, smectite, kaolinite, vermiculite, and goethite (Uddin, 2017; Wu *et al*., 2016). Phosphate fertilizer is another interesting immobilizing agent since it can also be a fertilizer. Phosphate fertilizer can dissolve in water. The soluble phosphate can migrate only a short distance. It can then combine with various elements in soil and form solid compounds. This study investigated the efficiency of phosphate fertilizer in stabilizing lead, cadmium, and manganese in acidic sandy loam. The fertilizer was rock phosphate ($Ca_{10}(PO_4)_6(OH)_2$), di-ammonium phosphate ($(NH_4)_2HPO_4$), and monopotassium phosphate (KH_2PO_4). The benefit of this research is that it can help to reduce the contamination of metals in plants grown in contaminated soils and thus to reduce the health risk of people who consume those plants.

2. Materials and Methods

The collection of the soil sample was from Chum Saeng District, Rayong province. The exact location was at the latitude 12°57’22.7“N and the longitude 101°32’12.2“E. The collection was by composite sampling method from the soil surface to a depth of 30 cm. Preparation of the soil sample using the method developed by the Department of Land Development (2014). The soil was synthesized to contaminate with 50 mgCd /kg_{soil}, 550 mgPb /kg_{soil}, and 2,000 mgMn /Kgsoil. After leaving the contaminated soil at room temperature for 1 month, rock phosphate (RP), di-ammonium phosphate (DAP) and monopotassium phosphate (MPP) in the amount of 2.5 g/kg_{soil}, 5.0 g/kg_{soil}, and 7.5 g/kg_{soil} were added. The mixed soils were left at room temperature for 1 month. A six-step sequential extraction method was then carried out to investigate forms of metals in those mixed soil samples (Tessier *et al*., 1979). A single-step extraction method was also performed using 1M NH_4OAc, 0.05 M EDTA, 0.005 M DTPA, and 0.01 M $CaCl_2$ (Zhang *et al*., 2010).

Table 1. Soil characteristics

Parameters	Results	Parameters	Results
Moisture (%)	10.80 ± 0.30	Particle distribution	
Bulk density (g/cm^3)	1.88 ± 0.06	Sand (%)	66.89
pH	3.20 ± 0.01	Silt (%)	4.53
Organic matter (%)	3.50 ± 0.15	Clay (%)	28.58
SiO_2 (%)	94.6	Soil type	sandy clay loam
CEC (meq/100g)	2.80 ± 0.53	Cd (mg_{Cd}/kg_{soil})	0.03 ± 0.06
Total N (%)	0.0024 ± 0.002	Pb (mg_{Pb}/kg_{soil})	22.17 ± 1.51
Total P (mg_P /kg_{soil})	0.61 ± 0.08	Mn (mg_{Mn}/kg_{soil})	35.34 ± 1.99

Table 2. Modifier characteristics

Parameters	Modifier		
	phosphate rock	di-ammonium phosphate	monopotassium phosphate
Moisture (%)	2.68 ± 0.09	3.85 ± 0.25	0.17 ± 0.02
pH	6.43 ± 0.13	7.36 ± 0.03	4.22 ± 0.05
CEC (meq/100g)	44.31 ± 2.33	7.53 ± 0.05	4.86 ± 0.12
Available P (g/kg)	90.11 ± 5.00	375.36 ± 27.88	456.52 ± 15.31
Total P (g/kg)	162.90 ± 2.89	404.46 ± 2.43	465.50 ± 6.08
Cd content (mg/kg)	7.17 ± 0.26	4.45 ± 0.12	2.93 ± 0.15
Pb content (mg/kg)	89.88 ± 0.37	10.03 ± 0.78	17.58 ± 0.27
Mn content (mg/kg)	3,788.83 ± 71.13	473.85 ± 15.47	3.10 ± 0.28

Table 3. Soil pH before and after adding modifiers (Mean ± S.D.)

Modifier	Adding amount (g/kg_{soil})	Sign	pH
No modifier (control)	0	CK	3.60 ± 0.01
rock phosphate	2.5	RP1	6.13 ± 0.05
	5.0	RP2	6.27 ± 0.06
	7.5	RP3	6.54 ± 0.04
di-ammonium phosphate	2.5	DAP1	5.36 ± 0.02
	5.0	DAP2	6.41 ± 0.01
	7.5	DAP3	7.01 ± 0.01
mono-potassium phosphate	2.5	MPP1	4.29 ± 0.01
	5.0	MPP2	4.78 ± 0.02
	7.5	MPP3	5.20 ± 0.01

2.1 Chemical characterization of soil and phosphate fertilizers (modifiers)

The moisture content, pH, cation exchange capacity (CEC), available phosphorus were characterized using the method developed by the Department of Land Development (2014). The determination of total phosphorus was by the method developed by the Department of Agriculture (2008). The investigation of total metal was by Atomic absorption spectrophotometry (AAS) (US. EPA, 1996). The analysis of soil was also on bulk density, organic matter, inorganic materials, total nitrogen and soil distribution using the method developed by the Land Development Department (2014).

2.2 Statistical analysis

Two-way ANOVA analysis using MINITAB version 16 tested the difference of data at 95% confidence level by analyzing comparative data within the experimental set and between the experimental set before and after the soil modification by rock phosphate, di-ammonium phosphate, and monopotassium phosphate. Each sample experimented in triplicate. A standard deviation was observed to identify the precision of the experiment. The average was used to critique the results.

3. Results and discussion

Table 1 and 2 showed the characteristics of soil and modifier, respectively. The soil from Rayong Province was an acid sandy clay loam soil, rather high in organic matter, low CEC value, and low fertility. The Cd, Pb and Mn content did not exceed the standard for agricultural soil. From Table 2, the pH, CEC value and heavy metals (Cd, Pb, and Mn) content of monopotassium phosphate was the lowest. In contrast, the total and available phosphorus content were highest. Cao *et al*. (2009) reported the percentage of P in phosphate rock was 14% which was a little lower than the rock phosphate in this research.

3.1 Soil pH affected by modifiers

After adding fertilizers to the soil and leaving at room temperature for 1 month, the pH of mixed soil was examined. The results were shown in Table 3.

The soil pH increased after adding rock phosphate to the strong acid soil. The results of this study were consistent with the research conducted by Huang *et al*. (2016), which added rock phosphate to soil and resulted in a significant increase in soil pH. The reasons were partly from exchanging of hydroxide ligand of iron and aluminum oxyhydroxide with H_2PO_4. Hydroxide ion was then released. The pH of rock phosphate and di-ammonium phosphate were about 6-7. The soil pH increased after adding such modifiers to the soil (Table 2). The pH of mono-potassium phosphate was quite low (pH 4.22). When added it to the soil, the pH of the soil increased. However, the soil was still the strong acid soil.

3.2 Changing of metal forms in soil

The method of six-step sequential extraction was performed to identify forms of Cd, Pb, and Mn in soil both before and after adding modifiers. The form of heavy metal in the soil can be divided to water soluble form (F1), exchangeable form (F2), carbonate bound form (F3), Fe-Mn oxide bound form (F4), organically bound form (F5), and residual form (F6). According to the ability of heavy metals to move in the environment, the form of metal can be classified as an unstable form (F1, F2, and F3) and a stable form (F4, F5, and F6).

Forms of Cd

Without adding any modifier, cadmium was found the most in soluble form (59.15%) (Figure 1). In the research of Sungur et al. (2014), up to 96% of cadmium was found to be in an unstable form. The cation exchange capacity value of this studied soil was moderate and this can cause Cd in exchangeable form was moderate too. Chen *et al*. (2007) studied of Cd-contaminated soils and Cd was mostly found in the soluble and exchangeable form.

After adding of rock phosphate in the soil, nearly all soluble form of Cd was diminished and changed to other forms. The exchangeable form of Cd increased. The radius of cadmium ion (100 pm) is close to the calcium ion (90-130 pm). Cadmium ion can exchange with calcium ion of $Ca_{10}(PO_4)_6(OH)_2$ and converted to the form of $Ca_{10-x}Cd_x(PO_4)_6(OH)_2$.

Cadmium in unstable forms after adding rock phosphate, di-ammonium phosphate, and monopotassium phosphate was in the range of 50 - 64%, 38-48%, and 20-45%, respectively. The percentage of the unstable form of Cd after adding modifiers was statistically significantly less than without adding any modifier. Cadmium in the stable form was found the most when adding 7.5 g_P/kg_{soil} of rock phosphate. The conclusion was using phosphate rock at 7.5 g_P/kg_{soil} was appropriate and effective in reducing cadmium mobility in soil.

Since the studied soil contains iron oxide and organic matter in relatively high amount, Cd was then tending to bind to organic matter and iron oxide. Cd in stable form thus increased by 45%. Mignardi *et al*. (2012) studied the modification of metal contaminated soil with rock phosphate, which reduced the metal concentration in soluble form by 92-99% and increased the F5 and F6 fraction. The results were similar to those of Huang *et al.* (2016). There was also a mechanism of precipitation of cadmium as shown in equations 1 and 2 (Xu and Schwart, 1994). The more stable compound formed.

$$_xCd^{2+} + (10-x)Ca^{2+} + 6H_2PO_4^- + 2H_2O \rightarrow (Cd_xCa_{10-x})(PO_2)_6(OH)_2 + 7H^+ \quad (1)$$

$$_xCd^{2+} + (10-x)Ca^{2+} + 6H_2PO_4^{2-} + 2H_2O \rightarrow (Cd_xCa_{10-x})(PO_4)_6(OH)_2 + 4H^+ \quad (2)$$

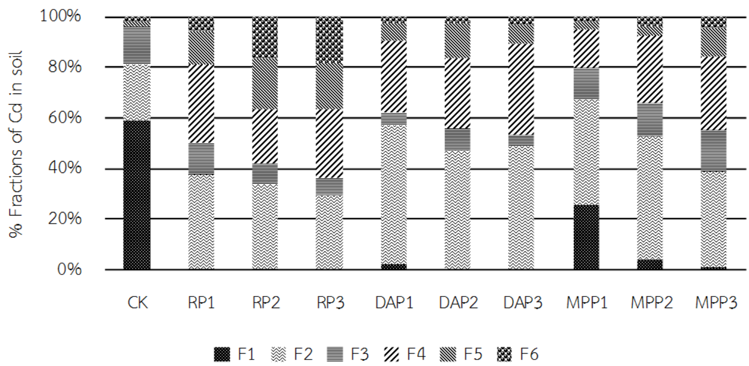

Figure 1. Forms of Cd after adding modifiers to soil (water soluble form (F1), exchangeable form (F2), carbonate bound form (F3), Fe-Mn oxide bound form (F4), organic bound form (F5) and residual form (F6))

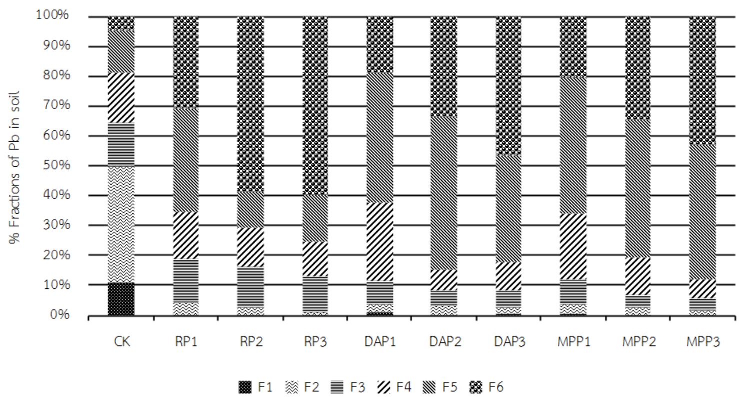

Figure 2. Forms of Pb after adding modifiers to soil (water soluble form (F1), exchangeable form (F2), carbonate bound form (F3), Fe-Mn oxide bound form (F4), organic bound form (F5) and residual form (F6))

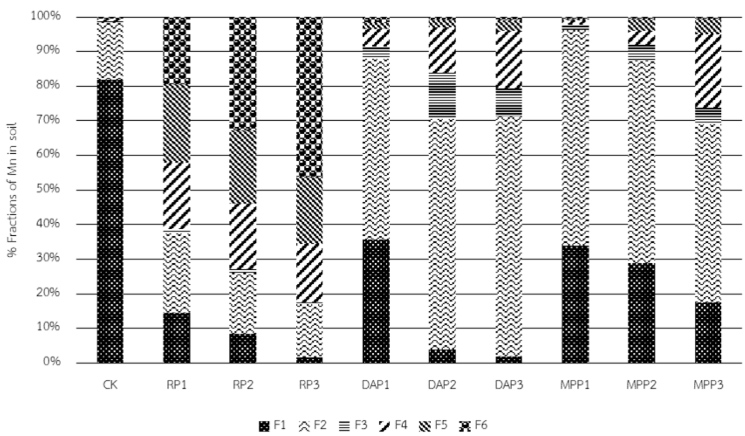

Figure 3. Forms of Mn after adding modifiers to soil (water soluble form (F1), exchangeable form (F2), carbonate bound form (F3),Fe-Mn oxide bound form (F4), organic bound form (F5) and residual form (F6))

Addition di-ammonium phosphate and monopotassium phosphate, Cd was more in stable form in comparison to the control. However, when compared to rock phosphate, Cd was found less in the stable form. Yan *et al.* (2015) studied on using di-ammonium phosphate to stabilize metals in sandy soils and found that di-ammonium phosphate has a good ability to transform metals from a form that can move easily to a more stable form.

Forms of Pb

Figure 2 showed that Pb in the control was in a soluble form (11%) less than in the case of Cd (59%). The reason may be Pb concentration was several times higher than Cd. The amount of Pb and Cd dissolved in soil may not be very different but when calculating in term of the percentage, it was very different. About 65% of Pb in the control was in an unstable form.

Lead in a stable form significantly increased after adding of the phosphate fertilizers. The more fertilizer, the more Pb in the stable form. Lead was in a stable form (82-88%) when mixing the soil with rock phosphate. Adding 5.0 g_P/kg_{soil} and 7.5 g_P/kg_{soil} monopotassium phosphate into the soil resulted in no significant difference at 95% confidence level. Lead in the stable form increased 60%. The main mechanism could be the precipitation of Pb with rock phosphate to highly stable pyromorphite [$(Pb_5(PO_4)_3)Cl$] (Zhang *et al.*, 2015).

Forms of Mn

Figure 3 showed Mn ions in the control (CK) was mostly in a soluble form (81.76%), followed by an exchangeable form (16.65%).

Adding rock phosphate 7.5 g_P/kg_{soil}, 83% of Mn changed from an unstable form to a stable form as high as 83%. The reasons were the same as in the case of Cd. Rock phosphate and monopotassium phosphate had a good ability to reduce the movement of Cd, Pb, and Mn in the acid soil. However, using rock phosphate could decrease the risk of eutrophication occurring due to its lower water-soluble (Hettiarachchi *et al.*, 2001: Seshadri *et al.*, 2017).

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3.3 The metal ions potential to move into the biosystem

The study was carried out by performing a single step extraction method. Four extraction solutions were used as follow: 0.05 M Ethylenediaminetetraacetic acid (EDTA), 0.005 M Diethylenetriamine pentaacetic acid (DTPA), 0.01 M Calcium chloride (NH_4OAc). The results were presented in Figure 4-6.

EDTA can extract metals in soluble form, exchangeable form, carbonate bound form and partly of Fe-Mn oxide bound form and organically bound form (Chang *et al.*, 2014). It can be used to assess the ability of metals to move in the environment. Ammonium

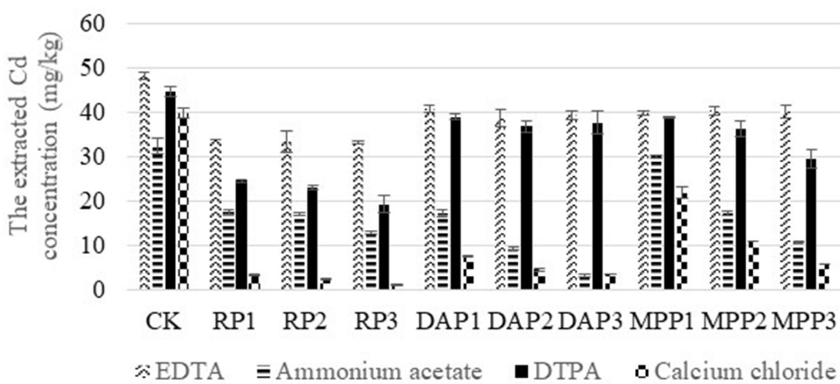

Figure 4. Cd concentration when extracted with EDTA, ammonium acetate, DTPA, and calcium chloride

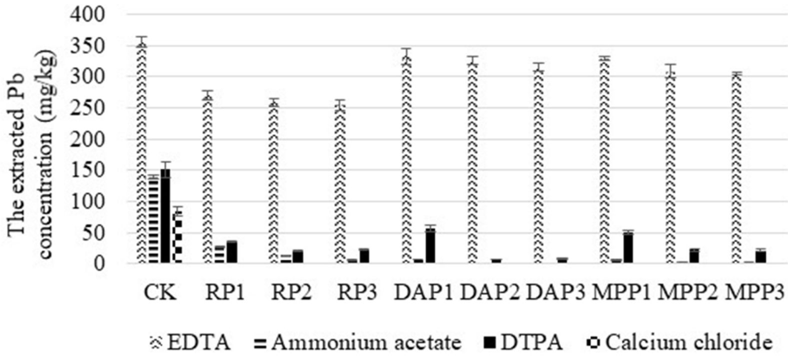

Figure 5. Pb concentration when extracted with EDTA, ammonium acetate, DTPA, and calcium chloride

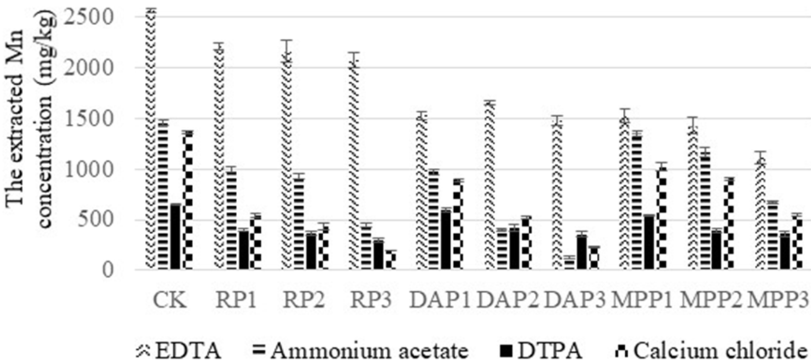

Figure 6. Mn concentration when extracted with EDTA, ammonium acetate, DTPA, and calcium chloride

acetate can extract metals in soluble form and exchangeable form (Zhang *et al.*, 2010). It can be used to assess the exchangeability of metals. DTPA can extract metals in soluble form, exchangeable form, and partly of organically bound form. $CaCl_2$ can only extract metals in soluble form. DTPA and $CaCl_2$ can be used to assess the phytoavailability (Tica *et al.*, 2011). From Figure 4, the concentration of cadmium in solutions extracted with EDTA, DTPA, and $CaCl_2$ was the lowest when adding rock phosphate to the soil. This means that rock phosphate was effective in reducing the cadmium potential to move from soil to plant.

Figure 6 showed that rock phosphate could be the best modifier to reduce the movement of Mn to plants.

The value of the extracted metals from RP3 by $CaCl_2$ solution (non-detected for Cd and Pb, 3 mg/kg for Mn) was close to the F1 portion when extracted by sequential extraction method (2 mg/kg for Cd, non-detected for Pb, 6 mg/kg for Mn). When extracted by sequential extraction method, the F1 + F2 portion of Cd, Pb and Mn was 30, 2 and 18 mg/kg, respectively, which was close to the concentration of metals when extracted by NH_4OAc solution (30 mg/kg for Cd, 3 mg/kg for Pb, 21 mg/kg for Mn).

4. Conclusions

Rayong soil sample used in this study was an acid sandy loam soil. The addition of 7.5% rock phosphate and monopotassium phosphate resulted in increasing the soil pH to 6.5-7. The soil was still strong acid after adding the diammonium phosphate. Formation of Cd, Pb, and Mn in soil changed after adding modifiers. Metals in unstable forms reduced and in stable forms increased. The 7.5 g*P*/kg*soil* of rock phosphate was the best modifier to reduce mobility, exchangeability, and phytoavailability of Cd, Pb, and Mn ions.

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References

Cao X, Wahbi A, Ma L, Li B, Yang Y. Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid. Journal of Hazardous Materials 2009; 164: 555–564.

Chang YT, Hseu ZY, Zehetner F. Evaluation of phytoavailability of heavy metals to Chinese cabbage (Brassica chinensis L.) in rural soils. The Scientific World Journal 2014; 2014: 309-396.

Chen S, Xu M, Ma Y, Yang J. Evaluation of different phosphate amendments on availability of metals in contaminated soil. Ecotoxicology and Environmental Safety 2007; 67(2): 278-285.

Department of Agriculture. Guide to chemical fertilizer analysis. Institute of Agricultural Research and Development. Department of Agriculture. Ministry of Agriculture and Cooperatives. Bangkok. Thailand. 2008.

Department of Groundwater Resources. Final report: Contamination study and networking of surveillance of contaminant contamination in underground water resources in Amphoe Tab Kola, Amphoe Wang Sai Poon, Pichit Province and Amphoe Wang Pong, Phetchaboon Province. Department of Groundwater Resources. Ministry of Natural Resources and Environment. Bangkok. Thailand. 2011. Available at: http://www.dgr.go.th/newproject/53/FinalReport.pdf. [Accessed March 1, 2018]

Department of Land Development. Manual of soil analysis, soil fertility, soil improvement materials and analysis to certify the product. Department of Land Development. Ministry of Agriculture and Cooperatives0. Bangkok. Thailand. 2014.

Hettiarachchi GM, Pierzynski GM, Ransom MD. In situ stabilization of soil lead using phosphorus. Journal of Environmental Quality 2001; 30(4): 1214-1221.

Huang G, Su X, Rizwan MS, Zhu Y, Hu H. Chemical immobilization of Pb, Cu, and Cd by phosphate materials and calcium carbonate in contaminated soils. Environmental Science and Pollution Research 2016; 23(16): 16845-16856.

Mignardi S, Corami A, Ferrini V. Evaluation of the effectiveness of phosphate treatment for the remediation of mine waste soils contaminated with Cd, Cu, Pb, and Zn. Chemosphere 2010; 86(4): 354-360.

Mulligan CN, Yong RN, Gibbs BF. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. Engineering geology 2001; 60(1): 193-207.

Notification of the National Environment Board No. 25. Soil quality standards. 2004. Available at: http://www.onep.go.th/topics/20748. [Accessed February 13, 2018]

Seshadri B, Bolan NS, Choppala G, Kunhikrishnan A, Sanderson P, Wang H, Kim K. Potential value of phosphate compounds in enhancing immobilization and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. Chemosphere 2017; 184: 197-206.

Sirichamorn Y, Phuekvilai P, Yookongkaew N. Potential of heavy metal uptake and accumulation in dominant herbaceous plants around gold mine areas in Pichit Province. Science and Technology Journal 2017; 25(1): 110-123.

Sun Y, Zhou Q, Xie X, Liu R. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. Journal of hazardous materials 2010; 174(1): 455-462.

Sungur A, Soylak M, Ozcan H. Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability. Chemical Speciation & Bioavailability 2014; 26(4): 219-230.

Tessier A, Campbell PG, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry 1079; 51(7): 844-851.

Tica D, Udovic M, Lestan D. Immobilization of potentially toxic metals using different soil amendments. Chemosphere 2011; 85(4): 577-583.

Uddin MK. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chemical Engineering Journal 2017; 308: 438–462.

US. EPA. Acid digestion of sediments, sludges and soil / SW-846 Method 3050b. 1996. Available at:
https://www.epa.gov/sw-846/pdfs/ 3050b.pdf. [Accessed November 11, 2017]

Wu YJ, Zhou H, Zou ZJ, Zhu W, Yang WT, Peng PQ, Zeng M, Liao BH. A three-year in-situ study on the persistence of a combined amendment (limestone + sepiolite) for remedying paddy soil polluted with heavy metals. Ecotoxicology and Environmental Safety 2016; 130: 163–170.

Xu Y, Schwart FW. Lead immobilization by hydroxyapatite in aqueous solutions. Journal of Contaminant Hydrology 1994; 15(3): 187-206.

Yan Y, Zhou YQ, Liang CH. Evaluation of phosphate fertilizers for the immobilization of Cd in contaminated soils. PloS one 2015; 10(4): 124-132.

Zhang MK, Liu ZY, Wang H. Use of single extraction methods to predict bioavailability of heavy metals in polluted soils to rice. Communications in Soil Science and Plant Analysis 2010; 41(7): 820-831.

Zhang Z, Guo G, Teng Y, Wang J, Rhee JS, Wang S, Li F. Screening and assessment of solidification/stabiliza tion amendments suitable for soils of lead-acid battery contaminated site. Journal of hazardous materials 2015; 288: 140-146.