THE JOURNAL OF SOLID WASTE TECHNOLOGY AND MANAGEMENT

Formerly The Journal of Resource Management and Technology (Volumes 12-22) Formerly NCRR Bulletin (Volumes 1-11)

August 2009	Volume 35	Number 3
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THE JOURNAL OF SOLID WASTE TECHNOLOGY AND MANAGEMENT

ISSN: 1088-1697

Indexed/Abstracted by: Chemical Abstracts; Engineering Abstracts; Environmental Abstracts; Environmental Periodicals Bibliography; Pollution Abstracts, All-Russian Institute of Scientific and Technical Information (VINITI, REFERATIVNYI ZHURNAL)

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EFFECTS OF PHOSPHATE CHEMICALS TREATMENTS ON AUTO BATTERY WASTE CONTAMINATED SOIL IN NIGERIA

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ABSTRACT

Auto battery waste contaminated site poses potential threats to the environment and biological life through lead toxicity, thus making remediation imperative. The possibility of using phosphate chemicals to reclaim a grossly lead-contaminated site was explored. The study site was an abandoned lead-acid battery waste dumpsite in Nigeria. Phosphate chemicals were applied at 5 and 10% phosphorus levels to the contaminated soil collected from the site in incubation experiments. The air-dried sub-samples of the incubated soils were analyzed for pH, P, bioavailable Pb and TCLP- extractable Pb. Results showed that 99.5% of the applied phosphorus was removed by the end of the first week of incubation. Incubation time showed less effect on Pb immobilization. A 10% phosphorus application resulted in reductions of water soluble Pb between 77.8% and 86.4% thus eliminating to a reasonable extent, the hazard to living things and the environment. TCLP extractable Pb was reduced from 50.2 mg/L in untreated soil to below the acceptable value of 5.0 mg/L. An application of 10% CHP produced overall effectiveness in the reduction of bioavailable Pb, TCLP-extractable soil Pb. This treatment also had little effect on soil acidification and resulted in the least residual P. Results therefore indicated that phosphorus can be used as potential chemical remediation for cleanup of battery waste contaminated soils.

Keywords: Lead; contaminated soil; battery waste; remediation; phosphate chemicals; speciation

INTRODUCTION

Contamination by heavy metals is a global concern due to its threats to all living things and the environment. There are documented reports identifying waste from industrial activities as the major route by which heavy metals reach the soil at the levels that are precarious to living organisms and the general environment (Balkrishena et al, 1999; Andy and Roberts, 2002; Boularbah et al., 2006; Everhart et al., 2006; Sanghoon, 2006; Li et al., 2005; Peplow and Edmonds, 2005; Chopin et al., 2003). Lead contamination particularly is of great concern owing to its outcome on human health in terms of neurological, metabolic and behavioral changes produced in children (Kaul et al., 1999; ATSDR, 2005).

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The effectiveness of phosphate chemicals in immobilizing bioavailable Pb in Pb contaminated soils has been well documented. Many bench scale batch, continuous flow column, incubation, pot and field experiments have been conducted by researchers on lead-contaminated soils to determine the rate and extent of lead immobilization with phosphorus amendments (Ma et al. 1995; Ma and Traina, 1999; Berti and Cunningham, 1997; Ownby et al., 2005; Laperche et al., 1996; McGowen et al., 2001; Brown et al., 2004; Chen et al., 2003; Yang and Mosby, 2006). Pyromorphites have been reported to be stable over a wide range of environmental conditions and are biologically inert. In addition, they do not dissolve in the human digestion system even when ingested, but rather pass through unabsorbed without being deleterious (Ma et al., 1995; Zhang and Ryan, 1998).

The site for the present study was polluted with auto battery waste by a defunct automobile battery manufacturing company located at Lalupon, Ibadan, Nigeria. The company dumped slag obtained from the lead smelting operations spanning from 1996 to 1998. A huge pile of waste by the company was left in the open and untreated. The preliminary study showed that lead levels ranged from 120-124 000 and 25.4-4300 mg Pb/kg soil in the waste and the surrounding soils respectively, indicating levels higher than the clean-up level (400 mg/Kg) of Pb in soil. Based on the pilot study, the site constituted a potential hazard to the environment and biologic life, hence the need for decontamination of the site. The objective of the study was to evaluate the remediation effects of phosphate chemical treatments on the auto battery waste contaminated soil.

Materials and methods

Site description

A lead-acid battery manufacturing company located at Lagelu Local Government area of Ibadan. Nigeria dumped solid waste slag on a hectare of land in a disused quarry situated in Lalupon on the outskirts of Ibadan. The company had since gone into liquidation. Selected waste and soil samples tested for Toxicity characteristic Leaching procedure (TCLP) had mean values of leachable lead of 171 and 63.9 mg Pb/L respectively. These values categorized the waste and the surrounding soils as hazardous and requiring remediation.

Experimental materials

The sample used for this experiment was collected from slag guided by the results of preliminary studies of total environmentally available metal determination. The phosphorus sources used included soluble diammonium hydrogen phosphate (DAP): $(NH_4)_2HPO_4$, less soluble calcium hydrogen phosphate (CHP): CaHPO₄ and the combination of the two (DAP + CHP). Less soluble CHP and soluble DAP were chosen as the phosphate chemical amendments because H⁺ and PO₄³⁻ ions are easily more released than the insoluble apatite and phosphate rock used in other studies (McGowen et al., 2001).

Soil properties

Total environmentally available Pb was assessed in the experimental soil using 2 M HNO₃. Soil pH was measured in a 1:1 ratio of soil to water (w/v) using a glass electrode pH meter. Available phosphorus was extracted with Olsen's reagent (0.5 M NaHCO₃ adjusted to pH 8.2, 1:20 soil/solution ratio) and determined colorimetrically by molybdenum blue ascorbic acid method (Stewart, 1989). The hazardous status of the soil was tested using Toxicity Characteristic Leaching procedure (TCLP, SW-846 Method 1311) (USEPA 1992).

Addition of phosphate chemicals

In preliminary optimization experiments, the different P sources at application rates of 0%, 5%, 10%, 15% and 20% were applied to the experimental soil to determine the extent of reduction of bioavailable Pb. Through this experiment, it was discovered that there was no significant difference between the effects produced by 10% and 15% phosphorus application. This formed the basis for choosing the following phosphorus amendment treatments in the form of DAP, CHP and DAP + CHP, each at application rates of 0%, 5%, and 10%. An application rate of 0% represented the control, which was contaminated soil without the addition of an amendment.

Seven treatments with 100 % duplicates were examined: 1. 0% (1.0 kg soil + 0.0 g amendment);

- 2. 5 % P as DAP (1.0 kg soil + 28.1 g DAP);
- 3. 10 % P as DAP (1.0 kg soil + 56.3 g DAP);
- 4. 5 % P as CHP (1.0 kg soil + 29.9 g CHP);
- 5. 10 % P as CHP (1.0 kg soil +59.7 g CHP);
- 6. 3.75 % P as DAP + 1.25 % P as CHP (1.0 kg soil + 21.1 g DAP + 7.5 g CHP);
- 7. 5 % P as DAP + 5 % P as CHP (1.0 kg soil + 28.1 g DAP + 29.9 g CHP).

Procedure

A large quantity mixture of soil and waste sample was collected from the area of highest contamination as revealed by the pilot study. This mixture was air dried, homogenized by grinding and then sieved through a < 2 mm pore sieve. An analysis of the sample for environmentally available Pb showed that the soil sample contained about 95700 mgPb/kg soil. One kilogram samples of the air-dried, sieved soil were weighed into 1 L polyethylene containers. The soil amendments were applied to the soil in the plastic containers at rates of 0 %, 5.0 % and 10.0 % phosphorus from the phosphorus sources. The contents of the containers were mixed thoroughly and deionized water was added to obtain 20 % gravimetric moisture containers were covered partially to reduce moisture loss and to allow for gas exchange.

The soil samples were incubated at room temperature for 12 weeks. Sub-sampling of the incubated soils was done after one week and subsequently at 4 weeks intervals. The water content of 20 % per Kg soil was ensured by re-watering each

container once weekly. The soils were thoroughly mixed at weekly intervals. At the different incubation times sub samples of approximately 100 g were taken from the containers after thorough mixing,. The sub-samples were air-dried, sieved to < 2 mm and analyzed for pH, Oslen-exractable P, Pb fractions and TCLP-extractable Pb.

Quality control: All treatments and analyses were carried out in duplicate. For every batch of samples processed, a method blank was included and appropriate corrections made.

Determination of pH of the incubated soil

Soil pH was measured in a 1:1 ratio of soil to water (w/v) using a glass electrode pH meter.

Ten grams of the air-dried soil samples was added to 10.0 mL of deionized water. The pH was measured after the mixture was stirred at 10 minutes interval for 30 minutes and then left standing for 1 hour.

Determination of available phosphorus in the amended soils

The available phosphorus in the amended soils was extracted with Olsen's reagent (0.5 M NaHCO₃ adjusted to pH 8.2, 1:20 soil/solution ratio) and determined colorimetrically by molybdenum blue ascorbic acid method (Stewart, 1989).

Leaching of incubated soils

The effectiveness of the chemical treatments in immobilizing lead in the incubated soils was tested by comparing the concentrations of lead in the chemically treated soils to those of the untreated soils. The sequential extraction procedure developed by Tessier et al (1979) was modified for the study. The procedure was modified to separate heavy metals into six operationally defined fractions: water extractable, extractable with water ; exchangeable, extractable with 1.0 M MgCl₂ at pH 7; specifically sorbed and carbonate bound, extractable with 1.0 M (CH₃COONa) adjusted to pH 5.0; metals associated or sorbed or occluded mainly on iron or extractable with hydroxylamine manganese oxides, (NH₂OHHCl in HNO₃); strongly complexed by organic matter, extractable with H_2O_2 in HNO₃; and residual extracted with 4 M HNO₃.

Toxicity testing of the incubated soils

Samples of 2.5 g of air-dried incubated soil, sieved to < 2

mm, were weighed into sealed wide-mouth 100 mL polyethylene jars. Fifty millilitres of 0.1M sodium acetate buffer was added and the mixture was agitated on an end-to-end shaker for 18 hours at 30 rpm. The extracts were stirred with a glass rod after the required period had elapsed. The extracts were transferred into polyethylene centrifuge tubes and separation was done by centrifuging at 5,000 rpm for 30 minutes. The supernatants were acidified by 0.2 conc. HNO₃ to pH < 2 until analysis when they were analyzed with AAS.

Statistical analysis

Data were analyzed using one-way ANOVA of SPSS statistical package version 14.0. Significant means were separated using Duncan multiple range F-test.

RESULTS AND DISCUSSION

Soil properties

The analytical parameters of the experimental soil are shown in Table 1. The estimated level of Pb that could be available and cause injury in the environment was found to be 95700 mg/kg soil. The pH of the experimental soil was mildly acidic. Phosphorus content of the soil indicated that the soil was deficient in phosphorus. This can be an added advantage to the choice of phosphate remediation of the contaminated site. The high concentration of TCLP extractable Pb presents the site as hazardous and requires remediation.

Effect of phosphate amendments on Soil pH

The pH of the incubated soils was monitored to verify the impact of the amendments on soil acidification. This was to ensure that during field application, some other toxic metals that might be present in the soil would not be made active due to increased acidity of the amended soil, thereby creating an additional environmental risk. The pH of the experimental soils, including that of the control, varied slightly with time as shown in Figures 1 and 2. The reason for the variation was unknown, although it might be due to the effect of microbial activities. The pH varied according to the type of phosphorus sources and the amount added to the experimental soils. The pH ranged from 5.17-5.26 (control), 4.88-5.58 (DAP), 5.01-5.50 (CHP) and 4.83-5.52 (DAP+CHP). The highest change was observed at week 8. After one week of P application, all

TABLE 1					
Analytical	parameters of the experimental so	il			

Pb (mg/kg)	pН	P(mg/kg)	TCLP extractable Pb (mg/L)
95700	5.2	2.83	50.4

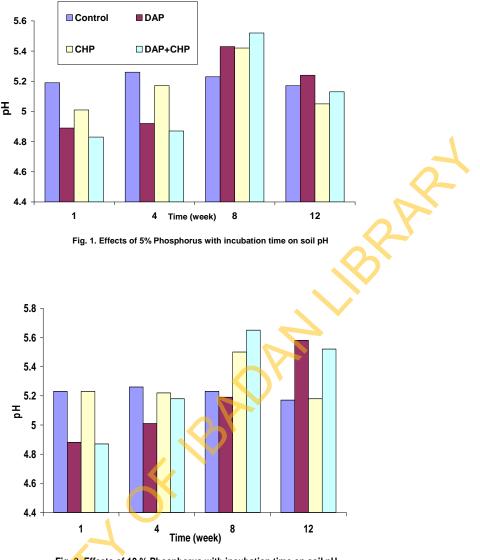


Fig. 2. Effects of 10 % Phosphorus with incubation time on soil pH

the amendments except 10 % CHP caused a slight decrease in the pH of the treated soils from 5.19 (control) to a minimum of 4.83 (DAP + CHP). The application of DAP and DAP+CHP produced the highest decrease in the pH of the treated soils. It was apparent that the reduction in pH produced by the mixture was influenced primarily by the presence of DAP. Bolan and Duraisamy (2003) and Pierzynski and Schwam, (1993) documented similar observations with DAP. The initial reduction in pH observed with the phosphate treated soils may be explained by the following soil reactions in the generation of protons during pyromorphite formation:

$$(NH_4)_2 HPO_4 (s) + H_2O (l)$$
 dissolution

 $2NH_4^+$ (aq) + $H_2PO_4^-$ (aq) + OH^- (aq) (Diammonium hydrogen phosphate)

$$2HNO_3 + 6H^+(aq) \xrightarrow{\text{Nitrification by microbial action}} 2NH_4^+(aq) + 3O_2(g)$$

Ca HPO₄ + H₂O (1)
$$\leftarrow$$
 Ca²⁺ (aq) + H₂PO₄ (aq) +

OH⁻ (aq)(Calcium hydrogen phosphate)

$$5Pb^{2+}(aq) + 3H_2PO_4(aq) + H_2O(l)$$

 $[Pb_5(PO_4)_3OH](s) + 7H^+(aq)$
(pyromorphite)

These equations show that the initial reduction in pH produced by the phosphate treated soils resulted from the generation of protons during pyromorphite formation. Ammonium ions produced during DAP dissolution were nitrified to nitric acid (HNO₃) by soil microbes. This is suspected to be the reason why the reduction in pH was more pronounced with DAP. In contrast, such soil reaction was not observed to occur with the CHP treated soil. This acidifying power of nitrogen fertilizers was reported to be partially neutralized during field application when plants took up the resulting NO₃⁻ ions (Bolan and Duraisamy, 2003).

As the week of the incubation period increased, the pH of the amended soil adjusted naturally towards the pH of the control soil. It is worth noting that during the pyromorphite formation, hydroxyl ions were created thereby clarifying the pH adjustment towards the neutral side. At the end of incubation period, all other amendments except CHP produced slight increments in the pH of the soil. For example, 5 %, 10 % DAP and 10 % mixture of DAP and CHP shifted the pH of the soil from 5.16 to 5.24, 5.58 and 5.52 respectively. The pH of the soils treated with 10 % CHP (5.16) at the end of the incubation period was comparable to the pH of the untreated soil (5.17). Apart from the fact that the pH of the experimental soil itself was acidic as observed with the untreated soil, none of the amendments can be said to produce any undesirable effects on pH of the soil. The initial lowering of pH and eventual increment induced by DAP-containing amendment may be an added advantage for a near neutral Pbcontaminated soil. The dissolution of soil Pb was complimented by reduced pH, and stability of the Pb pyromorphite formed was enhanced at near neutral pH (Chen et al., 2003; McGoween et al., 2001). The implication was that if the right proportion of any of the experimented amendments was used on normal soil, it might not significantly alter the pH of the soil. Thus, the application of soluble phosphorus salts to leadcontaminated soil may not require liming every time. Nevertheless, field applications of any of these chemicals on acidic soil as in the present study might require liming in order to enhance the stability of the pyromorphite minerals formed.

Effect of time on extractable phosphorus

Removal of the available P from incubated soils over time was recorded to estimate the effect of time on the pyromorphite formation in the treated soils. This was necessary to estimate the length of time the amendment would take to produce the desired results on the field applications. Reduction in the amount of phosphorus remaining in the soil with incubation time was evident with all the amendments (Table 2), implying that a reaction actually occurred in the soil between lead and phosphorus. This removal was most likely a result of lead phosphate mineral formation. Some authors have also identified such phenomenon in both laboratory and field trials (Zhang and Ryan, 1999; Zhang et al., 1997; Cao, et al., 2002; Chen et al., 2003). This however was contrary to the opinion of other reports that the shaking during the sequential extraction to evaluate the effectiveness of the amendments might be a major contributor to the formation of pyromorphite.

The results in Figure 3 show that immobilization of Pb as indicated by P removal was about 99.5 % completed by the

% P in P source	Chemical weight (g) P added (mg/kg)		Sodium bicarbonate-extractable P (mg/kg)			
			Week 1	Week 4	Week 8	Week 12
		,0	DAP			
0.0	0.0	0.0	2.90	2.56	3.25	2.62
5.0	28.1	6600	34.7	26.9	25.9	25.3
10.0	56.3	13200	67.9	52.2	51.4	53.1
			CHP			
0.0	0.0	0.0	2.90	2.56	3.25	2.62
5.0	29.9	6800	33.6	26.8	24.9	22.4
10.0	59.7	13600.0	68.9	62.2	59.2	52.1
		I	DAP + CHP			
0.0	0.0	0.0	2.90	2.56	3.25	2.62
5.0	28.6	6650	38.8	28.3	28.0	25.5
10.0	58.0	12400	60.5	47.9	46.9	47.1

 TABLE 2

 Effects of phosphate amendments on soil residual phosphorus

DAP = Diammonium hydrogen phosphate

CHP = *Calcium hydrogen phosphate*

end of the first week of incubation. Hettiarachchi et al (2001) also reported similar observations that the reaction between soil Pb and P was likely to have occurred within the first three days of incubation and the change was not significant thereafter. This indicated that there was rapid dissolution of soil lead aided by the reduced pH, presumably with a consequent reaction with the solution phosphorus to form pyromorphite minerals. Larperche et al (1996) corroborate that the conversion of lead (II) oxide (PbO) to pyromorphite was most rapid at pH 5.0. The almost complete reaction observed within the first week of application suggested the appropriate time frame is one week to lime an acidic lead-contaminated soil for optimum effective phosphate remediation technology. The application of lime to phosphate treated soil earlier than a week of application may increase the soil capacity for binding Pb, thereby limiting the release of Pb to react with the solution P. Many reports investigating soluble phosphates as sources of P for lead immobilization in contaminated soils applied lime at different times (Yang and Mosby, 2006; Hettiarachchi et al., 2001; McGowen et al., 2001). This work, however, showed the first week of the treatment as the best time to apply lime. It was also speculated that the addition of lime after the phosphate treatment could augment the stabilization of excess added phosphate by the formation of calcium phosphate or apatite which prevents the excess phosphate from leaching out of the remediated soils (Yang and Mosby, 2006).

Phosphorus sources and rates in relation to soil residual phosphorus

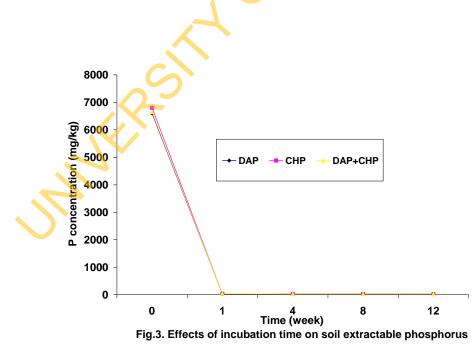
There is need for caution when carrying out in-situ immobilization of Pb in contaminated soil with the use of phosphate chemicals. Excess P in the environment may stimulate excessive growth of algae on surface water which may lead to depletion of oxygen and blockage of sunlight available to aquatic life (Cao et al., 2002; Hettiarachchi et al., 2001; McGowen et al., 2001). This necessitates the need to monitor the residual phosphorus in the phosphate remediated soils. Testing of soil P revealed that the concentration of phosphorus in the untreated soil was about 2 mg/kg, showing that the soil was deficient in phosphorus. Thus, there was an additional advantage in choosing phosphate remediation methods to decontaminate this site.

The residual P in the treated soils ranged from 22.4-53.1 mg/kg, which accounted for less than 0.5 % of the P applied to the contaminated soil. This range is far less than the range of total P concentrations of 200 to 5000 mg/kg soil normally encountered in soil as cited by Hiettiarachchi et al (2001), suggesting that the application of regulated amounts of any of these phosphate chemicals to the contaminated site may cause little or no undue P increment in the environment. The concentration of the residual P in the present study was in proportion to the amount of P applied, corroborating the need to be cautious in the amount of P introduced into the soil.

The application of P as CHP yielded the least residual P at the end of the incubation period while DAP produced the highest. This might have resulted from the formation of calcium phosphate $[Ca_3(PO_4)_2]$ or apatite $[Ca_5(PO_4)_3OH]$; both are reported to be environmentally stable alongside with pyromorphite formation (Yang and Mosby 2006).

Fractionation of Pb in an incubated soil

The effectiveness of 5 % and 10 % P applications as DAP, CHP and DAP + CHP in the incubated soils was evaluated using chemical fractionation procedure. The fractions of lead in the control soils were compared with the fractions of lead in the treated soils. The results are as presented in Figure



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4. Sequential extraction of the untreated soil showed that Pb was associated mainly with the residual fraction (85300 mgPb/kg), followed by the Fe-Mn oxide (31900 mgPb/kg), carbonate bound (24300 mgPb/kg), organic matter bound (12700 mgPb/kg), exchangeable (5680 mgPb/kg) and water soluble (266 mgPb/kg) fractions. Generally, the added phosphate chemicals reduced the concentrations of Pb in water soluble, exchangeable, carbonate bound and Fe-Mn oxide fractions, and increased residual Pb concentrations in the treated soils when compared with the fractions of the untreated soil. This is consistent with the results of Ma and Rao (1997) who reported that phosphate rock transformed Pb from non-residual forms to residual forms. Others document similar results that treatment of Pb-contaminated soil with phosphate chemicals results in the formation of pyromorphites (lead phosphate) which has low water solubility (Berti and Cunningham, 1997; McGowen et al., 2001; Ma et al., 1995). The effects of reduction were primarily on water soluble Pb followed by the Fe-Mn oxide bound fraction. Melamed et al (2003) and Chen et al (2003) observed a significant decrease in Fe-Mn oxide bound Pb upon applications of phosphorus. They attributed the decrease to the dissolution of the oxides and release of sorbed Pb as a result of low pH initiated by the soluble phosphates. The reduction in the distribution of Pb in the treated soil was less than expected, which might be due to the influence of the low pH of the experimental soil. This reiterates the need for liming of acidic soil for effective phosphate chemical remediation. Five percent DAP, CHP and DAP + CHP produced 50.9, 61.6 and 79.1 % reduction in water soluble extractable Pb respectively while 10 % DAP, CHP and DAP + CHP produced 77.8, 84.2, 86.4 % reduction in water soluble Pb respectively. The main objective of the remediation technique is to eliminate or lower the most available form of contaminant in the polluted soil, as noted in the present study.

Five percent DAP, CHP and DAP + CHP reduced the sum of the water soluble, exchangeable, carbonate bound and Fe-Mn oxide bound fractions by 22.6%, 34.6% and 25% respectively while a 10 % P application as DAP, CHP and DAP + CHP caused 24.7%, 47.3% and 42.5% reductions respectively. The higher percentage of transformation of nonresidual Pb to residual Pb resulting from a 10 % P application corroborated the theory that pyromorphite forms rapidly when sufficient Pb and P are present in aqueous solutions (Ma et al., 1993). When comparing the effectiveness of the P sources, CHP was more effective in transforming nonresidual Pb to residual fraction. Ten percent CHP produced the highest reduction in Pb concentration in the fractions. It produced 84.2, 27.8, 55.5, and 44.2% reductions in water soluble, exchangeable, carbonate bound and Fe-Mn oxide Pb fractions respectively while DAP produced the least effectiveness. Duncan one-way analysis of variance showed that there were significant (p < 0.05) differences between the Pb fractions in the treated soils and Pb fractions in the untreated soils. The analysis also confirmed 10 % P application to be the most effective and CHP to produce more effectiveness than others.

All the amendments at the different rates caused a slight increase in the Pb concentrations in organic fraction, with 5

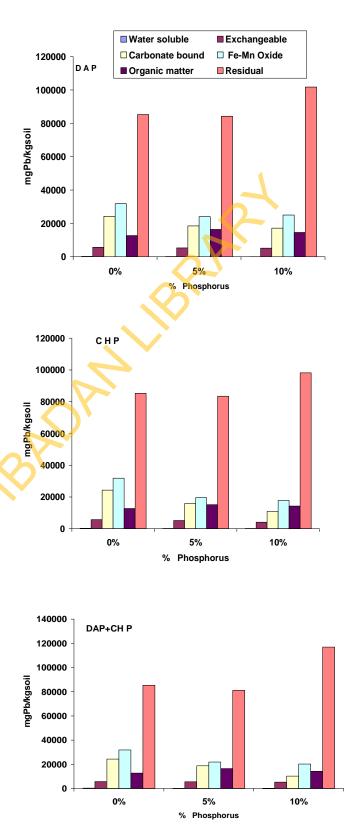


Fig. 4. Effects of phosphate chemicals on the distribution of Pb in the incubated soils at 12 weeks

% P application causing the highest increase. This observation may be connected with acidic nature of the incubated soils. The pH of the soils that received 5 % DAP, CHP and DAP + CHP at the end of the 12 weeks incubation period were 5.24, 5.05 and 5.13 respectively, and those of 10 % DAP, CHP and DAP + CHP were 5.58, 5.16 and 5.52 respectively. These observations demonstrated that increases in pH would favor stability of the newly formed lead phosphate. This inference further emphasizes the need to lime acidic soil.

Toxicity characteristics leaching procedure

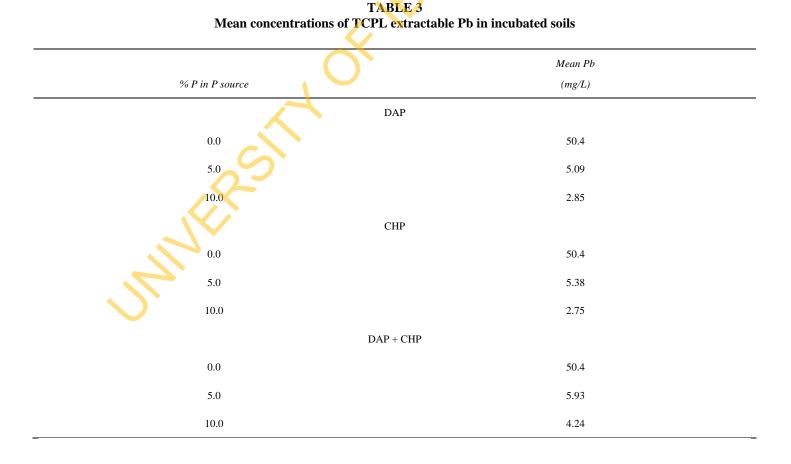
Toxicity characteristics leaching procedure (TCLP) of untreated soils was 50.4 mg/L and was noticed to be well above the critical level of 5 Pb mg/L recommended by the United States Environmental Protection Agency (Chen et al., 2003). The addition of phosphate chemicals at the different rates significantly reduced the TCLP extractable Pb. A 5 % P application of all the phosphate chemicals reduced the leachable lead from 50.4 mg/L to below 6 mg/l, and a 10 % P addition reduced it to below 5 mg/L, the regulatory limit of toxicity characteristic leaching procedure (Table 3). The highest reduction in TCLP extractable Pb concentration (2.75 mg/L) was caused by 10 % CHP, indicating that a 10 % P application as CHP is more effective at reducing the hazardous status of the soil than other applications. This was consistent with the results for fractionation of Pb in the incubated soils where CHP produced the overall effect of reducing bioavailable Pb with little or no impact on soil acidification and least residual P.

CONCLUSION

The application of phosphorus sources in incubation studies did not result in soil acidification. Consequently, the re-mobilization of metals in field applications using this technology is almost ruled out. The application of phosphate chemicals at the experimented rates did not show excessive residual soil phosphorus; therefore, undue environmental impact is not anticipated in the field application of the method. The addition of phosphate chemicals to the contaminated soils reduced the concentrations of Pb in water soluble, exchangeable, carbonate bound and Fe-Mn oxide fractions, as well as increased residual Pb concentrations when compared with the fractions of the untreated soil. This demonstrates effectiveness in reducing potential bioavailable lead.

The addition of phosphate chemicals at the different rates significantly reduced the TCLP extractable Pb below the USEPA regulatory levels of 5.0mg/L, predicting potential reduction in the hazardous status of the site during field application.

Considering the reduction of bioavailable Pb in the treated soil, the low contents of the residual phosphorus, and



the excellent reduction in TCLP leachable Pb with little or no impact on soil acidification, 10 % phosphorus amendments as DAP, CHP and DAP+CHP, especially CHP, can be promising remediation techniques for the studied site. Upon determining the total Pb concentrations in a particular Pb contaminated soil, the amount of the phosphate amendment required can be extrapolated based on the results of this study.

REFERENCES

- 1. Agency for Toxic Substances and Disease Registry, 1988. The nature and extent of lead poisoning in children in the United States: A report to Congress. U.S. Public Health Service, Washington, DC.
- Agency for Toxic Substances and Disease Registry, 2005. Toxicological Profile for Lead. U. S Department of Health and Human Services. Public Health Service, Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine/Applied Toxicology Branch 600 Clifton Road NE, Mailstop F 32, Atlanta, Georgia 30333.
- Andy, R., D. Roberts, 2002. "Health effects and landfills." Issues in *Environmental Science and Technology*, Volume 8, pp. 103-139.
- Balkrishena, K., S.S. Randhir, D. Conrado, R. Franklin, 1999. "Follow-Up Screening of Lead-Poisoned Children near an Auto Battery Recycling Plant, Haina, Dominican Republic." *Environmental Health Perspectives*, Volume 107, pp. 917-920.
- 5. Berti, W.R., S.D. Cunningham, 1997. "In-place inactivation of Pb in Pb contaminated soils." *Environmental Science and Technology*, Volume 31, pp. 1359-1364,
- 6. Bolan, N.S., V.P. Duraisamy, 2003. "Role of inorganic and organic soil amendments on immobilization and phytoavailability of heavy metals: a review involving specific case studies." *Australian Journal of Soil Science*, Volume 41, pp. 533-555.
- Boularbah, A., C. Schwartz, G. Bitton, W. Aboudrar, A. Ouhammou, J.L. Morel, 2006. "Heavy metal contamination from mining sites in South Morocco: 2. Assessment of metal accumulation and toxicity in plants." *Chemosphere*, Volume 63, pp. 811–817.
- Brown, S., R.L. Chaney, J.G. Hallfrisch, J.A. Ryan, W.R. Berti, 2004. "In Situ Soil Treatments to Reduce the Phyto- and Bioavailability of Lead, Zinc, and Cadmium." *Journal of Environmental Quality*, Volume 33, pp. 522-531.
- Cao, X., L.Q. Ma, M. Chen, S.P. Singh, W.G. Harris, 2002. "Impacts of phosphate amendments on lead biogeochemistry at a contaminated site." *Environmental Science and Technology*, Volume 36, No. 24, pp. 5296-5304.
- Centers for Disease Control, 1991. Preventing lead poisoning in young children. Atlanta, GA, U. S. Department of Health and Human services, public Health service, Centers for Disease Control and Prevention. Accessed from <u>http://wonder.cdc.go/wonder/prevguid/p0000029</u>/0000029.asp May 18, 2007.

- Chen, M., L.Q.S.P. MaSingh, R.X. Cao, R. Melamed, 2003. "Field demonstration of in situ immobilization of soil Pb using P amendments." *Advances in Environmental Research*, Volume 8, pp. 93–102.
- Chopin, E.I.B., S. Black, M.E. Hodson, M.L. Coleman, B.J. Alloway, 2003. "Preliminary investigation into mining and smelting impacts on trace element concentrations in the soil and vegetation around Tharsis, SW Spain." *Mineralogical Magazine*, Volume 67, No. 2, pp. 279-288.
- Everhart, J.L., M.J. David, E. Peltier, D. Van der Lelie, R.L. Chaney, D.L. Sparks, 2006. "Assessing nickel bioavailability in smelter-contaminated soils." *Science of the Total Environment*, Volume 367, Nos. 2-3, pp. 732-744.
- 14. Hettiarachchi, G.M., G.M. Pierznski, 2000. The use of phosphorus and other soil amendments for in-situ stabilization of soil lead. Proceedings of the 2000 conference on Hazardous Waste Research: Environmental challenges and Solutions to Research Development, Production and Use, Great Plains/Rocky Mountain Hazardous Substance Research Center, Denver, CO, May 20-23, 2000. 125-133.
- Hettiarachchi, G.M., G.M. Pierznski, M.D. Ransom, 2001. "In situ stabilization of soil lead using phosphorus." *Journal of Environmental Quality*, Volume 30, pp. 1214–1221.
- 16. Kaul, B., R.S. Sandhu, C. Depratt, F. Reyes, 1999. "Follow-up screening of lead-poisoned children near an auto battery recycling plant, Haina, Dominican republic." *Environmental Health Perspectives*, pp. 107: 917-920.
- Laperche, V., T.J. Logan, P. Gaddam, S.J. Traina, 1996. "Chemical and mineralogical characterizations of Pb in a contaminated soil: reactions with synthetic apatite." *Environmental Science and Technology*, Volume 30, pp. 3321-3326.
- Li, J., Z.M. Xie, Y.G. Zhu, R. Naidu, 2005. "Risk assessment of heavy metal contaminated soil in the vicinity of a lead/zinc mine." *Journal of Environmental Science*, Volume 17, No. 6, pp. 881-885.
- Ma, Q.Y, S.J. Traina, T.J. Logan, 1995. "Lead immobilization from Aqueous Solutions and Contaminated Soils Using Phosphate Rocks." *Environmental Science and Technology*, Volume 29, pp. 1118-1126.
- Ma, Q.Y, S.J. Traina, T.J. Logan, J.A. Ryan, 1993. "In situ lead immobilization by apatite." *Environmental Science and Technology*, Volume 27, pp. 1803–1810.
- Ma, Q.Y., G.N. Rao, 1997. "Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils." *Journal of Environmental Quality*, Volume 26, pp. 788–794.
- 22. Ma, Q.Y., S.J. Traina, 1999. "Aqueous Pb reduction in Pb-contaminated soils by Florida phosphate rocks." *Water, Air, and Soil Pollution*, Volume 110, pp. 1–16.
- McGowen, S.L., N.T. Basta, G.O. Brown, 2001. "Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil." *Journal of Environmental Quality*, Volume 30, pp. 493-500.
- 24. Ownby, D.R., K.A. Galvin, M.J. Lydy, 2005. "Lead and

zinc bioavailability to Eisenia fetida after phosphorus amendment to repository soils." Environmental Pollution, Volume 136, pp. 315-321.

- 25. Peplow, D., R. Edmonds, 2005. "The effects of mine waste contamination at multiple levels of biological organization." Ecological Engineering, Volume 24, Nos. 1-2, pp. 101-19.
- 26. Pierzynski, G.M., A.P. Schwab, 1993. "Bioavailability of zinc, cadmium and lead in a metal-contaminated alluvial soil." Journal of Environmental Quality, Volume 22, pp. 247-254.
- 27. Sanghoon, L., 2006. "Geochemistry and partitioning of trace metals in paddy soils affected by metal mine tailings in Korea." Geoderma, Volume 135, pp. 26-37
- 28. Stewart, E.A. 1989. Chemical analysis of ecological materials. 2nd Ed. Great Britain: Buller and Tanner.
- 29. Tessier, A., Campbell, P.G.C., Benon, M., 1979. "Sequential extraction procedure for the speciation of par-June ticulate trace metals." Analytical Chemistry, Volume 51, pp. 844-851.
- 30. US Environmental Protection Agency Method 1311. SW-846, 1992. Toxicity Characteristic Leaching Proce-

dure.

- 31. Yang, J., Mosby, D.E., 2006. "Field assessment of treatment efficacy by three methods of phosphoric acid application in lead-contaminated urban soil." Science of the Total Environment, Volume 366, pp. 136-142.
- 32. Yang, J., Mosby, D.E., Casteel, S.W., Blanchar, R.W., 2001. "Lead immobilization using phosphoric acid in a smelter contaminated urban soil." Environmental Science and Technology, Volume 35, pp. 3553-3559.
- 33. Zhang, P. Ryan, J.A., Bryndzia, L.T., 1997. "Pyromorphite formation from goethite adsorbed lead." Environmental Science and Technology, Volume 31, No. 9, pp. 2673-2678.
- 34. Zhang, P., Ryan, J.A., 1998. "Formation of pyromorphite in anglesite-hydroxyapatite suspensions under varying pH conditions." Environmental Science and Technology, Volume 32, No. 21, pp. 3318-3324.
- 35. Zhang, P., Ryan, J.A., 1999. "Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite." Environmental Science and Technology, Volume 33, No. 4, pp. 618-624.