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Green approach of chemical immobilization of lead in metal - contaminated soils of NCT of Delhi using rock phosphate

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ABSTRACT

In Chemical immobilization, an *in situ* remediation method, inexpensive chemical e.g., rock phosphate is used to reduce contaminant solubility in contaminated soil. We investigated the effectiveness of rock phosphate (RP), to reduce extractability and gastrointestinal (GI) bioavailability in two Cd- and Pb- contaminated soils from industrial sites in NCT of Delhi. The effect of soil treatment on metal extractability was evaluated by TCLP and on human GI availability of Pb from soil ingestion by the Physiologically Based Extraction Test (PBET). Rock phosphate GI-available Pb in both gastric and intestinal solutions was, 23 and 92%, respectively. Rock phosphate decreases risk from exposure to Pb via the soil ingestion pathway. Leachability of metals in treated soil was measured by using a combination of batch and bench tests to evaluate the immobilization capability of applied treatments. For efficient immobilization, pH reduction with H_3PO_4 became necessary to dissolve carbonate-bound metals and make them readily available for the geochemically stable metal phosphate formation.

INTRODUCTION

The soil is a key component of natural ecosystems because environmental sustainability depends largely on a sustainable soil ecosystem[1]. When soil is polluted, the ecosystem is altered. Throughout the last decade manufacturing industry, fertilizer application, sewage discharges and sludge disposal have resulted in the deposition and accumulation of trace metals in soils in NCT of Delhi. Over time, the Pb loading rate in soil exceeds its natural removal rate by more than 20- fold[31]. A soil is generally considered contaminated with lead (Pb) when its total lead (Pb) concentration exceeds 400 mg kg^{-1}[42], and remediation is required at this level[33]. Metal contaminants either accumulate in or leach from soils, polluting surface and subsurface water bodies. Options available for remediating metal-contaminated soils are numerous, but most often the contaminated soil is capped in situ or is excavated and removed. These engineering techniques are expensive and too expensive or logistically impracticable in many instances; they are also invasive and can prevent the restoration of environmental equilibrium. An alternative is to apply amendments to the soil. These in situ treatments take advantage of the soil's natural mechanisms for controlling the mobility and bioavailability of metals and reducing to some extent the toxicity of metals to humans and the environment. Metal bioavailability is related to solubility rather than total concentration, which must be taken into account when developing remediation strategies[39]. For example, a major limitation for in situ Pb immobilization in contaminated soils is the limited solubility of Pb minerals present in the existing soil environment. Lead carbonate (cerrusite) has been identified as a major Pb mineral in many contaminated soils, particularly from battery recycling sites[29,35]. Effective Pb immobilization using phosphorus amendments requires enhanced solubility of the existing Pb minerals by inducing acidic conditions to promote pyromorphite $[Pb_{10}(PO_4)_6(OH,F,Cl)_2]$ formation, with the Pb in the pyromorphite being much less bioavailable than Pb associated with cerrucite. These resulting acidic conditions will also enhance the mobility of other heavy metals, increasing the risk of their leaching to ground water. Phosphatic clay possesses a high potential to adsorb these metals. Phosphatic clay could also have the secondary benefits of improving fertility, structure, and soil moisture-holding capacity when added to sandy soils[21].

This approach, though not changing the concentrations in total, is an effective, more realistic, and cost effective choice for industrial sites and surrounding rural land, dumping grounds, or highly contaminated soils[43]. The use of rock phosphate to help soils and sediments to retain metals has been investigated more extensively.

The objective of determining the effectiveness of different application methods on Pb immobilization in a soil using a mixture of PR and PA as P source was accomplished by (i) determining Pb leaching characteristics and (ii) its bioavailability using PBET. Phosphate has been shown to effectively immobilize Pb in contaminated soils[2,4,15,16,17,18,23,26,38,44]. Its effectiveness is based on P-induced conversion of reactive Pb into less labile lead phosphate. In the presence of adequate P, lead-phosphates are at least 44 orders of magnitude less soluble than galena (PbS), anglesite ($PbSO_4$), cerussite ($PbCO_3$), and litharge (PbO), which arecommon Pb minerals in contaminated soils[24,36]. Natural lead-phosphate minerals have been identified in contaminated soils[15,16,18,17,37,19]. In light of their intrinsically low solubilities, efforts have been made to form lead phosphates in lead-contaminated soils through P addition. Highly soluble forms of P (e.g. Na_2HPO_4 or KH_2PO_4) can significantly reduce Pb bioavailability[3,34] via formation of lead-phosphate[15,16,18]. Ma et al.[26] showed that less soluble hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ effectively immobilizes aqueous Pb via formation of hydroxypy romorphite. Phosphate rock [PR, primarily $Ca_{10}(PO_4)_6F_2$] is also shown to effectively immobilize Pb from aqueous solution and lead contaminated soils. The main mechanism of Pb immobilization is via dissolution of PR and subsequent precipitation of pyromorphite-like minerals $[Pb_{10}(PO_4)_6X_2$, X = Cl, Br, OH] [5,27,45].

MATERIALS AND METHODS

Site characterization

The soil used for this study was collected from a Pb contaminated site in an industrial area of Naraina and Mayapuri in the NCT of Delhi. Industrial activities, which included a recycling operation for lead batteries, industrial activities, which included paints and recycling operation for lead batteries, have all contributed to the contamination of this site.

The total Pb concentrations in the soil ranged from 1875 to 6625 mg kg^{-1}. Lead concentration decreased with soil depth, with the majority of the Pb present near the soil surface (0-20 cm).

Soil analysis

Experimental procedures

Soil samples were collected from the top 20 cm at the industrial sites at Mayapuri. They were collected from a location where high concentrations of Pb are present. They were air-dried, sieved through a 2-mm stainless steel sieve and stored at room temperature. The soil sample was thoroughly mixed to ensure uniformity.

Metal concentration

They were then digested using the microwave digestion procedure (USEPA Method 3051) for total Pb concentration using Scientific microwave Anton Paar Multiwave 3000. The clean soil sample was collected from Himalayan region. Concentrations of Pb, in the extracts were analyzed with AAS (acetylene air flame) (Perking Elmer A Analyst -100) with addition calibration.

Electrochemical properties

Electric conductivity (EC) and pH were measured in water suspensions and in 0.01 M $CaCl_2$. (Elico CM 180 and Elico LI 127)

The Pb contents and pH in the clean and contaminated soils were 165 and 6625 mg kg^{-1}, and 7.5 and 8.11, respectively.

Clay content

The clay content was determined by sedimentation analysis using a hydrometer after dispersion in sodium polyphosphate.

The Toxicity Characteristics Leaching Procedure (TCLP) was used to evaluate the efficiency of P amendments on lead toxicity[40,41].

Analytical procedures

In our preliminary laboratory experiments these soil samples were subjected to Pb immobilization optimization by testing P sources and application rates using both batch and bench experiments

Batch test

Four grams of air-dry soil were placed into 40mL polycarbonate centrifuge tubes. Phosphate amendment solution was prepared by dissolving $Ca(H_2PO_4)_2\,H_2O$ into 0.05 M H_3PO_4 and 0.002 M $CaCl_2$ solution so that 20 mL solution may be equivalent to 22.5 tons of phosphate per acre. Phosphate amendment solution was added to a centrifuge tube. In addition to soluble phosphate sources, 5% phosphatic rock was also used. Samples were equilibrated on a reciprocating shaker for 24 h at 25^0C. Supernatants pH reading was taken after suspensions were allowed to settle. Samples were centrifuged at 10,000 rpm for 20 minutes using *Centrifuge Machine model no KI-199* and filtered through 0.45 μm membrane filters. A fraction of the filtered supernatant was analyzed for dissolved organic carbon (DOC) and soluble orthophosphate was determined using the molybdate ascorbic acid method[32] (results not included). The remaining supernatant was acidified and analyzed for metals by using flame atomic absorption spectrometer (*Perkin Elmer A Analyst -100*). After batch equilibration, the residue was evaluated by using a toxicity characteristic leaching procedure (TCLP).

Bench test

In this investigation, column tests were used to evaluate the effectiveness of selected treatments for further detailed evaluation. A total of 25 g air-dry soil was mixed with $Ca(H_2PO_4)_2$ H2O salt at an application rate equivalent to 22.5 ton per acre for the contaminated soil. After uniform mixing, mixture was placed in 60-mL syringes containing 0.5 g coarse washed-sand to prevent soil loss during leaching. Mixed solution of 0.005 M H_3PO_4 and 0.001 M $CaCl_2$ was added to bring soil to near field capacity. Each column was covered with polyurethane film to avoid moisture loss but allow adequate air exchange. It was incubated at room temperature. After one week of incubation, 25 mL of deionized water was leached through columns under gravity and samples were returned for continued incubation and were extracted after 4 week.

Leachate was filtered through 0.45 μm membrane filters. The supernatant was analyzed for dissolved organic carbon (DOC), phosphate, and metals as described above. The TCLP test was used to evaluate the effectiveness of applied treatment by taking soil sample from one of the column replicates.

RESULTS AND DISCUSSION

Application rate of P amendments will depend on the contamination levels as well as soil physicochemical properties and soil mineralogy. It also depends on the percentage of metals present in their labile forms because proposed *in situ* remediation technology minimizes the mobility of target contaminants by transferring them to non-labile phases via chemically induced transformations. Reactive sinks that compete for soil additives such as P amendments and coal fly ash, however, can reduce the effectiveness of metal precipitation. Based on our batch and bench experimental data, combined application of $Ca(H_2PO_4)_2\,H_2O$, $CaCl_2$ and H_3PO_4 was sufficient to immobilize target contaminant (Pb) to below its regulatory level. Applied treatment is not only effective for Pb, but it also immobilized other metals such as cadmium, copper and zinc to a significant extent (data not shown).

Selected chemical properties of the collected surface soil (0-20 cm) are listed in TABLE 1.

The soil is very sandy, with a pH of 8.11, which is within the range typical of Delhi soils. Lead was the main contaminant with a concentration of 6625mg kg^{-1},

TABLE 1: Selected physicochemical properties of the contaminated and control soil samples*

Reference soil	pH^a	Conductance (μS)	OM^b	Sand	Silt	Clay	Pb_T^c (mg kg^{-1})
Contaminated sample MAYA	8.11	0.39	2.63	77.5	5	17.5	6625
Controlled sample HIM	7.55	0.23	3.51	77.5	7.5	15	165

***Data represent an average of twelve replicates with a standard deviation. [a]pH was determined with a 1:1 ratio of soil/water. [b]Organic matter. [c]Total concentration**

TABLE 2: pH of soil after treatment

Soil	RP0	RP1	RP2
MAYA(0-10cm)	5.51	5.53	5.87
MAYA (10-20cm)	5.56	5.65	5.90
MAYA (20-30cm)	5.52	5.63	5.85
HIM (top soil)	5.1	5.21	5.45

RP0- Only phosphoric acid (PA), RP1-phosphoric acid (PA) + $Ca(H_2PO_4)_2$, RP2 - phosphoric acid + rock phosphate (RP)

TABLE 3: Lead concentration (mg L^{-1}) in TCLP solution of soil after treatment

Soil	Control	RP0	RP1	RP2
MAYA(0-10 cm)	145.7	55.8	9.8	8.9
MAYA(10-20 cm)	122.6	12.6	4.2	4.3
HIM	85.1	10.3	3.5	3.8

Control – without remediation

TABLE 4: Lead concentrations (mg L^{-1}) in the PBET for soil after treatment

Soil layer	Unamended soil	RP1	RP2
MAYA(0-10 cm)	45.8	26.5	25.3
MAYA(10-20 cm)	49.2	27.6	24.5
HIM	28.5	16.2	15.4

which exceeds the critical level for industrial soils (1,400 mg kg^{-1}). Generally, Pb, was concentrated on the surface soil (0-20 cm) and their concentrations decreased with soil depth. However, a substantial amount of Pb (>2,000 mg kg^{-1}) was found at depths below 30 cm. In the long run, it is possible that the metals may leach downward to the subsurface soil[15,16,18,5,10,11].

Soil pH after remediation

As expected, soil pH was reduced in all P-treated soils due to the addition of H_3PO_4. Among all treatments, RP0 promoted the greatest decrease in soil pH, while RP2 promoted the least decrease. The range of pH values at the surface, varied from 6.25 in RP2 to about 5.21 in RP1 and 5.1 in RP0 for the Himalayan soil and for the Delhi industrial site soil the values were 5.87, 5.53 and 5.51 respectively. As expected, application of $Ca(H_2PO_4)_2$ or phosphate rock combined with H_3PO_4 maintained soil pH slightly higher than H_3PO_4 alone. (cf. TABLE 2)

Although application of H_3PO_4 caused a decrease in soil pH, it was necessary to reduce soil pH to near 5-6 for efficient metal immobilization in this demonstrate site. Lead in this site was mainly associated with carbonate. Therefore, it was essential to add H_3PO_4 to the soil to dissolve carbonate-associated Pb for the subsequent precipitation of insoluble pyromorphite like mineral. Concerning the precipitation of the pyromorphite-like mineral, at a given lead and phosphate concentration, more pyromorphite-like mineral was formed at pH 5 than at pH 6 or 7[24].

TCLP lead in soil profiles

The concentration of Pb from phosphorus amended soils decreased sharply and remained below their regulatory levels in drinking water. Applied P amendments were effective not only to limited surface layer, but remained effective > 10 cm depth from surface. Without P treatments, TCLP-extractable Pb concentrations in the surface soils (0-10 cm) far exceeded 5 mg^{-1} critical level of hazardous waste[41]. This is possibly because most of the Pb is in the carbonate fraction, which would readily dissolve in the acidic TCLP solution[28]. Similar to the distribution of total Pb, the highest concentration of TCLP extractable Pb was observed at 10-20 cm. Phosphate amendment was effective in reducing the TCLP Pb to below the critical level in the sub surface soil samples. These results are of great significance with respect to the disposal of the soil, because they show that P amendments can amend the soil to a material that would be considered non-hazardous.(cf TABLE 3)

Lead bioavailability

Incidental ingestion of Pb-contaminated soil has been reported as a primary exposure pathway to humans for elevated blood Pb levels[14]. A physiologically-based extraction test has been used to estimate Pb bioavailability (*in vivo*), which simulates Pb dissolution under gastrointestinal conditions using a chemical extraction[44]. Lead bioavailability in contaminated soils has been shown to vary with its mineralogical forms[20]. *In vivo* and in vitro assays have indicated that the mammalian gastrointestinal availability of Pb is controlled by the form and relative solubility of Pb solids[37]. The PBET has been used to assess the Pb bioavailability in a contaminated soil after receiving various amounts and sources of P[23]. The bioavailability of soil Pb is associated with its solubility and dissolution rate in the gastrointestinal tract. Bioavailable Pb in the contaminated soil based on PBET was reduced after P application. The control soil showed 45-49 mg kg^{-1} of bioavailable Pb while P-treated soils showed reduction of PBET-Pb by 25-42%, which was similar to the 25-35% reduction reported by Hettiarachchi et al.[23] and 39% by

TABLE 5: Pb concentration (mgL^{-1}) in batch and bench leachates and in the TCLP solution in MAYA soils

Treatments	Batch Tests		Bench tests	
	Leachate Pb (µg L^{-1})	TCLP Pb (mg L^{-1})	Leachate Pb (µg L^{-1})	TCLP Pb (mg L^{-1})
RP0	51.8	13.8	15.9	14.4
RP1	49.2	12.2	13.4	11.4
RP2	48.3	12.6	12.8	12.3

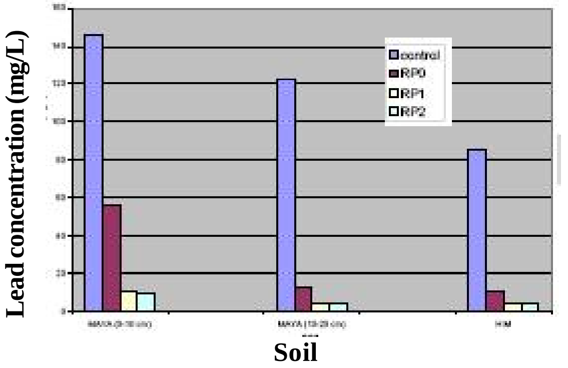

Figure 1 : Lead concentration (mg/ L) in TCLP solution of soil after treatment

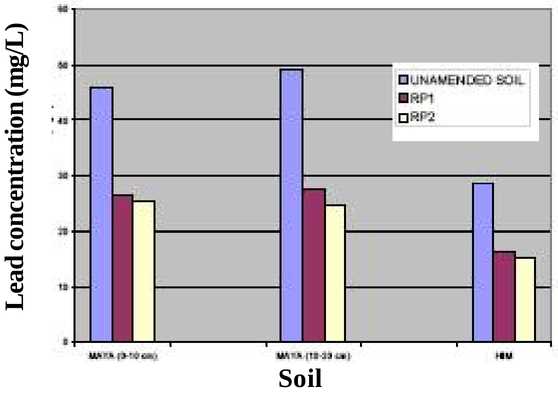

Figure 2 : Lead concentrations (mg /L) in the PBET for soil after treatment

Yang et al.[44]. (cf. TABLE 4)

The results of the bench and batch scale study (summarized in TABLE 5), at this particular site, indicate that P amendments were efficient in transforming more bioavailable Pb (non-residual) into a less-bioavailable form (residual). Although H_3PO_4 is needed to catalyze the dissolution of meta-stable Pb, making it available for further immobilization reactions, its use should be taken with caution. Phosphoric acid decreased soil pH, especially for low-buffering sandy soils, and consequently may cause leaching of heavy metals. Thus, low pH and other heavy metals leaching may be potential drawbacks of its indiscriminate utilization. On the other hand, a mixture of H_3PO_4 and calcium phosphate or rock phosphate had excellent efficiencies, and both treatments had less impact on soil pH. A strategy, which could work better than the one used in this study, would be to invert the sequences of phosphate application, i.e. to add calcium phosphate and phosphate rock first and then apply the phosphoric acid, thus producing the dissolution of cerussite and the more soluble P amendments at the same time. (cf. TABLE 5) Effective remediation technology entails minimizing both leaching and bioavailability.

The results from both the batch and column experiments demonstrated that application of soluble phosphorus equivalent to 2700 kg P per acre obtained from H_3PO_4 immobilized soil Pb concentration to below its regulatory levels. Additional column experiments will be required to test the hypothesis that metals mobilized from surface soil under resulting acidic conditions are sorbed back onto subsurface soils. Readsorption should reduce metal concentration in leachates to below drinking water regulatory levels. Column experiments will be conducted to evaluate the vertical effectiveness of these applied treatments.

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