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COMPARISON OF PHOSPHATE AMENDMENTS FOR Pb AND Cd IMMOBILIZATION IN HEAVY METAL IMPACTED SOIL

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Abstract: Various phosphate compounds have been known as highly beneficial amendments for soils contaminated by heavy metals (Pb, Zn, Cu, Cd). Considering their application in agriculture as nutrient source (fertilizer) and potential for soil remediation, they have been a focus of several studies. In this work, we have attempted to evaluate the efficiency of three phosphates (a commercial product TCP, and pure phosphates MPP and DAP) to reduce the bioavailability of Pb and Cd pollutants in contaminated soil. Evaluation was made on the basis of two most common tests for leachability and extractability of heavy metals: TCLP and sequential extraction analysis. Data indicates that all three amendments can reduce concentration of extractable Pb and Cd, and MPP and DAP can be somewhat more efficient.
Keywords: soil pollution, immobilization, heavy metals, TCLP

1. INTRODUCTION

Heavy metal (HM) contamination in soil has become one the most pressing issues in modern agriculture and environmental sciences. While the Earth's crust is naturally abundant with these elements, anthropogenic sources of heavy metals causes more concerning and threatening harm to the entire ecosystem. During 20th century, due to increased demand and expansion of steel industries and industrial revolution overall, the use of these metals has increased rapidly. Additionally, in some developing countries, the–end–of–life recycling is performed at lower rates mostly due to the lack of necessary technologies and infrastructure. Thus, alarming amounts of metal waste are being introduced into the environment causing substantial health risks and environmental toxicity.

Unlike organic molecules, metals are inert to microbial or chemical transformation, and their concentration in soil persists for extended periods of time after their introduction [1]. Their presence can adversely impact water resources, soil ecology, and agricultural products quality, while simultaneously causing many damaging effects on human health. High lead risk to children or other exposed organism is linked to ingestion of contaminated soil, and absorption of lead into the blood [2]. Other significant sources of lead, directly affecting human health, include house paint, leaded gasoline, Pb smelters, etc. It affect various organs in both adults and children, and it cannot be entirely removed from the body, but its quantities can be considerably lowered with medical therapies [3]. Cadmium (Cd) can lead to bone damage, kidney scaring, and cause various cancers (e.g., breast and ovarian cancer) by disrupting calcium metabolism and endocrine system [4,5].

Heavy metals are not biodegradable, and their bioavailability and toxicity depends on their chemical form and type. Therefore, the main purpose of heavy metal remediation is to reduce the biological toxicity, as well as metal contents in the soil. In situ remediation has been successfully applied for moderately contaminated soils, and those methods include soil flushing [6], microbial remediation [7,8], phytoremediation, [9], electrokinetic extraction [10], encapsulation [11], and chemical immobilization. With the merits of being cost–effective and environmentally benign, in situ chemical immobilization is a promising remediation strategy that reduces the extractable potential of heavy metals. The method is essentially based on utilization of readily available and inexpensive materials which can substantially reduce bioavailability and mobility of heavy metal species in contaminated soil [13]. In the recent years, there has been renewed interest in the immobilization of metals using diverse environmentally friendly compounds, such as lime, phosphate (P) compounds (e.g., apatite rocks), and alkaline waste materials; and organic compounds with exceptional quality (bio–solids) [12–14].

Numerous research accounts regarding the capability of phosphate salts to reduce the amounts of soluble metals due to rapid formation of stable metal phosphates, such as pyromorphite, have been published in the recent years [15–17]. At present, these phosphates are widely recognized as one of the most advantageous amendments for several heavy metals (Pb, Cu, Zn, Cd). Additionally, many phosphate based amendments have been utilized in agriculture as nutrient source and are considered and registered as

phosphate fertilizers. When facing a complex pollutant matrix in highly impacted areas, combined technologies will likely be necessary.

Generally, the addition of P amendments can cause a chemical reaction between metal ions in soil and phosphates [22,23,24]. They can also alter soil properties, i.e. pH value, available phosphate concentrations, and surface charge. Consequently, phosphate addition can shift the chemical balance from more labile forms towards inert mineral species [25,26,27]. Considering Pb, introduction of phosphates to contaminated soil generates pyromorphite, fluoropyromorphite or apatite [16,18,19,20]. Cd–levels are, on the other hand, affected by precipitation reaction with phosphate ions [21].

With the growing public concern for the impact of contaminated soils on human health and environment, there has been increased interest within scientific community in the transformation and fate of metals in soils, and the development of strategies to remediate and reclaim contaminated sites. Although P amendments have mainly been applied to remediate Pb–contaminated soil, they are also applicable to other metals such as Zn, Cu, and Cd. Phosphates effectively remove Zn and Cd from aqueous solutions, but the removal mechanism is different from that of Pb. In this work, we investigate most commonly used phosphates for remediation, and compare their effectiveness in reducing the extractability of Pb and Cd.

2. METHODOLOGY AND MATERIALS

Chemical tests used to evaluate the efficiency of immobilization of Pb and Cd with phosphates were:

▨ the reduction of extractable Cd and Pb concentrations (procedure adapted from EPA TCLP protocol), and

▨ Pb and Cd content changes associated with specific soil fractions using sequential extraction analysis.

Soil sample preparation: the soil sample, from vegetable plot, was collected from the surface layer, transferred to plastic bags, and transported to the laboratory. Air–dried samples were mixed and passed through sieve. The soil was prepared by adding cadmium nitrate ($Cd(NO_3)_2$) or lead nitrate ($Pb(NO_3)_2$) to yield a concentration of approximately 100 mg/kg. Prepared soil was then left at 25°C for seven days, and after a week air–dried samples were stored in plastic containers for further immobilization test.

Three phosphates calcium phosphate tribasic ($Ca_3(PO_4)_2$, TCP) potassium phosphate monobasic (KH_2PO_4, MPP) and diammonium phosphate (($NH_4)_2HPO_4$, DAP) were evaluated in immobilization test. The phosphate loadings was calculated on the basis of the molar ratio of PO_4^{3-} to the total concentration of Cd/Pb in the soil samples (1:1). Each immobilization test included 50g of soil, a precalculated weight ratio of phosphate added to air–dried soil sample (1 molar phosphates to 1 molar Pb/ Cd), and the amount of deionized water sufficient to reach homogenous and saturated mixture.

Samples prepared in this manner were kept in plastic container until laboratory tests were performed.

Standard EPA toxicity characteristic leaching procedure (TCLP) is an analytical method used to verify the presence, and contents, of hazardous compounds in waste and environmental samples. The test is based on simulation of leaching process through a landfill, and indicates whether present hazardous materials are dangerous for the environment. In the present case, modification of the original method described by USEPA (1986) was applied. This modified TCLP method uses the pH value of the soil to differentiate between two extraction procedures. In cases where pH < 5, extraction solution contains 5.0 ml of glacial acetic acid and 65 ml of 5 M sodium hydroxide, and then diluted to 1.0 L with deionized water (pH values of the resulting extraction solution is ~5). Extraction solution, for samples where pH > 5, containes 5.7 ml of glacial acetic acid diluted to 1.0 L with deionized water (pH of the resulting extraction solution is ~2). 20 ml of extraction solution was used for 1 g of sample prepared as described above.

Sequential Extraction Analysis, developed by Tessier *et al.* [28], is used to evaluate the availability and speciation of Pb and Cd forms present in the analyzed samples. Extraction procedure differentiates metals associated with five soil fractions:

▨ soluble–exchangeable (SE),

▨ weakly specifically adsorbed or bound to carbonates (WSA),

▨ bound to Fe–Mn oxides (OX),

▨ bound to organic matter (OM), and

▨ residuals (RES).

Extractions are carried out on 1.000 g of test soil using specific extraction solutions as detailed in Table 1.

Table 1. Sequential Extraction Analysis. (Adapted from Tessier et al. [28].)

Step	Fraction	Extraction procedure
1	Soluble–exchangeable (SE)	1M $MgCl_2$, pH=7, rt
2	Bound to carbonates (WSA)	1 M NaAc, pH=5, rt
3	Bound to Fe–Mn oxides (OX)	0.04 M $NH_2OH \cdot HCl$, pH=2, 96°C
4	Bound to organic matter (OM)	0.02 M HNO_3, H_2O_2, 3.2 M, CH_3COONH_4
5	Residual (Res)	HF–$HClO_4$, digestion

3. RESULTS AND DISCUSSION

TCLP Extractability After Treatment With Different Phosphates

The results of TCLP extractability of Pb and Cd after treatment with three different phosphates, after 50 days of immobilization, are shown in the Figure 1. Among the three phosphates screened, the application of $(NH_4)_2HPO_4$ (DAP) affords the most significant decrease in TCLP leachability of both Pb and Cd chemical species. More precisely, in the case of Pb reduction of extractable concentration drops from 71 mg/kg to 41 mg/kg, and for Cd from 50 to 24 mg/kg. The efficiency of phosphates to reduce TCLP concentration of extractable Pb and Cd follows roughly the order: $(NH_4)_2HPO_4 > KH_2PO_4 > Ca_3(PO_4)_2$ The reason might be partially attributed to the fact that $(NH_4)_2HPO_4$ is highly water–soluble and can therefore release appreciable amounts of phosphate for complexation of heavy metals. In contrast, $Ca_3(PO_4)_2$ is a water–insoluble compound and cannot provide sufficient amounts of phosphate for significant immobilization of Pb and Cd concentration. However, the effect of calcium ion on the stability of Cd(II) can be observed (Fig 2.). Such increase in stability of heavy metal species in the presence of Ca^{2+} has been well documented by other authors [29, 30]. It can also be speculated that ammonium ions, present in $(NH_4)2HPO_4$, can further decrease Cd/Pb bioavailability, most likely due to formation of more complex mineral forms.
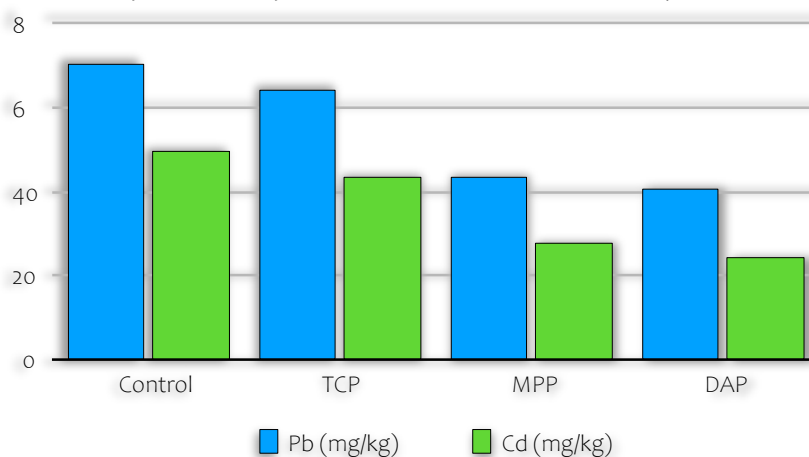

Figure 1. TCLP Extractability of Pb and Cd with Different Phosphates

It should also be noted that the addition of phosphates amendments alters the pH value of soil which can disturb the stability of metal–phosphate complexes and increase their solubility and extractability. Namely, pH value is a parameter which affect metal precipitation [31], occlusion [32], and movement and sorption [31]. Thus, difference in effectiveness levels of phosphates to affect extractability of specific metal can be traced to the nature of the phosphate compounds, and the amounts of phosphate that it releases into the soil.

Sequential Extraction Analysis

Sequential extraction procedure is often applied for studying the relative availability of soil–sorbed metals by revealing the operationally defined speciation of metal in solid phase [33]. The trace metals detectable in water–soluble and exchangeable fractions (SE) are considered more mobile and biotoxic than those found in other fractions. Figure 2 And 3 show the distribution of Pb and Cd in four different fractions of extracted material.

In the case of Cd (Fig. 2), it is apparent that the addition of all three amendments can induce reduction of SE fraction of Cd, while the levels of residual fraction (RES) have somewhat increased. More significant decrease of SE when TCP has been utilized can be attributed to the presence of Ca^{2+} cations [34].
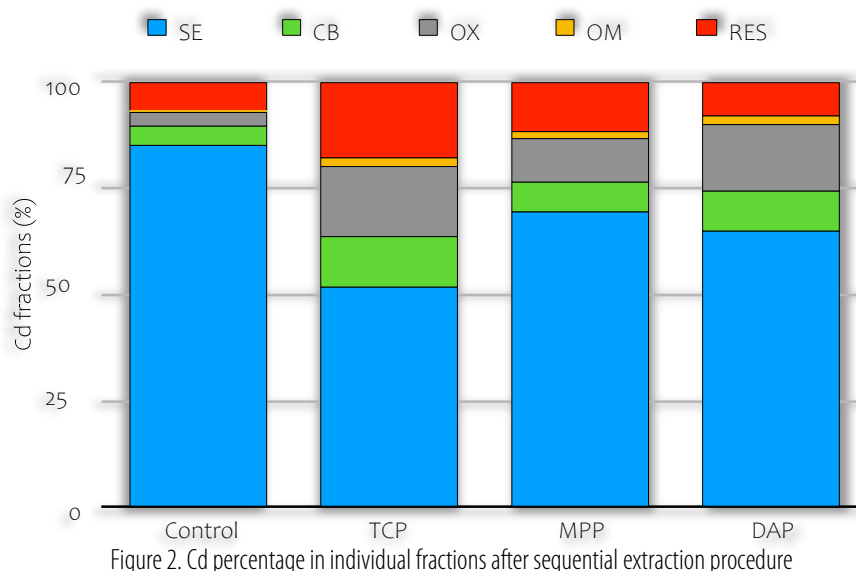
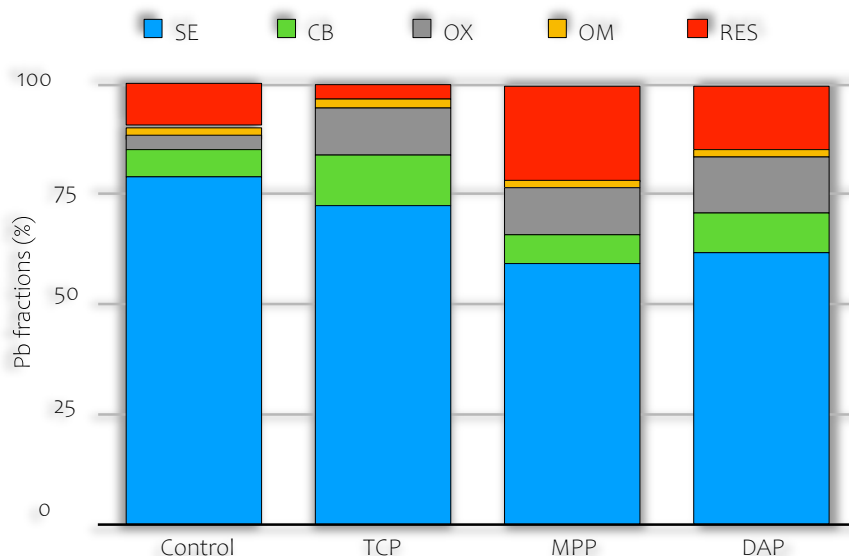Figure 2. Cd percentage in individual fractions after sequential extraction procedure

Figure 3. Pb percentage in individual fractions after sequential extraction procedure

The reduction of SE fraction of Pb after phosphate application can be attributed to the transformation of soluble Pb to insoluble Pb–phosphate species. One plausible explanation for such significant shift from extractable Pb to the residual Pb is due to the formation of pyromorphite [15, 35].

As shown in Fig. 2 and Fig. 3, Cd and Pb exhibit similar behavior in the presence of phosphates, and show propensity towards formation of low solubility forms. One can envision several factors which are play in both case. Namely, a change in pH value of resulting soil can directly affect the solubility of metal phosphates. Additionally, complexation and co–precipitation have been suggested as most likely chemical mechanism which occurs in these processes [13].

3. CONCLUSION

The results shown here indicate that extractable concentration of both Pb and Cd, in contaminated soil, can be significantly reduced after phosphate treatment. These observations are supported by both reduced TCLP extractable concentrations of Pb and Cd, as well as sequential extraction data. Among phosphate amendments screened, $(NH_4)_2HPO_4$ provides most promising results, most likely due to its high solubility in aqueous media. Similar trend can be observed in MPP. It should be also noted that these compounds have been used in p.a. form (neat compounds). In contrast, $Ca_3(PO_4)_2$ would not be the first choice of amendment, even though it can affect the immobilization of heavy meal. One reason for such low efficiency observed with $Ca_3(PO_4)_2$ can be attributed to stabilizing Ca^{2+} affect.
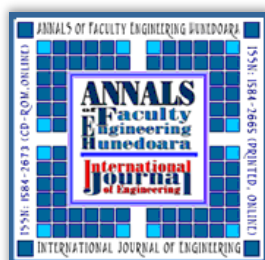
Additionally, TCP material used in this study was a commercial fertilizer which can, arguably, contain impurities or unspecified amounts of phosphate.

In the future, it would be beneficial to focus research on the combination of amendments to formulate immobilization strategy for sites contaminated with multiple metallic species or complex pollution matrix.

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