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Assessment on the Degree of Immobilization of Heavy Metals in Contaminated Urban Soils by Selected Phosphate Rocks of Different Particle Sizes

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ABSTRACT

The efficiencies of different particle sizes (< 63, 63-93, 93-106 and 106-125 µm) of mined phosphate rock (PR), as well as other phosphate sources (processed and biogenic) as a chemical stabilization remediation technology and stability (in terms of heavy metals) were assessed in contaminated urban soils. The results demonstrate that the application of PR substrate with smaller particle size (< 63 µm) was significantly more effective than larger particle size for Cu, Co, Cd and Pb immobilization. Depending on phosphate solubility, the decrease in of metal availability was highest in biogenic ground fish bones) (0.02; 0.0; 0.005 and 0.017 mg kg^{-1} for Pb, Cd, Co and Cu, respectively) and processed phosphates (0.05; 0.02; 0.22 and 2.01 mg kg^{-1} for Pb, Cd, Co and Cu, respectively) than mined phosphate rock (0.03; 0.011; 1.11 and 0.005 mg kg^{-1} for Pb, Cd, Co and Cu, respectively). It is noted that lower dissolution of phosphate rock may be advantageous for long term maintenance.

Keywords: Mined PR, processed PR, biogenic PR, TCLP, sequential extraction study

INTRODUCTION

Heavy metals pollution is a major environmental problem which requires our immediate attention. As a result of widespread industrialization, soil pollution with toxic metals such as cadmium has accelerated dramatically. Clean up of the polluted areas is necessary in order to remediate these soils and minimize the entry of potentially toxic elements into the food chain (Manousaki *et al*. 2008). While soil clean-up methods such as isolation and containment, mechanical separation, chemical treatment, or soil flushing have proven to be effective in small areas, they require special equipment and are labour intensive. Furthermore, these technologies are not only costly, but also cause soil disturbance, and are not readily accepted by the general public (Gardea-Torresdey *et al.* 2004).

In soils, toxic metals are present in various chemical forms and generally exhibit different physical and chemical behaviours in terms of chemical interactions,

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mobility, biological availability and potential toxicity. This chemical speciation plays a vital role in the solubility and potential bioavailability of metals in soils (Tandy *et al.* 2004). Unlike organic compounds, toxic metals are not degradable in the environment, and can persist in soils for decades or even centuries. The contamination of soils by metals can have long-term environmental and health implications (Leštan *et al.* 2007). It is highly desirable to apply suitable remedial approaches to polluted soil, which can reduce the risk of metal contamination. The demand for soil treatment techniques is consequently growing and the development of new low-cost, efficient and environmentally friendly remediation technologies has generally become one of the key research activities in environmental science and technology. In selecting the most appropriate soil remediation methods for a particular polluted site, it is of paramount importance to consider the characteristics of the soil and the contaminants (Leštan *et al*. 2008).

Chemical stabilization involves fixing up the contaminants in stable sites by mixing or injecting inorganic or organic soil amending agents (e.g., liming molecules, organic materials, aluminosilicates, phosphates, iron and manganese oxides, coal fly ashes, etc.). Due to the effects of a change in pH, such agents are effective in decreasing the bioavailability of metals by introducing additional binding sites for toxic metals. Stabilized metals then become less available for plants, and their bioconcentration through the food chain is reduced (Guo *et al.* 2006). However, toxic metals remain in the soil and can be harmful when soil dust is ingested or inhaled. Many of the amendments used in soil stabilization are by-products of industrial activities, and are therefore inexpensive and available in large amounts. Reviews on previously successfully applied amending agents and their effectiveness of different metals have been given by Knox *et al.* (2001) and Puschenreiter *et al.* (2005). In the last few years, significant research has focused on this topic. Several soil additives have been tested: eight substrates (calcium carbonate, bentonite, kaolinite, charcoal, manganese oxide, iron oxide, zeolite, phosphate) to reduce metal availability and study the change in metal speciation in different forms (Fawzy, 2008), zeolites (Rebedea and Lepp 1994; Chlopecka and Adriano 1996b; Boisson *et al.* 1999), beringite (Vangronsveld *et al.* 1991;1995a; b; 1996; Mench *et al*. 1994a), and steel shots (Mench *et al*.1994b; Sappin-Didier *et al.* 1997). Ma *et al*. (1993) and Laperche *et al*. (1996) showed that the application of synthetic hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ leads to immobilisation of dissolved Pb in contaminated soils. In aqueous solutions, HA leads to immobilization of Al, Cd, Cu, Fe (II), Ni and Zn as well (Suzuki *et al*. 1981; Takeuchi and Arai 1990; Middelburg and Comans 1991; Ma *et al* 1994); Xu and Schwartz 1994). Therefore, HA appears to be a promising soil additive for immobilizing metals in polluted soils.

Many studies have been conducted to understand the mechanism of this immobilization (Suzuki *et al*. 1981; Xu and Schwartz 1994; Laperche *et al*. 1996). However, a chemical and physical evaluation of the efficiency of HA application as a remediation technique is not sufficient. Biological evaluation methods are necessary to assure that immobilization results in lower soil to plant transfer and

phytotoxicity. Moreover, these methods can give indications about possible adverse effects (toxicity, deficiency of other elements) of HA application. Chlopecka and Adriano (1996a; b) showed that the addition of apatite (0.4% by weight) to a Zn, Cd and Pb polluted soil led to an increasing yield and lowered the Zn, Cd and Pb content in three week-old-maize plants (*Zea Mays*), in mature maize tissues (roots, young leaves, old leaves, stems, grains) and in barley (*Hordeum vulgare*). The addition of HA (0.6%, 1.16%, 1.74%, and 2.32% by weight) to Pb polluted soils led to a strong decrease in Pb concentrations in shoots of sorghum (*Sorghum bicolor* L. Moench) while Pb concentrations in the roots decreased only at low application rates of HA.

Phosphate Rock (PR) is a natural inexpensive source of phosphorus but its solubilization rarely occurs in non-acidic soils. However, microbial mediated processes involving chelation and exchange reactions are able to solubilize inorganic P forms (RodrõÂguez *et al.* 1999)

The objectives of this study were: 1) To evaluate the effectiveness of particle size fractions of phosphate rock in decreasing heavy metal (Pb, Cd, Co and Cu) mobility, 2) Quantifying the purity of different phosphate sources; and, lastly 3) To compare the suitability of different phosphate sources for remediation of metal-contaminated soils by determing the total metal concentrations in different phosphate sources, the tendency of these trace impurities to leach, and the apparent amendments for stabilizing contaminants.

METHODOLOGY

Quality Assurance

Precautions were taken to prevent sample contamination and to ensure reliability and quality of analytical results. Soil samples were collected using tools made of stainless steel and stored in non-metallic containers, such as glass bottles or polyethylene bags. For all analysis, standard samples were run during and at the end of the measurements to ensure continued accuracy.

For analytical precision, the samples were run in triplicates. The blanks were run all the time. All chemicals used were of analytical grade. Concentrated acids were provided by BDH Chemicals Ltd. (Poole, UK), while salts were provided by Sigma (Missouri, USA). All glassware were cleaned in 10% HNO_3 (w/v) prior to usage in each experiment.

Samples Collection

Surface soils (0–30 cm in depth) were collected from an urban area (ca 20 samples), in Aswan city, in South-eastern Egypt. The soils were enriched with heavy metals, including Pb, Cd, Co and Cu due to a high population density

Three types of phosphate materials were investigated: mined, processed, and biogenic. Mined phosphate refers to phosphate rock (31% P_2O_5), processed phosphate rock fertilizers were in granular form (125 µm) and the source of biological phosphate was ground fish bones, 125 µm (*Tilapia nilotica*), from Lake Nasser, Egypt.

Analysis of Soil

The soil samples were air-dried and then ground to pass through a 2-mm sieve prior to use. Soil pH (soil: water; 1:2.5) was measured using a pH-meter (Orion Research, Model SA520, U.S.A.). Electrical conductivity was measured in the sample suspension obtained from pH determination using conductivity meter (HANNA Instruments, HI 8033 Italy). Calcium carbonate was determined by back-titrating an excess of 0.5M HCl added to 1 g of the sample (Nelson 1986), and organic matter content was determined by the wet oxidation (Nelson and Sommers 1982), respectively. Particle size analysis (percent sand, silt, and clay) was determined by the micropipette method.

Analysis of Phosphate Materials

Mined phosphate rock (PR) was sieved through < 63, 63-90, 90-106, and 106-125 μm, respectively. Each phosphate source was analyzed for pH (in 1:1 mineral/water equilibration solution), solubility, total metal content and toxicity characteristic using the toxicity characteristic leaching procedure (TCLP) (U.S. EPA 1992).

The measured metal solubility of each phosphate source was tested in 25 mL polyethylene tubes with 1 g of well mixed phosphate sample and 10 mL of distilled water. The samples were placed in a shaker for 12 days, centrifuged and decanted. Consequently metal concentrations in the decanted solutions were referred to as the apparent solubility of these elements. Total metal concentrations were determined using complete acid mixture (digestion of 0.6 g of phosphate material with concentrated acids, 10 mL of HNO_3, 4 mL of H_2SO_4 and 2 mL of HCl). The same elements were also extracted from the phosphate materials with the standardized TCLP (U.S. EPA 1992). The TCLP leaching solution consisted of 0.1 M glacial acetic acid and 0.0643 M NaOH and had a final pH of 4.93. Forty ml of leaching solution were added to 2 g of phosphate material; the mixture was agitated on a shaker for 18 h at 25°C and then centrifuged. All tests were duplicated.

Sequential Extraction Study

Mobility of metal in contaminated (T0) and treated soil with mined PR of grain size 106-125 μm (T1), 90-106 μm (T2), 63-90 μm (T3) and < 63 μm (T4), processed (T5) and biogenic (T6) were evaluated using sequential extraction procedure. This procedure is used to operationally define heavy metal into different geochemical phases, usually in the order of increasing stability. A five-step sequential chemical extraction procedure was proposed for harmonization and validation of the methods used for speciation studies in soils and sediments (Tessier *et al*. 1979). It was designed based on $MgCl_2$, pH7 (step 1), hydrogen peroxide oxidation and ammonium acetate extraction (step 2), sodium acetate, pH5 (step 3), 0.175M ammonium oxalate and 0.1M acetic acid (step 4) and conc. acids mixture, $HCl/HNO_3/HF$ (3:1:2, v/v/v) (step 5). These extractions are associated with the exchangeable, organic-bound, acidic, amorphous Fe/Al oxides-bound and the residual form, respectively. It is acknowledged that the

reactivity and potential bioavailability of heavy metals generally increase with increasing solubility. Thus, the first form is usually considered the most mobile form of metals in soils and the other three fractions are relatively immobile and more stable, but may sometimes become mobile and bioavailable with changes in soil conditions.

All the steps and the operational fractions of metal are displayed in Table 2. The sequential extraction was carried out in triplicate, on 1 g of soil, in 85 ml polyethylene tubes. After each extraction step, the suspensions were centrifuged at 8000 rpm for 15 min. The supernatants were carefully removed and stored in polyethylene bottles at 4°C. The residues were washed with ultrapure water before the addition of the next extracting agent.

TABLE 1
Some chemical soil properties

Item	Mechanical Analysis %			$CaCO_3$ mg g^{-1}	O.M mg g^{-1}	CEC (μScm^{-1})	pH
	Sand	Silt	Clay				
Urban Soil	35	36	38	2.5	23	920	6.8

TABLE 2
Procedure of the five step sequential extraction of metals from the urban soil and corresponding phases

Phase/Association	Abbreviation	Operational Definition
Exchangeable	EX	16 ml $MgCl_2$, pH7.0, shaking 1h
Organic-bound	OB	10 ml 30 % H_2O_2 (pH2), then 10 ml 30 % H_2O_2 (pH2) cool, add 50 ml mol/1ammonium acetate (pH2)
Acidic	AC	16 ml 1M NaOAC, pH5.0 with HOAC, shaking 5h
Amorphous Fe/Al oxides-bound	OX	40 ml 0.175M $(NH_4)C_2O_4$/0.1M $H_2C_2O_4$, shaking 4h in the dark
Residual	RES	Acid mixture[a]

[a] the residual from step 4 was digested in 15 ml $HCl/HNO_3/HF$ (3:1:2, v/v/v) at 150 °C

Elemental Analysis and Instrumental Technique

Metal concentrations in all extracting solutions of contaminated and amended soil samples were determined by the atomic absorption spectrophotometer (Model Solaar 969, ATI Unicam Comp.). The standard addition calibration method and extraction blanks were employed to avoid interferences in the measurements.

RESULTS AND DISCUSSION

The Effect of Particle Size of Phosphate Rock for Metal Immobilization

Sequential Extraction Procedure

The percent distribution of measured metals in contaminated (T0) and amended soil (T1-T6) with PR are displayed in *Fig. 1*. Metal levels indicate relatively high metal contamination of the study area because it was subjected to urban activities and wastewater effect. The application of the sequential extraction technique can help to investigate metal distribution in the various soil compartments. To illustrate the results in more detail, we compared the extractable forms as a function of efficiency of different grain sizes for remediation of the contaminated soil.

The leached metals concentrations in different forms are in the order: residual > amorphous Fe/Al oxides-bound > organic bound > acidic > exchangeable (*Fig. 1*). The residual metal content was significantly higher as compared to the available metals in exchangeable phase or those that bound to Fe/Mn oxides fraction. Total metal content is still used as an important index in the long run, which, together with the changing environmental condition (both soil and plant factors), determines the bioavailability of heavy metals (Haiyan and Stuanes 2003). Elevated concentrations of heavy metals in soils are of potential long-term environmental and health concerns because of their associated toxicity to biological organisms (Wong and Li 2003).

In general, the analytical results of the sequential chemical extraction indicate that all measured metals were primarily associated with residual and amorphous Fe/Al oxides fraction and secondary with the organic fraction, and the Pb, Cd, Co and Cu in the exchangeable fraction represented small percentages of the total metal content (*Fig. 1*). Results suggest that high percentages of measured metals were relatively significantly associated with the non-residual fractions (Table 2), where the contaminated metals in these fractions might be moderately soluble and potentially bioavailable (with changes in different soil characteristics influencing the heavy metal solubility e.g. pH, organic matter, CEC, carbonate and clay mineralogy), representing the metal fraction of potential environmental concern.

Fawzy *et al.* (2006) studied the relation of the mobility and distribution of metals between Tamarix parts and their crystal salts-soil system and applied sequential extraction on the different soil samples to obtain a better understanding of the geochemistry of heavy and trace metals in soil. They concluded that the hydrous Fe and Mn oxides may hold significant proportions of some heavy metal ions. These oxides are known to exist as separate phases, and there is evidence from electron microprobe analysis of surface soils that Pb is concentrated in the Mn oxides, whereas Cu is concentrated and distributed approximately equally between the Fe and Mn oxides. Comparing the concentrations of metals in the non--residual fraction (the sum of the first four fractions) by residual fraction (RES) indicated that the metal concentrations in available form were decreased after treatment (by change its form in exchangeable fraction to other chemical

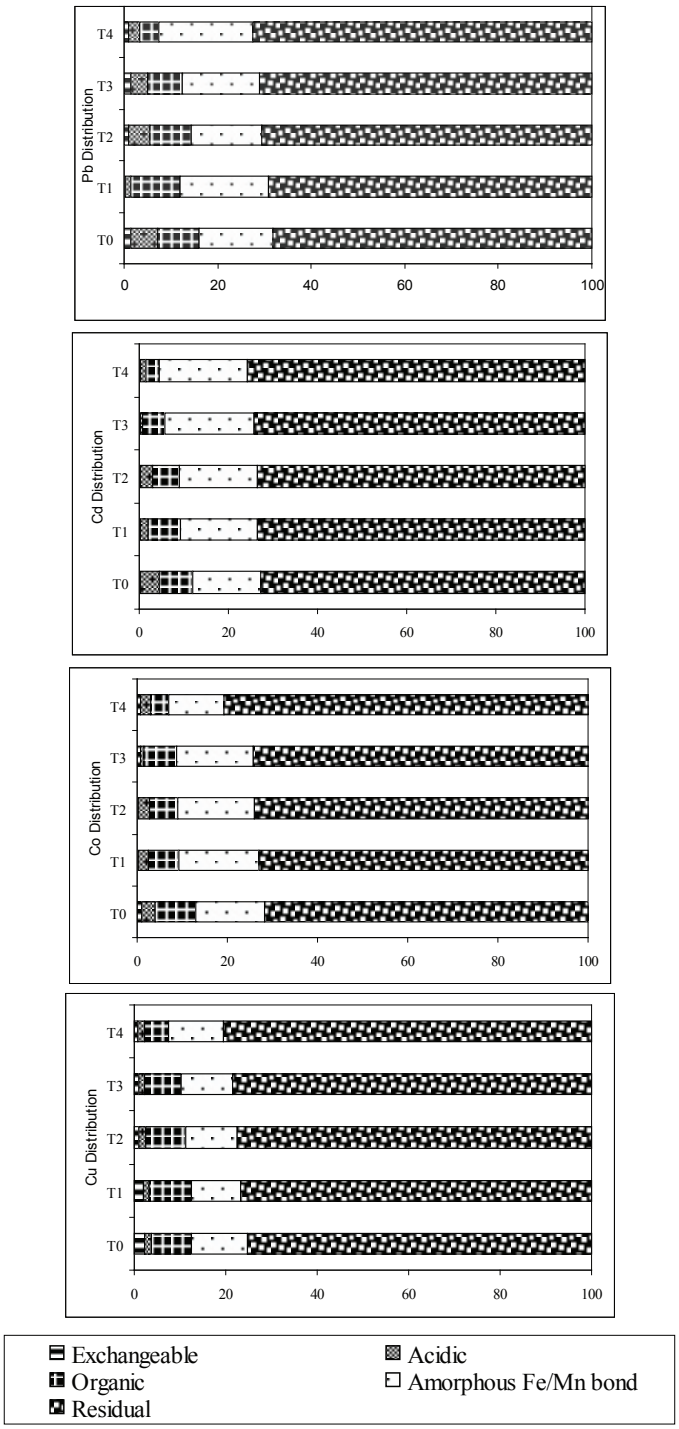

Fig. 1: Percentage of Pb, Cd, Co and Cu in contaminated and treated soil

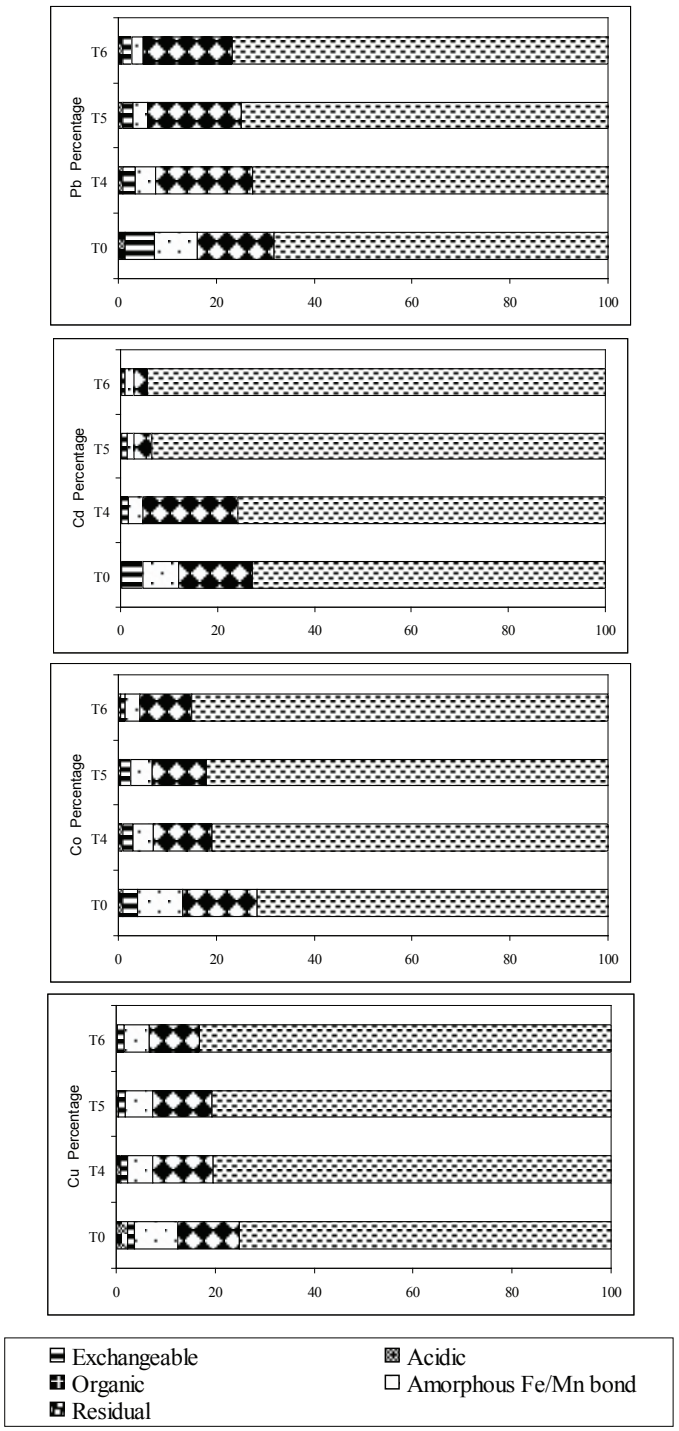

Fig. 2: Comparison of metals percentage in different phosphate sources.

forms (Table 3). The proportion of Pb in the non-residual fractions of control soil represented about 31.86% of the total metal concentration (Table 3); this leached lead content was lower than the control, because it shifted from the mobile fractions to the residual fraction. Lead stabilization may have been due to the formation of sparingly soluble lead phosphate mineral phases (Badawy *et al*. 2002; Spuller *et al.* 2007). Lead hydroxypyromorphite (log K_{sp}= -76.8) and lead chloropyromorphite (log K_{sp}= -84.4) are important lead sequestering minerals of very low solubility which have been identified in phosphate amended soil (Spuller *et al.* 2007). A pronounced immobilization of Co and Cu were observed in the phosphate amended samples compared to the control (Table 3). Cadmium also showed a same trend (*Fig. 1*). Makino *et al.* (2006) developed a new, three-step soil-wash process for Cd-contaminant paddy sorts. They assumed that cadmium has a good capacity to form complexes with various anions such as Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, organic acids, and fulvic acid. Immobilization or transformation of soil metals especially Pb to low soluble species that reduces metals dissolution and leachability in soil system may be a remedial strategy for metal contaminated soil which safeguards human and ecosystem from contamination (Yang and Mosby 2006). The real effectiveness of in situ remediation of metal-contaminated soils can be assessed using a fractionation scheme (Chen *et al*. 2006). Among the four particles sizes of phosphate rock, T4 (< 63 μm) was the most effective in transferring metals from the non-residual fractions to the residual fraction, while

TABLE 3
Measured metals percentage in the non-residual (EX+OB+AC+OX) and residual fractions (RES).

Treatment	Cu	Co	Cd	Pb
T0	24.8	28.3	27.2	31.86
	75.20	71.73	72.8	68.15
T1	23.27	26.98	26.45	30.84
	75.73	73.00	73.60	69.17
T2	22.43	26.08	26.4	29.4
	77.60	74.00	73.60	70.6
T3	21.5	25.72	25.84	28.85
	78.50	74.30	74.2	71.15
T4	19.6	19.13	24.3	27.53
	80.43	80.88	75.7	72.5
T5	19.3	17.97	6.34	25.2
	80.70	82.03	93.7	74.9
T6	16.76	14.94	5.59	23.37
	83.24	85.1	94.41	72.64

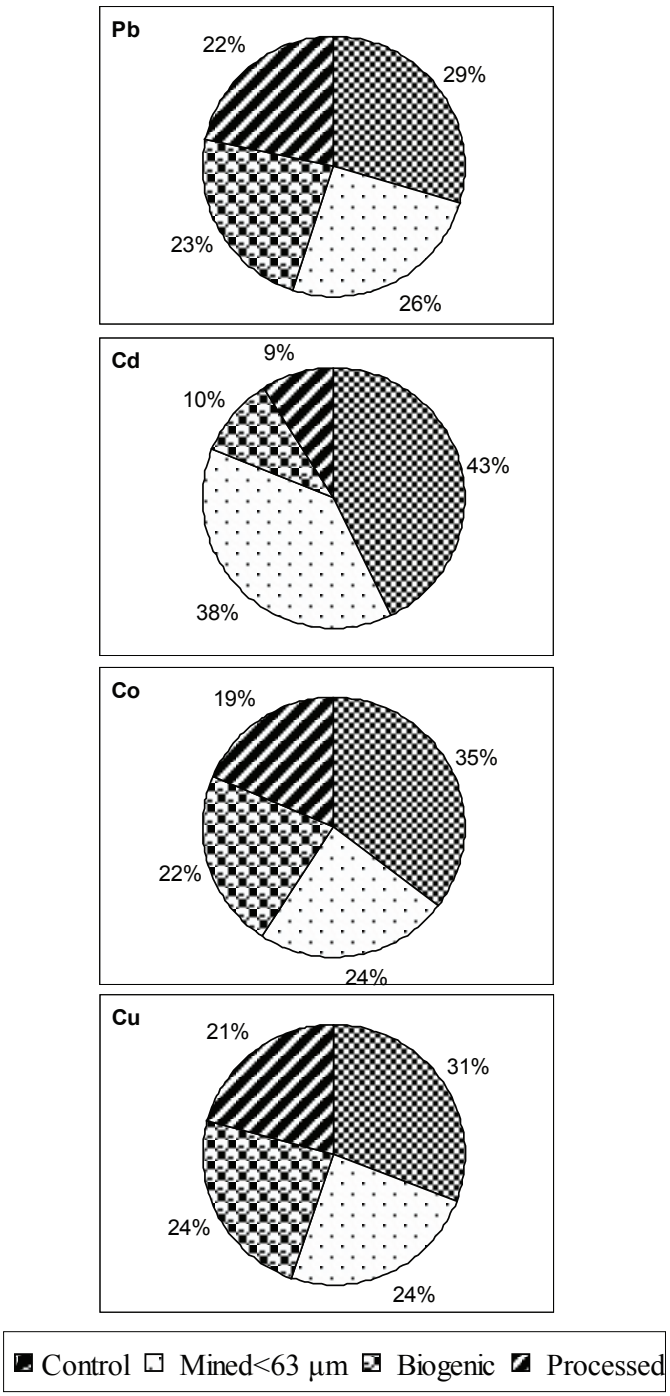

Fig. 3: Comparison of percentage of Pb, Cd, Co and Cu, respectively in the non-residual fraction of the unamended and treated soils

T1 (125-106 µm) was the least effective, indicating that the potential bioavailability of Pb, Cd, Co and Cu in PR treatments decreases with increasing rock grain size.

Comparison of Different Phosphate Sources Suitability for Remediation of Contaminated Soils

Treatment T5, phosphate fertilizers-treated soil and biogenic (T6) showed a marked decrease in contaminant metal concentrations compared to the control (Table 3); a similar trend was observed in these substrates. All determined metals decreased in the following order: mobile < acidic organic bound < amorphous Fe/Al oxides-bound < residual (*Fig. 2*). The difference in extraction efficiency of metal concentrations between the six substrates (T1-T6) reflects that biogenic phosphate is the most effective amendment for the remediation of metal contaminated soil (*Fig. 3*). This ability of biogenic phosphates to re-adsorb metals from the contaminated soil may result from the capacity of induce metal-binding role such as metallothioneins (Canli and Atli 2003). By mixing different phosphate sources with contaminated soil, biogenic phosphates are the preferential sites to re-adsorbed metals from contaminated soil. Soltan *et al*. (2005) studied nilotica fish as a bio-indicator to evaluate heavy metal concentrations in the ecosystem of some bights at Lake Nasser, Egypt. They proved that Tilapia can be used as a bioindicator species due to its abundance and accumulation capacity for heavy metals.

Evaluation of Purity of Different Phosphate Sources

Availability of Metals in Phosphate Sources

Soluble impurities pose a greater hazard than strongly bound materials because they readily enter soil water where they are potentially available for plant or animal uptake. Chabbi (2003) studied metal concentrations in soil water of the Lusatian Lignite mining sediments and internal metal distribution in *Juncus Bulbosus* L. and indicated that iron in the pore waters was very likely present as iron oxhydroxides or being bound to phosphates; Cu was probably in oxidized form. From the monitoring results of analysis of different phosphate sources, the concentration of Co and Cd show significantly low content in solubility test (Table 4).

Available metal concentrations reflected relatively high lead and copper levels (Table 4). Elevated lead in soil has been identified as a threat to human health and ecosystem (Cotter-Howells and Thorton 1991; US EPA 1998). The ecological threat is associated with Pb mobility in the soil system (Yang and Mosby 2006), which is controlled by the chemical or mineralogical associations of soil Pb and their solubility (Ruby *et al.* 1992; Davis *et al*. 1993). Immobilization of soil Pb can be achieved by formation of pyromorphite through phosphate amendments. Based on the results, a pronounced mobilization of Pb, Cd, Co and Cu was observed in mined phosphate compared to other phosphate sources (Table 4). This characteristic points to the release of mobile constituents into aqueous

phase during the solubility test. The solubility of phosphate materials is important because dissolution is dependent on the contaminant, a necessary step in the immobilization of contaminants (Knox *et al*. 2006).

TABLE 4
Total, Water Soluble and TCLP Mean Concentrations (μg g^{-1}) of Impurities in Different Sources of Phosphate Materials.

Element	TCLP regulatory limit	Average Shale, 1961	Biogenic Mean	Processed Mean	Mined Mean
pH			6.98	6.41	8.89
Water Soluble					
Pb			0.02	0.05	0.03
Cd			0.0	0.02	0.011
Co			0.005	0.22	1.12
Cu			0.017	2.01	0.005
Total Digestion					
Pb		20.00	1.15	3.93	2.15
Cd		0.03	0.021	0.09	0.13
Co		19.0	0.021	0.76	16.23
Cu		45.00	2.3	3.6	45
TCLP					
Pb	5.0[a]		0.23	0.27	1.0
Cd	1.0[a]		0.01	0.01	0.067
Co			0.11	0.52	0.087
Cu			0.088	1.2	3.0

TCLP: Toxicitycharacteristic leaching procedure limits (a — 40 CFR 261.24, U.S. EPA 1999).

Total Concentration of Impurities in Phosphate Sources

As in the solubility test, the results (Table 4) showed markedly higher Cd, Co, Pb and Cu concentrations in mined and processed phosphate sources than those in uncontaminated soils. The concentrations of metals in the mined, processed and biogenic phosphate sources were higher than measured concentrations in the soluble form. These elevated concentrations of metals in some phosphate materials were as expected because of isomorphic substitution into the flexible structure of apatite minerals (Knox *et al*. 2006). The biogenic phosphate contained low levels of most elements (Pb, Cd, Cu and Co) compared to the other phosphate sources. Mined and processed sources had relatively higher levels of elements (Table 4); this would be expected to increase impurity levels because of the tendency of phosphate to scavenge elements. Some of the variations among the metal contents of phosphate sources are likely to be due to the different geological origins of the phosphate rock materials (Knox *et al.* 2006).

The observed Cd content in processed phosphate may be expected because phosphate fertilizers are considered the most important source of metal contamination in agricultural lands (Adriano 2001). Fertilizers made from magmatic phosphate tend to have only negligible concentrations of Cd, whereas those from sedimentary phosphate tend to have higher Cd concentrations (Adriano 2001). Metal contents re-adsorbed in mined and processed phosphate sources

reflect large differences between total and soluble contaminant levels. Overall the studied trace metal concentrations were lower than in natural back ground levels (Table 4).

The TCLP Test

The TCLP was designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This test reflects the availability of contaminants under extreme environmental conditions, such as low pH, that could cause the release of contaminants that would otherwise be stable. Data in Table 4 show that metal concentrations in the TCLP extracts are much lower than concentrations in the total digestion extracts and similar to or slightly higher than concentrations in the water soluble extract. The TCLP is a regulatory test used widely to classify solid waste materials as hazardous or non-hazardous (U.S. EPA 1992) based on their potential to leach certain toxic elements. Measured metals in mined and processed phosphate materials showed relatively higher concentrations than corresponding values in biogenic phosphate (Table 4). However, even in this case, metal contents in different phosphate sources are still under the EPA regulatory levels (U.S. EPA 1992) and thus allowed to be used for remediation purpose.

Knox *et al.* (2006) studied the suitability of phosphate sources for remediation of contaminated soils. They concluded that rapid phosphate release would be advantageous when a rapid immobilization of contaminants is necessary. Conversely, a slow-release phosphate source may be preferred for long-term treatment. Combination of phosphate sources having high, and the other, of slow dissolution rates, may provide a rapid immobilization of contaminants while providing a slow release of phosphate for continued long-term treatment and maintenance.

CONCLUSION

Based on these results, it can be concluded that:

- The phosphate rock (PR) substrate with smaller particle size (<63 μm) is more effective than larger particle sizes in transforming large amounts of Pb, Cd, Co and Cu from non-residual fraction to residual ones.
- Biogenic apatite has lower concentrations of impurities than mined and processed phosphate. These differences between mined, processed, and biogenic phosphate are obvious in total impurities concentrations test (TCLP Test). Nevertheless, all the phosphate sources are below the EPA allowed levels to be used for remediation purposes.
- Further research should be conducted on the stabilization mechanisms in which the durability of surface complexes and precipitates in contaminated soil are subjected to changing soil conditions, e.g. acidification, to evaluate the long-term stability of the amendment process.

REFERENCES

Adriano, D.C. 2001. *Trace Elements in Terrestrial Environments: Biochemistry, Bioavailability and Risks of Metals*. New York: Springer.

Badawy, S.H., M.I.D. Helal, A.M. Chaudri, K. Lawlor and S.P. McGrath. 2002. Soil solid-phase controls leads activity in soil solution. *Journal of Environmental Quality.* 31: 162-167.

Boisson, J., A. Ruttens, M. Mencha and J. Vangronsveld. 1999. Evaluation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils. Part 1. Influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation. *Environmental Pollution*.104: 225-233.

Canli, M. and G. Atli. 2003. The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. *Environmental Pollution.* 121: 129 – 136.

Chabbi, A. 2003. Metal concentrations in pore water of the Lusatian lignite mining sediments and internal metal distribution in juncus bulbosus. *Water, Air, and Soil Pollution*. 3: 105 – 117.

Chen, S.B., Y.G. Zhu and Y.B. Ma. 2006. The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils. *Journal of Hazardous Materials* B. 134: 74–79.

Chlopecka, A. and D.C. Adriano.1996a. Mimicked in situ stabilization of metals in a cropped soil: bioavailability and chemical forms of zinc. *Environmental Science and Technology.* 30: 3294-3303.

Chlopecka, A. and D.C. Adriano. 1996b. Influence of zeolite, apatite and Fe-oxide on Cd and Pb uptake by crops. *Science of the Total Environment.* 207: 195-206.

Cotter-Howells J. and I. Thorton. 1991.Source and pathways of environmental lead to children in a Derbyshire mining village. *Environmental Geochemistry and Health.* 13(2):127–35.

Gardea-Torresdey, J., J. Peralta-Videa, M. Montes, G. de la Rosa, B. Corral-Diaz. 2004. Bioaccumulation of cadmium, chromium and copper by Convolvulus arvensis L.: Impact on plant growth and uptake of nutritional elements. *Bioresource Technology*. 92:229–235

.

Guo, G., Q. Zhou and L.Q. Ma. 2006. Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: A review. *Environmental monitoring and Assessment*. 116: 513-528.

Davis A, J.W. Drexler, M.V. Ruby and A. Nicholson. 1993. Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environmental Science and Technology.* 27: 1415–25.

Fawzy, E.M., M.E. Soltan and S.M. Sirry. 2006. Mobilization of different metals between Tamarix parts and their crystal salts – soil system at the banks of river Nile, Aswan, Egypt. *Toxicological and Environmental Chemistry*. 88(4) : 603–618.

Fawzy, E.M. 2008. Soil remediation using in situ immobilization techniques. *Chemistry and Ecology*. 24: 147–156.

Haiyan, W. and A. Stuanes. 2003. Heavy metal pollution in air-water-soil-plant system of Zhuzhou city, Hunan Province. China. *Water, Air and Soil Pollution.* 147: 79–107.

Laperche V, S.J. Traina, P. Gaddam and T.J. Logan. 1996. In situ immobilization of lead in contaminated soils by synthetic hydroxyapatite: chemical and mineralogical characterizations. *Environmental Science and Technology*. 30: 3321– 6.

Knox, A.S., J.C. Seaman, M.J. Mench and J. Vangronsveld. 2001. Remediation of metal-and radionuclides-contaminated soils by in situ stabilization techniques. In: *Environmental Restoration of Metals-Contaminated Soils*, ed. I.K. Iskandar, pp.21-60. Boca Raton: CRC Press LLC.

Knox, A.S. D.I. Kaplan and M.H. Paller. 2006. Phosphate sources and their suitability for remediation of contaminated soils. *Science of the Total Environment.* 357: 271– 279.

Laperche V, S.J. Traina, P. Gaddam and T.J. Logan. 1996. In situ immobilization of lead in contaminated soils by synthetic hydroxyapatite: Chemical and mineralogical characterizations. *Environmental Science and Technology*. 30: 3321– 6.

Lesăţan, D., C. Luob and X. Li. 2008. The use of chelating agents in the remediation of metal-contaminated soils: A review. *Environmental Pollution.*153 (1): 3-13.

Ma Q.Y., S.J. Traina and T.J. Logan. 1993. *In situ* lead immobilization by apatite. *Environmental Science and Technology*. 27: 1803– 10.

Ma Q.Y., S.J. Traina, T.J. Logan and J.A. Ryan. 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environmental Science and Technology.* 28: 1219–28.

Makino, T. K. Sugahara, Y. Sakurai, K. T. Takano Kamia, K. Sasaki, T. Itou and N. Sekiya. 2006. Remediation of cadmium contamination in paddy soils by washing with chemicals: Selection of washing chemicals. *Environmental Pollution.* 144: 2-10.

Mench, M., V. Didier, M. LoÈer, A. Gomez and P.J. Masson. 1994a. A mimicked in situ remediation study of metal contaminated soils with emphasis on cadmium and lead. *Journal of Environmental Quality*. 23: 58-63.

Mench, M., J. Vangronsveld, V. Didier and H. Clijsters. 1994b. Evaluation of metal mobility, plant availability and immobilization by chemical agents in a limed, silty soil. *Environmental Pollution*. 86: 279-286.

Middelburg, J.J. and R.N.J. Comans. 1991. Sorption of cadmium on hydroxyapatite. *Chemical Geology.* 90: 45-53.

Miller W.P. and D.M.Miller. 1987. A micro-pipette method for sediment mechanical analysis. *Communications in Soil Science and Plant Analysis*. 8(1): 1 –15.

Manousakia, E., J. Kadukovab, N. Papadantonakisc and N. Kalogerakis. 2008. Phytoextraction and phytoexcretion of Cd by the leaves of *Tamarix smyrnensis growing on contaminated non-saline and saline soils. Environmental Research.* 106: 326–332.

Nelson, R.E. 1986. Carbonate and gypsum. In: *Methods of Soil Analysis*, Part 2, ASA ed. A.L. Page, R.H. Miller and D.R. Keeney, pp. 181–197.

Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon and organic matter. In: *Methods of Soil Analysis, Part 2. Chemistry and Microbiological Properties* (2nd ed.), eds. A.L. Page, R.H. Miller, and D.R.Keeney. Agronomy Monograph, Vol. 9, pp. 539–577.

Puschenreiter, M., O. Horak, W. Friesl and W. Hartl. 2005. Low-cost agricultural measures to reduce the heavy metal transfer into human food chaine a review. *Plant, Soil and Environment*. 51: 1-11.

Rebedea, I. and N.W. Lepp. 1994. The use of synthetic zeolites to reduceplant metal uptake and phytotoxicity in two polluted soils. In: *Biochemistry of Trace Elements,* ed. D.C. Adriano, Z.S. Chen and S.S. Yang, pp. 81-87. Science and Technology Letters. Northwood, UK,

RodrõÂguez, R., N. Vassilev, N. and R. AzcoÂn. 1999. Increases in growth and nutrient uptake of alfalfa grown in soil amended with microbially-treated sugar beet waste. *Applied Soil Ecology.* 11: 9-15.

Ruby MV, A. Davis, J.H. Kempton, J. Drexler and P.D. Bergstrom. 1992. Lead bioavailability: dissolution kinetics under simulated gastric conditions. *Environmental Science and Technology.* 26: 1242–8.

Sappin-Didier, V., M. Mench, A. Gomez and C. Lambrot. 1997. Use of inorganic amendments for reducing metal availability to ryegrass and tobaco in contaminated soils. In: *Remediation of Soils Contaminated with Metals* ed. I.K. Iskandar and D.C. Adriano, pp. 85-98. Science and Technology Letters. Northwood, UK.

Soltan, M.E., S.M.N. Moalla, M.N. Rashed and E.M. Fawzy. 2005. Physicochemical characteristics and distribution of some metals in the ecosystem of Lake Nasser, Egypt. *Toxicological and Environmental Chemistry*. 87(2): 167–197.

Spuller, C., H. Weigand and C. Marb. 2007. Trace metal stabilization in a shooting range soil: Mobility and phytotoxicity. *Journal of Hazardous Materials* .141: 378-387.

Suzuki, T., T. Hatsushika and Y. Hayakawa. 1981. Synthetic hydro-xyapatites employed as inorganic cation-exchangers. *Journal of the Chemical Society, Faraday Transactions*. 77: 1059-1062.

Tandy, S., K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack. 2004. Extraction of heavy metals from soils using biodegradable chelating agents. *Environmental Science and Technology*. 38: 937-944

Takeuchi, Y. and H. Arai. 1990. Removal of Coexisting Pb2+, Cu2+ and Cd2+ Ions from Water by Addition of Hydroxyapatite Powder. *Journal of Chemical Engineering of Japan.* 23: 75-80.

Tessier, A., P.G.C. Campbell and B. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Journal of Analytical Chemistry.* 51:844-851.

Turekian, K.K. and K.H. Wedepohl. 1961. Distribution of the elements in some major units of the Earth's crust. *Bulletin of the Geological Society of America.* 72: 175 – 192.

U.S. E.P.A 1998. Jasper County Site Area Wide Baseline Ecological Risk Assessment, Jasper County, Missouri. Kansas City, KS7 US EPA Region VII.

U.S. E.P.A. 1992. Toxicity characteristic leaching procedure. Method 1311, Rev. In : SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Washington7 Office of Solid Waste. U.S. EPA. Identification and Listing of Hazardous Waste, Toxicity.

Vangronsveld, J., F. Van Assche and H. Clijsters. 1991. Reclamation of a `desert like' site in the north east of belgium: evolution of the metal pollution and experiments in situ. In: *Proc. Int. Conf. Heavy Metals in the Environment*, ed. J.G. Farmer. CEP Consultants, Edinburgh, UK, 58-61.

Vangronsveld, J., J. Sterckx, F. Van Assche and H. Clijsters. 1995a. Rehabilitation studies on an old non-ferrous waste dumping ground: Effects of revegetation and immobilization by beringite. *Journal of Geochemical Exploration*. 52: 221-22.90

Vangronsveld, J., F. Van Assche and H. Clijsters. 1995b. Reclamation of a bare industrial area contaminated by non-ferrous metals: in situ metal immobilization and revegetation. *Environmental Pollution*. 87: 51-59.

Vangronsveld, J., J.V. Colpaert and K.K.Van Tichelen. 1996. Reclamation of a bare industrial area contaminated by non-ferrous metals: physicochemical and biological evaluation of the durability of soil treatment and revegetation. *Environmental Pollution*. 94: 131-140.

Xu, Y. and F.W.Schwartz. 1994. Lead immobilization by hydroxyapatite in aqueous solutions. *Journal of Contaminant Hydrology.* 15: 187– 206.

Yang, J. and D. Mosby. 2006. Field assessment of treatment efficacy by three methods of phosphoric acid application in lead-contaminated urban soil. *Science of the Total Environment*. 366: 136– 142.

Wong, S.C.C. and X. Li. 2003. Analysis of heavy metal contaminated soils. *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management.* 7(1) : 12-18

Wong, C.X., Z. Moa, H. Wanga, Z.J. Wanga and Z.H. Caob. 2003. The transportation, time-dependent distribution of heavy metals in paddy crops. *Chemosphere.* 50: 717–723.

Yu, K., L. Tsai, S.H. Chen and S.T. Ho. 200. Chemical binding of heavy metals in anoxic river sediments. *Water Research*. 35(17): 4086 – 4094.