

## Reducing Bioavailability of Some Heavy Metals in A Contaminated Soil Using Phosphate Amendments

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CHEMICAL remediation of heavy metals in contaminated soils is necessary in order to alleviate their potential risks that pose to both environment and human health. So, the present work was carried out to assess the immobilization efficiency of some selective P-agencies induced some heavy metals in a sewage effluent contaminated soil. Two phosphate compounds differ in their water solubility, *i.e.*, diammonium phosphate (DAP) and phosphate rock (PR) were evaluated for their ability to reduce Zn, Pb and Cd bioavailability in a contaminated soil under a wheat-maize cropping sequence installed through a greenhouse pot experiment. The treatments structure was associated with the intent for immobilizing the studied metals according to total P % in both applied agents and based on providing a specific  $P/M_{total}$  molar ratio. The corresponding applied rates of P were 0,400, 600 and 800 kg/fed for PR and DAP.

The obtained data showed that both applied phosphate agents of DAP and PR succeeded in reducing the bioavailability of Zn, Pb and Cd as well as those phytoavailability to the grown plants of wheat followed by maize. The bioavailable metal contents showed a tendency to decrease by increasing the applied amendment levels, with a rather greater response for DAP at the first crop (wheat) as compared to the second one (maize), suggesting that DAP has directly greater potential to immobilize the heavy metals. On the other hand, PR reacts with the tested heavy metals improved significantly with the progress of time, particularly under the presence of organic acids (soil organic matter content =7.82 %), however, DAP potential was almost coupled with the residual effect of PR in the second phase of the current experiment (maize). That was true, since the differences between their effects being insignificant on reducing the extractability of Zn, Pb and Cd in the case of maize plants due to the residual effect of PR was visible.

The previous beneficial effects of the studied amendments were actually reflected on increasing the plants ability for improving the vegetative growth parameters, *i.e.*, plant height and dry weights of shoot and root yields, with similar parallel trends for the heavy metals immobilization in soil and uptake by plant organs (shoots and roots). Likewise, phytotoxicity of Pb, Zn and Cd could be alleviated rather easily by increasing the levels of either DAP or PR on short and long-term of use, respectively.

Sequential extraction results indicated that the application of phosphate amendments led to convert significant amounts of the soil Zn,

Pb and Cd from non residual form (*i.e.*, water soluble, exchangeable, carbonate, Fe-Mn oxides and organic matter fractions) to residual one. DAP was more effective in transforming soil Zn, Pb and Cd from the non-residual to the residual phase than PR at the first phase of wheat-maize cropping sequence, and then the differences became in a narrow range.

From technical and economical point of view, chemical immobilization of heavy metals using DAP is an effective technique method of reducing heavy metals solubility and mobility on a short-term of use, but it is expensive due to the relative high cost of its production as a compound fertilizer for N and P. Thus, it could be recommended by using PR, however, its beneficial effect achieves through long-term of use and it is found as a natural shale formation available in large quantities at some desert locations of Egypt.

**Keywords:** Heavy metals, El-Gabal El-Asfar soil, Phosphate rock, Diammonium phosphate, Wheat, Maize.

Undoubtedly, long-term deposition of heavy metals in El-Gabal El-Asfar soils, Great Cairo, Egypt is more attributed to the continuous irrigation with sewage effluent. Also, bioavailability and mobility of significant fraction of such metals caused biotoxicity for the grown plants. Bioavailability is assumed to be static in nature, where most decisions on risk and remediation are based on laboratory estimations of bioavailable fractions, which may vary with time, nature of species as well as with temporal variation in environmental factors. Treating contaminated soils with certain amendments that enhance key biochemical processes in soils that effectively immobilize heavy metals have already been treated with lime, phosphate and biosolid amendments. Such soil chemical amendments enhanced natural remediation and resulting in substantially improved plant growth and reduced offsite metal transport. The immobilization efficiency induced by such assisted natural remediation may be offered some potential. A suite of chemical amendments are available to monitor the efficiency of assisted natural remediation as well as such technique is now available ensuring the long-term efficiency of a chosen cleanup tool.

The application of phosphate amendments to contaminated soils has been identified as a potentially efficient remediation method (Hettiarachchi *et al.*, 2001 and Cao *et al.*, 2003). This technique is to immobilize metals primarily through the formation of metal phosphates with reduced solubility and enhanced geochemical stability in a wide range of environmental conditions. Precipitation appears to be the predominant process of metal immobilization in the presence of different anions, *i.e.*, carbonate, hydroxide and phosphate, especially when the concentration of metal ion is high (Adriano, 2001). In this connection, precipitation as metal phosphates is considered to be one of the mechanisms for phosphate-induced immobilization of heavy metals. Although phosphate amendments have been

shown to effectively immobilize Pb from contaminated soils, they are also applicable to other metals such as Zn and Cd (Xu & Schwartz, 1994). Ma & Rao (1997) reported that diammonium phosphate  $[(\text{NH}_4)_2\text{HPO}_4]$  decreased Cd solubility in soil cadmium suspensions. Precipitations as metal phosphate have been proved to be one of the main mechanisms for the immobilization of metal, such as Pb and Zn in soils (McGowen *et al.*, 2001).

Recent studies have provided conclusive evidence for the mitigative value of both water-soluble (diammonium phosphate) and water-insoluble phosphates (phosphate rock) to immobilize metals in soils, there by reducing their bioavailability for plant uptake and mobility for transport (Bolan *et al.*, 2003a). Phosphate enhances the immobilization of metals in soils through various processes including: a) direct metal adsorption by the phosphate, b) phosphate anion-induced metal adsorption and c) precipitation of metals with solution phosphate as metal phosphates. Other technique has shown that highly soluble phosphate sources enhance the potential for formation of lead pyromorphite as compared to rock phosphate (Cooper *et al.*, 1998). A number of studies suggested that phosphate sources with higher solubility could be mixed with rock phosphate to increase the effectiveness of lead immobilization in contaminated soils (Ma *et al.*, 1993; Pierzynski & Schwab, 1993 and Hettiarachchi *et al.*, 2000).

Depending on the source, soil application of phosphate can cause direct adsorption of metals onto these compounds through increased surface charge and enhanced anion-induced metal adsorption. Adsorption of metals onto hydroxyapatite surfaces has been observed for a number of metals including Cd, and Zn. Therefore, this study was carried out to evaluate the effectiveness of Phosphate amendments differ in their water solubility, *i.e.*, using both water-soluble diammonium phosphate (DAP) and phosphate rock (PR) for Zn, Pb and Cd immobilization in a long-term irrigated soil by sewage effluent, with special interest to assess the response of their mobility and biological uptake by plants grown thereon to the applied chemical amendments.

## Material and Methods

### *a. Soil*

Soil sample was collected from the 0-25 cm surface layer at the agricultural farm of El-Gabal El-Asfer that is located adjacent to Great Cairo, Egypt and continuously irrigated with sewage effluent for a about 80 years. Soil sample was air dried and then ground to pass through a 2 mm sieve. Some physical and chemical analysis was carried out according to the standard methods undertaken by Black *et al.* (1965) and Page *et al.* (1982) the results are shown in Table 1.

TABLE 1. Some physical and chemical characteristics of the tested soil.

Soil characters	Value
<i>Particle size distribution %</i>	
Coarse sand	20.7
Fine sand	37.4
Silt	19.6
Clay	22.3
Texture class	Sandy clay loam
Soil moisture at water holding capacity %	15.35
CaCO <sub>3</sub> %	0.76
Organic matter %	7.82
Cation exchangeable capacity (c molc kg <sup>-1</sup> )	28.94
pH (1:2.5 soil water suspension)	6.78
E <sub>Ce</sub> (dS/m, soil paste extract)	1.86
<i>Soluble ions (me/l)</i>	
Ca <sup>++</sup>	6.45
Mg <sup>++</sup>	3.25
Na <sup>+</sup>	8.30
K <sup>+</sup>	0.80
CO <sub>3</sub> <sup>-</sup>	0.00
HCO <sub>3</sub> <sup>-</sup>	2.30
Cl <sup>-</sup>	9.15
SO <sub>4</sub> <sup>-</sup>	7.35

Also, 1.0 g of a homogenized soil sample was digested with 12.5 ml of aqua regia (HNO<sub>3</sub>: HCl: HClO<sub>4</sub> with a ratio 3:1:1), the samples were heated until the color became clear, dissolved with several drops of 1% HNO<sub>3</sub>, filtered, diluted to a volume of 50 ml with distilled water, and analyzed for the total content of Zn, Pb and Cd using flame atomic absorption spectrophotometer. Available Zn, Pb and Cd were determined in the experimental soil using ammonium bicarbonate DTPA extractable according to Soltanpour & Schwab (1977) and their contents in the obtained extract were measured by Atomic Absorption Spectrophotometer. Total and DTPA extractable contents of the studied heavy metals (Zn, Pb and Cd) in the contaminated soil under investigation are presented in Table 2.

TABLE 2. Total and DTPA extractable contents of the studied heavy metals (Zn, Pb and Cd) in the contaminated soil.

Total content of metals (mg kg <sup>-1</sup> soil)			DTPA extractable content of metals (mg kg <sup>-1</sup> soil)			Available content as a percentage of total amount		
Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd
274.20	184.95	2.85	29.86	16.73	0.56	10.89	9.05	19.65

#### b. P- agencies

Two Phosphate material differ in their water solubility [(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, DAP (55.47% P<sub>2</sub>O<sub>5</sub>%) and phosphate rock, PR (18.49P<sub>2</sub>O<sub>5</sub> %)] were used as soil amendments for reducing the potential mobility and biological uptake of Zn, Pb

and Cd. The treatments structure was associated with the intent to immobilize the studied metals in the experimental sludge-contaminated soil, based on Providing specific  $P/M_{total}$  molar ratio however, both phosphate amendments including different levels of added P according to its P-total content as a percentage in both added P-materials (El- Gendi, 2004). Hence, diammonium phosphate was added at levels represent about one third of those applied from phosphate rock. Thereby, the corresponding applied rate of P were 0, 400 , 600 & 800 kg fed<sup>-1</sup> which both individually mixed thoroughly with the experimental soil pots.

#### c. Greenhouse experiment

A greenhouse experiment was carried out on wheat Giza 7 (*Triticum aestivum* L.) followed by maize single cross 10 hybrid (*Zea maize* L.) as test crops were consecutively grown on the equilibrated soils under the prevailing conditions of greenhouse at Fac. of Agric., Cairo University, Egypt during November 2005-June 2006. Plastic pots of 28 cm diameter and 30 cm height were filled with 8 kg of sieved untreated and amended soils. The pots were categorized in a completely randomized block design (two plant species, two chemical amendments, three levels for each one, with three replicates), beside the untreated soil (control treatment). As for the wheat-maize cropping sequence, twenty wheat seeds were planted per pot on the 20<sup>th</sup> of November 2005, however, ten maize seeds were planted on the same previously used pots on the 20<sup>th</sup> of March 2006, and then watered daily with tap water. Ten days after sowing, seedlings were thinned to ten and five healthy plants per pot for wheat and maize, respectively. The amended soil pots as well as the untreated ones were rehydrated to 70 % of the water holding capacity through all the experiment period. The conventional agricultural practices, especially the fertilization with the recommended doses of N and K, were applied.

Plant shoots and roots were harvested after 60 days from planting, at which time there was sufficient plant material for analysis. Plant organs were rinsed in distilled water and then dried at 60-70° for 24 hr, dry weights were recorded. The plant samples ground and wet digested with an acids mixture (HNO<sub>3</sub> and HClO<sub>4</sub>) according to Jackson (1973). Heavy metals under investigation (Zn, Pb and Cd) in clear digested solutions were determined using Perkin Elmer Inductively Coupled Spectrophotometer Plasma 400 (ICP). At the same time, DTPA extractable contents of the studied heavy metals were determined, as mentioned before, at harvest to evaluate the response of their potential mobility and biological uptake by grown plants to the applied chemical amendments.

#### d. Sequential extraction of soil samples

Sequential extraction was performed on air-dried soil samples for each pot using the methodology of Tessier *et al.* (1979). The extractions were carried out in 40 ml centrifuge tubes with 1 g of soil at the different treatments (before and after additions of phosphate amendments). The procedure was used to fractionate the studied metals into six operationally defined fractions, *i.e.*, water soluble, exchangeable, carbonate

bound, Fe-Mn oxides bound, organic matter and residual. After each extraction, the solution was separated from the solid by centrifugation at 8000 rpm for 20 min. A reference soil material (as abovementioned) was used to compare metal recovery based on sequential extraction with certified values. The results obtained were statistically analyzed according to Gomez & Gomez (1984).

## Results and Discussion

### *I. A general view on the prevailing conditions of the studied soil*

The use of treated Great Cairo sewage effluent as a source of irrigation for sand soils at El-Gabal El-Asfar farm was carried out since 1923 (Om Mohamed *et al.*, 2001). Continuously usage of this wastewater effluent caused long-term deposition of significant fraction of heavy metals as well as resulted in a decrease in soil pH (< 7), which enhances their potential mobility and biological uptake by grown plants (Tables 1 & 2). However, soils containing high available contents of these metals are suffered from serious problems for plant, animal and human (Adriano *et al.*, 2004).

Heavy metals, particularly those have been a considerable interest in the current study such as Zn, Pb and Cd, will continue their prominent role in our society as contaminants and as essential nutrients. A number of these metals are essential in plant, animal and human nutrition such as Zn. So far, no evidence is available to prove and beneficial role from Pb and Cd. A soil is generally considered contaminated with Zn, Pb and Cd when their total concentrations exceed 300, 260 and 10 mg kg<sup>-1</sup> soil respectively (EPA, 1993). According to the aforementioned permissible limits of the studied three heavy metals, it could be concluded that the application of the sewage effluent for the in situ accumulation of heavy metals led to Zn-excess in soil over the permissible limit, while both Pb and Cd are still within the permissible range (Table 2).

### *II. Effect of applied amendments on heavy metals immobilization in soil and their reflections on plant growth and metals uptake*

#### *a. Immobilization of bioavailable heavy metals*

The application of the studied amendment levels for both DAP and PR to immobilize Zn, Pb and Cd in situ might provide an effective and sustainable solution for remediation of contaminants in the experimental soil. The bioavailable metal contents showed a tendency to decrease by increasing the applied amendment levels, with a rather greater response for DAP at the first crop (wheat) as compared to the second one (maize) (Table 3). It is clear that there is a significantly decrease in bioavailable heavy metal contents as a result of applying the two remedies (DAP vs PR) reached at the highest level in the first phase of the experiment 58.34 vs 42.26% for Zn, 64.71 vs 52.82% for Pb and 67.92 vs 54.72% for Cd as compared with the untreated soil. The corresponding values in the second experimental phase were 59.73 vs 58.64 %, 70.08 vs 68.91 % and 72.55 vs 70.59 %, respectively.

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TABLE 3. DTPA extractable contents of Zn, Pb and Cd as affected by the applied chemical amendment levels.

Treatment	DTPA extractable contents (mg kg <sup>-1</sup> soil)					
	Wheat			Maize		
	Zn	Pb	Cd	Zn	Pb	Cd
Control	29.72	16.49	0.53	29.35	16.21	0.51
DAP1	18.05	9.95	0.32	17.64	9.48	0.29
DAP2	15.92	7.63	0.20	14.75	7.36	0.18
DAP3	12.38	5.82	0.17	11.82	4.85	0.14
PR1	24.70	12.97	0.39	17.96	10.12	0.31
PR2	21.45	10.56	0.28	15.07	7.98	0.20
PR3	17.06	7.78	0.24	12.14	5.04	0.15
L.S.D. at 0.05						
T-rate	2.41	2.51	0.012	3.12	2.56	0.02
P-induced	1.24	1.01	0.051	0.12	0.06	0.08
T x P	3.51	2.10	0.050	2.13	1.13	0.04

These results suggested that DAP has directly greater potential to immobilize Zn, Pb and Cd in the studied contaminated soil at the first phase of wheat-maize cropping sequence, however its potential was almost coupled with the residual effect of PR in the second phase. These results can be interpreted on the base that PR reacts with the tested heavy metals improved significantly with the progress of time, particularly under the presence of organic acids developed through organic matter decay (soil organic matter content =7.82 %). These findings are in harmony with those reported by Boisson *et al.* (1999) and Biswas & Narayanasamy (2006). It could be explained on the basis of apatites in commercial phosphate rocks are in the form of carbonate apatite with isomorphous substitution of carbonate for phosphate, F for hydroxyl anion, and minor substitution of Ca<sup>2+</sup> by Na<sup>+</sup> and Mg<sup>2+</sup> atoms. Therefore, metal adsorption onto phosphate rock is facilitated through the exchange of Ca<sup>2+</sup> from apatite particle with the metal cations in soil solution. These fairly stable-phosphate compounds have extremely low solubility over a wide pH range, which makes phosphate application an attractive technology for managing metal contaminated soils. The formation of new solid phase (precipitates) occurs when the ionic product in the solution exceeds the solubility product of that phase. Thereby, the ability of phosphate rock to immobilize heavy metals under consideration in contaminated soils through precipitation as metal-phosphate compounds has been well documented by Bolan *et al.* (2003b).

The inhibition of heavy metals availability could be emphasized by their adsorption on to P- rock as an inner sphere complexes, *i.e.*, Cd<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·OH and Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl, which have relatively low solubility product constants, *K<sub>sp</sub>*, *i.e.*, -38.1, -63.1 and -84.4, respectively

#### *b. Vegetative growth parameters*

The beneficial effects of the studied amendments were actually reflected on increasing the plant ability for both water and nutrients use efficiencies by wheat

and maize plants, consequently increased the vegetative growth parameters, *i.e.*, plant height and dry weights of shoot and root yields, as shown in Table 4.

TABLE 4. Plant height, dry shoot and root weights as affected by the applied chemical amendment levels.

Treatment	Plant height (cm)		Dry weight (g/pot)			
	Wheat	Maize	Wheat		Maize	
			Shoot	Root	Shoot	Root
Control	32.15	44.45	16.75	4.53	33.52	10.73
DAP1	39.08	53.12	24.48	6.62	40.05	12.83
DAP2	43.75	58.93	27.35	7.38	44.16	14.15
DAP3	46.94	64.85	29.47	7.96	47.38	15.36
PR1	36.51	52.97	20.93	5.65	39.89	12.76
PR2	38.82	59.06	23.86	6.47	43.97	14.07
PR3	41.15	63.85	25.01	6.81	46.95	15.05
L.S.D. at 0.05						
T-rate	3.21	4.51	0.65	0.73	1.11	0.54
P-induced	2.45	0.23	2.13	1.51	0.59	0.39
T x P	1.13	2.13	0.91	0.13	1.21	0.84

The obtained data indicate that the values of plant height and dry matter of both wheat and maize were significantly increased with increasing the applied levels of DAP and PR as compared to the control treatment. The treatments of DAP surpassed the PR ones for increasing wheat vegetative growth, while their effectiveness were almost similar for maize vegetative parameters. This was true, since the differences between the effects of parallel applied treatments for DAP and PR being insignificant in the case of maize plants due to the residual effect of PR on reducing the extractability of Zn, Pb and Cd was visible.

#### *c. Biological uptake of heavy metals*

Data presented in Table 5 reveal that the heavy metals response of Zn, Pb and Cd to uptake and accumulate in either shoot or root tissues showed a closely relationship to their corresponding reduction in the bioavailable contents in the experimental soil treatments as a result of applying the tested DAP and PR, (Tables 3 and 4). However, addition of DAP showing a relatively higher decreasing order as compared with PR in the first phase of wheat-maize cropping sequence. That is more closely with the obvious differentiations between both amendments for their immobilization efficiency for the studied heavy metals, which it was towards DAP at the first phase of the current experiment. Likewise, biological uptake of Zn, Pb and Cd can be alleviated rather easily by increasing the time and levels of PR due to its residual effect on immobilizing bioavailability of the studied metals as well as  $\text{Ca}^{2+}$  through phosphate rock competes with those metals for plant uptake, thereby reducing the uptake of them. In addition, the released  $\text{Ca}^{2+}$  causes an inhibition of the translocation of such metals from root to shoot.



Data presented in Table 5 also showed that the beneficial effect of applied both amendments on reducing the biological metals uptake in tissues of plant shoots was more pronounced than roots, this is mainly due to the slowly translocation of such metals from root to shoot. The formation of pyromorphite in the soil and association of P-amendments with the studied metals in the roots appear to be responsible for the reduction of their contents in plant shoots (Ma *et al.*, 1994). Such results are in harmony with those documented by various studies installed on different phosphate materials, such as phosphate rock (PR) fertilizers and other P-compounds have been widely used to immobilize some heavy metals in contaminated soils to reduce its phytotoxicity and accumulation by plants.

TABLE 5. Tissue Zn, Pb and Cd concentrations of wheat and maize as affected by the applied chemical amendment levels.

Treatment	Metal uptake (mg kg <sup>-1</sup> dry matter)					
	Zn		Pb		Cd	
	Shoot	Root	Shoot	Root	Shoot	Root
<b>Wheat</b>						
Control	93.56	115.74	10.45	17.92	0.47	0.73
DAP1	56.85	67.47	6.32	10.51	0.28	0.42
DAP2	44.73	56.93	5.08	8.67	0.23	0.35
DAP3	35.82	47.51	3.92	7.39	0.18	0.30
PR1	67.79	79.19	7.74	12.40	0.35	0.51
PR2	53.14	65.76	5.85	10.23	0.26	0.42
PR3	46.60	58.16	4.96	9.02	0.22	0.37
L.S.D. at 0.05						
T-rate	2.39	5.49	3.22	2.11	0.51	0.03
P-induced	1.73	2.21	0.82	0.95	0.02	N.S.
T x P	3.11	1.13	0.91	1.17	0.32	0.12
<b>Maize</b>						
Control	86.05	103.52	8.75	15.09	0.45	0.68
DAP1	52.86	61.94	5.27	9.74	0.26	0.39
DAP2	40.39	53.19	4.68	7.25	0.22	0.33
DAP3	32.94	41.72	3.35	6.20	0.16	0.28
PR1	53.25	62.35	5.93	10.12	0.27	0.40
PR2	41.17	54.74	5.02	7.96	0.24	0.34
PR3	33.65	42.31	3.89	6.87	0.17	0.27
L.S.D. at 0.05						
T-rate	3.33	5.12	0.93	0.81	0.03	0.05
P-induced	N.S.	N.S.	0.08	1.10	N.S.	N.S.
T x P	0.53	1.13	0.53	0.31	0.01	0.03

### III. Fractionation and mobility indexes of the studied heavy metals

Metal fractionations or sequential extraction schemes are commonly used to evaluate mobility and bioavailability of heavy metals in soils, and hence the efficiency of remediation treatments at the experimental end. Assuming the non-residual metal (sum the metal fractions of soluble, exchange, organic, carbonate,

amorphous Fe and Mn oxides) is more bioavailable than the residual one. Thus, the effectiveness of in situ remediation of metal contaminated soils can be assessed using a fractionation scheme (Ma & Rao, 1997; Basta & Gradwohl, 2000 and Cao *et al.*, 2003). This statement is emphasized by the illustrated data in Table 6, which showed Zn, Pb and Cd immobilization and the formation of phosphate compounds with low solubility resulting in their transformation from non residual fractions to residual ones.

TABLE 6. Zn, Pb and Cd fractionation and mobility indexes as affected by the applied chemical amendments after harvest maize plants.

Treatment	Metal fractions %						Mobility index*
	Soluble	Exchange	Carbonate	Fe-Mn oxides	Organic	Residual	
<b>Zn</b>							
Control	0.15	10.68	12.95	16.74	39.58	19.90	28.78
DAP1	0.06	7.12	9.56	11.62	36.19	35.45	16.74
DAP2	0.02	3.74	7.51	9.42	34.75	44.46	11.27
DAP3	0.00	2.65	5.71	7.15	30.03	54.43	8.36
PR1	0.08	7.96	9.82	12.64	38.67	30.83	17.86
PR2	0.03	3.54	8.47	10.53	37.04	40.39	12.04
PR3	0.00	2.93	6.02	8.31	36.80	45.90	8.95
<b>Pb</b>							
Control	0.08	9.54	15.26	12.97	32.06	38.09	22.88
DAP1	0.03	6.32	10.76	8.82	29.56	44.51	17.11
DAP2	0.00	2.75	7.95	7.14	27.98	55.78	9.90
DAP3	0.00	2.14	5.70	6.05	23.74	62.37	7.84
PR1	0.06	7.08	10.42	9.66	32.92	39.86	17.56
PR2	0.02	3.05	6.93	8.94	31.75	48.51	10.00
PR3	0.00	2.58	6.02	6.97	29.65	54.78	8.60
<b>Cd</b>							
Control	0.03	7.97	9.65	10.74	31.85	34.76	17.65
DAP1	0.01	5.31	7.16	7.43	29.36	50.73	12.48
DAP2	0.00	2.42	5.94	6.02	27.93	57.69	8.36
DAP3	0.00	1.75	4.25	5.01	24.47	64.52	6.00
PR1	0.02	5.89	7.68	8.17	31.15	47.09	13.59
PR2	0.00	2.63	6.34	7.03	29.83	54.17	8.97
PR3	0.00	2.18	4.75	5.42	28.34	59.31	6.93

\* (Soluble + exchangeable + carbonate fractions) / sum of the six fractions.

The residual fraction was the most important fraction; however, the addition of the tested phosphate amendments substantially increased its values for the studied metals in soil, which corresponded to the metal concentrations in tissues of both tested plants. The residual fraction reached the greatest percentages at the highest levels of DAP & PR, which containing approximately 54 & 46% for Zn, 62 & 55% for Pb and 65 & 59% for Cd. Also, the organic fraction was the next most important one, where its corresponding percentages amounted approximately 30 & 37 %, 24 & 30 % and 25 & 28 % due to applying DAP & PR for Zn, Pb and Cd, *Egypt. J. Soil. Sci.* 47, No.1 (2007)

respectively. In general, it could be categorized the different fractions of the studied metals in an ascending order: residual > organic >> Fe-Mn oxides > carbonate > exchangeable >>> soluble. Moreover, the narrow range between the mobility indexes at all applied parallel levels of both studied DAP and PR at harvest of the second experimental phase (maize) indicate that the PR reacts with heavy metals improved significantly with the progress of time, especially under the relatively high content of soil organic matter (7.82%). These findings are in harmony with those reported by Boisson *et al.* (1999).

From the technical point of view, chemical immobilization of heavy metals using DAP is an effective technique method of reducing heavy metals solubility and mobility on a short-term of use, but it is expensive due to the relative high cost of production as a fertilizer for N and P. Thus, it could be recommended by using PR, however, its beneficial effect achieves through long-term of use, and it is found as a natural shale formation available in large quantities at some desert locations of Egypt.

#### References

- Adriano, D.C. (2001) *"Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability and Risks of Metals"*, 2<sup>nd</sup> ed., Springer, New York, NY.
- Adriano, D.C.; Wenzel, W.W.; Vangronsveld, J. and Bolan, N.S. (2004) Role of assisted natural remediation in environmental cleanup. *Geoderma* 122: 121-142.
- Basta, N.T. and Gradwohl, R. (2000) Estimation of heavy metal bioavailability in smelter-contaminated soils by a sequential extraction procedure. *J. Soil Contam* 9: 149-164.
- Biswas, D.R. and Narayanasamy, G. (2006) Rock phosphate enriched compost: An approach to improve low-grade Indian rock phosphate. *Bioresource Technology* 97 : 2243-2251.
- Black, C.A.; Evans, D.D.; Ensminger, L.E.; White, J.L. and Clark, F.E. (1965) *"Methods of Soil Analysis"*, Amer. Soc. Agron. Inc., Pub., Madison, Wisc., USA.
- Boisson, J.; Ruttens, A.; Mench, M. and Vangronsveld, J. (1999) Valuation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils. I: influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation. *Environmental Pollution* 104 : 225 -233.
- Bolan, N.S.; Adriano, D.C.; Duraisamy, A. and Mani, P. (2003a) Immobilization and phytoavailability of cadmium in variable charge soils. III. Effect of biosolid addition. *Plant & Soil* 256 : 231-241.
- Bolan, N.D.; Adriano, D.C. and Naidu, R. (2003b) Role of phosphorus in immobilization and bioavailability of heavy metals in the soil-plant system. *Rev. Environ. Contam. Toxicol.* 177 : 1-44.
- Cao, R.X.; Ma, L.Q.; Chen, M.; Singh, S.P. and Harris, W.G. (2003) Phosphate-induced metal immobilization in a contaminated site. *Environ. Poll.* 122 : 19-28.

- Cooper, E.M.; Strawn, G.D.; Sims, T.J.; Sparks, L.D. and Onken, M.B. (1998) Effect of chemical stabilization by phosphate amendment on the desorption of P and Pb from contaminated soil. *Agronomy Abstracts*, 343, ASA, Madison, WI.
- El-Gendi, S.A.Z. (2004) Remediation of soil polluted with industrial wastes using an immobilization technique. *J. of Agric. Sci. Mansoura Univ.* 29 (8) : 4833-4843.
- EPA, Environmental Protection Agency of USA (1993) Standards for the use ore disposal of sewage sludge final rules. Federal Register Part II, 40 CFT Part 257.
- Gomez, K.A. and Gomez, A.A. (1984) "Statistical Procedures for Agricultural Research", John Wiley and Sons Inc., New York, USA.
- Hettiarachchi, G.M.; Pierzynski, G.M. and Ransom, M.D. (2000) In situ stabilization of soil lead using phosphorous and manganese oxide. *Environ. Sci. Technol.* 34: 4614-4619.
- Hettiarachchi, G.M.; Pierzynski, G.M. and Ransom, M.D. (2001) In situ stabilization of soil lead using phosphorus. *J. Environ. Qual.* 30 : 1214-1221.
- Jackson, M.L. (1973) "Soil Chemical Analysis", Prentice Hall of India Private Limited, New Delhi, Indian.
- Ma, Q.Y.; Traina, S.J. and Logan, T.J. (1993) In situ lead immobilization by apatite. *Environ. Sci. Tech.* 27 : 1803-1810.
- Ma, Q.Y.; Traina, S.J.; Logan, T.J. and Ryan, J.A. (1994) Effects of aqueous Al, Cd, Cu, Fe (II), Ni and Zn on Pb immobilization by Hydroxyapatite. *Environ. Sci. Technol.* 28 :1219-1228.
- Ma, L.Q. and Rao, G.N. (1997) Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. *J. Environ. Qual.* 26 : 788-794.
- McGowen, S.L.; Basta, N.T. and Brown, G.O. (2001) Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter contaminated soil. *J. Environ. Qual.* 30 : 493-500.
- Om Mohamed, A. Khafagi; Wafaas, I. El-Lawndy and Hanan, E. Abdel Aal (2001) Effect of irrigation with treated sewage effluent on the accumulation Cd, Cr, Cu, Pb and Zn in some vegetables. *Al-Azhar J. Agric. Res.* 33 : 171-187.
- Page, A.I. ; Miller, R.H. and Keeney, D.R. (1982) "Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties", 2<sup>nd</sup> ed., Amer. Soc. of Agron., Madison, Wisconsin, U.S.A.
- Pierzynski, G.M. and Schwab, A.P. (1993) Bioavailability of zinc, cadmium, and lead in a metal-contaminated alluvial soil. *J. Environ. Qual.* 22: 247-254.
- Soltanpour, P.N. and Schwab, A.B. (1977) A new soil test for simultaneous extraction of macronutrients in alkaline soils. *Comm. Soil Sci. and Plant Annal.* 8, 195.

Tessier, A.; Campbell, P.G. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particular trace metals. *Anal. Chem.* 51, 844.

Xu, Y. and Schwartz, F.W. (1994) Lead immobilization by hydroxyapatite in aqueous solution. *J. Contam. Hydrol.* 14 : 187-206.

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## خفض التيسر الحيوى لبعض العناصر الثقيلة فى تربة ملوثة باستخدام المصلحات الفوسفاتية

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المعالجة الكيميائية للأراضى الملوثة وتقييد حركة العناصر الثقيلة منها أصبحت ضرورة لتجنب مخاطرها على البيئة وصحة الإنسان ، لذا فإن هذه الدراسة قد أجريت لتحديد كفاءة بعض المركبات الفوسفاتية فى تقليل حركة وتيسر بعض من هذه العناصر فى أرض ملوثة بمياه الصرف الصحى. حيث تم تقييم مركبين من المواد الفوسفاتية المختلفة فى درجة ذوبانها فى الماء : الأولى (فوسفات ثنائى الأمونيوم-DAP) والثانية هي (صخر الفوسفات-PR) من حيث قابليتهما لخفض الصلاحية الحيوية لعناصر Zn, Pb and Cd تحت ظروف زراعة محصولى قمح-أذرة متعاقبين من خلال تجربة أصص خضرية ، وقد تم إختيار معاملات المعالجة تبعا للمحتوى الكلى من الفوسفور فى كلا المادتين المستخدمتين ، حيث كانت مستويات الإضافة صفر ، ٤٠٠ ، ٦٠٠ ، ٨٠٠ كيلو جرام فسفور للفدان .

وتوضح النتائج المتحصل عليها أن كلا المركبين الفوسفاتيين (DAP and PR) قد نجحا فى خفض التيسر الحيوى لعناصر Zn, Pb and Cd وكذا حركتها فى التربة المنزرعة بنباتات القمح وما تلاها من أذرة ، حيث أظهر المحتوى الميسر من تلك العناصر إتجاها متناقصا بزيادة مستويات الإضافة ، باستجابته أكثر فاعلية بالنسبة لمركب DAP فى حالة المحصول الأول (القمح) مقارنة بفترة المحصول الثانى (الأذرة) ، مبينا دور DAP المباشر والأكثر تأثيرا فى تقليل تيسر العناصر الثقيلة فى فترة قصيرة نسبيا. وعلى الجانب الآخر فإن تأثير PR على تقييد حركة العناصر الثقيلة فى التربة قد تحسن بدرجة معنوية مع تزايد فترة الإستخدام ، خاصة فى وجود الأحماض العضوية المنطلقة من تحلل مادة الارض العضوية (٧,٨٢٪) ، ويؤكد ذلك تقارب تأثير الـ DAP مع التأثير المتبقى للـ PR فى الجزء الثانى من

التجربة (الأذرة) وأن الفروق بين تأثيرهما في خفض تيسر عناصر Zn, Pb and Cd غير معنوية كنتيجة لوضوح التأثير المتبقى لصخر الفوسفات .

وبالطبع فقد ابعثت هذه التأثيرات المفيدة لكلا المحسنين على تحسين قياسات النمو الخضري للنباتات النامية ممثلة في أطوال النباتات والوزن الجاف للسيقان والجذور باتجاهات مشابهة وموازية لتأثير كلا المحسنين على تقييد حركة العناصر الثقيلة في التربة وخفض الكمية الممتصة منها في الأنسجة النباتية للسيقان والجذور، وعليه فان سمية هذه العناصر للنباتات النامية تناقصت بزيادة مستويات الإضافة من الـ DAP أو الـ PR على المدى القصير أو الطويل على الترتيب.

وتشير نتائج الإستخلاص المتتابع إلى أن إضافة تلك المحسنات الفوسفاتية قد أدى إلى تحول كميات محسوسة من العناصر الثقيلة في التربة من صورها غير المتبقية (الميسرة في صور ذائبة، متبادلة، مرتبطة بالكربونات ، مرتبطة بإكاسيد الحديد والمنجنيز، مرتبطة بالمادة العضوية) إلى الصورة المتبقية (غير الميسرة). كما وأن الـ DAP كان أكثر فاعلية في تحول تلك العناصر في التربة من الصور الميسرة إلى الصورة الأقل ذوبانا (المتبقية) مقارنة بالـ PR في الجزء الأول من التجربة (القمح) ، ثم أصبحت الفروق بين المعاملات الموازية ضئيلة ، كما وأن المدى الضيق لقيم دليل حركة تلك العناصر عند مختلف مستويات الإضافة الموازية لكلا المحسنين في الجزء الثاني من التجربة يؤكد أيضا أن تعامل الـ PR مع العناصر الثقيلة وتقليل حركتها وتيسرها قد تحسن بدرجة معنوية مع تزايد الزمن (فترة الإستخدام).

ومن الوجهة الفنية والاقتصادية ، فان المعالجة الكيميائية للعناصر الثقيلة باستخدام الـ DAP تعتبر طريقة فعالة ومباشرة خلال فترة قصيرة نسبيا من الإستخدام، ولكنها مكلفة نتيجة لإرتفاع تكاليف إنتاجه إستخدامه كسماد مركب (أزوتى-فوسفاتى) ، لذا يوصى باستخدام PR لما له من تأثير مفيد على المدى الطويل ، كما أنه يتواجد كخام طبيعي ميسر بكميات كبيرة في بعض الأماكن الصحراوية في مصر .