



Evaluation of monobasic calcium phosphate for the immobilization of heavy metals in contaminated soils from Lavrion

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Abstract

The objective of this work was to evaluate the efficiency of monobasic calcium phosphate for the stabilization of heavy metals in contaminated soils. The treatment was applied on a soil sample from the Lavrion mining area, Greece, heavily contaminated with Pb, Zn, Cd and As and characterized as toxic in respect to Pb according to the US EPA toxicity characteristics leaching procedure (TCLP). The efficiency of stabilization was evaluated based on two criteria: (a) the reduction of metals mobility below the TCLP regulatory limits; (b) the reduction of phytoaccumulation. Phytoaccumulation was evaluated both indirectly by applying leaching tests using EDTA, DTPA and NaHCO₃ solutions and directly by carrying out pot experiments with *Phaseolus vulgaris* as plant indicator. This treatment was found to immobilize Pb and Cd, whereas As and Zn were slightly mobilized. No effect on phytoaccumulation was observed. Moreover, the treatment had a negative effect on plants growth, which was combined with a strong deficiency of Ca in the tissue of leaves. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Contaminated soil; Stabilization; Lead; Phytoaccumulation; Phosphate

1. Introduction

The use of phosphates as stabilizing agent is particularly attractive for the case of soils, where the key-contaminant is Pb. This selection is based both on empirical observation and thermodynamic considerations and it is supported by several geochemical studies, which indicate that lead phosphate minerals are very stable under a wide range of environmental

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conditions. A classic and comprehensive study on this issue was published by Nriagu in 1973 [1]. Nriagu has concluded that lead phosphates and more particularly chloropyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, are the least soluble lead minerals under most natural subaqueous and aerobic conditions.

Based on the low lead phosphate solubility, a number of studies involving the use of phosphates for the stabilization of Pb in contaminated soils were carried out. Ying Ma et al. [2] investigated the use of apatite for in situ immobilization of Pb in contaminated soils and wastes. Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] and natural apatite were applied as stabilizing agents. The hydroxyapatite addition resulted in the reduction of soluble Pb from initial concentration of 2273 to 36 $\mu\text{g/l}$. Natural apatite was also effective in removing lead from aqueous solution. The optimal removal of aqueous lead was achieved when the pH of the solution was low enough to dissolve apatite and supply phosphorus to immobilize Pb, and high enough to keep the solubility of hydroxypyromorphite low. According to their results, the final product of the lead immobilization was $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$.

Rabinowitz [3] tested a solution of 0.03 M $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and 0.015 M NaCl to immobilize lead in soil. The treatment efficiency was tested by leaching with three different reagents: 10% HNO_3 ; 0.5% HCl; 10% citric acid. It was found that treatment with phosphates resulted in a significant reduction of Pb leachability in the hydrochloric and citric acid solutions. However, the strong nitric acid solution dissolved any lead phosphate formed.

In this experimental work, the phosphate treatment was tested as a potential cost effective remediation option for the rehabilitation of a heavily contaminated site in Lavrion, Greece. This site has been used in the past for the disposal of mining wastes and it is heavily contaminated with Pb, Zn, Cd and As. Moreover, the soil is characterized as toxic with respect to Pb following the toxicity characterization leaching procedure (TCLP) of US EPA. The land however is actually used as residential area with occasional agricultural activities. The objective of this work was to evaluate the efficiency of phosphates for the immobilization of lead, based on two criteria: (a) the reduction of metals mobility below the TCLP regulatory levels; (b) the reduction of phytoaccumulation to acceptable levels for the protection of human health. Phytoaccumulation was evaluated both indirectly by applying leaching tests and directly by carrying out pot experiment with *Phaseolus vulgaris* as plant indicator.

2. Materials and methods

2.1. Soil sampling and characterization

Soil samples were taken from the surface layer (0–0.20 m), air dried and homogenized. The most important characteristics are presented in Table 1. The sampled material was found to contain 16.3% of gravel size particles; the “soil” fraction (<2 mm) is characterized as sandy loam. It is a calcareous soil containing 25.6% of calcite equivalent and exhibiting pH value of 7.84. It is very poor in organic matter containing less than 0.76% of organic carbon. From the elemental analyses shown in Table 1, it is seen that the soil used in this experimental work is highly contaminated, mainly with Pb and Zn; their concentrations exceed by far all existing guidelines for soils.

Table 1
Characterization of the soil used in the experiments

Soil characteristics	
Texture	
>2 mm (%)	16.3
Sand 0.02–2 mm (%)	65.8
Silt 0.063–0.02 mm (%)	14.5
Clay <0.002 mm (%)	3.4
H-Alkalinity	
pH	7.84
CaCO ₃ (mg/g)	256
Organic matter	
Organic carbon (%)	0.76
Elemental analyses (%)	
Major elements	
Ca	12.7
Mg	0.9
Fe	7.0
Mn	0.5
Pb	2.43
Zn	1.86
Cd	0.013
As	0.30
Contaminants	
Pb	2.43
Zn	1.86
Cd	0.013
As	0.30

Mineralogical examination by X-ray diffraction revealed that the main constituents are quartz, calcite and fluorite, with minor amounts of muscovite, chlorite, albite and dolomite. Electron probe microanalysis revealed 13 minerals of Pb, Zn, Fe, Mn and Ba. Lead was found mainly in the form of carbonates (PbCO₃, Pb₃(CO₃)₂(OH)₂, Pb₂CO₃Cl₂) and oxides, or associated with limonite (FeOOH·xH₂O).

2.2. Phosphate treatment

A preliminary experimental study using pure chemical reagents (CaHPO₄·2H₂O and Na₂HPO₄·2H₂O) had shown that the calcium dibasic phosphate was more efficient as stabilizing reagent compared to the corresponding sodium salt. Based on these findings it was decided to use as source of phosphates a calcium phosphate salt for the experimental work presented in this paper. Moreover, to obtain a cheap and easily available product, a search in the Greek fertilizer market was performed. The product which was finally selected is a commercial fertilizer consisting mainly of monohydrate calcium oxyphosphate (Ca(H₂PO₄)₂·H₂O).

The phosphate dose was calculated based on the stoichiometric ratio of PO₄ ions to the total concentration of Pb in soil, i.e. 2.43 wt.% or 117.4 mmole Pb per kg of soil. The addition

of phosphates at a molar ratio 1.0 mole/mole corresponds to 14.8 g of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ per kg of soil for this particular soil sample.

The experiments were carried out in pots, each pot having a volume of approximately 1 l. An amount of 10 kg of soil was sieved at 2.5 mesh in order to remove the coarse material. A series of 12 pots were prepared as follows: 800 g of soil were thoroughly mixed with the proper quantity of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. Twelve molar ratios PO_4/Pb were tested: 0 (no addition), 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.5, 2.0 and 2.5. In order to promote the chemical reactions between the metal ions retained in soil and the phosphate additive, the pots were systematically hydrated and kept saturated for approximately 2 months.

2.3. Chemical tests

Following the treatment of soil with phosphates, representative samples from each pot were subjected to several leaching tests, in order to evaluate the toxicity and availability of contaminants.

2.3.1. Toxicity

The US regulatory test TCLP involves leaching of the sample with a buffer solution of acetic acid/acetic sodium 0.1 M, $\text{pH} = 5$, for 24 h at 5% pulp density. If the dissolved metals exceed the specified limits the material is characterized as toxic [4].

2.3.2. Phytoavailability

Two alternative leaching tests were applied to estimate the phytoavailable fraction of Pb, Zn and Cd, based on the use of EDTA and DTPA chelating reagents. In the EDTA leaching test [5] the extraction solution consisted of 0.02 M EDTA and 1N $\text{CH}_3\text{COONH}_4$ at $\text{pH} = 7.0$. Ten gram of soil were mixed with 100 ml of extraction solution in 300 ml flask and the slurry was agitated for 1 h at 100 rpm. The DTPA leaching solution contained 0.01 M CaCl_2 , 0.1 M triethylamine and 5×10^{-3} M DTPA at $\text{pH} = 7.3$ [6]. Ten milliliter of soil were mixed with 20 ml of solution and the mixture was shaken for 2 h at 160 rpm.

The phytoavailable fraction of As was evaluated using the NaHCO_3 leaching procedure [6]. Five gram of soil were mixed with 100 ml of extraction solution (0.5 M NaHCO_3 at $\text{pH} = 8.5$ regulated with 1N NaOH) and the mixture was shaken for 1 h at 100 rpm. Following the filtration of the slurries, the metals in the leachates were analyzed with atomic absorption spectroscopy (AAS).

2.4. Biological tests

In order to evaluate directly the effect of phosphate treatment on the accumulation of metal contaminants on plant tissues, plant growth tests were carried out using dwarf beans (*P. vulgaris Starazagorski gw*) as plant “indicator”. The seeds were sown after 24 h imbibition in deionised water. The seedlings were grown under artificial light (15 out of 24 h) in the laboratory environment and watering with deionized water was adjusted to the needs of plants.

The plants were harvested after a period of 22 days, when it was clear that their development was due to the nutrients uptake exclusively from soil and not from the initial germ.

The morphological parameters of the plants (root weight, leaf area, length and weight of the aerial parts) were measured and samples from roots and leaves were collected for the determination of metal concentrations, mainly Pb, Zn, Cd and As.

A wet digestion procedure was followed for the analysis of plant tissues. The dried and ground plant tissue was placed in a small beaker with 10 ml of concentrated HNO₃ and the mixture was allowed to stay overnight. The beaker was heated gently on a hot plate until the production of red NO₂ fumes was ceased. After that the beaker was allowed to cool and a small amount (2–4 ml) of 70% HClO₄ was added. Finally, the sample was heated again, allowed to evaporate to a small volume, transferred to a volumetric flask and diluted with distilled water. The metal concentrations were analyzed by flame AAS; a graphite atomizer was also used for low concentrations.

3. Results and discussion

3.1. Chemical tests

3.1.1. Toxicity

As previously mentioned the soil under examination consists mainly of mineral processing wastes, which have been deposited in the west side of Lavrion city during the first decades of the century. As a consequence it contains unusually high concentrations of metal contaminants. When subjected to the US toxicity characterization leaching procedure it is characterized as toxic, particularly for Pb, which clearly exceeds the regulatory limit of 5 mg/l. The treatment with phosphates was seen to stabilize efficiently Pb (Table 2). The dose required to reduce leachable Pb below the regulatory limit was found to be around the molar ratio PO₄/Pb = 0.6 mole/mole (Fig. 1), which corresponds approximately to an application rate of 0.9 wt.% Ca(H₂PO₄)₂·H₂O.

Table 2
The effect of phosphate treatment on the toxicity of soil [4]

Phosphate dose PO ₄ /Pb (mole/mole)	Concentrations in leachate (mg/l)		
	Pb	Cd	As
0.0	34.3	1.06	0.19
0.1	34.7	0.53	0.35
0.2	21.1	0.63	0.85
0.3	19.4	0.39	0.99
0.4	7.9	0.48	1.09
0.5	4.1	0.45	1.3
0.6	4.5	0.41	1.99
0.8	2.9	0.35	1.24
1.0	3.0	0.38	1.43
1.5	1.2	0.26	1.21
2.0	1.0	0.27	1.00
2.5	1.5	0.26	1.33
TCLP limit (mg/l)	5	1	5

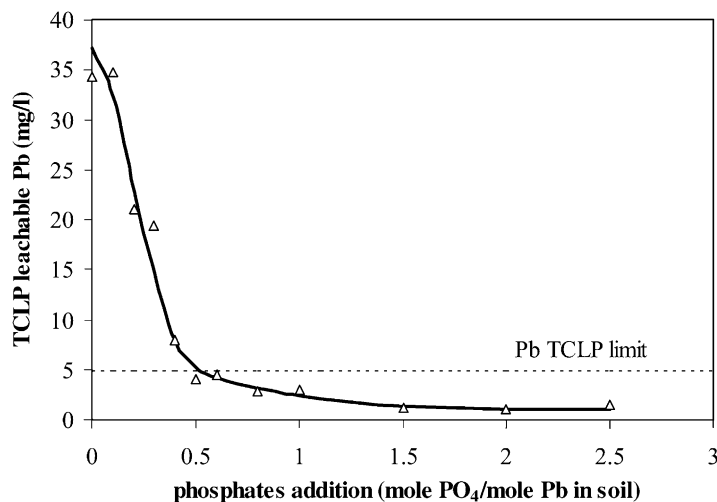


Fig. 1. Reduction of Pb toxicity with the phosphate treatment.

It is also seen in Table 2 that the treatment of soil with increasing rates of phosphates results in the stabilization of Cd, reducing its solubility from the initial value of 1.06 down to 0.26 mg/l. On the contrary, arsenic stability was adversely affected from this treatment. Its solubility increased from the initial value of 0.19 up to 1.35 mg/l at the highest phosphate dose of 2.5 mole/mole. The mobilization of As can be explained considering the close chemical similarity between the phosphate and arsenate ions. Traces of arsenate compounds, such as mimetite, $Pb_2(AsO_4)Cl$, have been identified during the mineralogical examination of the soil sample. The above results suggest a partial substitution of arsenate ions by phosphates during this intense phosphate treatment. The corresponding release of As remains however below the toxicity limit of 5 mg/l in the entire range of phosphate doses examined in this experimental work.

3.1.2. pH of soils and phytoavailability of contaminants

The availability of contaminants regarding their uptake by plants was estimated with leaching tests using chelating reagents (DTPA and EDTA) for Pb, Zn and Cd and a solution of $NaHCO_3$ for As. The pH of treated soils was also measured in order to evaluate the degree of acidification and eventual adverse effects, due to the application of the acidic phosphate salt, $Ca(H_2PO_4)_2 \cdot H_2O$. The results are presented in Table 3.

The application of phosphates was found to reduce efficiently the extractable fractions of Pb and Cd. On the contrary a slight increase of Zn solubility was observed increasing the phosphate dose. Finally, the solubility of As in $NaHCO_3$ remained practically constant with no obvious correlation with the application rate of phosphates.

The variation of Pb, Zn and Cd leachability as a function of phosphate dose is illustrated in Fig. 2. For comparison reasons the extractable fraction of metals, M , was “normalized” versus the initial concentration of extractable metal, M_c , in the untreated soil. Based on the DTPA results, approximately 70% of leachable Pb and 60% of leachable Cd can be

Table 3
Effect of phosphate treatment on the pH of the soils and the EDTA, DTPA and NaHCO₃ leachability of contaminants

Dose PO ₄ /Pb (mole/mole)	pH	Extractable metals (mg/kg of soil)						
		Pb		Zn		Cd		As
		DTPA	EDTA	DTPA	EDTA	DTPA	EDTA	NaHCO ₃
0.0	7.84	1294	5530	576	1895	9.56	28.4	21.0
0.1	7.52	1010	3670	524	2063	8.14	30.4	16.0
0.2	7.24	979	3930	560	1927	8.12	27.6	12.6
0.3	7.18	877	3050	590	1807	7.44	21.6	18.9
0.4	7.13	795	3190	557	1847	7.22	22.8	18.9
0.5	7.07	775	2710	600	1703	7.34	20.4	16.4
0.6	7.03	720	2920	599	2014	6.54	21.2	19.8
0.8	7.01	567	2560	550	1850	5.78	19.6	16.3
1.0	6.90	600	2540	621	2124	6.56	22	17.7
1.5	6.53	379	2695	643	1994	4.34	15.1	17.9
2.0	6.39	372	2646	740	2134	4.22	13.9	15.6
2.5	6.07	336	2684	615	2216	3.80	13.7	20.2

stabilized at PO₄/Pb molar ratios greater than 1.5. Following the EDTA leaching test the immobilization does not exceed 50% for both metals. It is also evident that stabilization is not improved significantly when phosphates are applied at large stoichiometric excess with respect to Pb, i.e. PO₄/Pb >1.0–1.5 mole/mole.

The increase of Zn solubility, up to 20%, is obviously related with the acidification of soil. Increasing the application rate of Ca(H₂PO₄)₂·H₂O the pH decreases from the initial value of 7.8 to 6.0 at the highest dose of 2.5 mole/mole.

3.2. Biological tests

3.2.1. Metal uptake in plant tissues

The concentrations of Pb, Zn, Cd and As on the leaves and roots of beans are shown in Table 4. The uptake of these contaminants was not significantly reduced with the treatment, up the application rate of 2 mole/mole. Lead accumulation in the leaves varied between 100 and 250 mg/kg dry matter, Zn between 100 and 480 mg/kg, Cd between 3 and 15 and As in the range 16–68 mg/kg, with no obvious correlation with the dose. Surprisingly high concentrations were measured in the leaves of the plant, grown at the soil that was treated with the maximum phosphate dose of 2.5 mole PO₄/mole Pb. A parallel decrease of the metal contents in roots was also observed.

The preferential retention of heavy metals, especially Pb, in the root system is often reported in the literature [8–12]. The plants, which exclude the translocation of metals from the roots to the above ground parts, are called “excluders”. According to Antosiewicz [12] the concentration of metals breaking this root barrier could be used in determining the threshold of phytotoxicity. Following this approach the toxic concentration of metals in leaves for *P. vulgaris* Starazagorski amounts to 490 mg/kg for Pb, 470 mg/kg for Zn and 40 mg/kg for Cd.

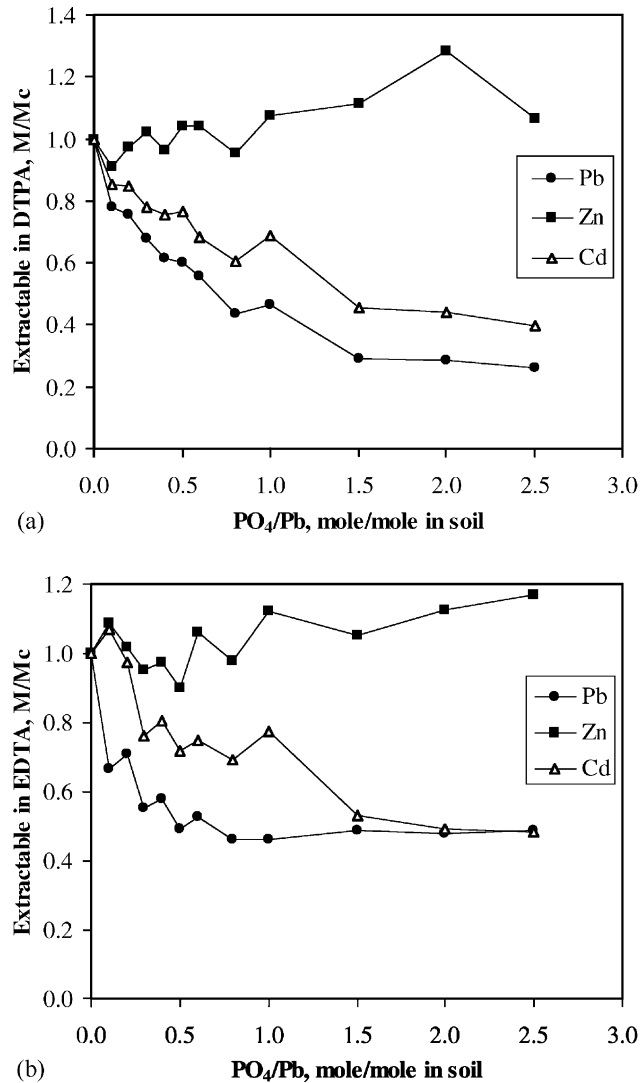


Fig. 2. The effect of phosphate application on the leachability of metals in the DTPA (2a) and EDTA (2b) solutions. M , extractable fraction in treated soil; M_c , extractable fraction in the control experiment.

It must be emphasized however that the concentration of metals accumulated in plant tissues, at phosphate doses below 2 mole/mole, may remain below the phytotoxicity threshold values, but there are still very high compared to the normal range encountered in the leaves of plants (Table 4). Based on these experimental results, risks for grazing animals and humans through food intake are not attenuated with this treatment.

It should be noticed also that this experimental work has not confirm the predictive value of chemical tests for the evaluation of phytoavailability, as it is evident comparing

Table 4
Metals contents in the primary leaves and the roots of 21-day-old bean seedlings

Dose PO ₄ /Pb (M)	Metals contents (mg/kg dry matter)							
	Pb		Zn		Cd		As	
	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots
0.0	240	9553	240	7284	4.16	94.6	27.5	881
0.1	252	8220	173	8717	3.79	92.7	30.0	1012
0.2	101	9839	484	9943	6.34	94.6	25.6	1067
0.3	95	10284	196	9695	3.69	93.2	16.6	1320
0.4	98	6944	188	7589	3.67	66.2	22.1	880
0.5	205	9604	221	8617	4.72	74.4	28.0	1914
0.6	184	9542	227	7942	15.8	77.9	38.8	1507
0.8	99	7575	148	5563	6.31	71.7	22.8	1035
1.0	135	9622	317	4274	6.80	69.9	21.9	1376
1.5	111	7609	100	5905	9.22	57.6	68.0	1034
2.0	149	8628	175	8982	6.15	84.1	–	1221
2.5	491	2384	473	2708	40.3	42.9	–	365
Normal range of concentration in plant leaves [9]								
	0.1–5.0		15–150		0.2–0.8		0.01–1.0	

the results of leaching tests in Table 3 and the analyses of metal contents in the plants in Table 4, at least for the concentration ranges examined in this study and for the case of beans which were used as plant indicator. The low positive correlation for Pb ($R = 0.49$) and the lack of any significant correlation for Cd in the case of DTPA test is illustrated in Fig. 3. The linear correlations proposed by Boon and Soltanpour [13] for the prediction of Pb and Cd concentrations in lettuce and spinach is also shown in the same figure. Though a large number of the experimental values concerning the DTPA extractable concentrations are within the range investigated by these researchers the response of beans was found to be completely different.

3.2.2. Dry-matter yield

The phosphate treatment had a pronounced negative effect on plant growth mainly for the above ground parts of the plants as seen in Table 5. This cannot be attributed to an increase of toxic metals uptake, since this effect was not observed from the analyses of plant tissues. In order to clarify the reasons for this pronounced negative effect on plants growth, selected samples of leaves were further analyzed for their content in essential nutrient elements. The elements analyzed were Ca, Mg, Fe, Cu and P. The results are presented in Table 6. The normal range of concentrations encountered in bean tissues are also shown in this table [7].

The most unexpected finding was that the phosphate treatment resulted in a strong and increasing deficiency of Ca in the tissue of leaves, although the phosphates were applied in the form of calcium salt and the treated soil contained a high percentage of calcite.

The analyses of leaves in the control experiment (no phosphate addition) has also shown that the plant grown in this soil take up an excess of Fe and is clearly deficient in P. The addition of phosphates has no effect on the accumulation of Fe and increases slightly the uptake of P, without however reaching the required levels.

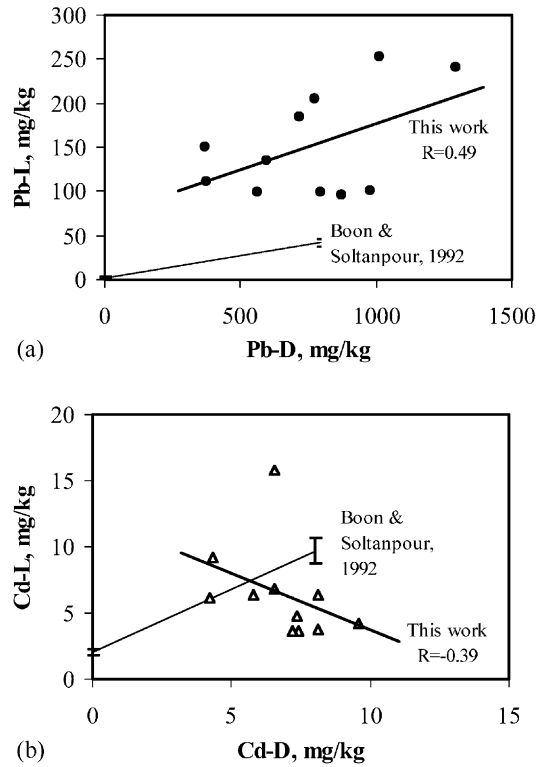


Fig. 3. Relationships between Pb (3a) and Cd (3b) concentrations in leaves (Pb-L, Cd-L) and the DTPA extractable fraction of these metals (Pb-D, Cd-D). The linear correlation proposed by Boon and Soltanpour [13] for the prediction of Pb and Cd concentrations in lettuce and spinach is also shown.

Table 5
Morphological parameters and dry-matter yield of *Phaseolus vulgaris* grown on the treated soils

Dose PO ₄ /Pb (M)	Root weight, DW (g)	Shoot length (cm)	Leaf area (cm ²)	Leaf weight, DW (g)
0.0	0.0425	31.1	113.0	0.1812
0.1	0.0753	22.2	108.0	0.1741
0.2	0.0560	19.1	78.9	0.1452
0.3	0.0740	17.9	79.5	0.1598
0.4	0.0468	19.7	87.1	0.1698
0.5	0.0632	19.6	76.9	0.1356
0.6	0.0655	16.2	50.0	0.0905
0.8	0.0767	14.6	47.7	0.0872
1.0	0.1058	12.9	46.1	0.0905
1.5	0.0573	14.2	32.5	0.0618
2.0	0.0226	16.0	40.9	0.0862
2.5	0.0233	11.7	8.25	0.0129

Table 6
The effect of phosphate treatment on essential nutrients

Dose PO ₄ /Pb (M)	Leaf weight (g)	Concentration in leaves, DW (mg/kg)					
		Ca	Mg	Fe	Mn	Cu	P
0.0	0.1812	10198	5077	1054	154.5	28.2	936
0.5	0.1356	5693	4417	1416	66.4	37.6	1446
1.0	0.0905	5263	4803	680	87.7	36.2	1779
1.5	0.0618	2909	4739	1340	98.0	39.2	2005
Normal range in leaves [7]							
Deficiency limit (<i>D</i>)		10000	3000	50	50	5	3500
Toxicity limit (<i>T</i>)		20000	10000	300	300	30	7500
Response in increasing phosphate rates							
<i>P</i> ↑		<i>D</i> ↑	✓	<i>T</i> ↔	✓	✓	<i>D</i> ↓

The above results suggest that the negative effect of phosphate treatment on plant growth is mainly due to the increased deficiency of Ca. Addition of a stabilizing additive with higher Ca/PO₄ molar ratio, for instance using a mixture of agricultural lime and Ca(HPO₄)₂·H₂O fertilizer, may be a solution to this productivity problem.

4. Conclusions

In this experimental work, the treatment of heavy metal contaminated soil with phosphates was tested as a potential cost effective remediation option. This treatment was seen to stabilize efficiently Pb. Pb and Cd leachability determined by the TCLP, EDTA and DTPA leaching tests decreased by increasing the phosphate addition rate. The required dose to reduce TCLP leachable Pb below the respective regulatory limit was found to be around the molar ratio PO₄/Pb = 0.6 mole/mole, which corresponds approximately to an application rate of 0.5 wt.% expressed as P₂O₅. However, an increase of Zn EDTA and DTPA leachability was observed which was attributed to the acidification of soil due to the addition of acidic calcium oxyphosphate.

The arsenic stability was also adversely affected by this treatment. The TCLP solubility increased from the initial value of 0.19 up to 1.35 mg/l at the highest phosphate dose. The mobilization of As can be explained considering the close chemical similarity between the phosphate and arsenate ions resulting in a partial substitution of arsenate ions by phosphates during this intense phosphate treatment. However, the As concentration in the TCLP leaching solution remained below the respective regulatory limit of 5 mg/l. Finally, the solubility of As in NaHCO₃ remained practically constant with no obvious correlation with the application rate of phosphates.

Regarding phytoaccumulation the experimental results indicated that the phosphate treatment had no effect on the uptake of contaminants in plant tissues. The concentration of contaminants in the leaves remained very high, exceeding by far the reported normal concentrations. Based on these experimental results, risks for grazing animals and humans through food intake are not attenuated by this treatment. Moreover, phosphates treatment

was found to have a pronounced negative effect on plant growth, which was combined with a strong deficiency of Ca in the tissue of leaves.

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