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Remediation of Pb and Cd Polluted Soils Using In Situ Immobilization and Phytoextraction Techniques

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In situ immobilization and phytoextraction techniques have been used for remediation of Pb and Cd polluted soils. Three rates (0.25, 0.5 and 1.0%) of seven immobilizing agents (cement, slag, phosphate rock, bitumen, Fe- and Al-gels, and δ-MnO_2) were tested on three soils containing various levels of Pb (48–192.0 ug/g) and Cd (0.75–3.45 ug/g). All immobilizing agents reduced the plant available Pb and Cd as extracted by DTPA (diethylenetriaminepentaacetic acid). The effectiveness of the various agents in immobilizing Pb and Cd followed the descending order: bitumen > cement > slag > Fe-gel > Al-gel > phosphate rock > δ-MnO_2. Cement and phosphate rock fixed Pb and Cd mainly in the carbonate form, whereas the slag, bitumen, Fe-gel, Al-gel and δ-MnO_2 fixed the metals mainly in the oxide form.

*The results of pot experiment proved the high ability of barnyard grass (*Echinnochloa stagninum*) to accumulate elevated amounts of Pb and Cd (ranging from 291–2421 and 6.1–45.9 ug metal/g dry matter, respectively). These amounts are higher than those reported for hyperaccumulators, particularly for Pb. The amounts of Pb and Cd removed by barnyard grass represent, on average, 46 and 72% of their initial total contents in the soils, respectively. These results proved that, without any other soil treatments, barnyard grass is highly efficient in removing considerable amounts of Pb and Cd from polluted soil within a reasonably short period of time. Therefore, use of barnyard grass for the phytoremediation of Pb and Cd polluted soils is feasible and recommended as an environmentally safe and cheap method. The most significant finding of this study is to name the barnyard grass as an efficient lead accumulator plant.*

Keywords Hyperaccumulators, barnyard grass, phytoremediation, heavy metals

Introduction

Soils, whether in urban or rural areas, represent a major sink for metals released into the environment from a variety of anthropogenic sources (Arendt *et al.*, 1990; Nriagu, 1991). Once in soil, some of these metals are immobile and persistent, while others are more mobile. Mobile metals may move down the soil profile, polluting ground water, or taken up by plants causing either phytotoxicity or health hazards to human (Davies and Wixson, 1988; Sherlock, 1991; Jackson and Alloway, 1992). Cadmium has considerably less affinity to be adsorbed on soil constituents than do Cu, Zn and Pb and might be expected to be more mobile in the environment than these metals (Adriano, 1986). The combination of generally high bioavailability in soils and very high toxicity to animals and humans has

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made Cd the element of greatest concern in considering the value of sewage sludge as a soil amendment (Jackson and Alloway, 1992; Ruby *et al.*, 1996, 1999). Lead is the least mobile heavy metal in soils, especially under reducing or non acidic conditions (Chaney *et al.*, 1989; Ruby *et al.*, 1999). The risk of Pb movement to the edible parts of the plant is believed to be low. Toxic effects of Pb on plants have not often been observed (Davies and Wixson, 1988; Chaney *et al.*, 1989; Ruby *et al.*, 1996). The health concern with Pb-polluted soils arises mostly from the contamination of plants by soil particles, and ingestion of soil by humans and grazing animals (Davies and Wixson, 1988; Sherlok, 1991; Ruby *et al.*, 1999).

Remediation of polluted soils has to be considered when potentially toxic elements or substances in soils impose adverse effects on biodiversity or human health. Contaminated soil can be remediated by chemical, physical or biological techniques (Impens *et al.*, 1991; Logan, 1992). The available remediation technologies includes: 1) soil capping and/or removal of the polluted layer; 2) solidification, vitrification and soil venting; 3) in situ chemical treatments, e.g., soil washing to remove the metal from the soil, and addition of immobilizing agents to fix the metal in immobile form; and 4) using plants with ability to absorb high amounts of the metals, e.g., hyperaccumulator (Baker and Brooks, 1989; Baker *et al.*, 1994; Brown, 1995). The immobilization of heavy metals in polluted soils can be achieved by complexation adsorption and/or precipitation processes. This requires addition of inorganic binders such as cement, fly ash, slag, lime, manganese oxide, phosphate rock, etc., or by organic binders such as bitumen (Kabata-Pendias and Pendias, 1992; USEPA, 1995; Hettiarachichi *et al.*, 1998; Hettiarachichi and Pierzynski, 2002; Mcgowen, 2000; Mcgowen *et al.*, 2001; Seaman *et al.*, 2001). Immobilization of heavy metals may be very successful in decreasing bioavailability of the metals in soil, but their concentration in soil remains unchanged.

Alternatively, plants may be used for removal of the metals from contaminated soils. Certain species of higher plants, known as hyperaccumulators, can accumulate very high concentrations of metals in their tissues without showing toxicity (Wu *et al.*, 1999; Klassen *et al.*, 2000; Bennett *et al.*, 2003). Such plants can be used successfully to clean up heavy metal polluted soils if their biomass and metal content are large enough to complete remediation within a reasonable period (Ebbs and Kochian, 1997). Hyperaccumulator species are defined as those whose leaves contain $>$100 mg Cd kg^{-1}, 1000 mg Pb, Ni and Cu kg^{-1}or $>$ 10000 mg Zn and Mn kg^{-1} (dry weight) when grown in metal-rich soils (Baker and Brooks, 1989; Baker *et al.*, 1994). Some of the most likely plant species for phytoremediation are members of the Brassicaceae family. *Thlaspi caerulescens* can tolerate as much as 4000 ppm Zn in the shoots (Chaney, 1983). *Brassica juncea* (Indian mustard), for example, has been shown to accumulate moderate levels of Se (Banuelos and Meek, 1990; Banuelos *et al.*, 1993), Pb, Cr, Cd, Ni, Zn and Cu (Nanda-Kumar *et al.*, 1995). Other Brassica species, namely *B. napas* and *B. rapa*, show a similar tendency to accumulate moderate levels of heavy metals (Brown, 1995). In Egypt, several authors (Radwan, 1993; Ali, 1996) have studied ditch bank plants grown in lakes and waterways to remediate heavy metal polluted water. These plants include the cattail (*Typha domingenisis*), the common reed (*Phragmites austrailies*), the nutsedge (*Cyprus longus* and *Cyprus alopecroide*), and the barnyard grass (*Echinnochloa stagninum*). The last grass is planted as fodder in the North Delta (Ali, 1996).

This study was undertaken to evaluate: 1) the efficiency of cement, slag, phosphate rock, bitumen, and oxide gels to stabilize Pb and Cd in polluted soils in nonavailable forms; and 2) the capability of several plants to clean up and detoxify soils polluted with Pb and Cd from different sources.

Materials and Methods

Soil

Twenty-five surface (0–30 cm) soil samples were collected from different locations in Egypt. The selected locations received continuous supply of heavy metals from either vehicle exhausts, industrial, or domestic wastes. The samples were submitted for chemical and physical analyses. Based on the contents of total and plant available Pb and Cd as extracted using DTPA (diethylenetriaminepentaacetic acid), three samples, out of the collected 25 ones, were chosen for the comprehensive study. The three samples (classification is Typic Torrifluvents) include: one sample treated with sewage sludge and irrigated with sewage effluent of Cairo city for more than 50 years; one sample representing a site that has been used to dump industrial wastes; and one representing side road soils on the Cairo-Alexandria road and subjected to heavy fallout of traffic exhausts. The locations of the soils and source of metal pollutants are given in Table 1.

Immobilizing Agents

Seven immobilizing agents are used in the present study. Four of these agents are commercial materials and include: 1) cement, produced by Toura Portland cement company; 2) slag, a by-product of the iron and steel factory, Helwan, its chemical composition is Fe_2O_3, Fe_3O_4, and $CaSiO_3$; 3) phosphate rock, obtained from Abou-Tartour phosphate ore and 4) bitumen, produced by the Company of Modern Building Chemicals, Cairo. The other three agents, i.e., iron-gel, aluminum-gel and synthetic δ-MnO_2 were prepared in the laboratory as follows: 1) iron gel: a stock suspension of iron gel was prepared by the rapid (15 min) neutralization of reagent grade Fe $(NO_3)_3$ with NaOH to pH 7 in a polypropylene beaker as described by Kinniburgh *et al.* (1975); 2) aluminum gel: a stock suspension of aluminum gel was similarly prepared as previously mentioned using $Al(NO_3)_3$ (Kinniburgh *et al.*, 1975); and 3) synthetic δ-MnO_2, was prepared by oxidation of manganous ion by permanganate

Table 1

Location, source of pollutants, and general characteristics of (air dried) soils

Soil no.	1	2	3
Location	El-gabal El-Asfar	Banha	Damanhour
Source of pollutants	S	I	V.E
PH (1:2.5)	7.0	7.7	7.7
EC (1:2.5) dS/m	0.6	1.4	0.5
OM%	4.9	0.6	1.0
Total carbonte content%	0.1	1.7	2.5
Silt%	13.0	22.7	27.8
Clay%	16.0	49.3	44.3
Total Pb (ug/g)	192.0	48.0	127.0
Total Cd (ug/g)	3.45	0.75	1.4
DTPA-Pb (ug/g)	72.0	10.2	44.0
DTPA-Cd (ug/g)	1.02	0.26	0.44

S: Sewage Wastes; I: Industrial Wastes; V.E: Vehicle Exhaust.

according to the reaction: $3\ Mn^{2+} + 2\ MnO_4^- + 2\ H_2O = 5\ MnO_2 + 4H^+$. The procedure of Gascoyne (1983) was followed as described by Gongmin *et al.* (1991).

Immobilization Technique

The studied soils were treated with the seven immobilizing agents individually at three rates of 0.25, 0.5 and 1.0%. 20 g of each soil were transferred to 100 ml glass bottles. Each bottle received 20 ml of deionized water containing 0.05, 0.1 or 0.2 g of the immobilizing agent. The treated soils were then dried in an oven at 40°C for 3.5 days, then alternatively wet with 10 ml portions of deionized water and dried; one wetting and one drying constitute a cycle. Each soil was subjected to four wetting and drying cycles (28 days), then the soils were air dried and crushed to pass through a 2 mm sieve, and analyzed for total, DTPA extractable-, as well as various fractions of Pb and Cd. All treatments were done in three replicates.

Greenhouse Experiments

A pot experiment was conducted in a greenhouse using three soil samples and two plants, barnyard grass and candy tuff. The general characteristics of samples are given in Table 1. One-kg portions of each of the three soils, as well as a nonpolluted alluvial soil used as control, were packed in proper plastic pots. A sufficient amount of deionized water was added to each pot to bring the moisture content to the field capacity. Three seedlings of candy tuff (one month old) or three stems of barnyard grass were planted in each pot. Two weeks after planting, candy tuff seedlings were thinned to one plant per pot. The soil moisture was maintained at field capacity, in the case of candy tuff, by frequent irrigation with deionized water, while barnyard grass plants were kept submerged. Throughout the growth period, the plants were supplied as needed with diluted (0.1) Hoagland nutrient solution containing macro- and micro- nutrients.

Four cuts were collected from barnyard grass plants at two-month intervals. In the case of candy tuff, the plants of soils 1 and 3 were harvested after only two months of planting due to their poor growth and degradation; at that time the experiment came to an end for this plant species in these two soils. Candy tuff plants of the other two soils gave normal growth and were harvested after four months of planting. In each case, the plants were cut one cm above the soil surface, rinsed once with diluted HCl and twice with H_2O. They were dried in an oven at 70°C for 24 hours and ground in porcelain mortar. All experiments were done in three replicates.

Analytical Methods

Soil analysis.

- A sequential extraction procedure proposed by Tessier *et al.* (1979) was used to partition Pb and Cd of the selected soil samples into five operationally defined fractions; exchangeable, bound to carbonates, bound to Fe and Mn oxides, bound to organic matter, and residual.
- Plant available Pb and Cd were extracted using 0.005 M DTPA (diethylenetriamine-pentaacetic acid) and 0.1 M TEA (triethanoleamine) at pH 7.3, as described by Lindsay and Norvell (1978). Total contents of Pb and Cd were extracted by aqua regia (HCl—HNO_3) according to the method described by Cottenie *et al.* (1982). Concentrations of Pb and Cd of the extracts were measured using Flame Atomic

Absorption Spectrophotometer (FAAS, type Perkin Elmer, 2830). Mechanical analysis was performed according to the pipette method, organic matter by oxidation with dichromate, and total carbonate content gasometrically using a Collins calcimeter (Dewis and Feritas, 1970). Soil pH was measured in a 1:2.5 soil: water ratio suspension using a glass electrode. Electrical conductivity (EC) was measured in 1: 2.5 soil: water ratio extracts.

Plant analysis. 0.5 g portions of plant material were digested using a digestion mixture of concentrated; HNO_3 (65%), $HClO_4$ (70%), and H_2SO_4 (96%), at a ratio of 40:4:1. The digestate was analyzed for Pb and Cd using Flame Atomic Absorption Spectrophotometry (FAAS, type Perkin Elmer, 2830).

Statistical Analysis

Data of DTPA extractable-Pb and -Cd of soils before and after treating with immobilizing agents were analyzed using linear model procedure of SAS program (SAS, 1996). The model consists of three factors, including: 1) seven immobilizing agents, 2) three rates of addition, 3) three soils, and 4) all possible interactions between the tested factors. The analysis of variance data showed that, DTPA extractable-Pb and -Cd were significantly ($P < 0.001$) affected by: 1) immobilizing agents, 2) rates of addition, 3) tested soils, and 4) interactions between both immobilizing agents and addition rates, immobilizing agents and soil, and rates of addition and tested soils. The least square means of DTPA extractable-Pb and -Cd are given in Table 2. Also, data of the chemical fractions of Pb and Cd of soils before and after being treated with immobilizing agents, dry matter yield, and total contents of Pb and Cd in plant samples were analyzed using the abovementioned linear model procedure of SAS program.

Results and Discussion

Immobilization of Pb and Cd

DTPA extractable-Pb and -Cd. Initial contents of either total- or DTPA extractable-Pb (Table 1) varied widely among the studied soils, and ranged from 48.0–192.0 and 10.0–72.0 ug/g soil, respectively. DTPA extractable-Pb increased as the total content increased. The results (Figure 1) show that all immobilizing agents were able to reduce the mobile pool of Pb of the treated soils as extracted by DTPA. The magnitude of reduction varied significantly ($P < 0.001$) according to the type of the immobilizing agent and rate of its addition. In general, and for all soils and all reagents, DTPA extractable-Pb decreased as the rate of application of the immobilizing agents increased. Low application rates of 0.25% were able to decrease the initial level of DTPA extractable-Pb by values that ranged from 27–56%, i.e., 44–73% of DTPA Pb remained in the soil. Higher application rates of 0.5% and 1.0% were rather effective in reducing DTPA extractable-Pb by values that ranged from 63–92 and 76–95% of the initial ones, respectively, i.e., only 8–37 and 5–24% of the initial DTPA-Pb remained in soil.

For moderately polluted soil (no. 2), and at an application rate of 0.5%, only three reagents (bitumen, slag and cement) were effective in reducing DTPA-Pb to levels ranging from 0.8–1.4 ug/g soil. These values are within the range of 0.78–2.46 ug/g soil reported by Aboulroos *et al.* (1996) for DTPA-Pb of nonpolluted soils of Egypt. USEPA (1995)

Table 2

Least square means for DTPA extractable-Pb and -Cd (mg/kg) in the three soils for different immobilizing agents and addition rates

Factors	LSM* Pb	LSM* Cd
Immobilizing agent		
Cement	18.12 ef	0.245 d
Slag	18.87 de	0.225 d
Rock phosphate	22.28 ab	0.290 b
Bitumen	16.72 f	0.225 e
Fe-gel	19.85 cd	0.270 c
Al-gel	21.12 bc	0.282 bc
δ-MnO2	23.27 a	0.307 a
SE**	0.517	0.00476
Addition rate		
0.0	42.07 a	0.573 a
0.25%	23.12 b	0.313 b
0.50%	8.62 c	0.103 c
1.00%	6.31 d	0.081 d
SE**	0.391	0.0036
Soil		
1-El-gabal El-Asfar	34.0 a	0.481 a
2-Banha	4.82 c	0.120 c
3-Damanhour	21.27 b	0.202 b
SE**	0.339	0.0031
RSD***	1.79	0.0165

*Least square means. Means with same letter are not significantly different ($P < 0.05$). **Standard error. ***Residual standard deviation.

reported that the mobility of heavy metals could be reduced by mixing contaminated soil with appropriate ratio of cement, Portland-type. This reduction could be attributed to the formation of insoluble hydroxides, carbonates or silicates. Also, Shanableh (1995) reported that cement was effective in reducing the leaching of Cd, Ni, and Pb. Leaching decreased as the added cement ratio and curing time increased. Arniella and Blythe (1990) reported that bitumen is commonly used by some authors for the in situ stabilization of heavy metals. The other four reagents of the present study—phosphate rock, Fe- and Al- gel, and δ-MnO$_2$—were effective, also, in this connection, since the obtained values of DTPA-Pb ranged from 2.2–3.4 ug/g soil. However, at an application rate of 1.0%, all immobilizing agents were able to reduce DTPA-Pb to values (ranging from 0.6–2.4 ug/g) matching those of nonpolluted soils.

In the case of heavily polluted soils (no. 1 and 3), an application rate of 0.5% was much less effective in reducing DTPA extractable-Pb to level matching those of nonpolluted soil. However, bitumen, slag, and cement are more effective than the other four reagents in reducing DTPA-Pb in heavily polluted soils. The obtained results show that DTPA extractable-Pb of the soils treated with bitumen, slag, and cement ranged from 4.2–9.8, against 9.2–22.0 ug Pb/g soil, for the other four reagents. An agreement with these results could be seen

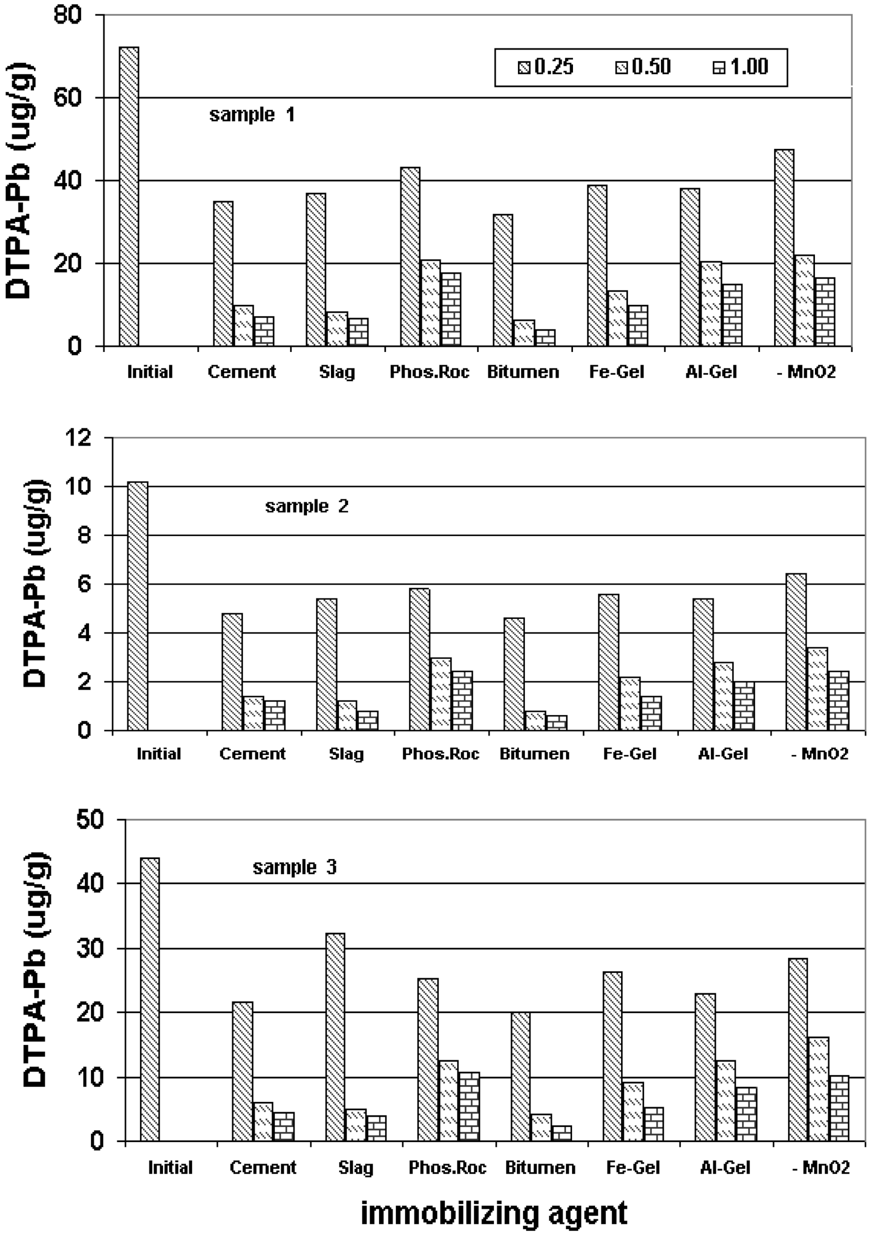

Figure 1. DTPA extractable-Pb of soils before and after treating with three rates of immobilizing agents.

from the results of Ma *et al.* (1997). They reported that addition of phosphate rock to heavily polluted soils (198–12523 mg Pb/kg) reduced Ca $(NO_3)_2$ and HOAc extractable, but had little effect on EDTA-NH_4OAc extractable Pb. On the other hand, the high efficiency reported by Hettiarachchi and Pierzynski (2002) for phosphorus in immobilizing Pb could be attributed to the fact that they used a more soluble form of P (triple superphosphate). An application rate of 1.0% of slag, cement and bitumen was able to reduce DTPA-Pb of the heavily polluted soils to 2.4–7.2 ug/g, against 5.2–17.6 ug/g for the other four reagents. Based on the obtained results, the tested reagents could be arranged according to their efficiency in immobilizing Pb of the studied soils, descending, as follows:

$$\text{bitumen} > \text{cement} > \text{slag} > \text{Fe-gel} > \text{Al-gel} > \text{phosphate rock} > \delta\text{-MnO}_2$$

It should be noted that the efficiency of the various agents in immobilizing Pb did not vary ($P > 0.05$) with the source of pollution among the different soils.

The effect of different immobilizing agents on the stabilizing mobile pool of Cd in the studied soils was almost similar to that on Pb. In general, the results (Figure 2) show that the efficiency of various immobilizing agents in stabilizing Cd increased as the application rate increased. Upon treating the soils with rates of 0.25%, the various agents decreased the DTPA extractable-Cd by values that ranged from 31–55% of the initial levels, i.e., 45–69% remained in soil. Higher application rates of 0.5 and 1.0% were rather effective in reducing the initial level of DTPA Cd by values that ranged from 71–95 and 77–100%, respectively, i.e., 5–29 and 0.0–33% remained in soil. Except for cement and slag, which had the same efficiency in reducing DTPA Cd (insignificant difference, $P > 0.01$, was shown for their DTPA Cd, Table 2), the efficiency of the tested reagents in immobilizing Cd had an order of magnitude similar to that found with Pb.

Chemical fractions of Pb and Cd. Studies on the speciation of heavy metals in polluted soils using sequential extraction techniques have increased in recent years (Tessier *et al.*, 1979; Shuman, 1985; Sposito *et al.*,1982), because these simple techniques provide knowledge about metal affinity to the soil components and the strength with which they are bound to the matrix (Narwal *et al.*, 1999). In the present study, distribution of Pb among the different soil chemical fractions was determined before and after treating the soils with immobilizing agents at application rate of 1% (Figure 3). The results show that the sum of the five fractions in the studied samples amounted to 81–110% of the corresponding total Pb. Highly significant correlation ($r = 0.988$) was obtained between total Pb and the sum of the five fractions. Tessier *et al.* (1979) found that the sum of Pb in the five fractions in two sediment samples amounted to 88–94% of the total Pb.

Comparison of different fractions before and after immobilization treatments show all agents caused a considerable and significant ($P > 0.01$) decrease in exchangeable fraction, the most mobile form, in all samples. All agents were able to reduce the exchangeable Pb by values that ranged from 6–75% of the initial ones. The highest reduction in exchangeable Pb (46–75% of the initial values) was found in the samples treated with slag and bitumen. The changes in the remaining Pb fractions varied among various agents used. Marked increases were obtained for carbonate-bound Pb upon treating the soils with cement, phosphate rock and bitumen. Contents of carbonate-Pb amounted to 302–369, 250–309 and 241–266% of the initial ones in the three soils, respectively. These increases were mainly at the expense of exchangeable-, organic- and, in some cases, oxide-Pb fractions. On the other hand, pronounced increases were observed in the contents of oxide-bound Pb of all soils after being treated with slag, Fe- and Al-gel, and δ-MnO$_2$. Contents of oxide-Pb amounted to 181–489, 198–532, 199–502 and 234–542% of the initial contents of this form in the three soils, respectively. These increases were at the expense of exchangeable-, carbonate- and, in a few samples, organic-fraction. Although the transformation of mobile Pb to carbonate form could be accepted in the case of cement and phosphate rock, it is questionable in the case of bitumen. Based on the chemical composition of bitumen (polynuclear aromatic hydrocarbon), the most accepted process in fixing mobile Pb is

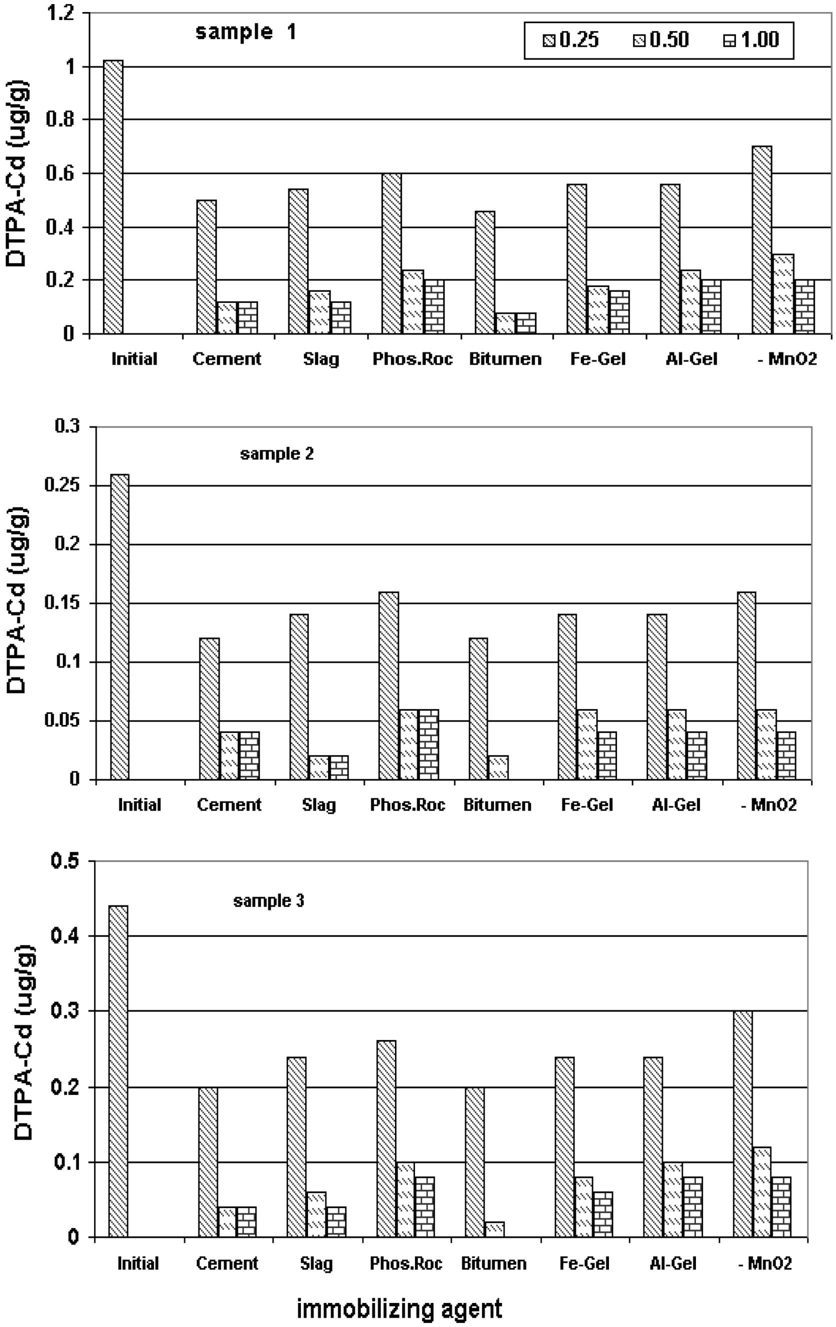

Figure 2. DTPA extractable-Cd of soils before and after treating with three rates of immobilizing agents.

complexation and/or chelation with either OH- or COOH-groups. The obtained results could be attributed to the method of extraction of carbonate form in which the sample was treated with 1M CH_3COONa (pH 5), which is sufficient to reprotonate the functional groups and release the complexed Pb.

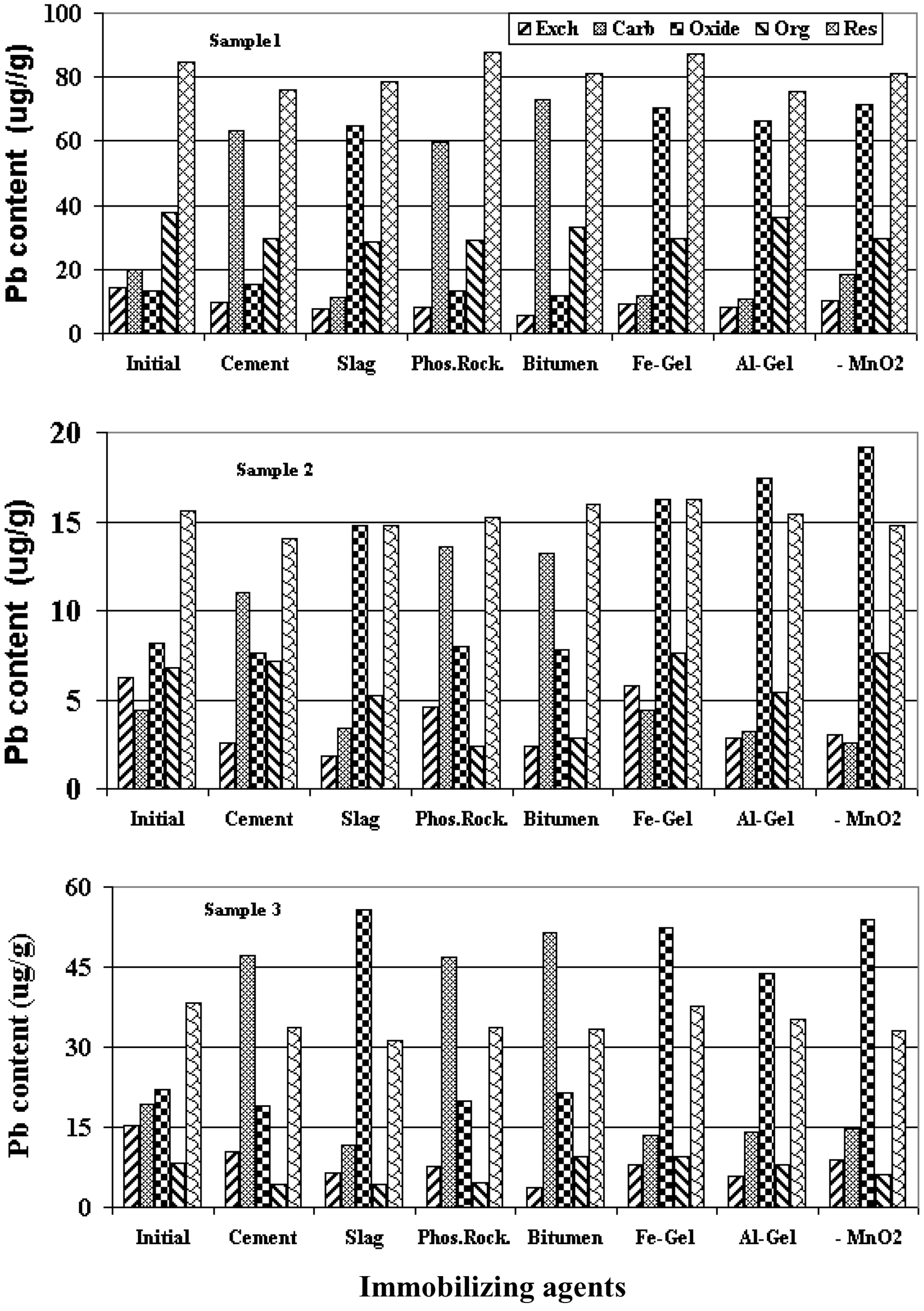

Figure 3. Chemical fractions of Pb of soils before and after treating with immobilizing agents at the rate of 1%.

Based on the fact that the release of carbonate-bound Pb is controlled by the solubility product of $PbCO_3$, which is relatively high ($pK_s = 13.5$) compared to other slightly soluble compounds, e.g., sulfide (PbS), $pK_s = 25.9$, hydroxide, Pb(OH)2, $pK_s = 15.0$, the utilization of cement and phosphate rock in immobilizing Pb may not be preferable. On the other hand, due to the hydroxylic surface nature of both Fe- and Al-gels, δ-MnO_2, and slag, the chemisorption of Pb on deprotonated hydroxyl group is the expected process for immobilization of Pb. Hence, desorption of chemisorbed Pb is more likely only in cases of sharp decreases in soil pH, a case that is difficult to attain in soils similar to the studied ones, i.e. having high buffering capacity due to high content of clay, $CaCO_3$, and in some cases organic matter. Therefore, the recommended effective immobilizing agents for the studied soils could be slag and bitumen. Even the moderately effective reagents, Fe- and Al-gels, are preferable than cement and phosphate rock in stabilizing Pb in such soils. This conclusion agrees with the statement of De Boodt (1991), who reported that, by comparing the composition of water suspensions with and without clay particles, but containing the same elements and the same high pH values, it was found that the concentrations of the elements were much higher in the supernatant liquid in equilibrium with metal precipitates than they were in the supernatants of the systems containing clay. Additional agreement was found with the statement of Mckenzie (1980), and Khattak and Page (1992). They reported that hydrous oxides of aluminum, iron and manganese are known to enhance metal immobility in soils. In this respect, Janssen *et al.* (1993) found that Zn and Pb can be adsorbed on a matrix containing clay and Al-hydroxide polymers on the clay surface. Sposito (1989) reported that these hydroxide compounds facilitated metal binding through specific adsorption. Therefore, selecting an immobilizing agent should consider not only the amount of metal fixed, but also the chemical form of the metal, which controls the future release of the immobilized Pb.

Due to the low content of total Cd of the studied soils (ranging from 0.70–3.45 ug/g soil), only two samples (no.1 and 3) of relatively high Cd content were chosen for the sequential chemical extraction procedure. The results show that the sum of the five fractions of the two studied soils ranged from 80–117% of the total Cd. A highly significant correlation ($r = 0.987$) was obtained between total Cd and the sum of the five fractions. Figure 4 shows the partitioning of Cd among different chemical forms for both treated and untreated samples. The results show a considerable decrease in exchangeable Cd of the treated samples compared with untreated ones. The exchangeable Cd of treated samples amounted to 0–70% of the initial ones. The effects of various reagents on the distribution of Cd among different fractions was almost identical to that of Pb. The carbonate form was the dominant chemical form of Cd of the samples treated with cement, phosphate rock and bitumen. In these samples, the carbonate-Cd form amounted to 188–352, 194–310 and 182–320% of the initial values, respectively. On the other hand, oxide-Cd was the dominant form in the two samples treated with slag, Fe- and Al-gels, and δ-MnO_2. The amounts of Cd bound to the oxides form in these samples were 153–202, 153–220, 160–207% of the initial ones, respectively.

Phytoextraction of Pb and Cd

The results of the pot experiment showed that the contents of the dry matter (DM) of candy tuff plants grown in the polluted soils ranged from 1.01–2.2 g/pot. These values amounted to 42–88% of the dry matter yielded by the corresponding plants grown in the non-polluted soil. Dry matter content decreased significantly ($^*P > 0.01$) as soil DTPA extractable-Pb increased. Lead concentration of the plants grown in the polluted soil varied from 49–73 ug/g DM and was approximately two to three times the value of the nonpolluted one. These values were much lower than the value of 1000 ppm recorded for hyperaccumulators of Pb (Baker and Brooks, 1989). For this reason, total mass of Pb removed by candy tuff from all soils was too low and varied between 0.07 and 0.13 ug/g soil. Similarly, the amounts of Cd removed by the growing plants were too low and ranged from 0.006–0.011 ug/g soil.

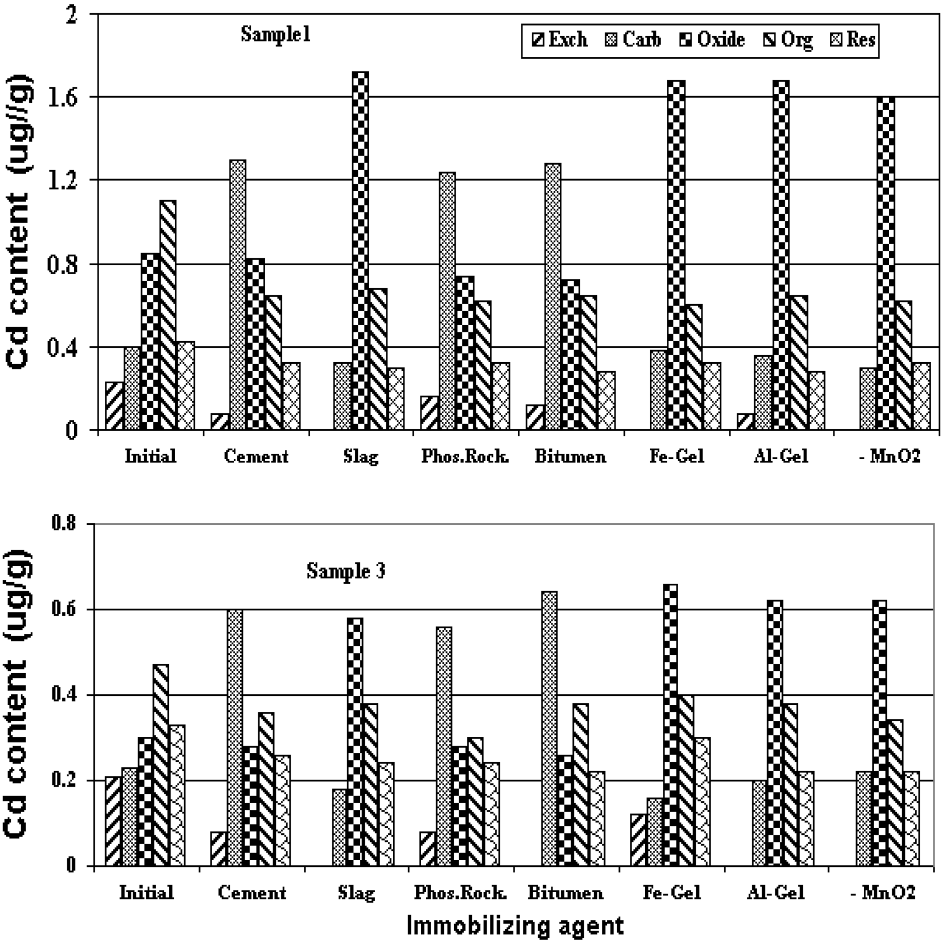

Figure 4. Chemical fractions of Cd of two representative samples before and after treating with immobilizing agents at the rate of 1%.

Thus, it could be concluded that the candy tuff plant (at least for the species used in the experiment) is not a good hyperaccumulator to be used for phytoremediation of Pb or Cd polluted soils.

The results of Table 3 showed that the biomass produced by barnyard grass (Nesela) varied between 6.56–25.17 g/pot. The marked drop in the yield of the second cut compared with the first one could be attributed to the fact that the experiment started with three seedlings having a total fresh weight of 20 g. Thus the yield of the first cut included the growth during the period of two months beside the initial weight of the three seedlings. Dry matter of the plants growing in polluted soils were, generally, lower than those of nonpolluted one. Among those growing in polluted soil, dry matter content decreased significantly ($P > 0.01$) as the soil DTPA-Pb increased. The marked increase shown in dry matter of the last two cuts could be attributed to the prevailing warm weather in April, May and June. Concentrations of Pb (Table 3) in barnyard grass plants grown in polluted soils varied widely and ranged from 291–2421 ug/g DM (the highest values were recorded for the highly polluted soil sample No.1 and 3). These values are higher (14–62 times,

Table 3

Dry matter yield, concentration, and uptake of Pb of four cuts of barnyard grass

	Cut number									
	1		2		3		4		Total uptake	
Soil no.	DM g/pot	Conc. ug/g	DM g/pot	Conc. ug/g	DM g/pot	Conc. ug/g	DM g/pot	Conc. ug/g	ug/pot	Ug/g soil
Control	29.36	34	20.26	39	24.71	29	25.66	21	3044	3.0
1	13.65	1560	6.56	2283	10.11	2421	10.56	2210	84290	84.3
2	25.17	291	14.00	316	19.74	351	20.09	300	24704	24.7
3	18.71	489	7.22	1191	11.98	1283	12.56	1040	52974	53.0

approximately) than those of non-polluted soil. The obtained values prove the high ability of barnyard grass plant to accumulate Pb in concentrations much higher than that reported for hyperaccumulators, i.e., >1000 ug/g DM (Baker and Brooks, 1989). Based on these results, barnyard grass should be named as lead accumulator plant. The results of total uptake in the four cuts showed that barnyard grass plants extracted enormous amounts of Pb, ranging from 24.7–84.3 ug/g soil (Table 3). These values are 1.2–2.6 times greater than the plant available Pb of the studied soils as extracted by DTPA (Table 1). The results of total uptake of Pb showed that barnyard grass plants accumulate approximately half of the total content of soil Pb (Table 1). These results proved that barnyard grass, without any other soil treatments, e.g. soil applied chelators or other soil treatments**,** is able to remove considerable amounts of Pb from polluted soils within a period of four cuts, which equals eight months. Therefore, phytoremediation process of Pb polluted soils using barnyard grass could be completed within a reasonable period of time.

Cadmium concentrations of barnyard grass grown in the polluted soils (Table 4) varied between 6.1-45.9 ug/g DM. These concentrations were approximately 14–92 times greater than those of the non-polluted soils. However, these values are much lower than the value of 164.8 ug Cd/g dry weight reported for the metal-tolerant fern (*Arhiyrium yokoscense*), growing on Cd contaminated soils (Nishizono *et al.*, 1987). Low Cd concentrations in barnyard grass could be attributed to the low Cd contents of the studied soils. Total Cd

Table 4

Dry matter yield, concentration, and uptake of Cd of four cuts of barnyard grass

	Cut number									
	1		2		3		4		Total uptake	
Soil no.	DM g/pot	Conc. ug/g	DM g/pot	Conc. ug/g	DM g/pot	Conc. ug/g	DM g/pot	Conc. ug/g	ug/pot	Ug/g soil
Control	29.36	0.5	20.26	0.4	24.71	0.5	25.66	0.4	44	0.04
1	13.65	25.6	6.56	45.5	10.11	45.9	10.56	42.0	1540	1.54
2	25.17	6.1	14.00	10.8	19.74	10.9	20.09	10.5	731	0.73
3	18.71	12.6	7.22	25.3	11.98	26.1	12.56	24.9	1045	1.05

Table 5
Total and DTPA extractable Pb and Cd (mg/kg) of the soils before and after pot experiment of barnyard grass

	Total Pb			DTPA-Pb			Total-Cd			DTPA-Cd		
Soil no.	Before	After	Red %	Before	After	Red %	Before	After	Red %	Before	After	Red %
1	192.0	104.5	45	72.0	5.6	92	3.45	2.00	42	1.02	0.02	98
2	48.0	22.0	54	10.2	1.2	90	0.75	0.1	87	0.26	Nil	100
3	127.0	67.5	47	44.0	3.2	93	1.40	0.35	75	0.44	0.02	95

uptake by the four cuts ranged from 0.73–1.54 ug/g soil, which are equivalent to 1.5–3 times the amount of plant-available-Cd as extracted by DTPA (Table 1), and representing an average of 74% of total Cd content of the soil.

For comparison, the soils of the pot experiment were analyzed at the end of the trial to determine the level of both total- and plant-available Pb and Cd. The results (Table 5) showed that the plant-available Pb was markedly reduced, even for the highly polluted soil (No. 1 and 3), to values as low as 1.2–5.6 ug/g soil. These values are similar to those of 0.78–2.46 ug/g soil reported for the uncontaminated soils of Egypt (Aboulroos *et al.*, 1996). Good agreement was observed between the results of Pb removed from soils based on soil analysis and those based on plant analysis. The amounts of Pb removed by plants as determined by plant uptake (ranged from 24.7–84.3 ug/g soil, Table 3) were identical to those calculated as difference between (soil Pb) before and after plant growth (26–87.5 ug/g soil, Table 4). A similar trend was observed with Cd. DTPA extractable-Cd remaining in soils after removing the plant decreased markedly and ranged from 0 to 0.02 ug/g soil. These values are close to the average values of 0.018 ug/g Cd extracted by DTPA for nonpolluted soils of Egypt (Aboulroos *et al.*, 1996). Also, total Cd contents remaining in soil after removing the plants represented only 13 and 25% of the initial values in case of soils 2 and 3, respectively, and 58% in case of soil no.1. The relatively low ability of the plants to detoxify Cd in soil no.1 is due to low dry matter content of the plants as a result of the very high Pb content of this soil. Meanwhile, good agreement was observed between the results of Cd removed based on soil analysis and that based on plant analysis. The amount of Cd removed by the plants as determined by plant uptake (range from 0.73–1.54 ug/g soils) was identical to those of 0.65–1.45 ug/g soil, calculated as the difference between total content of soil Cd before and after pot experiment.

Conclusion

The recommended effective immobilizing agents for the studied polluted soils are slag and bitumen. Even the moderately effective reagents, particularly Fe- and Al-gels, are rather effective in stabilizing Pb. Hydrous oxides of aluminum, iron and manganese are known to enhance metal immobility in soils (Mckenzie, 1980; Khattak and Page, 1992; Janssen *et al.*, 1993). Also, these hydroxide compounds facilitated metal binding through specific adsorption (Sposito, 1989). Therefore, selecting an immobilizing agent should consider not only the amount of metal fixed, but also the chemical form of the metal, which controls the future release of the mmobilized Pb. The most significant finding of this study is to name the barnyard grass (*Echinnochloa stagninum*) as an efficient lead accumulator plant. Barnyard grass has a high ability to tolerate and accumulate concentrations of Pb higher than those reported for hyperaccumulator plants without showing any toxicity effects. In the absence of any other soil treatments, barnyard grass was able to remove enormous amounts of soil Pb. Barnyard grass efficiently completed the remediation of Pb and Cd polluted soil within a reasonably short period of time. Therefore, use of barnyard grass for phytoremediation of Pb and Cd polluted soils is feasible and recommended as an environmentally safe and cheap method. However, progress in phytoremediation techniques needs more knowledge of basic plant remedial mechanisms and of the effect of agronomic practices on these mechanisms. In addition, a complete understanding of the biological nature of this approach is needed. For example, the potential for phytoremediation depends upon the interaction among soil, contaminants, microbes, and plants. This complex interaction, affected by a variety of factors such as climatic conditions, soil properties, and site hydro-geology, argues against generalization in favor of site-specific phytoremediating practices. Thus, an understanding of the basic plant mechanisms and the effect of agronomic practices on plant/soil/contaminant interaction would allow practitioners to optimize phytoremediation by customizing the process to site-specific conditions (Lasat, 2000).

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