Impact of some soil amendments on controlling heavy metals toxicity in some contaminated soils.

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ABSTRACT

A pot experiment was conducted under laboratory conditions at Desert Research Center, Cairo, Egypt. The aim of this experiment is to study the role of three soil amendments; i.e. rock phosphate, nano-hydroxy apatite and poultry litter manure on reducing the hazard effects of some heavy metals in contaminated soils and wheat plants grown in it. The investigated soils were alluvial silt clay and alluvial clay soils from El Salam canal and Bahr El-Baker drain areas, respectively as well as calcareous sandy clay loam from Ras Sudr. Sequential extraction was used to fractionate heavy metals, i.e., Cd, Pb and Zn to evaluate their mobility and bioavailability in such soils.

Results indicated that cadmium was predominantly associated with the crystalline Fe oxides fraction, while lead and zinc were predominantly associated with the residual fraction. By applying the modified degree of contamination index, it can be noticed that El Salam soil suffering from a high degree of contamination and Bahar El Bakar soil suffering from a very high degree of contamination, while Ras Sudr soil sample has a moderate degree of contamination.

Results also indicated that the application of rock phosphate, nano-hydroxy apatite and poultry manure reduced Cd, Pb and Zn mobility in all the investigated soils through metals transformation from non-residual to residual forms.

Mobility factor of heavy metals reduced due to the applied soil amendments and the efficiency of amendments on reducing such factor was in the following order: nano-hydroxy apatite > rock phosphate > poultry manure.

The present data showed that the addition of all the applied materials reduced the concentration of Cd, Pb and Zn in wheat roots and shoots.

It can be concluded that the toxicity of heavy metals does not depend only on its concentration in soil, but also depends on different forms in which metals are present. The applied soil amendments, especially nano hydroxy apatite have high effects on decreasing chemically available heavy metals in soil as well as decreasing their concentrations in wheat plant. Most of these materials are available in large amounts, So the application of such materials can be used as effective strategy to remediate soils polluted with heavy metals.

Key Words

Soil contamination, heavy metal fractionations, soil amendments, mobility factor, heavy metal immobilization.

Introduction

The contamination of soils with heavy metals is now worldwide concerned due to its hazard to ecosystem including soil, water, plant, animal and human life. Pollution and agriculture can be seen from two aspects; one is pollution by agriculture practices. The other is pollution to agriculture. Fields are often affected by offsite pollution, especially those, which lie near industrial zones and roads, FFTC (2002).

Heavy metals are found naturally in the soil mostly in its complexes or bound form. They enter the environment by human activities such as mining, purification of Zinc, lead and cadmium, steel production, coal burning, burning of wastes, discharges from industrial effluents, excessive use of fertilizer, pesticide application and use of raw sewage waste in farming, Okoronkwo et al. (2005).

The accumulation of heavy metals in surface soils is affected by many environmental variables, including parent material and soil properties, as well as by human activities, such as industrial production, traffic, farming, and irrigation. Accumulation of these metals in soils can degrade soil quality, reduce crop yield and the quality of agricultural products, and thus negatively impact the health of human, animals, and the ecosystem, Nagajyoti et al. (2010). Such metals are a real threat to the environment because they can not be naturally degraded like organic pollutants and persist in the ecosystem having accumulated in different parts of the food chain, Igwe et al. (2005). Therefore, it is an urgent necessity to develop effective strategies for lowering their risk on the environment.

Among various remediation techniques, in situ chemical immobilization technology is the relatively more operative and cost-effective remediation approach for the reduction of the mobility and bioavailability of heavy metals in contaminated soils, Basta et al. (2001). It was demonstrated that this method is considered to be feasible, more economically and gives very promising results without the need for soil removal, Yang et al. (2001). Immobilization of metals can be accomplished by the addition of soil amendments such as organic matter, phosphates, alkalizing agents, and biosolid to reduce contaminant solubility or bioavailability to the plants, Khan et al. (2012). The addition of such amendments is effective in lowering the metal toxicity of the soil and provides slow release of nutrient sources such as N, P. K to support plant growth, Chin et al. (2006). Moreover, nanoscale particle HAP (n-HAP) has been proven to be an extremely effective remediation material in heavy metal-contaminated soils since it has strong ability to fix heavy metals, Wang et al. (2012). Poultry waste materials also have been successfully employed in immobilizing heavy metals in contaminated soils. It may decrease the available concentrations of heavy metals in soils by precipitation, adsorption, or complexion processes, Hashimoto et al. (2008). The aim of the present study is to evaluate the role of some local soil amendments on reducing the hazard effects of some heavy metals in different soil types grown with wheat plants.

MATERIALS AND METHODS

Surface soil samples (0 - 20 cm) of three contaminated sites, i.e. alluvial silt clay soil of El-Salam Canal, alluvial clay soil of Bahar El-Bakar and calcareous sandy clay loam soil of Ras Sudr were sampled. These samples were air dried, crushed by mortar, passed through 2 mm sieve and stored for chemical and physical analyses and use in pot experiment. Table (1) depicts some physical and chemical properties of such soils.

It is clear that the differences in CEC and clay content between the three contaminated soils could imply that Bahar El-Bakar soil has a potentially stronger adsorption of heavy metals than El-Salam and Ras Sudr soils. Also, the concentration of chemically extractable and total Cd, Pb and Zn in Bahar El-Bakar soil was higher than that of both El-Salam and Ras Sudr soils, which means that Bahar El-Bakar soil is more contaminated than the other two soils.

Table (1). Some physical and chemical properties of the investigated soils.

Soil sampling site	pH	EC (dS/m)	Particle size distribution (%)			Texture	CEC (cmol/kg)	$CaCO_3$ (%)	OM (%)	Heavy metals content (µg/g)					
										Chem. extractable			Total		
			sand	silt	clay					Cd	Pb	Zn	Cd	Pb	Zn
El-Salam	7.22	5.17	17.11	38.64	44.3	slit clay	24.53	5.37	2.47	0.19	0.66	1.6	3.38	45.62	352.6
Bahar El-Bakar	7.28	36.80	16.05	36.59	47.4	clay	31.80	0.36	3.09	0.14	11.3	15.3	7.26	156	333.6
Ras Sudr	7.24	4.65	74.2	12.3	13.5	sandy clay loam	6.97	26.36	1.25	0.05	0.33	7.68	1.58	5.16	66.72

The remediation experiment

A pot experiment was conducted under laboratory conditions to compare and evaluate the effectiveness of chemical treatments on remediation of Cd, Pb and Zn in the contaminated soils. The experiment included 36 pots. Each pot filled with 500 g of one of the three contaminated soils under investigation, and then the pots divided into three groups. Each group (12 pots) treated with the following amendments:

1- Without adding amendment, donated as (control).

2- Rock phosphate at the rate of 10 mg/pot donated as (RP).

3- nano- Hydroxy apatite at the rate of 5 mg/pot donated as (n-HAP).

4- Poultry litter manure at the rate of 5 mg/pot donated as (PLM).

Each treatment replicated three times. Table (2) shows some characteristics of the applied amendments. n-HAP prepared by dissolution / precipitation of natural rock phosphate using nitric acid and ammonium solution (25%) according to El Asri. et al. (2009).

Table (2). Some characteristics of the applied soil amendments.

Soil amendments	pH	EC (dS/m)	CEC (cmol/kg)	OM (%)	$CaCO_3$ (%)	Total heavy metals (µg/g)		
						Cd	Pb	Zn
RP	8.02	1.64	10.18	-	4.32	0.34	0.92	22.2
n-HAP	7.12	7.28	26.77	-	0.64	0.38	0.91	23.5

PLM	7.46	8.94	23.73	37.56	7.46	0.74	1.97	26.4

The pots were laid out in a completely randomized block design under laboratory conditions and incubated for two months at room temperature (25°C) under irrigation with El-Salam Canal water. Table (3) reveals some chemical composition of such water. It is clear that such water having pH value of 7.28, EC value of 1.28 dS/m and SAR value of 4.26 which mean that it is in the safe side for irrigation according to Ayres and Westcot (1985). With respect to microelements concentration, it is clear that Cd, Pb and Zn were in sufficient concentration and less than the critical levels appointed by FAO (1992). So, such water is suitable to irrigate most of the field crops.

Table (3). Some chemical composition of the applied irrigation water.

pH	EC (dS/m)	Soluble Cations (me/l)				Soluble Anions (me/l)				SAR	Heavy metals content (mg/l)		
		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	CL^{-}	SO_4^{2-}		Cd	Pb	Zn
7.27	1.28	3.2	2.28	7.05	0.27	1.02	1.61	6.68	3.43	4.26	< 0.001	0.024	< 0.01

After the incubation period, sequential extraction of heavy metals was determined in soil samples of the pot experiment according to Matthew et al. (2000). Table (4) indicates the scheme of such sequential extraction. The procedure initiated using 1g dry weight of soil samples. After each extraction step, samples were certificated at 2400g for 15 min and the supernatant was filtered, acidified with concentrated HCl and analyzed for the concentrations of Cd, Pb and Zn. Samples remaining after each extraction step were washed with 10 ml of deionized water, certificated, decanted and discarded before the next extraction.

After sequential extraction of heavy metals, 10 seeds/pot of wheat (Triticum aestivum) Sakha 93 were sown on 6/10/2014 in pots of the three investigated soil samples. Plants were grown for 45 days then harvested. It was noticed that wheat seeds sown in Bahar El-Bakar soil did not grow due to the extremely saline of such soil (EC=36.8 dS/m). The harvested wheat roots and shoots of El-Salam and Ras Sudr soils were oven-dried at 60°C for 72h, then ground, digested and analyzed for the concentrations of Cd, Pb and Zn.

Table (4). Batch sequential extraction scheme for the studied heavy metals.

Fractions	Extractant	Soil/ Extractant	pH	^{0}C	Equil time (h)	Reference
water soluble	Deionized water	1:10	7	20	1	Tessier et al. (1979), (1985)
Exchangable	1 M $MgCl_2$	1:10	7	20	1	Tessier et al. (1979), (1985)
Organically bound	NaOCl	1:20	9.5	95±5	1	Shuman (1983)
Carbonate	1 M NaOc- HOAc	1:20	5	20	5	Tessier et al. (1979), (1985)
Mn oxides	0.1 M NH_2OH-HCl in 0.01 M HNO_3	1:25	2	20	4	Chao (1972) , Shuman (1982)
Amorphous Fe Oxides	0.02 M AOD	1:20	3	20	4	Jackson et al. (1986)
Crystalline Fe oxides	1 M NH_2OH-HCl in 25%(v/v) HOAc	1:30	-	95±5	6	Tessier et al. (1979), (1985)
Sulfide & Organic	0.02 M HNO_3+30% H_2O_2/NH_4OAC in 20% HNO_3	1:20	2	85±2	5	Tessier et al. (1979), (1985)
Residual	HNO_3-H_2SO_4-$HCLO_3$	1:20	-	-	-	Hesse (1972)

Methods of analysis:

Particle size distribution using the pipette method as outlined by Kilmer and Alexander (1949). Soil pH, in saturated soil paste and in water using pH-meter model Jenway 3305. EC in soil paste extract and in water using conductivity meter model Jenway 4310. Soluble ions in soil paste extract and in water according to Page et al. (1982). Soil OM using Walkley and Black method as described by Page et al. (1982). Total calcium carbonate using Collin's calcimeter according to Black (1965). Soil CEC using sodium acetate (pH 8.2) according to Rhoades (1982). Total and chemically available heavy metals extracted by ternary acids mixture Hesse (1972) and DTPA method Lindsay and Norvell (1978) respectively, then determined by Ionic Coupled Plasma. Concentrations of Cd, Pb and Zn in both soil fractions and plant digests were determined using Perkin Elmer Atomic Adsorption Spectrophotometer model 2380 according to page et al. (1982).

RESULTS AND DISCUSION

Assessment of heavy metal contamination of agricultural soils.

Contamination Factor (CF):

The assessment of soil contamination was carried out using the contamination factor (CF). CF is a single element index recognized by Hakanson (1980). It has four classes of contamination and can be calculated according to the following Equation: CF = C0 ⁄ Cn, Where C0 is the mean content of metals from at least five sampling sites and Cn is the pre-industrial concentration of the individual metal. Table (5) shows different contamination factor classes and levels.

Table (5). Different contamination factor (CF) for soil.

CF Value	CF level
CF < 1	Low contamination factor indicating low contamination
1 ≤ CF < 3	Moderate contamination factor
3 ≤ CF< 6	Considerable contamination factor
CF ≥ 6	Very high contamination factor

The assessment of the overall contamination of the studied agricultural soils was based on CF. Data in table (6) showed that the soil samples of El Salam canal area was classified as considerable contaminated with Pb and Zn where the CF values were 3.04 and 3.24 respectively, very highly contaminated with Cd (CF was 16.9). Data also cleared that Bahar El Bakar soil sample was classified as considerable contaminated with Zn (CF was 4.28) and very highly contaminated with Cd and Pb (CF were 36.3 and 10.4 respectively), while Ras Sudr was classified as low contaminated with Pb and Zn (CF were 0.344 and 0.86) and very highly contaminated with Cd (CF was 10.2).

Table (6). Average contamination factor (CF) values of the studied soils.

sampling site soil	Cd	Pb	Zn
El Salam	16.90	3.04	3.24
Bahar El-Bakar	36.30	10.40	4.28
Ras Sudr	10.20	0.34	0.86

Modified Degree of Contamination (mCD):

The assessment of soil contamination was also carried out using modified degree of contamination (mCD), recognized by Abrahim et al. (2008). It generalized form of the Hakanson (1980) equation for the calculation of the overall degree of soil contamination. It has seven classes of contamination and can be calculated according to the following Equation:

$$mCD = \left(\sum_{i=1}^{i=n} CF\right)/n$$

Where n is the number of analyzed elements and CF is the contamination factor . Using this generalized formula to calculate the mCD allows the incorporation of as many metals as the study may analyze with no upper limit. Table (7) shows different mCD classes and levels.

Table (7). Different modified degree of contamination (mCD) for soil.

mCD Class	mCD Level
mCD < 1.5	Nil to very low degree of contamination
$1.5 \leq$ mCD < 2	Low degree of contamination
$2 \leq$ mCD < 4	Moderate degree of contamination
$4 \leq$ mCD < 8	high degree of contamination
$8 \leq$ mCD < 16	Very high degree of contamination
$16 \leq$ mCD < 32	Extremely high degree of contamination
mCD ≥ 32	Ultra high degree of contamination

The mCD as proposed in the present study is based on integrating and averaging all the available analytical data for a set of soil samples. Therefore it can provides an integrated assessment of the overall enrichment and contamination impact of pollutant groups in the soil. Data in Table (8) shows the mCD values and levels of the three contaminated soil under investigation.

Table (8). Modified degree of contamination (mCD) of the studied soils.

Soil sampling site	mCD	mCD Level
El Salam	7.73	High degree of contamination
Bahar El-Bakar	16.99	Very high degree of contamination
Ras Sudr	3.8	Moderate degree of contamination

In Situ remediation experiment:

The efficiency of in situ remediation of metal contaminated soils can be evaluated by using fractionation procedures. The effectiveness of in situ remediation of metal-contaminated soils can be improved with more practical treatments that convert greater amounts of metal from the nonresidual to the residual fraction or from more bioavailable to less bioavailable forms, Rui-Juan et al. (2016).

When a particular heavy metal is in its labile state (soluble) it becomes readily available for plant uptake, but when the metal is transformed from available to unavailable state (residual) it becomes inactive, stable and unavailable for plant uptake. The non-residual fractions include; water soluble, exchangeable, organically bound, carbonate, Fe-Mn oxides and organic & sulfide fractions. Heavy metals bound or associated with the water soluble, exchangeable, weakly organically bound and carbonates are bioavailable to plant and environment. The remaining two fractions in the nonresidual fraction (Fe-Mn oxide and sulfide & organic) are not readily available except there are favorable chemical reactions like oxidation, reduction or dissolution of organic matter which could enhance the release of bound metals into soil solution, Aikpokpodion (2012).

Effect of the applied soil amendments on soil cadmium:

The mean concentration values of Cd found in different fractions with sequential extractions following treatment of the unamended soil are shown in Table (9). Results indicate that in the control treatment, the crystalline Fe oxides is the dominant chemical fraction in El-Salam and Bahar El-Bakar soils, while carbonate is the dominant chemical fraction in Ras Sudr soil.

Data also indicated a decrease in the mean values of carbonate- Cd fraction of Bahar El-Bakar and El-Salam soil samples due to RP application. As the rate of decrement in such fraction reached 54.34 and 63.4% for Bahar El-Bakar and El-Salam soil samples respectively as compared with the control treatment. In contrast, the highest increment rates in Cd were associated with residual fraction, where it reached 29.16, 53.65 and 49.27 % in El-Salam, Bahar El-Bakar and Ras Sudr soils, respectively. This may be due to that the available form of Cd can be transformed to unavailable form (amorphous, crystalline Fe oxides and residual fractions) after amendment with rock phosphate. These results are in agreement with those found by Thawornchaisit and Polprasertb (2009) who found that treating contaminated soils with RP decreased the leachable Cd concentrations and the mobile forms of Cd in such soils.

Table (9). Cd fractions distribution in the investigated soils as affected by the applied treatments.

Soil sampling site	Treat.	Cadmium fractions(µg/g)									MF (%)
		Water soluble	Exchan.	Organ. bound	Carbon.	Mn oxides	Amorph. Fe oxides	Cryst. Fe oxides	Sulfide & Organic	Resid.	
El-Salam	control	0.03	0.05	0.23	0.16	0.22	0.52	0.73	0.56	0.73	14.27
	RP	ND	ND	0.11	0.16	0.21	0.54	0.81	0.56	0.94	8.02
	n-HAP	ND	ND	ND	0.04	0.20	0.51	0.97	0.60	1.01	1.11
	PLM	ND	ND	0.13	0.16	0.21	0.52	0.75	0.70	0.88	8.41
Bahar El-Bakar	control	0.33	0.50	0.56	0.35	1.04	1.04	1.34	0.58	1.33	25.77
	RP	ND	ND	0.21	0.13	1.02	1.38	1.50	0.58	2.04	4.54
	n-HAP	ND	ND	0.14	0.10	1.00	0.98	1.95	0.68	2.55	3.30
	PLM	ND	0.12	0.28	0.18	1.13	1.26	1.38	1.35	1.57	6.41
Ras Sudr	control	0.02	0.03	0.03	0.36	0.06	0.25	0.35	0.15	0.34	27.99
	RP	ND	ND	ND	0.16	0.06	0.27	0.37	0.15	0.51	10.66
	n-HAP	ND	ND	ND	0.15	0.06	0.22	0.49	0.15	0.49	9.61
	PLM	ND	ND	ND	0.27	0.06	0.25	0.37	0.25	0.46	17.85

ND = not detected

The positive effect of RP on precipitating metal ions in soil may be due to the substitution of calcium with heavy metals divalent ions which is correlated to their ionic radius and electro negativity exist. Cd immobilization has been related to the ion exchange and complexation mechanisms, suggesting that the process results in the formation of Cd-containing phosphates, Marchat et al. (2007).

Concerning the effect of n-HAP treatment on soil Cd, data in the same Table indicate that the application of n-HAP to the three investigated soils help in reducing hazard effects of Cd in such soils through decreasing available fractions and increasing unavailable fractions of soil Cd. The highest decrement rates in Cd were associated with carbonate fraction, where it reached 76.88 and 58.82 % in El-Salam and Ras Sudr soils respectively. The highest Cd decrement rate in Bahar El-Bakar soil obtained by organic bound fraction, where it was 75.76%. On the other hand, the highest increment rates in Cd were associated with residual fraction in both Bahar El-Bakar and Ras Sudr soils, where it reached 91.8 and 43.99% respectively. In El-Salam soil, such rate was associated with crystalline Fe oxides fraction as it was 38.65%. These results in agreement with those found by He et al. (2013) who reported that addition of n-HAP reduced the water-soluble, bioaccessible, and phytoavailable Cd by forming the Cd phosphate (e.g. hydroxy pyromorphite-like mineral). The immobilization mechanism mainly involved both cation exchange and partial dissolution of the n-HAP amendment and precipitation of heavy metal-containing phosphates.

The above mentioned results were in agreement with those found by Chen et al. (2007) who reported that RP and natural hydroxyapatite amendments significantly reduced the bioavailability and increased the geochemical stability of soil Cd in contaminated soils.

Regarding the effect of poultry litter treatment on soil Cd, data in Table (9) indicated that the application of PLM to the investigated soils reduced the solubilization of Cd and the highest rates of such reduction were associated with organic bound fraction (45.89%) in El-Salam soil, exchangeable fraction (75.79%) in Bahar El-Bakar soil, carbonate fraction (23.53%) in Ras Sudr soil. It is worth to notice that there were significant increases in Cd associated with sulfide & organic fraction in all the three investigated soils due to PLM application, where the rate of increment in such fraction reached 25.99, 77.1 and 64.67 % in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively. The positive effect of PLM on Cd availability may be due to its higher content of organic matter (Table 2), which may retain Cd in the soil against both leaching and crop uptake Jones and Johnston (1989). These results were in agreement with Clemente et al. (2006) who found that heavy metal mobility can be reduced by the application of organic soil amendments.

The mobility of metals in soil samples may be assessed on the basis of absolute and relative contents of fraction weakly bound to soil components. The relative index of metal mobility was calculated as a mobility factor (MF) on the basis of the following equation, Kabala and Singh (2011).

$$MF = \{(F1 + F2 + F3 + F4) / \{(F1 + F2 + F3 + F4 + F5 + F6 + F7 + F8 + F9)\} \times 100$$

As regards the mobility factor of Cd, data in the same table showed that, the application of all the three soil amendments reduced such factor in all the three investigated soils. Data also revealed that n-HAP was the best amendment in this concern since it reduced the mobility factor from 14.27 to 1.11, from 25.77 to 3.3 and from 27.99 to 9.61 % in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively.

Generally, the efficiency of the applied materials on reducing mobility factor of Cd can be arranged in the following order: n-HAP > RP > PL.

Effect of the applied soil amendments on soil lead:

Lead is one of the most widely studied metals as a pollutant in the agriculturally contaminated soils. The relative distribution of Pb in the amended and non-amended soils with sequential extraction is shown in Table (10). The results indicate that Pb was mostly classified as bound to Fe–Mn oxides and residual fractions in the studied soils as it can be expected that the residual fraction of metals was the main soil fraction and strongly bound inner-sphere in the contaminated soils.

Data also indicated a decrease in the mean values of organic and carbonate Pb fractions of Bahar El-Bakar and El-Salam soil samples due to RP application. As the rate of decrement in such fractions reached 79.07 & 64.74% for Bahar El-Bakar soil sample and 61.97 & 86.61% for El-Salam soil sample respectively as compared with the control treatment. For Ras Sudr soil data also indicated a decrease in the mean values of carbonate-Pb fraction, as the rate of decrement in such fraction reached 53.4%.

Table (10). Pb fractions distribution in the investigated soils as affected by the applied treatments.

Soil	Treat.	Lead fractions(µg/g)									MF (%)
		Water soluble	Exchan.	Organ. bound	Carbon.	Mn oxides	Amorph. Fe oxides	Cryst. Fe oxides	Sulfide & Organic	Resid.	
El-Salam	Control	0.24	0.43	1.42	1.12	4.38	7.89	10.14	5.41	12.72	7.34
	RP	ND	ND	0.54	0.15	2.50	7.82	11.30	5.53	15.58	1.58
	n-HAP	ND	ND	0.23	0.12	2.46	6.60	12.55	5.63	17.16	0.83
	PLM	ND	0.06	1.24	0.76	2.42	6.39	10.16	9.40	12.99	5.39
Bahar El-Bakar	Cont	2.27	7.76	12.33	3.82	13.46	29.60	34.17	15.39	35.24	18.94
	RP	ND	ND	2.58	1.35	11.60	25.77	30.50	16.47	65.74	2.55
	n-HAP	ND	ND	1.55	1.25	11.33	22.32	36.96	16.76	67.85	1.82
	PLM	ND	1.30	5.78	1.54	12.42	28.32	35.27	23.04	38.22	5.59
Ras Sudr	Control	0.04	0.16	0.23	0.68	0.54	0.93	1.34	0.74	1.53	17.93
	RP	ND	ND	ND	0.31	0.54	0.83	1.48	0.76	2.37	6.73
	n-HAP	ND	ND	ND	0.21	0.40	0.69	1.76	0.79	2.04	3.45
	PLM	ND	ND	ND	0.54	0.42	0.83	1.35	1.21	1.74	8.87

ND = not detected

In contrast, the highest increment rates in Pb were associated with residual fraction, where it reached 38.21, 86.58 and 76.47 % in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively. This may be due to that the non-residual fractions of Pb were significantly transformed to residual fractions through formation of pyromorphite. These results are in agreement with those reported by Melamed et al. (2003) who found a decrease in the carbonate bound and Fe-Mn oxide bound fractions of soil Pb up to 40 and 10% respectively, while the residual fraction increased up to 60% due to RP application. The possible mechanisms of RP stabilizing Pb was suggested as a process including ion exchange processes at the surface of RP, surface complexation, and replacement of Ca in RP by Pb with formation of pyromorphite-type minerals, Cao et al. (2004).

Concerning the effect of n-HAP treatment on soil Pb, data in the same table indicate that the application of n-HAP to the three investigated soils help in reducing hazard effects of Pb in such soils through decreasing available fractions and increasing unavailable fractions of soil Pb. The highest decrement rates in Pb were associated with organic and carbonate fractions, where it reached 83.8 & 89.29% and 87.43 & 67.2% in El-Salam and Bahar El-Bakar soils respectively. The highest Pb decrement rate in Ras Sudr soil obtained by carbonate fraction, where it was 69.12%. On the other hand, the highest increment rate in Pb was associated with residual fraction in Bahar El-Bakar soil (92.56%), while in El-Salam and Ras Sudr soils, such rate was associated with crystalline Fe oxides (22.78 & 34.91%) and residual fraction (31.34 & 33.33%) respectively.

Regarding the effect of PLM on soil Pb, data in Table (10) indicated that the application of PLM to the investigated soils reduced the solubilization of Pb and the highest rates of such reduction were associated with carbonate fraction (86.05%) in El-Salam soil, exchangeable fraction (83.31%) in Bahar El-Bakar soil, carbonate fraction (20.59%) in Ras Sudr soil. It is worth to notice that there was an increase in Pb associated with sulfide & organic fraction in all the three investigated soils due to PLM application, where the rate of increment in such fraction reached 73.75, 85.96 and 63.51% in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively. The positive effect of PLM on Pb availability may be due to its higher content of organic matter (Table 2), which may retain Pb in the soil against both leaching and crop uptake, Jones and Johnston (1989).

As regards the mobility factor of Pb, data in the same table showed that, the application of all the three soil amendments reduced such factor in all the three investigated soils. Data also revealed that n-HAP was the best amendment in this concern since it reduced the mobility factor from 7.34 to 0.83, from 18.94 to 1.82 and from 17.93 to 3.45% in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively.

Generally, the efficiency of the applied materials on reducing mobility factor of Pb can be arranged in the following order: n-HAP > RP > PL

Effect of the applied soil amendments on soil Zinc:

The relative distribution of zinc in the amended and non-amended soils with sequential extraction is shown in Table (11). Zn bound to the organic matter fraction is the dominant chemical form among the non-residual fractions while Zn associated to residual is the major chemical form in the investigated soil samples followed by sulfide and organic fraction.

Data indicated also a highest decrease in the mean values of carbonate-Zn fraction of El-Salam, exchangeable fraction of Bahar El-Bakar and organic bound of Ras Sudr soil samples due to RP application. As the rate of decrement in these fractions reached 57.78, 89.06 and 58.91%, respectively, as compared with the control treatment. In contrast, the highest increment rates in Zn were associated with residual fraction, where it reached 18.59, 27.42 and 16.84% in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively. This may be due to the available form of Zn can be transformed to unavailable form (amorphous, crystalline Fe oxides and residual fractions) after amendment with rock phosphate.

Table (11). Zn fractions distribution in the investigated soils as affected by the applied treatmer

Soil	Treat.	Zinc fractions(µg/g)									MF (%)
		Water soluble	Exchan.	Organ. bound	Carbon.	Mn oxides	Amorph. Fe oxides	Cryst. Fe oxides	Sulfide & Organic	Resid.	
El-Salam	Control	1.04	1.94	28.33	4.53	22.42	27.80	36.90	62.89	166.64	10.17
	RP	ND	ND	11.96	2.87	11.90	24.75	37.74	65.64	197.63	4.21
	n-HAP	ND	ND	15.89	2.51c	11.98	22.39	31.15	66.41	209.63	3.10
	PLM	ND	ND	8.42	3.05	17.93	22.74	36.99	78.25	177.65	5.37
Bahar El-Bakar	Control	5.39	9.51	33.42	7.63	17.60	24.85	62.73	32.28	136.78	16.94
	RP	ND	1.04	11.11	2.30	14.67	22.96	68.41	35.47	174.29	4.38
	n-HAP	ND	0.17	18.57	2.27	12.30	21.93	72.41	36.95	177.01	2.90
	PLM	ND	ND	0.00	3.47	13.67	30.25	66.27	46.40	153.15	6.70
Ras Sudr	Control	0.54	0.64	1.29	6.62	2.51	5.91	13.77	14.07	21.56	13.58
	RP	ND	ND	0.53	4.53	1.85	5.81	14.58	14.42	25.19	7.56
	n-HAP	ND	ND	0.44	2.53	1.65	5.86	10.04	15.90	30.29	4.44
	PLM	ND	ND	0.71	5.01	1.45	5.80	13.88	22.18	17.88	8.55

ND = not detected

Concerning the effect of n-HAP treatment on soil Zn, data in the same table indicated that the application of n-HAP to the three investigated soils help in reducing hazard effects of Zn in such soils through decreasing available fractions and increasing unavailable fractions of soil Zn. The highest decrement rates in Zn were associated with carbonate fraction, where it reached 46.57 and 65.89% in El-Salam and Ras Sudr soils, respectively. The highest Zn decrement rate in Bahar El-Bakar soil obtained by organic bound fraction, where it was 78.16%. On the other hand, the highest increment rates in Zn were associated with residual fraction in all the investigated soils reaching 22.8, 29.41 and 27.89% in El-Salam, Bahar El-Bakar and Ras Sudr soils, respectively.

Regarding the effect of poultry litter treatment on soil Zn, data in Table (11) indicated that the application of PLM to the investigated soils reduced the solubilization of Zn and the highest rates of such reduction were associated with organic bound fraction where it reached 50.97 and 44.96% in El-Salam and Ras Sudr soils respectively. The highest Zn decrement rate (98.22%) in Bahar El-Bakar soil obtained by exchangeable fraction. It is worth to notice that there was an increase in Zn associated with sulfide & organic fraction in all the three investigated soils due to PLM application, where the rate of increment in such fraction reached 24.42, 43.75 and 29.21 % in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively. The positive effect of PLM on Zn availability may be due to its higher content of organic matter (Table 2), which may retain Cd in the soil against both leaching and crop uptake Jones and Johnston (1989). These results were in agreement with Clemente et al. (2006) who found that heavy metal mobility can be reduced by the application of organic soil amendments.

Regarding the mobility factor of Zn, data in the same table showed that such factor reduced in all the three investigated soils due to all applied soil amendments, especially that of n-HAP since it reduced the mobility factor from 10.17 to 3.1, from 16.94 to 2.9 and from 13.58 to 4.44% in El-Salam, Bahar El-Bakar and Ras Sudr soils respectively. Generally, the efficiency of the applied materials on reducing mobility factor of Zn can be arranged in the following order: n-HAP > RP > PL.

Effect of the applied soil amendments on wheat biomass.

Data in Table (12) show the effect of RP, n-HAP and PLM amendments on wheat biomass in both El-Salam and Ras Sudr soils. It is clear that both root and shoot biomasses of wheat plant increased with the application of such amendments. As the rate of increment in roots biomass of El-Salam soil reached 58.82, 94.12 and 76.47 % due to the application of RP, n-HAP and PLM, respectively, as compared with the control treatment, while the respective increases for shoots biomass reached 23.81, 57.14 and 33.33%. Concerning Ras Sudr soil, the respective increases reached 30, 65 and 10% in roots biomass, while it reached 18.52, 22.22 and 14.81% in shoots biomass. It can be noticed that the highest biomass of plant was associated with n-HAP treatment. This may be due to the role of n-HAP on alleviating the toxic effect of soil heavy metals on plant, resulting in increasing the biomass of wheat plant. Also, due to more phosphate nutrition supplement after n-HAP addition which can promote the growth of wheat plant. These results were in agreement with those obtained by Chen et al. (2007).

Table (12.). Dry weight and heavy metals content of wheat as affected by the applied soil amendments.

Treat.	Dry weight (g/pot)		Cd(µg/g)			Pb(µg/g)			Zn(µg/g)		
	Root	Shoot	Root	Shoot	MI	Root	Shoot	MI	Root	Shoot	MI
El-Salam Soil											
Control	0.17	0.21	0.13	0.23	1.77	0.21	0.45	1.16	1.30	2.45	1.88
RP	0.27	0.26	0.07	0.12	1.71	0.12	0.09	1.44	0.68	1.49	2.19
n-HAP	0.33	0.33	0.05	0.09	1.80	0.07	0.02	0.74	0.47	0.82	1.76
PLM	0.30	0.28	0.09	0.18	2.00	0.15	0.17	1.18	0.70	1.78	2.53
Ras Sudr soil											
Control	0.20	0.27	0.08	0.13	1.63	0.23	0.33	1.43	0.99	1.95	1.96
RP	0.26	0.32	0.03	0.08	2.67	0.02	0.02	1.20	0.66	0.93	1.41
n-HAP	0.23	0.33	0.02	0.03	1.50	0.01	0.01	0.73	0.44	0.67	1.52
PLM	0.22	0.31	0.05	0.10	2.00	0.18	0.18	0.96	0.75	1.22	1.64

Effect of the applied soil amendments on heavy metals content of wheat plant.

Data in Table (12) show the effect of RP, n-HAP and PLM amendments on Cd, Pb and Zn content of wheat plant grown on both El-Salam and Ras Sudr soils. It is clear that the application of all such amendments to both the two studied soils led to reduce Cd, Pb and Zn content in wheat roots and shoots. It is also clear that the highest decrements under the control treatment were associated with n-HAP treatment as compared with the other two amendments. As the rate of decrement in Cd, Pb and Zn content of wheat roots of El-Salam soil reached 61.54, 66.67 and 63.85%, respectively as compared with the control treatment, while the respective decreases in wheat shoots reached 60.87, 95.56 and 66.53%, respectively. Concerning Ras Sudr soil, the respective decreases in such elements reached 75, 95.65 and 55.56 % for roots, while it reached 76.92, 96.96 and 65.64%, for shoots, respectively.

It is worth to mention that the residual Pb soil fraction reached its high increase with the application of n-HAP, which demonstrated that conversion of soil Pb to more stable forms actually occurs in the field, Cao et al. (2002). This redistribution of Pb resulted in less phytotoxicity, as indicated by greater plant growth and lower metal concentration in plant tissue, Chen et al. (2007). Generally, the efficiency of the applied amendments on reducing the concentration of Cd, Pb and Zn in wheat roots and shoots can be arranged in the following order: n-HAP > RP > PLM.

Conclusions

From the present study it can be concluded that the toxicity of heavy metals does not depend on its concentration in soil, but depends on different forms in which metals are present. The applied organic amendments like PLM or inorganic additives like RP and n-HAP were found to reduce toxicity of metals by reducing available fractions, which in turn reduce heavy metal transfer to plants. Most of these materials are available in large amounts and its incorporation into soil is easy, however, repeated application may be necessary and the effectiveness is largely dependent on soil conditions and has to be proved periodically. From the practical and economic points of view, the n-HAP was the best treatment to immobilize Cd, Pb and Zn from all the studied polluted soils since it was more efficient in transferring bioavailable form of heavy metals into less bioavailable form than the other two amendments.

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تاثير بعض محسنات التربة في التحكم في سمية المعادن الثقيلة في الأراضي الملوثة

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أقيمت تجربة معملية بمركز بحوث الصحراء لدراسة تأثير إضافة الصخر الفوسفاتى (RP)، النانو هيدروكسى أباتيت (n-HAP) و سماد مخلفان الطيور (PLM) كمصلحات للتربة على خفض التلوث بمعادن الكادميوم و الرصاص و الزنك فى بعض الاراضى و نبات القمح النامى بها. أجريت التجربة على ٣ أنواع من التربة بنظام القطاعات كاملة العشوائية و كررت كل معاملة ٣ مرات. أضيفت مصلحات التربة و تم رى التجربة بمياه ترعة السلام و التحضين لمدة ٦٠ يوم. بعد فترة التحضين تم استخلاص الصور المرتبطة بالمعادن الثلاثة بطريقة الاستخلاص المتتابع و تقدير تركيزات هذه المعادن بالتربة. بعد ذلك تم زراعة نبات القمح لمدة ٤٥ يوم ثم حصاد النباتات لتقدير المادة الجافة لكل من السيفان و الجذور بالإضافة لتقدير محتواهما من العناصر الثلاثة محل الدراسة.

أوضحت النتائج أن معدن الكادميوم كان الأكثر ارتباطا مع The crystalline Fe oxides fraction ، فى حين كانت معادن الرصاص و الزنك الأكثر ارتباطا مع The residual fraction . بتطبيق دليل مدى التلوث (المعدل) يتضح أن درجة تلوث التربة عالية فى منطقة ترعة السلام ، فى حين أنها عالية جدا فى منطقة بحر البقر ، و متوسطة فى منطقة رأس سدر.

أوضحت النتائج أيضا أن إضافة المصلحات الثلاثة إلى التربة أدت إلى خفض حركة المعادن سالفة الذكر بالتربة ، و يمكن ترتيب هذه المصلحات تبعا لكفاءتها فى خفض قيم Mobility factor على النحو التالى: النانو هيدروكسى أباتيت > الصخر الفوسفاتى > سماد مخلفان الطيور .

أدت إضافة مصلحات التربة الثلاثة إلى زيادة وزن المادة الجافة لكل من جذور و سيقان نبات القمح بالإضافة إلى خفض تركيزات عناصر الكادميوم ، و الرصاص ، و الزنك بها.

أظهرت هذه الدراسة أنه من الناحية الاقتصادية و العملية أن معاملة التربة بالنانو هيدروكسى أباتيت هى أفضل معاملة لتثبيت معادن الكادميوم ، و الرصاص ، و الزنك فى التربة ، بالإضافة إلى خفض تركيزاتها فى النبات ، لذا فانه يمكن التوصية بإضافة هذه المادة إلى التربة الملوثة بهذه المعادن لتحسين صفات هذه التربة و خفض درجة التلوث بها.

الكلمات الدالة: تلوث التربة ـ عامل التلوث ـ مصلحات التربة ـ صور المعادن الثقيلة بالتربة ـ تثبيت المعادن الثقيلة فى التربة.