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MOBILITY OF HEAVY METALS (Pub and Cu) IN SOME CONTAMINATED EGYPTIAN SOILS TREATED WITH CERTAIN ORGANIC MATERIALS

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Abstract: Three contaminated soils at Helwan, El-Gabal El-Asfar (Cairo governorate) and Arab El-Madabeg (Assiut governorate) were chosen in a leaching column experiment for 8 weeks to study the effect of certain organic materials on the mobility of some heavy metals (Pb and Cu) in these soils. The organic materials including ethylene diamine tetra acetic acid (EDTA) as a synthetic organic material as well as poultry litter extract (PLE), vinasse (V) and humic acid (HA) solutions as natural organic materials, compared to distilled water as a control. These solutions were added to the column every week at levels of 2, 4 and 6 mmols/kg for EDTA, 25, 50 and 75 g/L for PLE , 1:2 and 1:1 dilutions of Vinasse to water as well as pure V, and 0.013, 0.019 and 0.025 % for HA.

The results indicated that leaching the studied soils with different organic materials at various levels of application resulted in increases in the mobility of soil Pb and Cu. The magnitude of soil Pb and Cu mobility varied depending upon the type of organic material, its application level and the soil type.

The studied organic materials differed in their efficiency in moving Pb and Cu from the top to the bottom of the soil columns. EDTA was found to be the most effective organic material, especially at its highest level.

Generally, the investigated organic materials had the order of EDTA > Vinase > PLE > HA in mobilizing soil Pb and Cu in the studied soils.

Key words: mobility, heavy metals, organic materials, contamination

Introduction

Heavy metals in the environment have been received considerable attention because of their potential effects on human and animal health. Heavy metals tend to accumulate in soils and sediments due to industrial activities, mining, and use of sludge, pesticides, agriculture chemicals, and automobiles (Bohn, 2001; Sun et al., 2001; Pandy et al., 2003).

Mobile metals in soils and sediments may be taken up by plants, or may contaminate ground water and estuarine water so that health associated problems may arise, especially when these forms of metals are present in toxic levels (Blaylock and Huang, 2000).

Heavy metal solubility in soils is mainly controlled by the soil pH, the amount and kind of sorption sites, and the total amount of heavy metals in the soil (Gray et al., 1999).

At higher soil pH levels, dissolved organics can increase the solubility of metal ions by formation of soluble organometallic complexes, which compet with the solid phases for metal ion (Almas et al., 1999). Thus, especially at higher pH, organic substances can contribute to heavy metal mobilization and accumulation (Schmidt, 2003). The solubilization of heavy metals through organic agents is mainly based on the ability of these organic chelating agents to form water-soluble metal-organic complexes (Martell and Calvin, 1958). By complexation, metals are extracted or desorbed from different soil components or from the surfaces of these components. Soluble metals are potentially bioavailable and can either be taken up by plants, leached into the groundwater, or desorbed again by the exchange sites of the soil. The mobility of Cu and Pb increased in the pH range of 6.5 to 7.5 due to the influence of soluble organic substances (Hornburg and Bruemmer, 1993).

The interaction of trace metals with the solid phase included chemisorptions on minerals, precipitation with different anions coprecipitation in minerals, and complexation with organic matter (McBride, 1989).

In a soil contaminated by lead, McBride and Hendershot (1998) studied the effect of levels of soil organic matter on the solubility of Pb within a pH range of 3 to 8. They showed that 30 to 50 % of dissolved Pb were present as soluble organic matter complexes at low pH and up to 80 to 99 % at near neutral pH (6.5-8).

The addition of some chelating agents including EDTA to the soil dramatically increased the solubility of Cu, (Wu et al., 1999; Lombi et al., 2001). Ligands that are sorbed to soil may increase ternary soil–ligand–metal complexes (Glover et al., 2002; Schwab et al., 2004). The presence of citrate and EDTA was found to decrease the adsorption of Pb to soil minerals although the addition of citrate increased Pb sorption to humus (Chen et al., 2003; Wu et al., 2003).

Reuse of agriculture drainage water, that are contaminated with heavy metals from the over application of fertilizers and pestisides and untreated sewage water in agriculture as well as soil application of sewage sludge that have high levels of heavy metals, may cause environmental problems concerning contamination of surface and groundwater as well as the grown crops with heavy metals. Moreover, the disposal of industerial wastes, that contain high levels of heavy metals, on the agriculture lands near the big cities could also result in environmental hazards. Excessive accumulation of heavy metals can also have deleterious effects on soil fertility, affect ecosystem function and constitute a health risk to human being and animal (Sun et al., 2001).

The main objectives of this study are to evaluate the effects of applying certain organic materials to some contaminated Egyptian soils on the movement and mobility of some heavy metals (Pb and Cu) in these soils.

Materials and Methods

I. Characterization of Soil and Organic Materials

Three contaminated soils at Helwan, El-Gabal El-Asfar (Cairo governorate) and Arab El-Madabeg (Assiut governorate) were chosen-based on their content of heavy metals- from twenty contaminated surface soil materials that were collected from different locations in Egypt to evaluate effects of certain organic materials on the mobility of two heavy metals (Pb and Cu) in these soils. The soils at these locations are receiving a continuous supply of heavy metals as domestic (El-Gabal El-Asfar and Arab El-Madabeg) and/or industrial wastes (Helwan). Soil samples were collected from the surface layer (0-30 cm) of these soils air- dried, crushed with a wooden roller, sieved to pass through a 2 mm sieve and kept for analysis and for the leaching experiment. Some chemical and physical properties of these soils are present in Table 1.

Four organic materials were used to investigate their effects on the mobility of these metals in the studied contaminated soils. They include ethylene diamine tetra acetic acid (EDTA) as a synthetic organic material as well as poultry litter extract (PLE), vinasse (V) and humic acid (HA) solutions as natural organic materials. The poultry litter (PL) was collected from the poultry farm of Assiut University, Assiut. Vinasse, a by-product of sugar industry, was obtained from Abu-korkas Sugar Factory, El-Minya governorate. Moreover, the humic acid solution was brought from the Agriculture Company for Recycling Agriculture Residues, El-Minya governorate. Table 2 shows some properties of these investigated organic materials and their total content of lead (Pb) and copper (Cu).

II. A leaching column experiment

This experiment was carried out in PVC columns of 7.5 cm in diameter and 35 cm in height to study effects of added levels of the investigated organic materials to the

Table(1): Some chemical and physical properties of the soils at the different studied locations.

Property	Soil location		
	Helwan	El-Gabal El-Asfar	El-Madabeg
Particle size distribution			
Clay (%)	24.74	12.00	4.91
Silt (%)	17.32	12.64	7.35
Sand (%)	57.94	75.36	87.74
Texture	Silty clay loam	Loamy sand	Sandy
$CaCO_3$ (%)	5.37	2.50	6.8
pH (1:2.5)	8.11	6.71	7.59
Organic matter (%)	2.18	5.70	2.80
EC (1:1 dS/m)	5.18	1.86	1.7
Soluble cations and anions (mmol/L)			
Na^+	17.31	7.97	4.18
K^+	12.46	3.79	4.37
Ca^{+2}	12.75	3.75	3.97
Mg^{+2}	0.48	0.39	0.22
HCO_3^-	4.12	2.89	3.9
Cl^-	16.62	6.83	6.31
SO_4^{-2}	17.74	5.15	3.36
DTPA-extractable metals (mg/kg)			
Pb	2.70	45.51	6.16
Cu	3.21	3.75	6.07
US.EPA-extractable metals (mg/kg)			
Pb	45.60	247.20	86.10
Cu	36.10	191.20	38.30
Total metals (mg/kg)			
Pb	56.80	261.00	95.00
Cu	55.00	195.00	45.00

Table (2): Some properties of the investigated organic materials and their total content of Pb and Cu.

Organic Material	Pb	Cu	EC (dS/m)	pH	OM (%)
	mg/Kg				
PLE (25 g/L)	0.40	0.10	1.65	7.46	1.90
PLE (50 g/L)	0.40	0.13	3.02	7.50	2.10
PLE (75 g/L)	0.51	0.15	4.20	7.66	2.25
Vinase	0.39	1.15	14.70	4.45	5.11
Humic acid	0.12	0.10	25.90	12.90	3.10

studied soils on the mobility of Pb and Cu in these soils during a leaching process. The investigated soil materials were packed uniformly in the PVC columns to a height of 30 cm. The bulk density of the soil materials in the columns was 1.59, 1.42 and 1.60 Mgm^{-3} for Helwan, El-Gabal El-Asfar and El-Madabeg soils, respectively. Nylon mesh contained a glass wool was used as a filter in the bottom of each column. A filter paper, that was slightly smaller than the inner diameter of the column was placed on the top of each soil column to minimize surface disturbance of the soil particles during the leaching process. The experiment had a completely randomized design and contained 156 soil columns of three different soil materials treated with four organic materials (EDTA, PLE, V and HA) having three levels for each one for 8 weeks. The control treatment for each soil had soil columns treated with distilled water. Each treatment for each soil column had 4 replications. At the end of experiment, the leachate samples were collected and stored un the refrigerator for analysis as well as the soil material in each column was divided into three equal parts (3 layers). Soil samples were taken from different layers of each soil column for chemical analysis. Soil Pb and Cu extracted by the US. EPA method (3050) were determined in the different soil layers.

Concentrations of these metals were also estimated in the leachate samples.

- **Preperation of organic material treatments.**

EDTA was applied every week at levels of 2, 4 and 6 mmol/kg soil. The respective powder amount of EDTA was dissolved in the required amount of distilled water that brought each soil to its saturation capacity resulting in respective levels of 16, 32 and 48 mmol/kg soil at the end of the experiment (8 weeks).

The collected poultry litter (PL) was air-dried, sieved through a 2 mm sieve and stored in a plastic bag. Levels of poultry litter extract (PLE) were prepared using 25, 50 and 75 g of the PL suspended in one litter of distilled water, steered for 2 h., filtered by filter paper, and stored in the refrigerator at 6 °C for use. The amount of PLE at each level to make each soil to reach its saturation capacity was added weekly to each soil column.

Three solution levels of vinasse, (1:2 and 1:1 dilutions of vinase to distilled water) as well as pure vinase were used in this experiment. The weekly added amount of each level was to make each soil to reach its saturation capacity.

The humic acid solution that contained 2% HA was kept in a plastic container at 6 C° in the refrigerator for use. This solution was used to gave HA levels in the soil at the end of the experiment (8 weeks) of 0.1, 0.15 and 0.2 %. The right amount of HA for each level was divided into 8 doses for 8 weeks to give weekly respective levels of 0.013, 0.019 and 0.025%. Each dose of HA for each level was mixed with the required amount of distilled water to make each soil to reach its saturation capacity and then added weekly to each soil column.

Addition of extra amount of 10 ml of distilled water was also added to each soil column, immediately after applying each treatment every week, to ensure leaching the organic materials through the soil columns.

Results and Discussion

1. Lead (Pb)

(a) Lead in the soil

The effect of the studied organic materials on the mobility of soil Pb in Helwan, El-Gabal El-Asfar and El-Madabeg soils is shown in Tables 3. Leaching the studied soils with different organic materials at various application levels for 8 weeks significantly increased the mobility of soil Pb.

Highly significant differences was observed between concentrations of Pb in the deepest layer (L3) and the upper two layers (L1 and L2) of all studied soil columns which were caused by the organic materials and their application levels compared to the control treatment. Concentrations of soil Pb was increased with column depth as a result of leaching the studied soil columns by the investigated organic materials. So, these organic materials have the ability to mobilize Pb in the studied soils. Moreover, Pb levels in most of the upper soil layers (L1 and L2) of the studied soil columns that leached with different levels of the investigated organic materials were lower than those of the control treatment. Conversely, the deepest layer (L3) of all columns of the studied soils leached with these materials at various levels contained

Table (3): Leaching effect using some organic materials on the mobility of soil Pb (mg/kg) of Helwan, ElGabal El-Asfar and El-Madabeg Soils.

Tretment		Helwan soil				El-Gabal El-Asfar soil				El-Madabeg soil			
		Soil layer				Soil layer				Soil layer			
Organic material	Level	L1	L2	L3	Mean	L1	L2	L3	Mean	L1	L2	L3	Mean
	Control	45.9	45.7	45.2	45.6	248.0	247.0	247.9	247.6	84.8	85.1	34.9	84.9
EDTA	2mmol/Kg	34.0	38.3	49.9	40.7	210.7	226.2	266.4	234.4	75.9	77.9	95.9	83.2
	4mmol/Kg	30.2	37.4	48.0	38.5	192.9	200.2	289.0	227.4	66.7	76.6	95.9	79.7
	6mmol/Kg	29.2	35.9	40.6	35.2	185.3	194.8	308.7	229.6	59.8	74.4	91.9	75.3
	Mean	31.1	37.2	46.2	38.1	196.3	207.0	288.0	230.5	67.4	76.3	94.6	79.4
Poultry litter extract	25 g/L	40.0	47.0	51.0	46.0	235.4	247.3	261.4	248.0	80.1	79.8	95.9	85.2
	50 g/L	35.8	48.0	53.9	45.9	231.3	239.8	273.4	248.1	79.0	80.8	97.4	85.7
	75 g/L	31.8	48.0	58.0	45.9	225.9	235.8	282.0	247.9	72.0	77.5	108.2	85.9
	Mean	35.9	47.6	54.3	45.9	230.8	241.0	272.3	248.0	77.0	79.4	100.5	85.6
Vinase	2:1	39.3	43.6	53.1	45.3	233.1	236.9	274.3	248.1	74.6	79.3	100.7	84.8
	1:1	31.2	47.1	58.1	45.4	229.1	233.4	282.0	248.1	70.3	73.3	114.0	85.8
	Pure	30.6	44.0	63.2	45.9	225.4	229.5	291.4	248.7	65.1	71.7	120.5	85.7
	Mean	33.7	44.9	58.1	45.5	229.2	233.2	282.6	248.3	70.0	74.7	111.7	85.5
Humic acid	0.013 %	40.5	46.0	50.5	45.7	240.9	247.8	255.4	248.0	81.0	82.0	93.0	85.3
	0.019 %	37.3	46.5	52.8	45.5	236.3	243.3	265.4	248.3	80.0	81.1	95.1	85.4
	0.025 %	34.3	49.4	53.8	45.8	234.0	241.3	270.0	248.4	76.7	79.2	100.4	85.4
	Mean	37.4	47.3	52.3	45.7	237.0	244.1	263.6	248.2	79.2	80.7	96.2	85.4
$L.S.D_{0.05}$													
Organic material (OM)		1.0				0.8				0.9			
Level		0.8				0.6				0.7			
OM x Level		1.7				1.4				1.6			
Layer (L)		0.8				0.6				0.7			
OM x L		1.7				1.4				1.6			
Level x L		1.3				1.0				1.3			
OM x Level x L		3.0				2.3				2.8			

higher levels of Pb than that of the control. However, the amounts of soil Pb that were moved varied according to the type of organic material, its added level and the soil type.

The studied organic materials varied in their ability to mobilize soil Pb within soil columns. In most cases, EDTA was the most effective organic material in moving soil Pb downward in all investigated soil columns, except El-Madabeg ones. Its ability to chelate soil metals usually much larger than those of other studied natural organic materials (poultry litter extract, vinasse and humic acid). EDTA was reported to be superior in terms of solubilizing soil Pb for root uptake and its translocation into the aboveground biomass due to its strong chemical affinity for Pb (Luo et al, 2005). Blaylock et al. (1997) stated that EDTA is one of the strongest synthetic chelating agents for metals. Its chelating ability is usually much lager than the naturally occurring organic ligands (Stevenson, 1991).

The amounts of soil Pb that were transported from the upper layer (L1) of the studied soil columns to the lower ones (L2 and L3) increased with increasing the application level of the investigated organic material. The highest application level of EDTA (6 mmol/kg) significantly decreased soil Pb in the upper layer after 8 weeks of leaching from 45.95 mg/kg to 29.2 mg/kg for Helwen soil, from 248.0 mg/kg to 185.3 mg/kg for El-Gabal El- Asfar soil, and from 85.5 mg/kg to 59.8 mg/kg for El-Madabeg soil compared to the control treatment. The same trend was observed with other various natural organic materials. Vinase was in the second order in mobilizing Pb in all studied soils, except El-Madabeg soil where it was the most effective one. Pure vinase significantly decreased El-Madabeg soil Pb in the first and second layers after 8 weeks of leaching from 84.5 mg/kg to 65.1 and 71.7mg/kg, respectively. Poultry litter extract (PLE) and humic acid (HA) followed vinase in their effect on the soil Pb mobility. The relative reduction or increase in soil Pb of each soil layer varied according to the type of the organic material, its level of application and the type of the soil which was leached. The leaching with EDTA at a level of 6 mmol/kg showed the highest relative reduction of soil Pb in the upper two layers of the studied soil columns, except for El-Madabeg ones where pure vinase gave the highest values of relative reduction. The relative reduction values of soil Pb in the upper soil layer (L1) after 8 weeks of leaching using the highest level of EDTA were 36.3% for Helwan soil, 25.3% for El-Gabal El-Asfar soil and 29.5% for El-Madabeg soil. The respective values using pure vinase were 33.4% for Helwan soil, 9.1% for El-Gabal El- Asfar soil, and 23.3% for El- Madabeg. Meanwhile, soil Pb in the upper soil layer (L1) after 8 weeks of leaching using the highest level of PLE was relatively reduced by 30.6%, for Helwan soil, 8.9%, for El-Gabal El-Asfar soil, and 15.2% for El-Madabeg soil. Moreover, leaching the studied soil columns with the highest level of HA for 8 weeks relatively decreased soil Pb in the upper layer (L1) by 25.2% for Helwan soil, 5.7% for El-Gabal El-Asfar soil, and by 9.6% for El-Madabeg soil. On the other hand, soil Pb in the deepest layer (L3) after 8 weeks of leaching using the highest level of EDTA and pure vinase relatively increased by 24.5 and 17.5%, respectively, for El-Gabal El-Asfar soil, and by 8.0 and 41.7%, respectively, for El-Madabeg soil. In Helwan soil, the highest level of EDTA relatively decreased Pb in the deepest layer after 8 weeks by 10.2 % whereas pure vinase relatively increased Pb in this layer by 39.9%.

It is obvious that the highest level of EDTA was the most effective organic material in reducing soil Pb in the upper two soil layers of all studied soils. Meanwhile, the highest level of all investigated organic materials was efficient in mobilizing Helwan soil Pb.

Organic material is considered the most efficient in mobilizing soil Pb within soil columns as well as leaching it out of the soil columns.

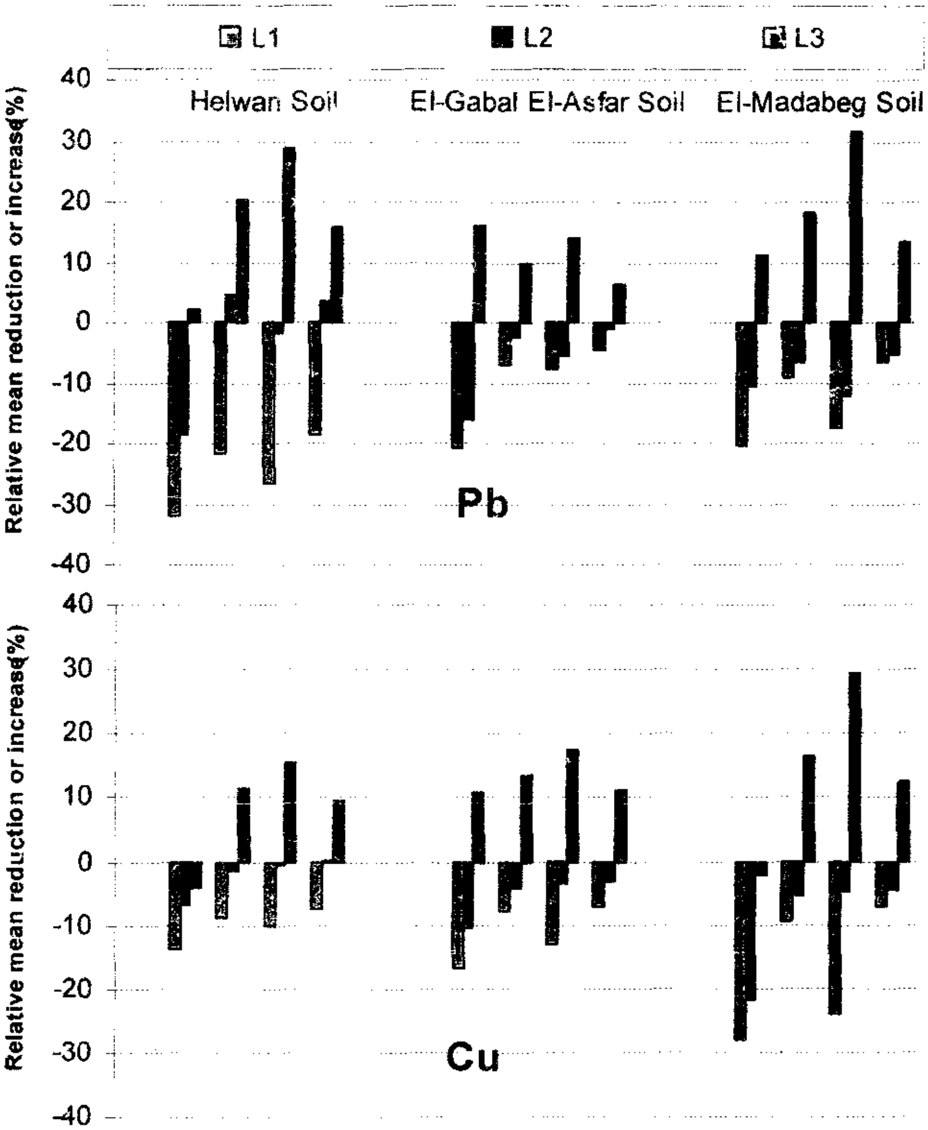
The highest level of EDTA caused 28.4 mg/column of Helwan soil Pb, 60.3 mg /column of El-Gabel El-Asfar soil Pb, and 35.3 mg/column of El-Madabeg soil Pb to be leached out after 8 weeks. These results agree with those obtained by Allen and Chen (1993). They indicated that pure vinasse was the most efficient organic material in mobilizing Helwan and El-Madabeg soil Pb. Pure vinase came after the highest level of EDTA in the ability to transport El-Gabal El-Asfar soil Pb. The high salt content, the low pH and the dissolved organics of vinasse could be the reasons behind its high efficiency for mobilizing soil Pb. Helal et al. (1996) and El-Desoky (1997) reported that saline irrigation water enhanced the release and solubility of soil metals. In all studied soils, the highest level of humic acid was the least effective organic material in mobilizing soil Pb. It may be attributed to its high pH value.

The relative mean reduction or increase of soil Pb in the different layers of the studied soil columns after 8 weeks of leaching using the tested organic materials is illustrated in Figure 1. Generally, EDTA was the most efficient organic material in mobilizing soil Pb of the upper two soil layers (L1 and L2) of all studied soils after 8 weeks of leaching. The results obtained by Luo et al. (2005)

demonstrated that EDTA was the most effective in increasing shoot Pb concentration in corn and beans due enhancing metal solubilization from the soil. On other hand, humic acid was the least productive organic material in removing soil Pb from the upper two Layers. The mean soil Pb in the upper two soil layers (L1 and L2) was reduced by 32.1 and 18.7%, respectively, in Helwan soil, by 20.8 and 16.2%, respectively, in El-Gabal El-Asfar soil, and by 20.5 and 10.4%, respectively, in El-Madabeg soil after 8 weeks of leaching using EDTA. On the other hand, humic acid caused 18.5% of Helwan soil Pb, 4.4% of El-Gabal El-Asfar soil Pb, and 6.6% of El-Madabeg soil Pb to mobilize from the upper layer (L1) after 8 weeks of leaching.

(b) Lead in the leachate

The leaching effect using the investigated organic materials on the amounts of soil Pb that were leached out the studied soils is shown in Table 4. Substantial amounts of soil Pb were leached out the studied soil columns after 8 weeks of leaching by EDTA, especially at its highest application level. However, traces of soil Pb were leached out all studied soil columns using the other three organic materials. It was noticed that amounts of soil Pb that moved by these three organic materials from the upper layer (L1) of each soil accumulated in most cases in the second layer (L2) and sometimes in the deepest one (L3). So, EDTA is considered the only effective organic material in leaching soil Pb. EDTA was reported to have a high binding capacity for Pb (Blaylock et al, 1997; Huang et al, 1997; Wu et al, 1999). The highest application level of each that the removal of toxic heavy metals from a soil matrix by the addition of EDTA was an effective mean of remediation. The use of EDTA was found to give a marked increase in the concentration of soluble Pb in Pb contaminated soils and subsequently enhanced Pb uptake by plants with high biomass production (Blaylock et al, 1997). El-Gabal El-Asfar soil had the highest values of Pb that were leached out with EDTA. Then, Helwan soil came in the second order with respect of amounts of soil Pb that were leached out by EDTA and El-Madabeg one was in the end. These differences may be attributed to the variation in soil texture, soil pH and soil CEC as well as soil Pb content. Sorption studies on Pb by soils indicated that clay, organic matter, CEC and pH are important soil parameters determining the fixation capacity of soils (Adriano, 1986). Lead was reported to have strong affinity to the clay fraction compared to the sand and silt ones. It was ranked by Anderssen (1979) as clay > silt > sand. It is noticed that soil Pb was increased in the deepest layer of each soil after 8 weeks of leaching using all investigated organic materials. Most of soil Pb



Figure(1): The relative mean reduction (-) or incrase (+) percentages (%) in soil Pb and Cu within different soil column layers of the studied soil inducesd by 8 weeks of leaching using some organic materials.

that eluviated from the upper layers illuviated in the deepest one (L3), especially with using the natural organic materials. The investigated organic materials are ranked as EDTA > vinase > PLE > HA in mobilizing Pb of all studied soils (Figure 1 and Table 4). Although the soil Pb content follows the order of El-Gabel El-Asfar > El- Madabeg > Helwan, the relative reduction values of soil Pb in the upper layers and the relative increase ones in the deepest layer have the rank of Helwan > El-Madabeg > El-Gabel El-Asfar

Table(4): Leaching effect using organic materials on the leached Pb (mg/soil column) out of the studied soils after 8 weeks of leaching.

Treatment	Level	Helwan	El-Gabal El-Asfar	El-Madabeg
	Control	0.00	0.80	0.08
EDTA	2 mmol/kg	13.14	35.40	17.82
	4 mmol/kg	17.89	55.85	26.28
	6 mmol/kg	28.45	60.30	35.33
	Mean	19.82	50.52	26.47
Poultry litter extract	25g/L	0.20	0.15	0.22
	50g/L	0.23	0.13	0.24
	75g/L	0.25	0.42	0.41
	Mean	0.23	0.23	0.29
Vinase	1:2	0.23	0.17	0.49
	1:1	0.44	0.19	0.53
	Pure	0.46	0.27	0.54
	Mean	0.38	0.21	0.52
Humic acid	0.013 %	0.27	0.10	0.15
	0.019%	0.43	0.14	0.17
	0.025%	0.45	0.29	0.35
	Mean	0.38	0.18	0.22
L.S.D.$_{0.05}$	Treat.	0.05	0.15	1.46
	Level	0.11	0.35	3.24

2. Copper (Cu)

(a) Copper in the soil

The influence of the studied organic materials on the mobility of soil Cu in Helwan, El- Gabal El-Asfar and El-Madabeg soils is present in Table 5. All organic materials were able to mobilize soil Cu in all studied soils. The magnitude of Cu mobility varied according to the soil type, the type of organic material and its application level. The mobility of soil Cu significantly was increased with leaching the studied soils using the different levels of the investigated organic materials for 8 weeks. So, concentrations of soil Cu was increased with column depth. Also, the results obtained by Pruschenreiter et al. (2001) and Chen et al. (2003) indicated that EDTA can be used to increase metal mobility, thereby enhancing uptake of many heavy metals including Cd, Cr, Cu, Pb and Zn.

In addition, soil Cu levels in the upper layers (L1 and L2) of the studied soil columns that were leached with different levels of the investigated organic materials were lower than those of the control. On the other hand, the soil Cu, in most cases, was higher in the deepest layer than that of the control. In few cases using EDTA, the soil Cu in the deepest layer was lower than that of the control treatment.

The obtained data indicated that EDTA as a synthetic organic material was able to increase the mobility of Cu in all studied soils more than other natural organic materials (vinase, PLE and HA). Elliot and Shastri, (1999), Heil et al. (1999) and Papassiopi et al. (1999) reported that EDTA is effective in mobilizing and removing Cu from contaminated soils. The extraction efficiency for an organic material was reported by Sun et al. (2001) to depend on many factors, such as the lability of heavy metals in the soil, the strength of that organic material, electrolyte, pH and soil matrix. Their laboratory studies showed that EDTA was effective in removing Pb, Zn, Cu and Cd from contaminated soils. The upper two layers of the studied soil columns contained lower amounts of Cu after 8 weeks of leaching with all organic materials. The highest values of soil Cu mobility were recorded with the highest application level of all investigated organic materials, especially the highest level of EDTA followed by pure vinasse. The results obtained by Mahmoud. (1988) and Abd El-Kaway (2006) revealed that the application of vinasse increased the micronutrients in all plant parts because of its low pH. So, application of vinase may increase the availability of micronutrients in the soil. The highest level of EDTA significantly decreased the soil Cu in the upper layer after 8 weeks of leaching from

Table(5): Leaching effects using some organic materials on the mobility of Cu (mg/kg) of Helwan, El-Gabal El-Asfar and El-Madabeg Soils.

Tretment		Helwan soil				El-Gabal El-Asfar soil				El-Madabeg soil			
		Soil layer				Soil layer				Soil layer			
Organic material	Level	L1	L2	L3	Mean	L1	L2	L3	Mean	L1	L2	L3	Mean
	Control	36.0	36.1	36.5	36.2	185.4	184.0	184.9	184.8	37.8	38.4	38.8	38.3
EDTA	2mmol/Kg	33.2	34.1	34.7	34.0	169.2	174.5	199.7	181.1	29.6	31.0	42.3	34.3
	4mmol/Kg	32.8	34.0	34.9	33.9	148.5	166.5	205.6	173.5	27.9	31.8	37.2	32.3
	6mmol/Kg	27.1	32.9	35.3	31.8	144.5	153.9	210.2	169.5	24.3	27.5	34.2	28.7
	Mean	31.0	33.6	35.0	33.2	154.0	165.0	205.1	174.7	27.2	30.1	37.9	31.7
Poultry litter extract	25 g/L	35.1	36.6	37.1	36.2	175.7	181.6	199.5	185.6	36.2	37.8	41.5	38.5
	50 g/L	32.0	36.8	41.5	36.8	169.6	175.7	212.6	186.0	34.2	36.8	45.0	38.6
	75 g/L	31.3	33.4	43.7	36.1	168.3	170.8	218.3	185.8	32.5	34.3	48.9	38.6
	Mean	32.8	35.6	40.8	36.4	171.2	176.0	210.0	185.8	34.3	36.3	45.1	38.6
Vinase	٢:١	35.2	36.9	37.4	36.5	168.5	184.5	203.6	185.5	30.9	36.5	47.5	38.3
	١:١	32.0	36.9	41.9	36.9	160.9	178.4	217.6	185.6	28.0	39.3	48.5	38.6
	Pure	29.9	34.0	46.9	36.9	154.4	170.6	229.7	184.9	27.3	33.9	54.5	38.6
	Mean	32.3	35.9	42.1	36.8	161.2	177.8	217.0	185.3	28.7	36.6	50.2	38.5
Humic acid	0.013 %	35.0	36.6	37.0	36.2	177.3	183.2	192.7	184.4	36.7	37.8	40.4	38.3
	0.019 %	33.3	36.3	39.9	36.5	170.6	175.4	210.7	185.6	36.5	37.7	41.7	38.6
	0.025 %	31.6	35.7	43.0	36.7	168.7	175.6	212.4	185.5	32.4	34.7	48.8	38.6
	Mean	33.3	36.2	39.9	36.5	172.2	178.0	205.3	185.1	35.2	36.7	43.6	38.5
$L.S.D_{0.05}$													
Organic material (OM)		0.3				0.5				0.7			
Level		0.3				0.4				0.5			
OM x Level		0.6				0.9				1.2			
Layer (L)		0.3				0.4				0.5			
OM x L		0.6				0.9				1.2			
Level x L		0.5				0.7				0.9			
OM x Level x L		1.0				1.6				2.1			

36.0 mg/kg to 27.1 mg/kg for Helwan soil, from 185.4 mg/kg to 144.5 mg/kg for El-Gabal El-Asfar soil, and from 37.7 mg/kg to 24.3 mg/kg for El-Madabeg soil compared to the control. Vinase followed EDTA and then PLE and HA in their effect on soil Cu mobility.

The relative reduction or increase in soil Cu of each soil layer differed according to the type of the organic material, its application level and the soil type. The use of EDTA at its highest level in leaching the studied soil columns resulted in the highest relative reduction values of soil Cu in the upper two layers (L1 and L2). However, the highest level of humic acid was recorded to give the lowest relative reduction values of soil Cu. Leaching the studied soil columns with the highest level of EDTA for 8 weeks relatively decreased soil Cu in the upper layer (L1) by 24.7% for Helwan soil, by 22.1% for El-Gabal El-Asfar soil, and by 35.8% for El-Madabeg soil. Meanwhile, soil Cu in this layer (L1) after 8 weeks of leaching with pure vinase was relatively reduced by 17.1% for Helwan soil, by 16.7% for El-Gabal El-Asfar soil, and by 27.9% for El-Madabeg soil. However, the relative reduction values of soil Cu in the upper layer after 8 weeks of leaching using the highest level of PLE were 13.2% for Helwan soil, 9.2% for El-Gabal El-Asfar soil, and 14.0% for El-Madabeg soil. Moreover, the respective values using the highest level of HA were 12.4% for Helwan soil, 9.0% for El-Gabal El-Asfar soil, and 14.4% for El-Madabeg soil. On the other hand, soil Cu in the deepest layer (L3) of Helwan and El-Madabeg soils was relatively reduced by 3.3 and 11.9%, respectively, but it was increased by 13.7% in El-Gabal El-Asfar soil after 8 weeks of leaching with the highest level of EDTA. However, pure vinasse caused increases in soil Cu of the deepest layer of Helwan, El-Gabal El-Asfar and El-Madabeg soils by 28.5, 24.2 and 40.5%, respectively, after 8 weeks of leaching.

It is clear that the highest level of EDTA is the most effective in reducing soil Cu in the upper two layers of all the studied soils. Meanwhile, pure vinasse is efficient in mobilizing El-Madabeg soil Cu. The highest level of both PLE and HA mobilized few amounts of soil Cu of all studied soils. The addition of some chelating agents including EDTA to the soil dramatically increased the solubility of Cu (Wu et al., 1999; Lombi et al., 2001). Although El-Gabal El-Asfar soil had the highest level of soil Cu, all studied organic materials at their highest level mobilized only few amounts of its soil Cu. On the other hand, the highest level of studied organic materials eluviated reasonable amounts of soil Cu from

El-Madabeg soil even though it had the lowest content of soil Cu.

The relative mean reduction or increase of soil Cu in the different layers of the studied soil columns after leaching using the investigated organic materials is shown in Figure 1. In general, EDTA mobilized the highest amounts of soil Cu from the upper two layers (L1 and L2) of all studied soil columns. It was the most effective organic material in soil Cu mobility. Vinasse was efficient in removing soil Cu from the upper layer (L1) of El-Madabeg soil. However in all soils, HA was the least effective organic material in mobilizing soil Cu from the upper two layers.

The mean soil Cu in the upper two layers (L1 and L2) was reduced by 13.9 and 6.8%, respectively, for Helwan soil, 16.9 and 10.4%, respectively, for El-Gabal EL-Asfar soil, and 28.0 and 21.7%, respectively, for El-Madabeg soil after 8 weeks of leaching with EDTA. Vinasse was effective to remove highest amounts of soil Cu from the upper layer of El-Madabeg soil accounted by 24.1. Reasonable amounts of soil Cu accounted by 10.2 and 13.0% migrated from the upper layer of Helwan and El-Gabal El-Asfar soils, respectively, after 8 weeks of leaching with vinase. On the other hand, PLE and HA removed relatively low soil Cu levels from the upper layer of averages accounted by 8.9 and 7.6%, respectively, for Helwan soil, 7.7 and 7.1%, respectively, for El-Gabal El-Asfar soil, and 9.3 and 7.0%, respectively, for El-Madabeg soil.

(b) Copper in the leachate

Table 6 shows the effect of the organic materials and thier application levels on the amounts of soil Cu that leached out the studied soil columns. The organic materials increased the amounts of Cu and that could move downward from the upper layers and accumulated in the deepest layer and/or leached out from the soil columns. Considerable amounts of Cu were leached out the studied soil columns by EDTA, especially at its highest application level. Conversely, traces of soil Cu were leached out all soil columns using other organic materials. Therefore, EDTA is considered the most efficient organic material in transporting soil Cu within soil columns as well as in leaching it out soil columns. The highest level of EDTA significantly leached amounts of Cu of 11.36 mg/column out Helwan soil, 43.80 mg/column out El-Gabal El-Asfar soil, and 25.37 mg/column out El-Madabeg soil after 8 weeks of leaching. On the other hand, pure vinasse caused only 2.2 mg/column of El-Gabal El-Asfar soil Cu to be leached after 8 weeks. Meanwhile, the amounts of Cu leached by this material out other tested soils (Helwan and El-Madabeg) were negligible. It is obvious that the mobilized soil Cu from the upper layers accumulated in the deepest one, especially with using the natural organic materials (PLE, vinase and HA). Tremendous amounts of soil Cu were leached out soil columns and lower Cu levels compared to the control were in the deepest layer using the highest level of EDTA. The investigated organic materials had the order of EDTA > Vinasse > PLE > HA in mobilizing soil Cu in all studied soils. The relative reduction values of soil Cu in the upper layer and the relative increase ones in the deepest layer had the order of El-Madabeg > Helwan > El-Gabal El-Asfar soil. Although the soil Cu content followed the rank of El-Gabal El-Asfar > El-Madabeg > Helwan. So, Cu

Table(6): Leaching effect using organic materials on the leached Cu (mg/soil column) out of the studied soil after 8 week leaching.

Treatment	Level	Helwan	El-Gabal El-Asfar	El-Madabeg
	Control	0.10	0.13	0.15
EDTA	2 mmol/kg	5.64	8.18	10.11
	4 mmol/kg	6.95	30.38	16.12
	6 mmol/kg	11.36	43.80	25.37
	Mean	7.98	27.45	17.20
Poultry litter extract	25g/L	0.10	0.22	0.24
	50g/L	0.19	0.22	0.32
	75g/L	0.29	0.39	0.38
	Mean	0.19	0.28	0.31
Vinasse	1:2	0.10	0.16	0.21
	1:1	0.13	0.38	0.24
	Pure	0.41	2.19	0.29
	Mean	0.21	0.91	0.25
Humic acid	0.013%	0.20	0.23	0.18
	0.019%	0.24	0.40	0.32
	0.025%	0.48	0.34	0.40
	Mean	0.31	0.32	0.30
L.S.D.$_{0.05}$	Treat.	0.62	0.37	0.41
	Level	0.68	0.82	0.93

mobility of El-Madabeg soil was higher than that in others. It may be attributed to its coarser texture (sand) in comparison with other soils.

All results indicate that metal-organic complexes could modify the solubility of metals in the soil solution and consequently their transport in the soil profile. This was assumed to explain the increased heavy metal transport in drainage waters following a sludge application (Lamy et al., 1993). Based on the distribution coefficient, the relative migration velocities of the heavy metals were increased by the presence of dissolved organic carbon (Christensen et al., 1996).

Conclusion

It could be concluded from the obtained results that organic materials play an important role in mobilizing the heavy metals in soils. The pH of the soil is not the only factor that controls the mobility of Pb and Cu in these soils. These materials may contain soluble organic acids and other soluble organics that form soluble organic complexes with these metals resulting in their mobility in the soils

Additions of these organic materials or their disposal on heavy metal contaminated soils, especially near sewage water plants and industrial areas can cause hazard problems with respect of environmental pollution. The soluble organic complexes of these metals can contaminate the surface water and the groundwater resources as well as enhancing the plants and crops that are grown on these contaminated soils to absorb and take up high amounts of these hazardous heavy metals. These contaminated water resources and plants may cause heath problems for Human, animals and livestocks. Therefore, it should be recommended to dispose any organic material far from the sites that have heavy metal contaminated soils. The organic wastes such as sewage wastes should be separated from industrial ones during their disposal and treatments.

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حركة العناصر الثقيلة(الرصاص والنحاس) في بعض الأراضي المصرية الملوثة والمعاملة ببعض المواد العضوية

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لقد تم اختبار ثلاث أنواع من الترب المصرية الملوثة هي حلوان والجبل الأصفر (محافظة القاهرة) ، وعرب المدابغ (محافظة أسيوط) لدراسة تأثير بعض المواد العضوية على حركة العناصر الثقيلة (الرصاص ، النحاس) في هذه الترب الملوثة وقد شملت هذه المواد العضوية الـ EDTA كمادة عضوية صناعية وكذلك مستخلص فرشة الدواجن (PLE) والفيناس وحامض الهيوميك (HA) كمواد عضوية طبيعية مقارنة بالماء المقطر. وتم اضافة هذه المواد لكل عمود من أعمدة التربة كمحاليل بتركيز ٢ ، ٤ ، ٦ مليمول/كجم من EDTA و ٢٥ ، ٥٠ ، ٧٥ جسم/لتر من PLE وتخفيفات ١:١ ، ٢:١ من للفيناس الي الماء بالاضافة الي الفيناس النقي وكذلك ٠,٠١٣ ، ٠,٠١٩ ، ٠,٠٢٥ % من حامض الهيوميك.

ويمكن تلخيص النتائج كما يلي :ـ

أدى غسيل الترب تحت الدراسة بالمواد العضوية المختلفة عند مستويات الإضافة المختلفة إلى زيادة حركة الرصاص ، النحاس في هذه الترب . كما اعتمدت حركة الرصاص ، النحاس في التربة على نوع المادة العضوية ومستوى إضافتها وعلى نوع التربة بالإضافة إلى فترة الغسيل.

اختلفت المواد العضوية في كفاءتها على حركة هذه العناصر في الترب تحت الدراسة فكان EDTA عند أعلى مستوى إضافة أكثر المواد العضوية تأثيرا في زيادة حركة الرصاص والنحاس وتقليل تركيزهما في الطبقتين العلويتين في كل الترب.

عموما يمكن ترتيب المواد العضوية من حيث دفعها لحركة هذه العناصر الثقيلة في الترب تحت الدراسة كما يلي : EDTA > الفيناس > مستخلص فرشه الدواجن > حامض الهيوميك . كما كان الفيناس ذو فاعلية في تحريك الرصاص والنحاس في تربة عرب المدابغ بعد ٨ أسابيع من الغسيل ، وكقيم متوسطة ، فقد أدى الفيناس لتحريك ١٧,٨ ، ٢٤,٠ % من الرصاص والنحاس على التوالي في الطبقة العليا لهذه التربة مقارنة بالقيم ٢٠,٧ ،٢٧,٩ % من هذه العناصر على التوالي في هذه الطبقة لنفس التربة بعد ٨ أسابيع غسيل بواسطة EDTA .