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Changes in Soil Zn and Mn Forms of Some Contaminated Egyptian Soils Treated with Organic Materials.

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Abstract

An incubation experiment using three contaminated soils from Helwan, El-Gabal El-Asfar (Cairo governorate) and Arab El-Madabeg (Assiut governorate) was conducted for 16 weeks to evaluate effects of four organic materials including ethylene diamine tetra acetic acid (EDTA) as a synthetic organic material as well as poultry litter extract (PLE), vinase (V) and humic acid (HA) solutions as natural organic materials on zinc (Zn) and manganese (Mn) forms of thesecontaminated soils. The studied chemical metal forms were soluble plus exchangeable (S+EXCH), carbonate bound (C-bound), Mn oxide bound (MnO-bound), organic bound (O-bound,), Poorly crystalline Fe oxide bound (PCFeO-bound) and crystalline Fe oxide bound (CFeO-bound) and residual forms.

The results showed that the transformation of soil Zn among its chemical forms was great in all studied soils treated with EDTA. Vinase was in the second order, with respect of the change efficiency, followed by PLE and HA. Increase in the soluble and exchangeable Zn induced by EDTA weretransformed mainly from PCFeO-bound and residual formsinHelwan soil, from C-bound, O-bound, PCFeO-bound and CFeO- bound forms in El-Gabal El-Asfar soil, and from C-bound,MnO-bound, PCFeO-bound and residual in El-Madabeg soil. The distribution order of Mn forms in all studied soils according to Mn abundance changed with using various organic materials. As it isindicated with Zn, EDTA was the most effective organic material in increasing the soluble plus exchangeable Mn in all tested soils. The increases in the soluble and exchangeable form of Mn induced by EDTA were on the expense of decreasing mainly the Mn-oxide (33.8%), and poorly crystalline Fe oxide (31.4%) forms, and partially the crystalline Fe oxide (7.0%), organically bound (20.41%) and residual (9.7%) forms in Helwan soil.

Keywords: *Transformation, fractionation Soil Zn and Mn, organic materials, contaminated soils.*

1. Introduction

Heavy metals in the environment have been received considerable attention because of their potential effects on human and animal health. They 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).Total heavy metal concentrations may give insufficient information about soil pollution and metal leaching when soils comprise horizons of different textures (Mokma *et al*. 2000). The determination of total heavy metal content does not provide useful information about the risks of bioavailability, the capacity for remobilization and the behavior of the metals in the environment (Sims and Sklin, 1991; Singh, 1997; Hsu and Lo, 2001). The speciation of trace elements in the soil is related to their chemistry inherited from parent materials as well as the time of impaction. Atomic properties also have a significant role in the cation speciation resulting from the formation of metal-ligand complexes. The binding mechanisms for trace metals in soils are manifold and vary with the composition of soils and their physical properties. Thus, a metal may form different species accordingto whether it is bound to various soil compounds, reacting surfaces, and external or internal binding sites with different bonding energy (Kabata-Pendias and Pendias, 1992).Unlike the single extraction technique, the sequential extraction gives information about both mobile and stable fractions of metals in soils, which it evaluates the actual and potential mobility of metals. Moreover, the speciation of heavy metals allows the estimation of heavy metal bioavailability and its relation to the different natures of the metals, as well as their bonding strength, as a free ionic form, complexed by organic matter or incorporated in the mineral fraction of the soil sample (Amir *et al.,* 2005). The dynamics of how elements move from one chemical form to another, in response to changing soil conditions, it can be also studied using fractionation techniques (Shuman, 1979).

Compost treatments lead to the development of microbial populations, which cause numerous physicochemical changes within the mixture. These changes could influence the metal distribution in soils through releasing heavy metals during organic matter mineralization or the metal solubilization by decreasing the pH, metal biosorption by the microbial biomass, metal complexation with the newly formed humic substances and/ or other factors (Hsu and Lo, 2001; Zorpas *et al*., 2003).

In soil columns leached by H_2O, $CaCl_2$, EDTA, and poultry litter extract (PLE) solutions, Li and Shuman (1997a) showed that the EDTA redistributed Zn, Cd and Pb from the exchangeable, organic matter and Mn oxide fractions to the water soluble fraction. Using a sequential extraction for soil samples that previously leached in soil columns with poultry litter extract (PLE), Li and Shuman (1997b) also indicated that the application of PLE to metal-contaminated soils caused Zn and Cd to be redistributed from the exchangeable to the water soluble fraction and enhanced the metal mobility. The PLE usually solubilize more Zn and Cd from the exchangeable fraction than $CaCl^2$.

The irrigation with sewage wastewater for 4 years was reported to transform soil metals from the carbonate form towards the exchangeable form, Fe-Mn oxide bound and organically bound forms for Zn (Usman and Ghallab, 2006). Also, the use of organic wastes as sources of organic matter for agricultural or ecological benefit is a way of recycling them (CEC, 1996). The effects of organic matter on heavy metal fractionation in the soil are pH-dependent. For example, at high soil pH, the formation of soluble organo-metallic complexes can increase the metal solubility (Gregson and Alloway, 1984).

This studyaims to investigated the addition effects of certain organic materials (EDTA, poultry litter extract, vinase and humic acid) to some Egyptian contaminated soils on the transformations of different soil Zn an Mn forms.

2. Materials and methods

2.1 Soil samples and organic materials.

Three different contaminated soils samples were collected from Helwan, El-Gabal El-Asfar (Cairo governorate) and Arab El-Madabeg (Assiut governorate) fromthe surface layer (0-30 cm) to study effects of certain organic materials on the changes in soil Zn and Mn forms. 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). The collected soil samples were air-dried, crushed with a wooden roller, sieved to pass through a 2 mm sieve and kept for analysis and experimentation. Table 1 shows some physicaland chemicalproperties of these soils according Jackson (1970).

Four organic materials including ethylene diamine tetra acetic acid (EDTA) as a synthetic organic material as well as poultry litter extract (PLE), vinase (V) and humic acid (HA) solutions as natural organic materialswere used in this study.

The poultry litter (PL) was collected from the poultry farm of Assiut University, Assiut. Vinase, a by-product of sugar industry, was obtained from Abu-korkas Sugar Factory, El-Minya governorate. The HA solution was brought from the Agriculture Company for Recycling Agriculture Residues, El-Minya. Some chemical properties of these organic materials are present in Table 2.

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	Sand
$CaCO_3$ (%)	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)			
Zn	11.91	5.63	4.10
Mn	3.86	1.22	3.93
US.EPA-extractable metals (mg/kg)			
Zn	202.90	585.30	139.10
Mn	282.10	313.50	223.80
Total metals (mg/kg)			
Zn	216.00	618.00	165.00
Mn	304.00	420.00	375.00

Table 2. Some properties of the investigated organic material solutions and their total content of Zn and Mn.

Organic Material	Zn	Mn	EC	pH	OM
	mg/kg		(dS/m)		(%)
PLE (75g/L)	0.22	0.27	4.2	7.66	2.25
Vinase	4.18	5.82	14.7	4.45	5.11
Humic acid	0.34	0.43	25.9	12.9	3.1

2.2 Preparation of organic material treatments.

EDTA was applied every week at level of 6 mmol/kg soil. The respective powder amount of EDTA was dissolved in the required amount of distilled water thatbrought each soil to its saturation capacity resulting in respective levels of 48 mmol/kg soil at the end of the experiment (16 weeks).

The collected poultry litter (PL)

were air-dried, sieved through a 2 mm sieve and stored in a plastic bag. Levels of poultry litter extract (PLE) were prepared using 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 ^{o}C for use. The amount of PLE to make each soil to reach its saturation capacity was added weekly to each soil plastic cups. Pure vinase were used in this experiment. The weekly added amount of each organic material was to make each soil to reach its saturation capacity.

The humic acid (HA) solution that contained 2% HA was kept in a plastic container at 6 C^{o} in the refrigerator for use. This solution was used to gave HA in the soil at the end of the experiment (8 weeks) of 0.2 %. The right amount of HA was divided into 8 doses for 8 weeks to give weekly respective level of 0.025%. The dose of HA 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 plastic cup.

2.3 An incubation experiment

This experiment was conducted to investigate the transformations among various soil Zn and Mn forms due to treating the soils with organic materials. The design of this experiment was completely randomized with 3 replications.

So, samples of 200g of each studied soil material were put in plastic cups, watered every weekwith a solution containing EDTA, PLE or HA at a levels of 6 mmol/kg, 75g/L or 0.025% respectively, to reach the watersaturation capacity of each soil samples. However, vinase was added to each soil samples as a pure liquid without dilution to reach its saturation capacity.The treated soil samples were incubated at the Lab temperature for 8 weeks. Then, the soil samples in the plastic cups were continued in the incubation for another 8 weeks with adjusting the water content of each soil material to 60% of the saturation capacity by the daily addition of ionized water during this incubation period. At the end of the experiment (16 weeks), samples from the incubated soil materials were taken, air-dried, sieved through a 2 mm sieve and kept for the Zn and Mn fractionation using sequential extractions.

2.4 Soil Zn and Mn fractionation

Two grams of each soil material were weighed and placed in a 50 ml polyacarbnate centrifuge tube. Sequential extractions of soluble and exchangeable (S+EXCH, Kabala and Singh 2001), carbonate specifically-bound (C-bound, Ahnstromand Parker, 1999), Mn oxide bound (Mn O-bound, Sims *et al.* 1986), organic bound (O-bound, Shuman 1979), poorly crystalline Fe oxide bound (PCFeO-bound, Shuman 1979) and-crystalline Fe oxide bound (CFeO-bound, Kittric and Hope, 1963) forms of Zn and Mn were performed. The total amount of Zn and Mn in the studied soil materials was determined after digestion using concentrated acids of HF, HNO_3 and HCl (Shuman, 1979). The residual formwas estimated by the difference between the total amount of a metal in the soil samples and sum of the six extracted forms of this metal. Zinc and Mnin the soil digests were determined using a model 906 of GBC atomic absorption spectrophotometry. Data were subjected to statistical analysis according to Sendecor and Cochrana (1980). The means of treatments were compared using the least significant difference (LSD) values at a 5% level of significance.

3. Results and Discussion

3.1 Soil Zinc

The effect of some organic materials on the different chemical Zn forms of Helwan, El-Gabal El-Asfar and El-Madabeg soils is shown in Table 3. The investigated organic materials significantly increased Zn levels in the soluble plus exchangeable form of the studied soils except PLE and HA in Helwan soil and HA in El-Gabal El-Asfar soil, compared to the control treatments.

EDTA as a synthetic chelating agent induced the highest increases in the soluble plus exchangeable Zn of all studied soils followed by vinase as a natural organic materialsand then PLE. On the other hand, humic acid was the least effective in all soils. Soluble plus exchangeable Zn is adsorbed as a cation by the electrostatic attraction to the negatively charged sites on the colloidal mineral solids and organic matter of soils (Adriano, 1986). The most common and mobile Zn in the soil is believed to be Zn^2+, but several other ionic species may occur in soils (Kabata-Pendias and Pendias, 1992).

The increase in the soluble and exchangeable Zn of Helwan soil treated with EDTA was mainly on the expense of the poorly crystalline Fe oxide (41.1%), and residual (22.2%) forms, and partially on the cost of the crystalline Fe oxide (35.8%) and organically bound (53.6%) forms. However, the increase in the soluble plus exchangeable Zn of El-Gabal El-Asfar soil due to EDTA was mainly on the expense of decreasing the organically bound (74.1%) and poorly crystalline Fe oxide (20.0%) forms, and partially on the charge of the carbonate bound (24.9%), crystalline Fe oxide (21.7%) and residual (4.4%) forms. Moreover, in El-Madabeg soil treated with EDTA, the soluble plus exchangeable Zn increased mainly on the expense of decreasing the poorly crystalline Fe oxide (55.36%) and partially on the charge of the residual (24.7%), carbonate bound (55.4%), Mn oxide (85.4%) and organically bound (22.6%) forms. Vinase treated Helwan soil had increases in the soluble and exchangeable and carbonate bound forms of Zn on the charge of decreases in the poorly crystalline Fe oxide form (12.8%). However, vinase caused Zn increases in the soluble plus exchangeable, carbonate bound and poorly crystalline Fe oxide forms of El-Gabal El-Asfar on the expense of decreasing the organically bound (3.8%), crystalline Fe oxide (18.7%), and residual (15.0%) forms. In El-Madabeg soil treated with vinase, the soluble plus exchangeable Zn form increased on the cost of decreasing the Mn oxide (39.7%) and residual (10.4%) forms.

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Table 3. Effect of some organic materials on the redistribution of zinc (Zn) among various forms of the studied soils.

Soil	Treatment	Zn forms (mg/kg)								
		S+EXCH	C-bound	MnO	O-bound	PCFeO	CFeO	Sum	Residual	Total
Helwan	control	1.63	3.66	1.48	2.65	79.63	16.04	105.10	110.90	216.00
	EDTA	52.94	16.82	1.53	1.23	46.87	10.30	129.69	86.31	216.00
	PLE	2.86	15.63	1.31	1.96	71.40	12.91	106.07	110.22	216.28
	Vinase	11.16	10.03	1.33	2.28	69.46	17.34	111.60	109.64	221.24
	HA	1.98	4.93	1.48	3.39	85.47	16.14	113.39	102.65	216.03
	$LSD_{0.05}$	2.16	1.60	0.33	0.48	3.63	1.72	-	2.35	-
El-Gabal El-Asfar	control	12.41	79.67	18.66	102.67	160.63	34.75	408.79	209.21	618.00
	EDTA	155.56	59.83	20.10	26.63	128.57	27.21	417.90	200.10	618.00
	PLE	14.61	64.30	19.92	111.53	181.53	29.78	421.68	196.62	618.30
	Vinase	26.70	89.97	20.26	98.73	182.17	28.18	446.00	177.77	623.77
	HA	13.83	87.75	20.77	106.7	169.73	26.45	425.23	192.81	618.04
	$LSD_{0.05}$	2.01	6.81	2.12	3.33	4.47	4.22	-	1.32	-
El-Madabeg	control	3.21	19.28	8.56	4.38	76.97	14.71	127.10	37.90	165.00
	EDTA	76.17	8.59	1.25	3.39	34.40	12.66	136.45	28.55	165.00
	PLE	5.63	19.05	8.81	3.77	76.30	14.67	128.24	36.91	165.15
	Vinase	16.80	18.51	5.16	4.01	75.17	14.24	133.89	33.97	167.86
	HA	4.82	18.63	8.39	3.96	76.80	15.75	128.36	36.67	165.03
	$LSD_{0.05}$	0.51	2.63	0.73	0.55	4.45	2.15	-	0.69	-

Poultry litter extract in Helwan soil caused an insignificant increase in the soluble plus exchangeable Zn and a significant increase in the carbonate bound Zn on the cost of decreases in the organically bound (26.0%), poorly crystalline Fe oxide (10.3%) and crystalline Fe oxide (19.5%) forms of Zn. Moreover, PLE induced Zn increases in the soluble and exchangeable, organically bound and poorly crystalline Fe oxide forms of El-Gabal El-Asfar soil on the expense of decreases in the carbonate bound (19.3%), crystalline Fe oxide (14.3%) and residual (6.0%) forms. An increase in the soluble plus exchangeable Zn of El-Madabeg soil treated with PLE occurred on the charge of decreasing both the organically bound (13.9%) and residual (2.61%) forms.

Humic acid induced lowest increases in Zn forms of all studied soils. In Helwan soil, insignificant Zn increases in the soluble plus exchangeable, carbonate bound, Mn oxide and crystalline Fe oxide forms occurred by HA on the expense of decreasing the residual form. Insignificant Zn increases in the soluble and exchangeable and Mn oxide forms but significant ones in the carbonate bound, organically bound and poorly crystalline Fe oxide forms were induced by HA in El-Gabal El-Asfar soil on the charge of decreasing the crystalline Fe oxide and residual forms. On the other hand, HA caused only an increase in the soluble plus exchangeable Zn of El-Madabeg soil on the expense of decreasing the residual form of Zn.

Table 3 also shows that the poorly crystalline Fe oxide was the dominant form in the non-residual Zn forms of Helwan and El-Madabeg soils. On the other hand, the dominant Zn forms in El-Gabal El- Asfar were the organically bound and poorly crystalline Fe oxide. This result may be attributed to the high content of organic matter (5.07%) in the latter soil. Zinc was reported to have relatively high affinity for sorption on the surfaces of Fe and Mn oxides, especially with an increase in the pH (Shuman, 1995; Luo and Christie, 1998).

The relative distribution of various Zn forms as a percentage of the total Zn after treating the studied soils with the investigated organic materials is present in Figure 1. EDTA caused Zn increases in the soluble plus exchangeable (from 0.76 to 24.51% of the total) and carbonate bound (from 1.70 to 7.79% of the total) forms of Helwan soil, but Zn decreases in the poorly crystalline Fe oxide, crystalline Fe oxide and residual (from 36.87 to 21.70%, from 7.42 to 4.77% and from 51.34 to 39.96%, respectively, of the total Zn) forms. In El-Gabal El-Asfar soil, EDTA released Zn levels from the carbonate (from 12.89 to 9.68%), organically bound (from 16.61 to 4.31%), poorly crystalline Fe oxide (from 25.99 to 20.80%), crystalline Fe oxide (from 5.62 to 4.40%) and residual (from 33.85 to 32.38%) forms and transformed them to the soluble and exchangeable form (from 2.01 to 25.17%). Meanwhile, the increase in the soluble plus exchangeable Zn (from 1.94 to 46.16%) of El-Madabeg soil induced by EDTA was due to releasing Zn levels from the carbonate bound (from 11.68 to 5.21%), poorly crystalline Fe oxide (from 46.65 to 20.85%), crystalline Fe oxide (from 8.91 to 7.67%) and residual (from 22.85 to 17.30%) forms.

The results show that Zn increases in the soluble plus exchangeable form induced by EDTA were transformed mainly from the poorly crystalline Fe oxide and residual forms in Helwan soil, from the carbonate bound, organically bound, poorly crystalline Fe oxide and crystalline Fe oxide forms in El-Gabal El-Asfar soil, and from the carbonate bound, Mn oxide, poorly crystalline Fe oxide and residual forms in El Madabeg soil. Sun *et al.* (2001) indicated that soil Zn level decreased in all fractions after leaching with EDTA. However, Li and Shuman (1997a) pointed out that EDTA redistributed Zn from the exchangeable, organic bound and Mn oxide fractions to the water soluble fraction. Generally, Zn levels that were transformed by EDTA in Helwan, El-Gabal El-Asfar, El Madabeg soils were 29.86, 33.39 and 44.22%, respectively, of the total. The soils may be ordered depending upon the progress degree of Zn transformation by EDTA as: El Madabeg soil > El-Gabal El-Asfar soil >Helwan soil.

Vinase in Helwan soil caused some Zn levels to release from the poorly crystalline Fe oxide (from 36.87 to 31.39% of the total) and the residual (from 51.34 to 49.56% of the total) forms and to be transformed to the soluble and exchangeable and carbonate bound forms (from 0.76 to 5.05% and from 1.70 to 4.53% of the total, respectively). Zinc levels were made free from the organically bound, crystalline Fe oxide and residual (from 16.61 to 15.83%, from

5.62 to 4.52% and from 33.85 to 28.50%, respectively) forms of El-Gabal El-Asfar soil by vinase to be redistributed on the soluble plus exchangeable (from 2.01 to 4.28%), carbonate bound (from 12.89 to 14.42%), and poorly crystalline Fe oxide (from 25.99 to 29.20%) forms. In El-Madabeg soil, vinase induced Zn increase only in the soluble and exchangeable form from 1.94 to 10.01% of the total on the expense of decreasing Zn occluded in the Mn oxide, poorly crystalline Fe oxide and residual forms (from 5.19 to 3.08%, from 46.65 to 44.78% and from 22.97 to 20.24%, respectively). Generally, the levels of Zn that were transformed by vinase in Helwan, El-Gabal El-Asfar, El Madabeg soils were 7.54, 7.42 and 8.07%, respectively, of the total. The studied soils have almost the same progress degree of Zn transformation induced by vinase.

Poultry litter extract (PLE) gave very low Zn increases in the soluble plus exchangeable form of Helwan and El-Madabeg soils. However, Zn increase in the carbonate bound (from 1.70 to 7.23%) induced by PLE in Helwan soil was mainly on the charge of decreasing the poorly crystalline Fe oxide (from 36.87 to 33.01%) and crystalline Fe oxide (from 7.42 to 5.97%) Zn forms. There was not any Zn increase in the soluble plus exchangeable form induced by PLE in El-Gabal El-Asfar soil but there was an increase in the organically bound and poorly crystalline Fe oxide forms (from 16.61 to 18.04%, and from 25.99 to 29.20%, respectively). Levelsof Zn that were redistributed by PLE among various forms were 6.09, 3.92 and 1.61% of the total in Helwan, El-Gabal El-Asfar, El Madabeg soils, respectively.

Humic acid caused transformations very low Zn levels only from the residual form (from 51.34 to 47.51%) to the poorly crystalline Fe oxide form (from 36.87 to 39.56%) in Helwan soil, from the crystalline Fe oxide (from 5.62 to 4.28%) and residual (from 33.85 to 31.20%) forms to the carbonate bound (from 12.89 to 14.20%) and poorly crystalline Fe oxide (from 25.99 to 27.46%) forms in El-Gabal El-Asfar, and from the other forms to the soluble plus exchangeable (from 1.94 to 2.92%) and crystalline Fe oxide (from 8.91 to 9.55%) forms in El-Madabeg soil. Usman and Ghallab (2006) showed that irrigating the soil with sewage wastewater caused Zn transformation from the carbonate bound form towards the exchangeable, easily Fe-Mn oxide bound and organically bound forms. The levels of Zn that were transformed by HA among the chemical forms of Helwan, El-Gabal El-Asfar and El Madabeg soils were 3.77, 4.00 and 1.62%, respectively, of the total. These results agree with those obtained by Dudka and Chlopecka (1990). They reported that, in a loamy sand soil amended with Zn-enriched sewage sludge, an increase was observed in the easily available Zn species, from 3 to 21%, and in the weakly bound or exchangeable Zn species, from 21 to 34 % of the total Zn content.

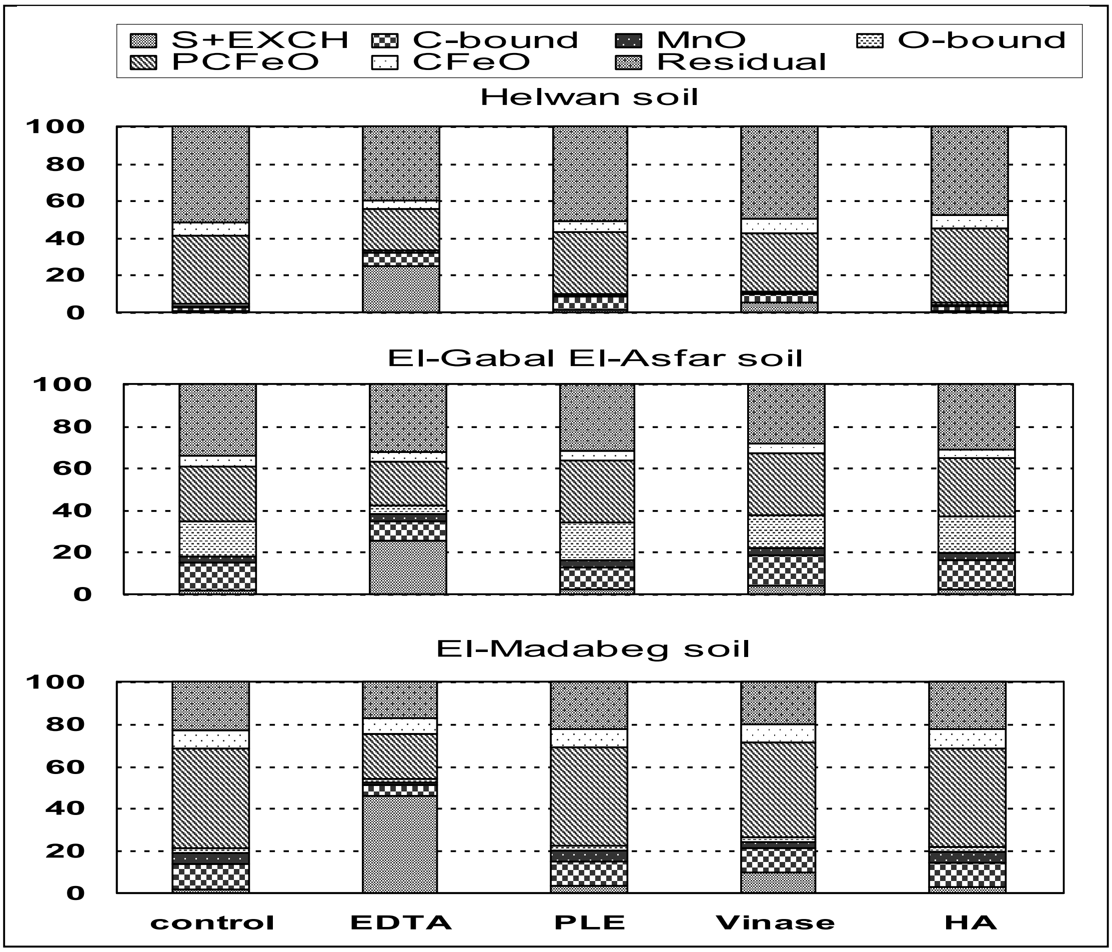

Figure 1. Redistribution of Zn (as a percentage of the total content) among its chemical forms of the studied soils treated with some organic materials.

In general, the transformation of soil Zn among its chemical forms was great in all studied soils treated with EDTA. Although the changes among Zn forms were low with vinase, especially in Helwan and El-Gabal El-Asfar soils, vinase was in the second order, with respect of the efficiency, followed by PLE and HA.

3.2 Soil Manganese

Levels of Mn in various chemical forms of Helwan, El-Gabal El-Asfar and El-Madabeg soils treated with the investigated organic materials are presented in Table 4. The concentration of soluble plus exchangeable Mn in the studied soils varied according to the used soil and the investigated organic material compared to the control treatment.

As it was shown earlier with Zn, EDTA was the most effective organic material in increasing the soluble plus exchangeable Mn in all tested soils. Vinase came in the second order and then the poultry litter extract. On the other hand, humic acid was the least efficient one in increasing the soluble and exchangeable Mn.

The increases in the soluble and exchangeable form of Mn induced by EDTA were on the expense of decreasing mainly the Mn-oxide (33.8%), and poorly crystalline Fe oxide (31.4%) forms, and partially the crystalline Fe oxide (7.0%), organically bound (20.41%) and residual (9.7%) forms in Helwan soil. However, EDTA induced increases in El-Gabal El-Asfar soil that were on the cost of decreasing mainly the organically bound (63.0%), poorly crystalline Fe oxide (44.4%) and residual (42.5%) forms. Meanwhile, in El-Madabeg soil, they were on the charge of decreasing mainly the Mn-oxide (80.6%), and partially the other forms.

Vinase was the second organic material causing increases in the soluble and exchangeable Mn of the studied soils. Manganese increases occurred in the soluble plus exchangeable and carbonate forms by vinase on the charge of the decreases mainly in the Mn oxide (28.6%) and poorly crystalline Fe oxide (43.5%) forms and partially in the organically bound (40.3%) and crystalline Fe oxide (17.8%) forms in Helwan soil, on the expense of decreasing mainly the organically bound (54.9%) poorly crystalline Fe oxide (41.6%) and residual (8.7%) forms in El-Gabal El-Asfar soil, and on the cost of decreasing mainly the Mn oxide (82.8%) and organically bound (51.6%) forms and partially the residual (6.2%) form in El-Madabeg soil.

Poultry litter extract caused low Mn increases in the carbonate bound and soluble plus exchangeable forms in Helwan soil on the charge of decreasing the other forms. It also induced low Mn increases in the carbonate bound and soluble and exchangeable forms as well as the poorly crystalline Fe oxide of El-Madabeg soil on the expense of decreasing the Mn oxide and residual forms. In El-Gabal El-Asfar soil, it also produced low Mn increases in the carbonate bound and soluble plus exchangeable forms as well as the Mn oxide form on the cost of decreasing mainly the organically bound, residual and poorly crystalline Fe oxide forms. Moreover, humic acid induced very low Mn increases in the soluble plus exchangeable form of Helwan soil, and in the Mn oxide as well as carbonate bound forms of El-Madabeg soil on the expense of decreasing the residual form. However, in El-GabalEl-Asfar soil, it caused high Mn increases in the Mn oxide and organically bound forms but low ones in the carbonate bound and soluble and exchangeable forms on the expense of the residual and poorly crystalline Fe oxide forms.

The dominant forms of the non-residual Mn were the poorly crystalline Fe oxide and Mn oxide in Helwan soil, the organically bound in El-Gabal El-Asfar soil, and the Mn oxide in El-Madabeg soil. The organically bound form dominated in El-Gabal El-Asfar soil due to the relatively high content of organic matter (5.07%) as a result of the prolonged irrigation with sewage water. The carbonate form in Helwan soil was higher than the organically bound one due to its relatively high content of $CaCO^3$ as well as the industrial activity as a source of pollution. This result agrees with those obtained by Abou-Zied (1999) and Awad (2007).

The effect of the investigated organic materials on the redistribution of various Mn forms, as a percentage of the total Mn, of the studied soils is shown in Figure 2. Manganese levels were released from the Mn oxide, poorly crystalline Fe oxide and residual forms (from 23.14 to 15.32%, from 21.03 to 14.43% and from 30.86 to 27.87%, respectively, of the total content) of Helwan soil by EDTA and redistributed to the soluble plus exchangeable and carbonate forms which their Mn levels increased from 0.78 to 18.37% and from 8.98 to 10.42, respectively, of the total Mn. However, in El-Gabal El-Asfar soil treated with the EDTA, the levels of Mn decreased in the organically bound, poorly crystalline Fe oxide and residual forms from 33.14 to 12.27%, from 15.05 to 8.29% and from 39.53 to 22.74%, respectively, of the total Mn. The released Mn levels from these forms of this soil were transformed to the soluble plus exchangeable and Mn oxide forms resulting in Mn increases in theseforms from 0.40 to 39.32% and from3.76 to 9.68%, respectively, of the total Mn. Moreover, EDTA in El-Madabeg soil made Mn to be free from the Mn oxide, organically bound, poorly crystalline Fe oxide and residual forms (from 28.11 to 5.46%, from 9.23 to 4.86%, from 9.92 to 4.61% and from 42.64 to 40.25%, respectively, of the total Mn) and to transform to the soluble and exchangeable form which its Mn increased from 0.45 to 37.87% of the total Mn. Generally, levels of Mn that were transformed by EDTA in Helwan, El-Gabal El-Asfar and El-Madabeg soils were 19.03, 44.91 and 37.42%, respectively, of the totalsoil Mn. The studied soils may be ranked according to the progress degree in Mn transformation induced by EDTA as El-Gabal El-Asfar soil > El-Madabeg soil >Helwan soil.

Vinase in Helwan soil caused Mn levels mainly in the poorly crystalline Fe oxide (from 21.03 to 11.60% of the total) and Mn oxide (from 23.14 to 16.14% of the total) forms to transform to the soluble plus exchangeable and carbonate bound forms which their Mn increased from 0.78 to 10.76% and from 8.98 to 18.80%, respectively, of the totalsoil Mn. On the other hand, in El-Gabal El-Asfar soil, it released Mn levels from mainly the organically bound (from 33.14 to 14.65% of the total), poorly crystallineFe oxide (from 15.05 to 8.61% of the total) and residual (from 39.53 to 35.40% of the total) forms and redistributed them to the soluble plus exchangeable (from 0.40 to 8.40% of the total) and carbonate bound (from 2.60 to 23.60% of the total) forms. Moreover, it induced Mn transformations in El-Madabeg soil mainly from the Mn oxide form (from 28.11 to 4.77% of the total) and partially from the organically bound (from 9.23 to 4.42% of the total) and residual (from 42.64 to 39.56% of the total) forms to the soluble and exchangeable, and carbonate bound forms which their Mn levels increased from 0.45 to 13.22% and from 4.11 to 25.80%, respectively, of the total. Levels of Mn that were redistributed by vinase among the chemical forms of Helwan, El-Gabal El-Asfar and El-Madabeg soils were 19.80, 29.00 and 34.46, respectively, of the total. The studied soils could be ordered with respect to the progress degree in Mn transformation by vinase as El-Madabeg soil > El-Gabal El-Asfar soil >Helwan soil.

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Low Mn transformations among various forms induced by PLE occurred in the studied soils (Figure 2). Poultry litter extract caused low Mn levels of Helwan soil from the Mn oxide and poorly crystalline Fe oxide (from 23.14 to 16.14% and from 21.03 to 19.84%, respectively) forms to spread out to the carbonate bound and soluble plus exchangeable forms (from 8.98 to 17.25% and from 0.78 to 2.52%, respectively). In El-Gabal El-Asfar soil, it caused some Mn levels of the organically bound (from 33.14 to 21.72%) and residual (from 39.53 to 33.67%) forms to redistribute to the Mn oxide (from 3.76 to 12.53%), carbonate bound (from 2.60 to 8.76%) and soluble plus exchangeable (from 0.40 to 3.54%) forms. Meanwhile, few Mn levels of the Mn oxide (from 28.11 to 13.71%) and organicallybound (from 9.23 to 8.02%) forms of El-Madabeg soil were transformed by PLE to the carbonate bound (from 4.11 to 15.12%).

Table 4. Effect of some organic materials on the redistribution of manganese (Mn) among various forms of the studied soils.

Soil	Treatment	Mn forms (mg/kg)								
		S+EXCH	**C-bound**	**MnO**	**O-bound**	**PCFeO**	**CFeO**	**Sum**	**Residual**	**Total**
Helwan	control	2.38	27.31	70.33	12.30	63.93	33.94	210.20	93.80	304.00
	EDTA	55.85	31.67	46.57	9.73	43.87	31.58	219.27	84.73	304.00
	PLE	7.66	52.48	49.66	10.16	60.37	32.29	212.62	91.64	304.26
	Vinase	33.48	58.53	50.23	7.34	36.10	27.92	213.60	97.70	311.30
	HA	4.76	28.46	70.27	12.30	62.90	32.93	211.61	92.44	304.04
	$LSD_{0.05}$	0.88	1.73	3.79	1.33	3.46	2.75	-	0.88	-
El-Gabal El-Asfar	control	1.67	10.93	15.80	139.17	63.20	23.19	253.96	166.04	420.00
	EDTA	165.13	11.22	40.64	51.53	34.83	21.12	324.48	95.52	420.00
	PLE	14.89	36.82	52.67	91.30	59.37	23.38	278.42	141.88	420.30
	Vinase	35.94	101.00	21.03	62.70	36.87	18.97	276.51	151.52	428.03
	HA	18.13	13.48	70.47	164.57	48.83	24.22	339.70	80.35	420.05
	$LSD_{0.05}$	1.15	1.15	1.63	4.76	2.39	2.26	-	2.51	-
El-Madabeg	control	1.69	15.41	105.4	34.6	37.19	20.81	215.10	159.90	375.00
	EDTA	142.00	10.53	20.46	18.22	17.29	15.55	224.05	150.95	375.00
	PLE	20.49	56.74	51.45	30.09	41.12	19.29	219.17	155.98	375.15
	Vinase	50.10	97.78	18.09	16.73	31.03	15.34	229.07	149.92	378.99
	HA	2.66	20.3	118.43	32.78	31.15	20.33	225.67	149.38	375.04
	$LSD_{0.05}$	1.1	1.81	2.75	1.96	1.84	3.23	-	0.98	-

and soluble and exchangeable (from 0.45 to 5.46%) forms.

The levels of Mn that were transformed by PLE among the chemical forms of Helwan, El-Gabal El-Asfar and El Madabeg soils were 10.01, 18.07 and 16.02%, respectively, of the total Mn.

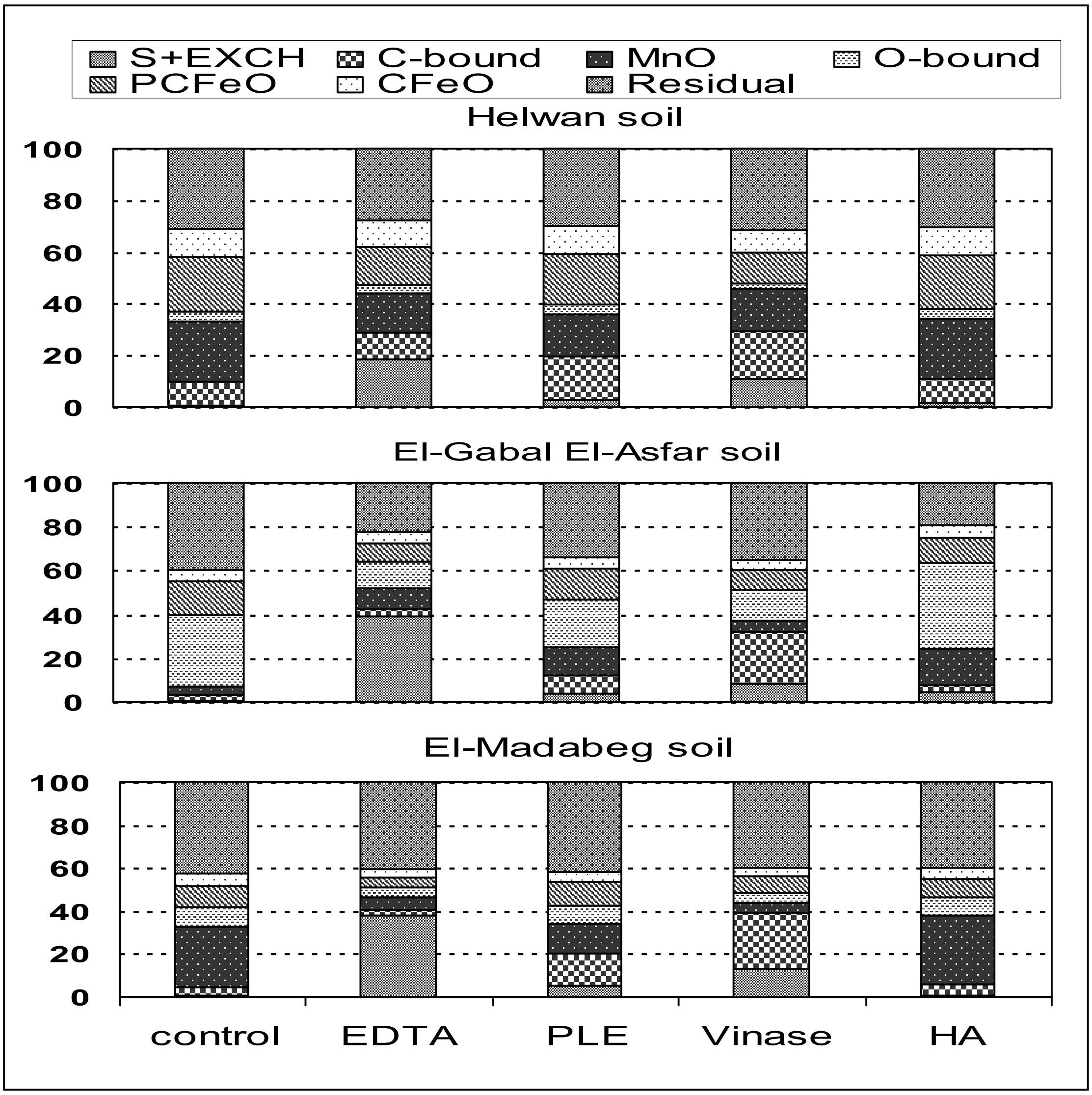

Figure 2. Redistribution of Mn (as a percentage of the total content) among its chemical forms of the studied soils treated with some organic materials.

Moreover, very low Mntrans-formations were induced by humic acid in Helwan and El Madabeg soils. Few Mn levels were transformed by HA in El Madabeg soil from the re-sidual and poorly crystalline Fe oxide forms mainly to the Mn oxide form. In El-Gabal El-Asfar soil, reasonable Mn levels were released by HA from the residual and poorly crystalline Fe oxide forms and redistributed to the Mn oxide, organically bound and soluble plus exchangeable forms. Manganese percentages that redis-tributed by HA among various forms of Helwan, El-Gabal El-Asfar and El Madabeg soils were 1.17, 22.98 and 5.46%, respectively, of the total Mn.

The distribution order of Mn in all studied soils according to Mn abundance changed with using vari-ous organic materials. However, it did not alter in Helwan soil treated with HA and it had very little shift induced by HA in El Madabeg soil. On the other hand, humic acid caused a great change in the distribution order of Mn forms in El-Gabal El-Asfar soil.

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تحولات صور الزنك والمنجنيز في بعض الأراضي المصرية الملوثة والمعاملة بمواد عضوية

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الملخص

تم إجراء تجربة تحضين باستخدام ثلاثة أنواع ترب ملوثة من حلوان، الجبل–الأصفر (محافظة القاهرة) وعرب المدابغ (محافظة أسيوط) لمدة ١٦ أسبوعاً لتقييم آثر اضافة أربعة مواد، شملت هذه المواد العضوية EDTA ، كمادة عضوية صناعية وكذلك مستخلص فرشة الدواجن (PLE) والفيناس(vinase) وحامض الهيوميك (HA) كمواد عضوية طبيعية على تحولات وإعادة توزيع الزنك والمنجنيز بين صورهما الكيميائية وهي الذائب المتبادل ، والمرتبط بالكربونات ، المرتبط بأكاسيد المنجنيز ، المرتبط بالمادة العضوية ، المرتبط بأكاسيد الحديد ضعيفة التبلور ، المرتبط بأكاسيد الحديد المتبلورة ثم المتبقي.أشارت النتائج الى ان تحولات الزنك بين صوره الكيميائية كان عظيما في كل الاراضى تحت الدراسة عند استخدام ال EDTA.

حدث زيادة فى الزنك الذائب + المتبادل بواسطة الEDTA نتيجة تحولات الزنك من المرتبط بصور اكاسيد الحديد ضعيفة التبلور والمتبقى فى أراضى حلوان ومن المرتبط بصور الكربونات والمادة العضوية واكاسيد الحديد ضعيفة التبلور والمتبلورة فى أراضى الجبل الاصفر ومن بصور الكربونات واكاسيد المنجنيز واكاسيد الحديد ضعيفة التبلور والمتبقى فى أراضى المدابغ. وكما هو موضح بالنسبة للزنك كان الEDTA هو اكثر المواد العضوية تاثيرا على زيادة صورة المنجنيز الذائب + المتبادل فى جميع الترب تحت الدراسة. كما كان الفينا س فى المرتبة الثانية ثم اتبعه مستخلص فرشة الدواجن وحامض الهيوميك. وكانت الزيادة فى صورة المنجنيز الذائب والمتبادل نتيجة اضافة الEDTA على حساب النقص في المنجنيز المرتبط بصور اكاسيد المنجنيز (٣٣,٨%) وأكاسيد الحديد ضعيفة التبلور (٣١,٤ %) والمتبلورة (٧%) والمادة العضوية (٢٠,٤ %) في تربة حلوان.