5 *Egypt. J. Soil Sci.* 44, No. 1, pp. 55-71 (2004)

Remediation of Certain Heavy Metals Status in Musturud and Elgabal-Elasfar Soils. I. Copper and Cobalt

M.A.O. Elsharawy and M.M. Elbordiny
Soils Department, Faculty of Agriculture, Ain Shams University, Cairo, Egypt.

THE AIM OF this work is to assess and evaluate the effect of certain amendments, *i.e.*, ground cotton stalks, rock phosphate, K_2EDTA and citric acid applied to contaminated soils at Qalubiya Governorate; namely Musturud, clay, Vertic Torrifluvents and Elgabal-Elasfar, sandy loam, Torriorthent; in soil columns experiment on the availability and mobility of Cu and Co and their transformation among the different soil fractions. All applied amendments altered concentrations of Cu and Co forms in the studied soils. Application of ground cotton stalks or rock phosphate amendment to metal-contaminated soils redistributed Cu and Co from potentially available form to the more complex one; thus reducing Cu and Co solubility and bioavailability. On the other hand, K_2EDTA and/or citric acid solubilized Cu and Co from relatively insoluble form indicating that these amendments have the ability to mobilize certain amounts of Cu from the upper to the lower layers of such contaminated soils. In both studied soils, ground cotton stalks were the best amendment in decreasing the DTPA-extractable Cu by about 57.4 and 55.1%, compared to control in Musturud and Elgabal-Elasfar soils, respectively. Cobalt extractability was effectively lowered by addition of citric acid treatment; values being 64.7and 50.8%, compared to control in Musturud and Elgabal-Elasfar soils, respectively.

Copper concentration was in the normal range for shoots of broad bean grown on Musturud soil, whereas that for Elgabal-Elasfar soil was higher than the normal range, except for ground cotton stalks and rock phosphate treatments. Cobalt concentration in plant shoots was excessive either for treated or untreated soils.

Keywords: Remediation, Contaminated soils, Copper, Cobalt, Fractions.

Concentrations of heavy metals in different plant parts are highly related to soil contamination. The prolonged period of irrigation with sewage water has markedly accumulated certain heavy metals in faba bean and citrus grown on Abu Rawash area (Khalil, 1990), bean plants grown on contaminated soils in Helwan, (Badawy and Helal, 1997) and corn and citrus grown on Elgabal-Elasfar farm (Mosalem, 1997). However, Elsokkary and Sharaf (1996) obtained similar findings for faba bean, clover and tomato grown on alluvial soil, Abo-Hommos area, Alexandria, irrigated with a mixture of agricultural drainage, domestic and industrial effluents. Recently, El-Motaium and Badawy (2000) found that heavy metals were concentrated mainly in the roots of cabbage plants and orange trees, which were irrigated for 80 years with sewage water in Elgabal-Elasfar soil. In cabbage plants, heavy metals content is arranged in the following order: roots> leaves> stems, whereas for orange trees the order is as follows: roots> leaves> fruit peel> fruit pulp.

Several authors have recently discussed methods for remediating metal-contaminated soils. For soils not heavily polluted with trace metals, the advisable methods to prevent plant tissue contamination are based on two processes- immobilization of mobile fractions of metals and leaching of easily soluble fractions. Treating soil with phosphate either in rock phosphate form or other P forms seemed to reduce heavy metals solubility and transformation in soil. Ma *et al.* (1995) showed that rock phosphate effectively immobilized Pb from aqueous solutions, with Pb immobilization ranging from 39 to 100 %. Chen *et al.* (1997) studied the sorption and desorption of dissolved Pb, Cd and Zn from aqueous solutions and contaminated soils by mineral apatite. Sorption results showed that apatite was very effective in retaining Pb and was moderately effective in attenuating Cd and Zn. On the other hand, the chelating agent EDTA is one of the strongest synthetic chelating agents and forms much stronger complexes with most metals than naturally occurring organic ligands. Li and Shuman (1997) leached Zn, Pb and Cd from polluted soils by H_2O, EDTA, and $CaCl_2$ solution and found that a large portion of these metals was leached, particularly Pb with EDTA solution.

The objective of this study is to improve contaminated soils by applying certain amendments to assess their effects on the bioavailability of Cu and Co. Mobility of the concerned metals was also evaluated.

Material and Methods

Soil columns experiment was carried out under greenhouse conditions using contaminated soil samples irrigated with wastewater for long period. Soil samples were collected from Musturud, clay, Vertic Torrifluvents, irrigated with industrial wastewater and Elgabal-Elasfar, sandy loam, Torriorthent, irrigated with sewage water, Qalubiya Governorate at a depth of 0-20 cm as the most contaminated layer in soil profile. Some characteristics of the selected soils are shown in Table 1a.

Application of soil amendments

Soil samples were air-dried and ground separately and thereafter were packed in PVC columns (60-cm long and 20 cm internal diameter). The column was vibrated during packing and the soil was packed to a height of 55 cm afterwards; moisture content was brought to field capacity using tap water. Each treatment was replicated three times. Five treatments with the characteristics shown in Table 1b were applied.

1- Control (soil- without amendments).

2- Ground cotton stalks (40 g. kg^{-1} soil).

3- Rock phosphate at a rate of 30 g. kg^{-1}soil.

4- K_2EDTA (di potassium ethylene di amine tetra acetic acid) at a rate of 1 g. kg^{-1} soil and the pH of the solution was adjusted to 7.0 using HCl 1:3 (acid: water).

5- Citric acid at a rate of 0.98 g. kg^{-1} soil. The amounts of citric acid were dissolved in irrigation water giving a solution of pH 6.5.

TABLE 1a. Some physical and chemical characteristics of the selected soils.

Area	Particle size distribution, %			Texture class	$CaCO_3$	O.M	pH (1:2.5)	ECe $dS.m^{-1}$	Total heavy metal, mg. kg^{-1}	
	Clay	Silt	Sand		%				Cu	Co
Musturud#	59.7	26.2	14.1	Clay	3.21	1.12	7.84	2.51	80.11	21.61
Elgabal-Elasfar	33.2	25.8	41.1	Sandy Loam	0.75	4.92	7.28	0.69	153.37	39.08

Musturud soil is irrigated from Musturud drain, while Elgabal-Elasfar soil is irrigated from Elgabal - Elasfar drain.

TABLE 1b. Concentration of some nutrients in different materials used as soil amendments.

Treatment	N	P	K	Fe	Zn	Cu	Co	Ni	Pb
	%			mg. kg^{-1}					
Ground cotton stalks	1.16	0.31	1.86	214.6	17.26	24.39	0.02	0.08	0.05
Rock phosphate	0.11	11.21	1.76	427.5	58.43	1.18	0.09	0.12	0.23
K_2EDTA	9.74	-	0.03	28.61	0.84	18.32	0.02	0.08	0.05
Citric acid	-	-	-	2.23	0.42	0.67	0.02	0.06	0.03

Ground cotton stalks treatment was applied through mixing with soil in the column; 45 days later, rock phosphate treatment was mixed with other soil columns. Moisture content of treated soil columns was kept at field capacity.

Then 45 days later (90 days from the first treatment application), K_2EDTA and/or citric acid treatments were added to soil in the columns through irrigation water.

The columns were cultivated with broad bean, *(Vicia faba* L., cv Giza 461*)*. Three seeds of broad bean were planted and soil moisture was maintained at field capacity. After germination, seedlings were thinned to one plant per column.

Soil samples were collected after 80 days from planting at depths of 0 to 15, 15 to 30 and 30 to 55 cm. The collected samples were air dried, crushed, sieved through a 2-mm sieve and stored for copper and cobalt determination.

Plant samples (shoots and roots) were collected at the same time of soil sampling. The plant samples were washed with tap water and 10^{-4} M HCl, then oven dried at 65°C for 48 hr. Plant materials were ground, mixed well and kept for copper and cobalt determination.

Sequential extraction

The method of sequential extraction used in this study was outlined by Tessier *et al.* (1979). Copper and cobalt were partitioned into five operationally defined fractions: exchangeable, bound to carbonates, reducible (bound to Fe-Mn oxides), oxidizable (bound to organic matter and/or sulphides) and residual. Each of these chemical fractions is operationally defined as follow:

Exchangeable (EXC): Soil (1g dry wt.) was extracted with 8ml 1.0 M $MgCl_2$ (pH 7) in teflon centrifuge tubes for 1 hr at 25^0C with continuous agitation.

Carbonate (CAB): Residue from exchangeable fraction was extracted with 8 ml of pH 5, 1.0 M sodium acetate for 5 hr at 25^0C with continuous agitation.

Reducible (OXD): Residue from carbonate fraction was extracted with 20 ml of 0.04 M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25 % acetic acid (v/v) for 5 hr at 96^0C with occasional agitation.

Oxidizable (ORG): Residue from reducible fraction was extracted with 2 ml of 0.02 M HNO_3 and 5ml of 30% H_2O_2 adjusted to pH 2 with conc. HNO_3. The mixture was heated to 85^0C for 2 hr with occasional agitation. Second 3-ml of 30% H_2O_2 (pH 2 with conc. HNO_3) were then added and the sample was heated again to 85^0C for 3 hr with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20 % (v/v) HNO_3 were added and the sample was diluted to 20 ml and agitated continuously for 30 min.

Residual (RES): Residue from the organic fraction was heated on a hot plate with 2 ml of conc. $HClO_4$ and 10 ml of conc. HF until almost dry; subsequently a second addition of $HClO_4$ (1ml) and HF (10 ml) were made and again the mixture was evaporated to near dryness. Finally, 1ml of $HClO_4$ was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 10 ml 12 M HCl and diluted to 25 ml.

Following each extraction or wash, mixtures were centrifuged at 12000 gravity for 30 min. prior to the start of the next extraction step, the residues were shaken with 8 ml water for 30 min., centrifuged and the wash solutions were discarded.

Total Cu and Co were determined after digestion with hydrofluoric/ perchloric acids mixture (Jackson, 1958). Chemically available forms of elements were evaluated by extracting the soil with DTPA according to Lindsay and Norvell (1978).

Copper and Co were determined in the wet acid digest of 2g of plant materials according to Chapman and Pratt (1961).

Heavy metals content of DTPA extract as well as digestion solutions of soil and plant samples were analyzed using Atomic Absorption Spectroscopy.

Results and Discussion

Copper and cobalt distribution in soil fractions

The behavior of heavy metals in soils depends not only on the level of contamination as expressed by the total content, but also on the form of the metal. Sequential extraction techniques which provide a useful tool to understand the chemistry of metals in soils. As described above, the partitioning of the metals in the studied soils is based on the sequential extraction procedure of Tessier *et al.* (1979) that evaluates the distribution of metals among the exchangeable, carbonate, oxide, organic and/ or sulphide and residual fractions or forms. Firstly, a high significant correlation coefficient value was obtained between the determined total metal in soil and sum of the different extracted fractions yielding 0.969 and 0.947, for Cu and Co, respectively. Therefore, the employed procedure succeeded in recovering amounts almost closed to the total contents of the different elements.

In untreated Musturud soil, Cu was mainly present in the RES and ORG-Cu fractions, while the lowest values were for EXC form, with the order being: RES> ORG> OXD= CAB> EXC, (Table 2). On average, the metal part existing in the RES, ORG, OXD, CAB and EXC fractions were represented by 47.6, 24.0, 11.1, 11.2 and 6.1 % of the sum of Cu fractions, respectively (Fig.1). It is well known that soil organic matter form very stable complexes with Cu compared to any other divalent transition metal as reported by Stevenson & Ardakani (1972) and McBride (1994). Dowdy *et al.* (1991) who reported that copper may either enter the exchange complex or be chelated by the organic matter. However, Co was mainly found in the RES form followed by OXD, while the lowest values were for EXC-Co. Mclaren *et al.* (1986) showed that soluble cobalt was clearly sorbed on the iron oxides present in soil. Grana *et al.* (1991) reported that cobalt bound to both iron and manganese oxides accounted for most of the total cobalt.

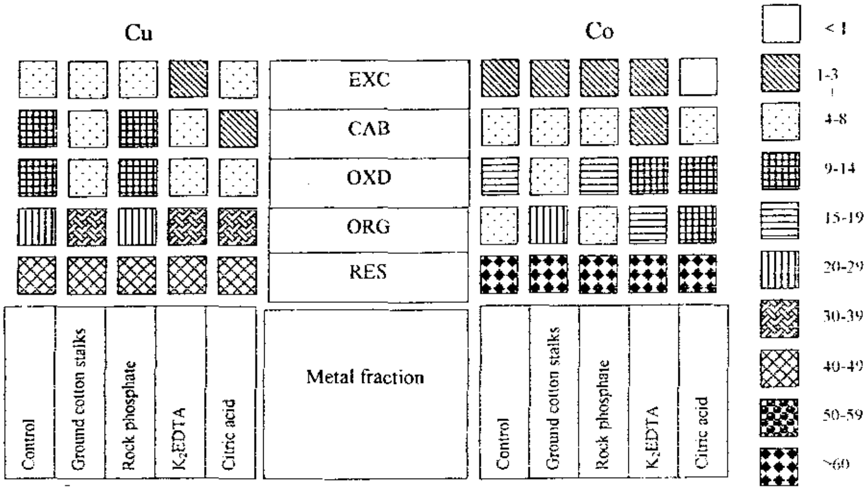

Fig. 1. Diagram showing the percentages of different forms of Cu and Co extracted by sequential extraction from Musturud soil.

Concerning Cu distribution in soil fractions due to application of different amendments through successive sections of Musturud soil, columns analysis data presented in Table 2 show that application of ground cotton stalks chelated certain amounts of Cu from EXC, CAB and OXD fractions. Thus, ground cotton stalks decreased EXC, CAB, and OXD-Cu fractions, while increased ORG-Cu in Musturud soil, which reached 44.5 % above the control; but RES-Cu apparently was not affected. Also, application of ground cotton stalks to Musturud soil decreased EXC, CAB and OXD-Co by 41, 32 and 76 % less than the control treatment, respectively. In contrast, ORG-Co increased with application of ground cotton stalks recording 3.4 fold that of the control treatment, while RES-Co seemed to be not affected.

Application of rock phosphate to the tested soil led to decrease EXC and CAB-Cu. Decreases represented 24 and 14% compared to the control, respectively. On the other hand, OXD-Cu was markedlyincreased with the application of rock phosphate reaching 23 % above the control, while ORG and RES-Cu fractions were not affected. However, application of rock phosphate decreased EXC, OXD and ORG-Co but increased CAB-Co and caused no change in RES-Co form.

TABLE 2. Effect of different amendments on Cu and Co fractions in Musturud soil.

Treatment	Depth, cm	Cu fractions						Co fractions					
		EXC[#]	CAB	OXD	ORG	RES	Sum	EXC	CAB	OXD	ORG	RES	Sum
		mg .kg^{-1}											
Control	0-15	3.96	7.21	8.20	19.20	36.22	74.79	0.28	1.16	3.28	1.18	12.52	18.42
	15-30	4.78	8.59	8.13	17.22	36.52	75.24	0.29	1.23	3.50	1.21	12.52	18.75
	30-60	4.95	9.35	8.76	17.81	34.71	75.58	0.31	1.24	3.66	1.25	12.53	18.99
Ground cotton stalks	0-15	2.21	5.94	5.12	25.14	36.10	74.51	0.12	0.87	1.09	4.04	12.41	18.53
	15-30	2.66	4.63	5.06	25.81	36.13	74.29	0.19	0.83	0.75	3.82	12.50	18.09
	30-60	2.83	3.18	4.32	27.33	36.23	73.89	0.21	0.75	0.63	4.34	12.50	18.43
Rock phosphate	0-15	3.16	7.43	10.21	18.00	36.13	74.93	0.25	1.25	2.88	1.06	12.42	17.86
	15-30	3.47	7.75	10.42	17.60	36.20	75.44	0.25	1.34	3.15	1.08	12.51	18.33
	30-60	3.73	6.44	10.33	17.62	36.41	74.53	0.22	1.38	3.12	1.13	12.62	18.47
K_2EDTA	0-15	1.88	4.35	6.05	25.01	36.20	73.49	0.16	0.38	1.69	2.98	12.53	17.74
	15-30	2.61	5.27	5.26	25.83	36.51	75.48	0.18	0.65	2.28	2.72	12.54	18.37
	30-60	2.87	3.92	3.57	28.61	35.78	74.75	0.25	0.73	2.32	2.55	12.51	18.36
Citric acid	0-15	1.30	2.19	6.97	28.03	36.00	74.49	0.05	0.46	2.50	2.92	12.52	18.45
	15-30	3.63	2.76	3.42	28.24	36.11	74.16	0.11	0.83	2.60	2.69	12.53	18.76
	30-60	4.06	2.16	3.65	30.32	36.32	76.51	0.17	1.15	2.77	1.85	12.51	18.45

[#] EXC, CAB, OXD, ORG and RES mean exchangeable, carbonate, reducible bound, organically bound and residual fractions.

Values of EXC, CAB and OXD-Cu were clearly reduced by increasing the solubilized amounts of certain Cu fractions as a result to K_2EDTA treatment. ORG-Cu was markedly increased with the application of K_2EDTA to the studied soil, while, RES-Cu was not affected. Christensen (1984) reported that organic ligands such as EDTA were effective in desorbing trace elements from adsorbed surfaces. He added that the metals were immobilized by organic ligands in the order: Cu > Zn > Pb and the immobilization effect depends on soil reaction and the kind of mineral components present in soils.

Similarly, citric acid also decreased EXC, CAB and OXD-Cu in Musturud soil, such decreases recorded 34, 72 and 44 % less than the control, respectively. Whereas, ORG-Cu increased by about 60 % over the control, but citric acid addition did not alter RES-Cu fraction. ORG-Co showed similar trend to those of Cu recording 127 or 106 % increase above the control treatment with K_2EDTA or citric acid additions for Musturud soil, respectively. While marked decreases in the EXC, CAB and OXD-Co were obtained and RES-Co did not show change. The lowest EXC-Cu and Co amounts were found in the upper layer (0-15 cm) of soil column treated with K_2EDTA or citric acid. This could be due to the increasing downward mobility of such metal-fraction.

Data of Cu and Co occurred in different fractions of Elgabal-Elasfar soil are presented in Table 3 and illustrated in Fig. 2. Copper in the light texture soil of Elgabal-Elasfar, irrigated for long time with sewage water, was mainly associated with the organic matter making ORG-Cu the dominant among metals fractions. Whereas, Co- fractions showed similar trend to that obtained for Musturud soil. Effect of soil texture and organic matter on the status of Cu was also reported by Shuman (1979) who obtained similar trend.

As have been found in Musturud soil, the applied treatments decreased amounts of EXC-Cu compared to control, whereas citric acid gave the lowest EXC-Cu values. The CAR-Cu fraction markedly decreased with all treatments, except for rock phosphate that did not alter CAB-Cu. Similar to that found for Musturud soil, except for rock phosphate, all the applied treatments markedly decreased the OXD-Cu values compared to control. Also, an obvious trend was observed for ORG-Cu values that ground cotton stalks, K_2EDTA and citric acid treatments increased Cu values, while rock phosphate resulted in an opposite effect.

The applied treatments decreased amounts of EXC-Co. The CAB-Co fraction increased only with rock phosphate application to soil recording 14% over the control treatment. Meanwhile, such Co fraction values were markedly decreased with the application of other treatments. Similar to that found for Musturud soil, all the applied treatments decreased the OXD-Co values compared to control one. It is interesting to note that, an obvious trend was observed for ORG-Co values as ground cotton stalks, K_2EDTA or citric acid treatments increased Co values, but rock phosphate decreased these values.

TABLE 3. Effect of different amendments on Cu and Co fractions in Elgabal-Elasfar soil.

Treatment	Depth, cm	Cu fractions						Co fractions					
		EXC*	CAB	OXD	ORG	RES	Sum	EXC	CAB	OXD	ORG	RES	Sum
		mg .kg^{-1}											
Control	0-15	11.10	18.42	13.32	67.43	39.10	149.37	0.91	0.57	3.22	11.00	19.11	34.81
	15-30	11.42	20.80	13.91	62.82	39.51	148.46	0.96	0.62	3.25	11.51	19.20	35.54
	30-60	11.93	21.10	12.60	63.10	39.51	148.24	1.02	0.58	3.58	11.11	19.23	35.52
Ground cotton stalks	0-15	5.61	12.11	10.30	80.30	39.12	147.44	0.51	0.41	1.47	13.22	19.20	34.81
	15-30	5.88	12.45	10.60	80.11	39.43	148.47	0.51	0.46	1.52	13.20	18.91	34.60
	30-60	6.40	12.78	10.12	80.60	39.61	149.51	0.74	0.51	1.61	13.21	19.42	35.49
Rock phosphate	0-15	9.22	19.01	13.73	67.10	39.10	148.16	0.89	0.64	2.19	10.63	19.94	34.29
	15-30	9.08	19.02	15.21	59.32	39.10	141.73	0.95	0.71	2.59	10.84	19.21	34.30
	30-60	9.54	21.90	14.80	62.44	40.32	149.00	0.59	0.67	2.62	10.91	19.40	34.19
K_2EDTA	0-15	7.14	9.32	10.11	85.21	39.22	151.00	0.25	0.32	0.38	13.82	18.82	33.59
	15-30	7.61	9.69	12.32	82.20	39.31	151.13	0.37	0.46	0.80	14.62	18.91	35.16
	30-60	9.22	9.75	11.32	80.31	39.54	150.14	0.51	0.49	1.15	17.93	19.10	39.18
Citric acid	0-15	2.58	6.144	12.21	89.22	39.24	149.39	0.03	0.14	1.24	13.50	19.32	34.23
	15-30	2.63	6.751	11.70	88.24	39.40	148.72	0.08	0.30	1.30	13.60	19.61	34.89
	30-60	9.98	14.22	12.40	75.02	39.52	151.14	0.11	0.35	1.84	13.21	19.71	35.22

* EXC, CAB, OXD, ORG and RES mean exchangeable, carbonate, reducible bound, organically bound and residual fractions.

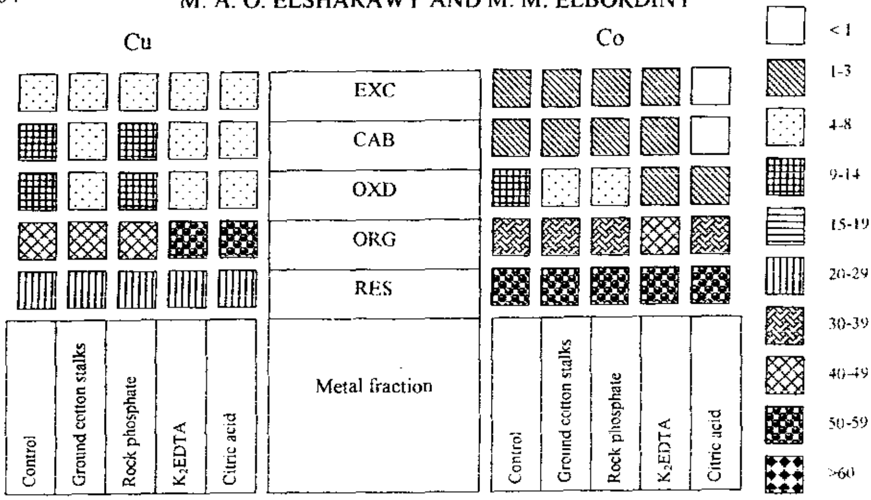

Fig. 2. Diagram showing the percentages of different forms of Cu and Co extracted by sequential extraction from Elgabal-Elasfar soil.

DTPA- extractable Cu and Co

Concerning chemically available Cu and Co in the studied soils as affected by application of different amendments, Table 4 and Fig. 3 show that chemically available Cu extracted from the upper section (0-15 cm) of the treated Musturud soil with ground cotton stalks was markedly decreased by about 57.4 % compared with control treatment. Chemically available form of Cu was affected due to rock phosphate addition. On average, the extracted amounts of Cu in the soil treated with rock phosphate were lower than that of control but higher than that of ground cotton stalks treatment. Gary *et al.*(1994) declared that the addition of phosphate could cause precipitation of the corresponding trace element containing solid phase which could be reflected on the bioavailability of the element. Application of K_2EDTA decreased amount of chemically available Cu in Musturud soil column compared to control treatment and this could be due to increasing Cu movement through soil column as a result to its complexation with the organic ligand. However, application of citric acid decreased amounts of chemically available Cu in the upper section (0-15 cm) by about 60 % less than the control. Decreasing DTPA-extractable Cu in soil column was accompanied by the downward movement of Cu as a result of increasing Cu solubility due to addition of K_2EDTA or citric acid. The chelating agent EDTA is one of the strongest synthetic chelating agents and forms much stronger complexs with most heavy metals than naturally occurring organic ligands, (Norvell, 1991). However, Wasay *et al.* (1998) reported that salts of citrate effectively removed Cu, Zn and Cd from contaminated soil as effectively as DTPA and EDTA. DTPA-extractable Co resulted from the ground cotton stalks treated soil was decreased compared with control treatment. This agrees with the findings of Bloomfield (1981) who noticed that soils rich in organic matter have low Co availability. Chemically available Co was decreased with rock phosphate addition. Application of K_2EDTA or citric acid decreased amount of chemically available Co in Musturud soil column due to increasing movement of EXC-Co from upper layer to the lower one.

TABLE 4. Values of DTPA-extractable Cu and Co of the studied soils as affected by different amendments.

Treatment	Depth, cm	Musturud soil		Elgabal-Elasfar soil	
		Cu	Co	Cu	Co
		mg .kg^{-1}			
Control	0-15	6.98	0.34	15.90	1.28
	15-30	7.16	0.35	16.33	1.37
	30-60	7.31	0.38	16.61	1.63
Ground cotton stalks	0-15	2.97	0.12	7.14	0.63
	15-30	2.80	0.16	9.53	0.72
	30-60	3.04	0.20	9.76	0.77
Rock phosphate	0-15	4.20	0.24	8.92	1.09
	15-30	4.75	0.25	11.10	1.04
	30-60	5.12	0.28	13.2	1.36
K_2EDTA	0-15	2.77	0.15	8.38	0.74
	15-30	2.95	0.21	10.72	0.78
	30-60	3.43	0.38	12.31	0.85
Citric acid	0-15	3.66	0.08	5.59	0.24
	15-30	4.69	0.12	12.21	0.35
	30-60	5.83	0.15	14.20	0.63

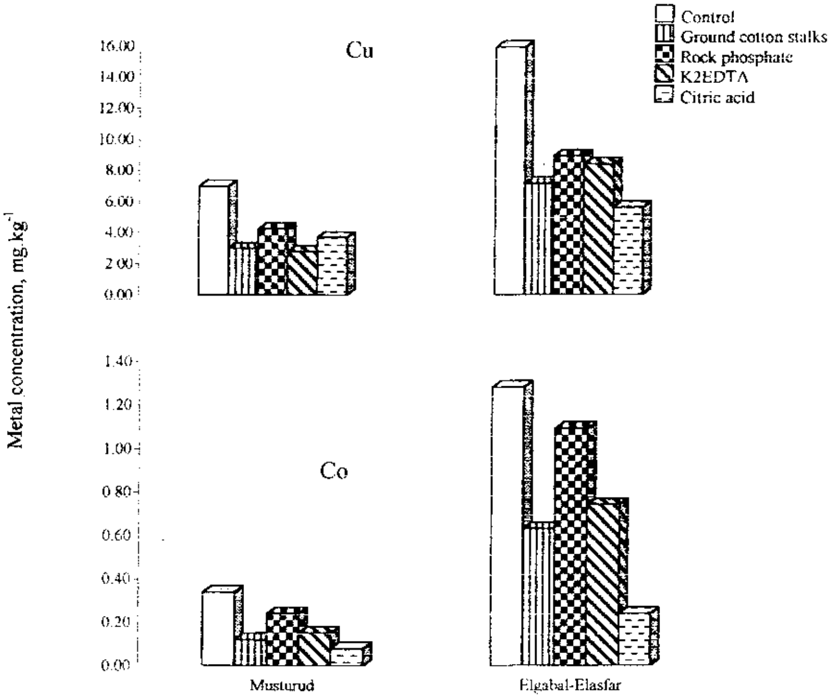

Fig. 3. Values of DTPA-extractable Cu and Co in the upper section (0-15 cm) of the studied soils as affected by different amendments.

Values of chemically available Cu extracted from Elgabal-Elasfar soil generally decreased with application of the different treatments with the highest amounts for ground cotton stalks and lowest one for K_2EDTA. The obtained results agree with those found by Allison (1973) who declared that the organic matter in coarse texture soils will also tend to reduce losses of added copper salts by leaching.

Also, values of chemically available Co extracted from the upper section (0-15 cm) of Elgabal -Elasfar soil, were generally decreased with application of ground cotton stalks, rock phosphate, K_2EDTA or citric acid amendments and recorded 51, 19, 42 or 81 % less than the control, respectively.

From the above-discussed results, it is clear that ground cotton stalks treatment resulted in obtaining the lowest chemically available Cu values in both soils. Thus, this treatment could be considered the best one. Meanwhile, citric acid treatment moved more Co from the soil column, which was reflected on reduction of the DTPA-extractable Co, particularly from the upper section.

Dry weight and Cu and Co content of broad bean

Dry weight and concentrations of Cu and Co in broad bean plant as affected by different amendments applied to the contaminated soils are shown in Table 5.

TABLE 5. Dry weight (g/ column) and Cu and Co concentrations (mg. kg^{-1}) of broad bean plants cultivated in Musturud and Elgabal- Elasfar soils as affected by different amendments.

Treatment	Dry weight of whole plant, g / column	Cu		Co	
		Shoots	Roots	Shoots	Roots
		Concentration, mg.kg^{-1}			
	Musturud soil				
Control	22.96	19.59	22.73	2.49	3.24
Ground cotton stalks	33.64	9.61	16.23	1.35	1.68
Rock phosphate	25.11	17.53	18.36	1.55	1.54
K_2EDTA	23.16	13.22	16.42	1.39	2.41
Citric acid	27.29	18.56	22.29	1.62	2.84
L.SD. $_{0.05}$	2.08	2.14	2.39	0.75	0.55
	Elgabal-Elasfar soil				
Control	29.75	24.14	36.66	4.16	7.99
Ground cotton stalks	36.88	10.99	18.79	1.97	2.50
Rock phosphate	33.71	16.05	23.37	3.10	4.52
K_2EDTA	31.81	20.25	21.07	2.13	4.22
Citric acid	35.12	22.26	26.75	3.80	4.52
L.SD. $_{0.05}$	2.12	0.91	0.93	0.11	0.35
Normal range, mg.kg^{-1}		5- 20*		0.05- 0.5**	

According to * Jones (1967) ** Kapata-Pendias and Pendias (1992)

Data illustrate that application of different amendments increased dry weight of broad bean plants prior to flowering compared to control. The highest increase resulted from ground cotton stalks treatment, which recorded 47 and 24% over the control for Musturud and Elgabal-Elasfar soils, respectively. The increases in plant dry weight due to ground cotton stalks application probably resulted from increasing macro and micro-nutrients availability needed for plant growth through organic matter decomposition as well as its positive effect on physical properties of the cultivated soils. Similar findings were also obtained by Barsoom *et al.* (1991). Also, the favorable effect of citric acid may be related to reducing soil pH, consequently increasing solubility and availability of some nutrients via plant roots absorption. The application of rock phosphate in both soils increased dry matter yield of broad bean plants by about 9 and 13 % over the control in Musturud and Elgabal-Elasfar soils, respectively and this may be due to increasing amounts of soluble phosphorus, particularly in Elgabal-Elasfar soil enriched with organic matter.

In general, Cu and Co concentrations in broad bean shoots and roots reflect the amounts of the chemically available metals present in the cultivated soils, which in turn are highly affected by both the sources of contamination and kind of amendment applied to those soils. However, the applied amendments tended to reduce concentration of Cu and Co in shoots and roots of broad bean plant compared to control treatment. Data show also that concentrations of Cu and Co in shoots of broad bean plant were markedly lower compared with those in roots. Several authors have shown that heavy metals tend to accumulate in roots of plants, among them Zhang & Wang (1991) and Wang *et al.* (1997).

Values of copper in bean plants were markedly decreased with application of different amendments particularly, with ground cotton stalks, which reached in shoots of plants to 51 or 54% from the control in Musturud or Elgabal-Elasfar soil, respectively. This may be due to the role of organic matter in reducing amount of Cu from soil solution. Allison (1973) declared that the organic matter can adsorb copper and thus eliminate any possible toxic effects of excess amounts added in fertilizers or in pesticides. On the other hand, organic matter can completely fix copper that the available supply is reduced below the needs of the crop. Application of rock phosphate decreased concentration of Cu in broad bean plant and this may be due to increasing pH of the soil which in turn decreased the mobility and solubility of copper in soils and increases copper adsorption on the surface of soil colloids as well as on the surfaces of $CaCO_3$ as has been reported by Das (2000). Tyler (1976) observed that application of phosphate precipitated Cu as its phosphates, beside the Cu-P antagonisms effect that occur in root media as phosphates have a strong tendency to adsorb Cu. Kabata-Pendias and Pendias (1992) reported that interaction between Cu and Ca are highly complex and apparently are cross-linked with the range of pH in the growth media.

Cobalt concentration was highly affected by ground cotton stalks or K_2EDTA addition to the studied soils as the decreases in the contents of cobalt in shoot of broad bean were 46 or 44% relative to the control for Musturud soil while were 53 or 49 % for Elgabal-Elasfar soil, respectively.

The beneficial effect of the applied amendments on reducing Cu and Co content in broad bean plants lead to compare the obtained data with the potentially toxic levels of heavy metals in plants according to Jones (1967) and Kabata-Pendias and Pendias (1992). Copper concentration was in the normal range for shoots of broad bean grown on Musturud soil, whereas that for Elgabal-Elasfar soil was excessive in the control, with K_2EDTA and citric acid treatments. Concerning Co concentration in plant shoots, it seems to be higher than that of the normal range either for treated or not treated soils of Musturud and Elgabal-Elasfar.

From the above discussion, it is clear that the concentration of Cu and Co in broad bean plants not only depended on amount of these metals in the contaminated soils but also on the chemically available heavy metals, distribution of forms and soil properties, which were affected by different amendments.

References

Allison, F.E. (Ed.) (1973) "*Soil Organic Matter and its Role in Crop Production*", Elsevier Scientific Publishing Co., New York, USA.

Badawy, S.H. and Helal, M.I.D. (1997) Impacts of heavy metals of sewage effluent on soils and plants of Helwan area. *J. Agric. Sci. Mansoura Univ.* **22**, 4737.

Barsoom, S.W.; Faiyad, M. N. and EL-Koumey, B.Y. (1991) Effect of organic matter addition on N and P uptake by wheat. *Munufiya. J. Agric. Res.* **16**, 1971.

Bloomfield, C. (1981) The translocation of metals in soils. In: "*The Chemistry of Soil Processes Green Land*", D.J. and M. H. B. Hayes (Ed.), pp. 463-478, John Wiley and Sons, New York.

Chapman, H.D. and Pratt, P.F. (1961) "*Methods of Analysis for Soils, Plants and Waters*", Berkeley, Univ. California, Division of Agric. Sci.

Chen, X.; Wright, J.V.; Conca, J. L. and Peurrung, L.M. (1997) Evaluation of heavy metal remediation using mineral apatite. *Water, Air and Soil Pollution* **98**(1-2), 57.

Christensen, T.H. (1984) Cadmium soil sorption at low concentrations. Reversibility, effect of change in solute composition, and effect of aging. *Water, Air and Soil Pollution* **21**, 115.

Das, D.K. (2000) "*Micronutrients: Their Behaviour in Soils and Plants*", Kalyani Publi-shers, New Delhi, India.

Dowdy, R.H.; Latterell, J.J.; Hinesly, T.D.; Grossman, R.B. and Suilvan, D. L. (1991) Trace metal movement in an Aeric Ochraqual following 14 years of annual sludge applications. *J. Environ. Qual.* **20**, 119.

El-Motaium, R.A. and Badawy, S.H. (2000) Effect of irrigation using sewage water on the distribution of some heavy metals in bulk and rhizosphere soils and different plant species: cabbage plants (*Brassica oleracea* L.) and orange trees (*Citrus sinesis* L.). *Egypt. J. Soil Sci.* **40**, 285.

Elsokkary, I.H. and Sharaf, A.I. (1996) Enrichment of soils and irrigated by wastewater by zinc and cadmium. *Egypt. J. Soil Sci.* **36,** 219.

Grana, M.J.; Barral, M.T. and Guition, F.E. (1991) Cobalt fractionation in soils. *Suelo-Y Planta* **2**, 303.

Gary, M.; Sims, J. and Vance, G. (1994) *"Soils and Environmental Quality"*, CRC Press, Inc. Boca Raton, London.

Jackson, M.L. (1958) *"Soil Chemical Analysis"*, Prentic-Hall, Inc. Englewood Cliffs, N. J. Library of Congress, USA.

Jones, J.B. (1967) *"Soil Chemical Analysis"*, Prentice-Hall, Pvt., Ltd., New Delhi, India.

Kabata-Pendias, A. and Pendias, H. (1992) *"Trace Elements in Soils and Plants"*, 2nd ed., CRC Press, Inc. Boca Raton, Florida. USA.

Khalil, M.E. (1990) Accumulation of some nutrients and heavy metals in Abu Rawash area, Giza Governorate. *M. Sc. Thesis*, Fac. Agric., Moshtohor, Zagazig Univ., Egypt.

Li, Z. and Shuman, L.M. (1997) Mobility of Zn, Cd and Pb in soils as affected by poultry litter extract. I- Leaching in soil columns. *Environ. Pollut.* **95**, 219.

Lindsay, W.L. and Norvell, W.A. (1978) Development of DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* **42,** 421.

Ma, Q.Y.; Logan, T.J. and Traina, S.J. (1995) Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environ. Sci. Technol.* **29**, 1118.

McBride, M.B. (1994) *"Environmental Chemistry of Soils"*, Oxford Univ. Press, Inc. New York. USA.

Mclaren, R.G.; Lawson, D.M. and Swift, R.S. (1986) Sorption and desorption of cobalt by soils and soil components. *J. Soil Sci.* **37**, 413.

Mosalem, T.M. (1997) Heavy metals pollution in sandy soil subjected to irrigation with sewage effluent. *J. Agric. Sci. Mansoura Univ.* **22**, 295.

Norvell, W.A. (1991) Reactions of metal chelates in soils and nutrient solutions. In: *"Micronutrients in Agriculture"*, J.J. Mortvedt; F.R. Cox; L. M. Shuman and R. M. Welch (Ed.), 2nd ed., pp.187-227, Soil Sci. Soc. Am., Madison, Wis., USA.

Shuman, L. M. (1979) Zinc, Manganese and copper in soil fractions. *Soil Sci.* **127**, 10.

Stevenson, F.J. and Ardakani, M.S. (1972) Organic matter reactions involving micronutrients in soils. In: *"Micronutrients in Agriculture"*, J.J. Mortvedt; P.M. Giordano and W. L. Lindsay (Ed.), pp.79- 114, Soil Sci. Soc. Am., Madison, Wis., USA.

Tessier, A.; Campbell, P.G.C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844.

Tyler, G. (1976) Heavy metal pollution, phosphatase activity and mineralization of organic phosphorus in forest soil. *Soil Biol. Biochem.* **8**, 327 (c.f. A. Kabata-Pendias and H. Pendias (Ed.),1992, *Trace Elements in Soils and Plants*. CRC Press, Inc. Boca Raton, Florida. USA).

Wang, P.; Qu, E.; Li, Z. and Larry, M.S. (1997) Fractions and availability of nickel in Loessail soil amended with sewage or sewage sludge. *J. Environ. Qual.* **26**, 795.

Wasay, S.A.; Barrington, S.F. and Tokunaga, S. (1998) Remediation of soils polluted by heavy metals using salts of organic acids and chelating agents. *Environ. Tech.* **19**, 369.

Zhang, S. and Wang, H. (1991) Nickel pollution to crops in soil with application of sewage sludge. *Acta Sci. Circumstantiate* **11**, 71.

Received 10/2002

معالجة أراضى مسطرد والجبل الأصفر من حيث محتواهـــا مــن النحاس والكوبالت

محمد على عثمان الشعراوى و محمود محمد البردينى
قسم الأراضي-كلية الزراعة-جامعة عين شمس- القاهرة- مصر .

تم إقامة تجربة أعمدة تربه بصوبة قسم الأراضي بالكلية لدراسة وتقييم تأثير إضافة بعض المحسنات مثل حطب القطن المطحون ، صخر الفوسفات، K_2EDTA ، حمض الستريك على صور وسلوك عنصري النحاس والكوبالت في أرضي مسطرد و الجبل الأصفر المروية بمياه ملوثه لفترات طويلة وتأثير ذلك على الكميه الميسرة كيميائيا وكذلك محتوى نبات الفول البلدي المنزرع من كلا العنصرين.

أوضحت النتائج أن المحسنات المستخدمة قد أدت إلى إعادة توزيع العنصرين بين الصور المختلفة واتضح أن استخدام أي من حطب القطن المطحون أو صخر الفوسفات أدى إلى زيادة تحول العنصرين إلى الصورة الأكثر تعقيدا بينما أدى استخدام كل من K_2EDTA أو حمض الستريك إلى زيادة ذوبان العنصرين وزيادة حركتهما إلى الطبقات السفلي من أعمدة التربة. كما أدى استخدام حطب القطن إلى انخفاض كمية النحاس الميسرة كيميائيا في كلا الارضين بنسبة ٥٧,٤ و ٥٥,١ ٪ في ارض مسطرد والجبل الأصفر على الترتيب مقارنـــة بالأعمدة الغــير معاملة . بينما أدت معاملة الأعمدة بحمض الستريك إلى خفض كمية الكوبالت الميسرة كيميائيا في كلا الأرضي بنسبة ٦٤,٧ و ٥٠,٨ ٪ في ارض مسطرد والجبل الأصفر على الترتيب مقارنة بالأعمدة الغير معاملة.

أدت إضافة حطب القطن إلى نقص تركيز النحاس فى المجموع الخضرى لنبات الفول البلدى النامى بارض الجبل الأصفر ليصل الى الحدود المسموح بها بينما كان تركيز الكوبالت فى كلا الأرضين سواء المعاملة بالمحسنات أو الغير معاملة أعلى من الحدود المسموح بها .