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CHEMICAL FORMS AND MOBILITY OF SOME HEAVY METALS IN SOME POLLUTED SOILS

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ABSTRACT

The present study was conducted to investigate the fractionation of some heavy metals (Cd, Cu, Pb and Zn) and their mobility in soils affected by different sources of pollution. The soil profile samples were collected from 3 sites from each of El-Gabal ELAsfar and Helwan areas which received sewage effluent and industrial wastes respectively for long time. The obtained results show that the soil pH and total carbonate content (TCC) are slightly decreased as the irrigation period increased. However, organic matter content increased.

The average percentage value of each particulate-bound metals species in all studied soils followed the order: residual (26.10 – 48.32 %) > organic-bound (6.27 to 52.48 %) > oxides-bound (4.95 to 33.15%) > carbonate-bound (0.67 to 22.05 %)> exchangeable (1 to 6 %) of the total present in the soils.

The percentage of distributed fractions from the surface layers showed that the deepest layer (100-120 cm) is amounted to approximately 20 % for Cd; 11% for Cu; 6% for Pb and 14% for Zn in El-Gabal El-Asfar which is higher than in Helwan which represents 15 % for Cd; 8.7 % for Cu; 3 % for Pb and 8% for Zn of their total contents in the surface layer (0-20 cm). The movement of Cd and Zn are more movable than Pb and Cu.

Keywords: pollution sourses, sewage effluent, industrial wastes, heavy metals, Cd, Cu, Pb, Zn, mobility, fractionation, forms.

INTRODUCTION

Assessment of heavy metal pollution can be approached by many ways. Total analysis of heavy metals do not generally provide any guide to the biological effectiveness or mobility of the metal under study, but do define unequivocally the total metal load of a polluted soil. For more useful data on the degree of soil pollution, the total concentration may be divided into different chemical components. More information approach is to identify nonlabile and labile forms. Although sequential extraction methods required more time consuming, its provide detailed information about the status of metal in soil (Kabala and Singh, 2001 and McLaren and Clucas, 2001). Several sequential extraction methods for soils and sediments have been discribed in the literature (El-Sokkary, 1979; Tessier *et al.*, 1979 and Salbu *et al.*, 1998)

El-Gendi, 1994 indicated that sum of the obtained fractions represented 92.8 and 88.7% of total Pb content for soil samples containing normal (18.0ppm) and high (42.5ppm) content of Pb, respectively. The level of each individual Pb fraction follows the order. Residual (42%) > bound to oxides (23%) > bound to organic matter (16%)> bound to carbonate (15%) >

exchangeable (3.0%), in the first sample, and residual = bound to oxides (26%) bound to carbonate (25%) > bound to organic matter (21%) > exchangeable (2%), in the other hand Miller *et al.* (1983) used a sequential extraction technique to characterize chemical forms of Cd, Zn, Cu, and Pb in heavy industrialized area of Indiana. They reported that the labile Pb (soluble + exchangeable) accounted for 8% of the total Pb, while the organic and carbonate fractions amounted 70% of total.

Needless to say that the factors which influence the downwords movement in soil profile are essentially those already modulot bioavailability. Soil pH considered to be one of the dominating factors controlling metal movement in soil profiles (Emmerich *et al.*, 1982). Welch and Lund (1987) mentioned that the movement of heavy metals was corrected positively with coarse fraction content and negatively with fine fractions. Also, the influence of the amount of the added sludge or number of years of application on movement of heavy metals were studied by many authors. Anderson and Nilson (1972) mentioned that all Cd remained in (20-cm) depth of a soil receiving sludge over a 12-yrs period. Chang *et al.*, (1984) mentioned that more than 90% of applied heavy metals, including Pb, were found in soil surface, 0-15 cm (the zone of application).

The influence of organic matter on the movement of heavy metals was studied by many authors, Arzahanova and Yelpat Yevskiy (1980) studied the forms in which some heavy metals migrate. They observed that, for example, Cu and Pb migrate mainly as colloidal phases, while Zn migrate mainly in truly soluble form. El- Gendi (1994) mentioned that the pattern of Pb distribution within the soil profile was mainly attributed to organic matter content. Like wise Pb, the distribution of Cu was closly associated with organic matter. Camobreco *et al.*, (1996) observed that the mobility of Cd, Zn, Cu and Pb may be ranked as follows: Cd > Zn > Cu > Pb.

The present study was carried out to assess short and long-term effects of two sources of pollution; farm-initiated source and inadvertent source on distribution of Zn, Cu, Cd, and Pb amongst the different fractions defined by sequential extraction procedure and their mobility in soil profiles.

MATERIALS AND METHODS

This study was carried out on two different locations in Egypt, which contaminated consequently by considerable amounts of toxic metals; one from El-Gabal El-Asfar farm is located at north east of Cairo Governorate, which is irrigated with sewage effluent of Cairo city since 1911. which received sewage sludge and sewage effluent for long time and the second from Helwan area endures of emissions of toxic metals from various industrial activities together with household sources which contaminated by industrial wastes.

Soil sampling and analysis:

The soil samples were collected from 3 sites from each of El-Gabal El-Asfar and Helwan area. Nine soil profiles were carefully dug to the depth of 120 cm for each location as the following; three profiles representing the oldest farm which has been irrigated for 70 and 20 years for El-Gabal El-Asfar and Helwan, respectivly; three profiles from a younger farm irrigated for 15 years for both sites; and three from unpolluted soil profile, i.e. un-irrigated site (background). Six sub-samples were taken from each soil and thoroughly homogenised before transporting to the laboratory and prepared for analysis.

Soil Analysis:

The general characteristics of soils:

Particle size distribution was carried out by the pipette method, pH, organic matter (OM) and total carbonate content (TCC), were determined using the standard methods outlined by Dewis and Freites (1970).

Sequential Chemical Extraction:

The sequential extraction procedure of Tessier *et al.*,(1979) was used to partition Cd, Cu, Pb and Zn in soils into five operationally defined fractions; 1) The exchangeable fraction: soils were extracted with 1M NaOAc, pH 8.2 at room temperature for one hour with continuous agitation; 2) The carbonate bound fraction: the residue from 1) was leached at room temperature for five hrs continuous agitation with 1M NaOAc, pH 5.0 ; 3) The Fe and Mn oxides bond fraction: The residue from 2) was extracted with 0.04 M NH_2 OH.HCl in 25% (v/v) HOAc at 96 ± 3 °C with occasional agitation for 5 hrs.; 4) The organic matter bound fraction: The residue from 3) was extracted with 0.02 M HNO_3 and 30% H_2O_2, pH 2.0 , for 2 hrs with occasional agitation at 85 ± 2 °C ; then 30% H_2O_2 for 3 hrs with intermittent agitation at 85 ± 2 °C ; after cooling 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added.; 5) The residue fraction: the residue from 4) was digested with HF-$HClO_4$ using the same procedure employed for total. The resulting supernatants from each fractionation step were filtered before analyzing the filtrates for metals by flame atomic absorption spectrophotometer and GF-ASS for Cd. using the standard addition technique.

RESULTS AND DISSCUSION

1. General characteristics of the soils:

The general properties, pH, clay, organic matter and total carbonate content of the studied profiles are given in Table (1). The results show that the pH varied from 8.60 to 8.77 and from 8.33 to 8.73 in the initial, nonpolluted soils of El-Gabal El-Asfar and Helwan respectively. The two soils had the highest pH values and then slightly decreased as the irrigation period increased.

The reaction of the soil was alkali (pH 8.75) in the beginning and changed to slightly acidic (6.11) after 70 years of irrigation with sewage effluent in El-Gabal El-Asfar soil, Also, the industrial wastes decreased soil pH from 8.33 to 7.45 in Helwan soil after 20 years. These changes in soil pH occurred in both surface and deepest layers. However at any given time, the surface layers showed slightly lower pH values than the subsurface ones. Generally, it can be seen that the drop in pH was very fast and clearly observed during the first 15 years of using sewage effluent in irrigation, further changes in pH with time were less sharp.

Table (1): Some physical and chemical characteristics of soil profiles in different locations.

Depth (cm)	Location											
	El-Gabal El-Asfar						Helwan					
	Time (Year)	O.M %	TCC %	pH (1:2.5)	Clay %	Texture Class	Time (Year)	O.M %	TCC %	pH (1:2.5)	Clay %	Texture Class
0-20	Control	**0.07**	**3.89**	**8.75**	**3.15**	**S**	Control	**0.32**	**23.55**	**8.33**	**25.23**	**SCL***
20-40		0.06	2.25	8.61	3.34	S		0.30	21.13	8.45	21.52	SCL
40-60		0.05	3.77	8.77	2.76	S		0.22	19.16	8.61	23.83	SCL
60-80		0.07	2.99	8.79	3.54	S		0.14	20.35	8.66	33.16	SCL
80-100		0.07	2.28	8.60	2.50	S		0.09	18.42	8.71	22.71	SCL
100-120		0.06	2.87	8.75	2.07	S		0.04	24.12	8.73	28.14	SCL
0-20	15	3.79	3.00	6.56	21.33	SCL	15	0.79	11.60	7.68	36.04	CL**
20-40		3.71	2.21	6.56	16.80	SCL		0.76	9.50	7.70	25.32	SCL
40-60		3.16	3.00	6.91	12.70	SCL		0.74	11.03	7.80	24.25	SCL
60-80		2.04	2.50	7.00	14.69	SCL		0.79	9.50	7.41	26.00	SCL
80-100		2.21	2.21	7.04	7.85	S		0.50	10.21	7.57	20.15	SCL
100-120		1.94	2.50	7.13	6.57	S		0.80	11.40	7.43	22.20	SCL
0-20	70	6.15	1.57	6.11	23.79	SCL	20	1.46	11.00	7.45	37.10	CL
20-40		6.29	1.60	6.20	20.00	SCL		1.05	10.51	7.70	35.41	CL
40-60		5.24	2.00	6.24	17.41	SCL		0.82	11.01	7.69	35.92	CL
60-80		3.22	1.51	6.30	14.50	SCL		0.83	10.00	7.64	36.50	CL
80-100		3.41	1.50	6.83	10.00	SCL		0.79	10.00	7.57	33.80	CL
100-120		3.09	2.30	7.10	14.40	SCL		0.83	10.00	7.51	33.00	CL

* Sandy Clay Loam ** Sandy Clay

The correlation coefficients between organic matter contents and soil pH values were highly significant (r = -0.92** and -0.88**) in El-Gabal El-Asfar and Helwan soils, respectively.

Also, total carbonate content (TCC) of the irrigated soils, ranging from 1.5 to 2.3 % are markedly lower than those, ranging from 2.28 to 3.89 %, of the initial ones in El-Gabal Asfar and ranging from 10 to 11 % are markedly lower than those, ranging from 18.42 to 24.12 %, of the initial ones in Helwan. This could be attributed to the dissolution of $CaCO_3$ as a result of interaction with organic acid exist in the sewage effluent or industrial wastes. Hence, the lowness observed in pH values could be a result of both; dissolution of $CaCO_3$ and the effect of organic acids. The correlation coefficients between soil organic matter contents and TCC were highly significant (r= -0.72** and -0.92**) in El-Gabal El-Asfar and Helwan soils, respectively.

On the other hand, both organic matter content (OM), and the particles of the clay-size fraction, are increasing with the irrigation period. In average, OM content ranging from 3.09 to 6.29 % after 70 years of irrigation are markedly higher than those, ranging from 0.05 to 0.07 %, of the initial ones in El-Gabal Asfar and ranging from 0.79 to 1.46% after 20 years of irrigation are markedly higher than those, ranging from 0.04 to 0.32%, of the initial ones in Helwan. Clay size- fraction content of the irrigated soils was approximately 1.5 and 6 times greater than those non-polluted soils.

2. **Fractionation of soil Cd, Cu, Pb and Zn**:

The sum of the five fractions amounted to 83-102% for Cd, 83-91% for Cu, 69- 90% for Pb and 87-97% for Zn of the total contents (Tables, 2, 3, 4 and 5). Tessier *et al.*, 1979; Krishnamurti *et al.*, 1995 and Badawy and Helal, 2002 reported that the sum of the extractable-Cd, Cu, Pb and Zn fractions were 88 to 104 % of the total Cd content.

The results (Tables, 2, 3, 4 and 5) of portioning of the studied metals in the deferent soil profiles among different pools show that, relatively small portions, ranging from 0.03 to 36.4 $mgkg^{-1}$ in different locations, of Cd, Cu, Pb and Zn exist in the exchangeable pool, readily available form. The highest exchangeable values were recorded for Zn, whereas the least ones belong to Cd. The exchangeable values of studied metals amounted to small portions, ranging approximatliy from 1 to 6 % of the total. The highest percentage of total was found in El-Gabal El-Asfar after 70 years with irrigation by sewage effluent (Fig.1). This is attributed to the acidity (pH = 6.11) of the soil. Onyatta and Huang, 1999 and Badawy and Helal, 2002 found that a negative relation between Cd-Exchangeable fraction and soil pH.

Carbonates bound-metal ranging from 0.03 to 157.4 $mgkg^{-1}$ in different locations, of Cd, Cu, Pb and Zn exist in the Carbonates pool. The highest values were recorded for Zn, whereas the least ones belong to Cd. The values ranging approximatliy from 0.67 to 22.05 % of the total. The highest percentages are recorded for Helwan soils followed by El Gabal El Asfar soils. This result could be attributed to high $CaCO_3$ which precipitate and adsorbed Cd, Cu, Pb and Zn (Fig 1).

Table (2): Cadmium associates with different chemical fractions at soil profiles of different locations.

Depth (cm)	Location													
	El-Gabal El-Asfar							Helwan						
	mg/kg soil (15 Yr.)							mg/kg soil (15 Yr.)						
	Ex.	Carb	Ox.	Org.	Res.	Sum.	Total	Ex.	Carb.	Ox.	Org.	Res.	Sum.	Total
0-20	0.28	0.38	0.98	2.07	1.49	5.20	5.65	0.31	1.52	2.20	0.62	2.71	7.37	7.99
20-40	0.16	0.15	0.58	1.21	0.83	2.94	3.17	0.17	0.89	1.31	0.33	2.23	4.49	4.86
40-60	0.08	0.13	0.49	1.00	0.62	2.33	2.37	0.09	0.53	0.74	0.17	1.30	2.58	2.57
60-80	0.06	0.08	0.38	1.15	0.62	2.05	2.30	0.07	0.35	0.50	0.14	0.88	1.76	1.99
80-100	0.03	0.03	0.21	0.85	0.59	1.67	1.85	0.04	0.25	0.35	0.09	0.64	1.25	1.44
100-120	0.03	0.03	0.16	0.77	0.52	1.49	1.58	0.04	0.23	0.30	0.09	0.60	1.13	1.23
	mg/kg soil (70 Yr.)							mg/kg soil (20 Yr.)						
0-20	0.40	0.50	1.33	2.89	2.03	7.16	7.35	0.45	2.02	2.73	0.96	3.10	9.26	9.16
20-40	0.25	0.22	0.89	1.94	1.42	4.69	4.70	0.27	1.20	1.63	0.57	2.18	5.81	5.68
40-60	0.25	0.22	0.89	1.94	1.42	4.69	4.70	0.27	1.20	1.63	0.57	2.18	5.81	5.68
60-80	0.09	0.12	0.56	1.58	0.98	3.30	3.33	0.10	0.45	0.71	0.22	1.03	2.49	2.99
80-100	0.04	0.04	0.29	1.18	0.81	2.29	2.46	0.05	0.39	0.50	0.15	0.86	1.91	2.24
100-120	0.03	0.03	0.16	0.74	0.51	1.41	1.47	0.04	0.28	0.38	0.11	0.57	1.36	1.38

* Ex. = Exchangeable; Carb. = bound to carbonates; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter, Res. = residual; Sum.= summation of extracted fractions.

Table (3): Zinc associates with different chemical fractions at soil profiles of different locations.

Depth (cm)	Location													
	El-Gabal El-Asfar							Helwan						
	mg/kg soil (15 Yr.)							mg/kg soil (15 Yr.)						
	Ex.	Carb	Ox.	Org.	Res.	Sum.	Total	Ex.	Carb.	Ox.	Org.	Res.	Sum.	Total
0-20	3.24	10.09	22.93	70.99	115.4	224.8	252.3	20.4	98.14	149.9	49.38	161.5	482.3	525.0
20-40	0.94	5.45	8.65	29.12	45.98	90.89	102.9	7.14	37.88	66.43	17.87	89.09	219.6	245.2
40-60	0.87	3.23	5.19	19.45	25.72	54.72	60.90	5.09	24.18	37.99	11.47	47.67	127.2	136.7
60-80	0.91	3.56	5.09	19.41	21.66	51.00	56.27	2.76	13.02	23.07	6.39	34.56	80.12	90.53
80-100	0.71	1.91	4.89	14.21	14.53	36.47	41.14	1.42	10.39	15.84	4.38	22.43	54.68	60.29
100-120	0.49	2.65	4.45	13.30	12.09	33.29	37.00	1.23	7.75	11.63	3.11	15.60	39.46	42.00
	mg/kg soil (70 Yr.)							mg/kg soil (20 Yr.)						
0-20	8.56	25.36	57.39	180.6	280.6	556.1	617.4	36.4	157.4	258.9	68.22	279.9	805.4	832.7
20-40	2.29	11.73	20.68	69.27	110.5	216.1	241.7	14.7	60.81	116.8	27.77	152.4	374.2	421.3
40-60	2.67	10.14	15.87	60.38	77.11	167.0	184.0	3.92	15.33	26.93	5.73	37.85	90.16	100.9
60-80	2.46	9.21	13.18	48.09	52.87	126.3	140.6	4.29	14.55	24.35	5.66	31.67	80.80	90.45
80-100	1.62	4.29	10.94	31.74	31.65	80.94	90.12	4.17	14.61	29.91	6.77	32.61	83.41	90.34
100-120	1.18	6.62	10.80	32.53	28.51	80.26	90.609	3.16	13.79	22.07	6.54	28.13	72.60	83.26

* Ex. = Exchangeable; Carb. = bound to carbonates; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter, Res. = residual; Sum.= summation of extracted fractions.

Table (4): Copper associates with different chemical fractions at soil profiles of different locations.

Depth (cm)	Location													
	El-Gabal El-Asfar							Helwan						
	mg/kg soil (15 Yr.)							mg/kg soil (15 Yr.)						
	Ex.	Carb	Ox.	Org.	Res.	Sum.	Total	Ex.	Carb.	Ox.	Org.	Res.	Sum.	Total
0-20	1.04	.0.56	8.44	36.61	35.08	84.27	94.91	4.35	28.24	40.58	15.09	45.65	134.2	153.9
20-40	0.71	0.21	3.43	14.99	11.09	30.60	34.20	1.69	11.04	17.54	5.23	20.90	56.55	65.92
40-60	0.44	0.29	4.21	13.54	11.41	30.14	34.92	1.36	7.23	10.67	3.39	14.08	36.80	40.34
60-80	0.54	.0.25	3.31	10.99	11.62	27.24	30.15	0.69	3.21	4.94	1.41	7.10	17.40	19.26
80-100	0.36	0.25	2.28	5.81	7.52	16.29	19.54	0.55	2.96	4.59	1.29	6.54	16.00	17.56
100-120	0.13	0.10	1.79	4.38	6.07	12.56	14.10	0.42	2.40	3.59	098	4.49	11.93	13.39
	mg/kg soil (70 Yr.)							mg/kg soil (20 Yr.)						
0-20	2.06	1.05	15.46	71.07	62.29	152.7	169.4	7.27	27.22	46.27	14.31	44.17	139.6	161.6
20-40	1.23	0.37	5.76	24.85	18.35	50.48	57.46	1.84	7.28	13.64	4.37	15.31	42.60	48.30
40-60	0.56	0.38	5.06	15.97	13.28	35.48	40.66	1.01	4.22	7.08	2.27	8.58	23.26	26.79
60-80	0.58	0.26	3.47	11.35	12.22	28.10	30.01	1.31	3.86	6.51	1.99	8.05	21.80	24.50
80-100	0.53	0.37	3.18	8.29	10.23	22.72	25.40	0.87	3.19	5.28	1.56	6.45	17.43	20.16
100-120	0.17	0.15	2.61	6.59	8.58	18.21	20.32	0.66	2.56	3.99	1.30	4.13	12.71	14.22

* Ex. = Exchangeable; Carb. = bound to carbonates; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter, Res. = residual; Sum.= summation of extracted fractions

Table (5): Lead associates with different chemical fractions at soil profiles of different locations.

Depth (cm)	Location													
	El-Gabal El-Asfar							Helwan						
	mg/kg soil (15 Yr.)							mg/kg soil (15 Yr.)						
	Ex.	Carb	Ox.	Org.	Res.	Sum.	Total	Ex.	Carb.	Ox.	Org.	Res.	Sum.	Total
0-20	0.84	1.75	2.12	21.85	15.36	42.14	49.00	2.92	11.29	13.78	6.31	21.56	56.12	66.48
20-40	0.26	0.52	0.68	6.46	4.92	12.92	15.92	0.57	2.39	3.56	1.55	5.78	13.92	15.52
40-60	0.29	0.56	0.71	4.99	3.39	10.02	12.07	0.41	2.14	2.95	1.18	4.56	11.28	14.60
60-80	0.34	0.54	0.80	4.11	3.11	8.94	10.14	0.28	1.75	2.05	0.89	3.24	8.22	9.15
80-100	0.14	0.27	0.43	2.05	1.64	4.56	5.46	0.18	1.01	1.38	0.49	2.07	5.15	7.45
100-120	0.12	0.26	0.37	1.04	1.05	2.86	3.42	0.09	0.42	0.64	0.23	0.89	2.28	2.92
	mg/kg soil (70 Yr.)							mg/kg soil (20 Yr.)						
0-20	2.62	4.93	5.11	54.19	36.41	103.3	120.2	1.29	14.23	20.71	8.43	12.79	82.50	97.62
20-40	1.03	1.75	2.46	18.21	12.63	36.09	43.10	0.62	3.23	5.16	1.87	8.81	19.74	23.45
40-60	0.68	1.23	1.56	11.07	7.52	22.06	25.10	0.39	2.33	3.41	1.24	5.41	12.82	15.20
60-80	0.51	0.83	1.19	5.78	4.05	12.36	14.26	0.29	1.63	2.09	0.73	3.67	8.46	10.12
80-100	0.28	0.59	0.85	3.87	3.11	8.70	10.30	0.18	1.07	1.53	0.55	2.63	5.97	7.07
100-120	0.24	0.59	0.87	2.37	2.75	6.82	7.94	0.09	0.44	0.66	0.19	1.01	2.41	2.86

* Ex. = Exchangeable; Carb. = bound to carbonates; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter, Res. = residual; Sum.= summation of extracted fractions.

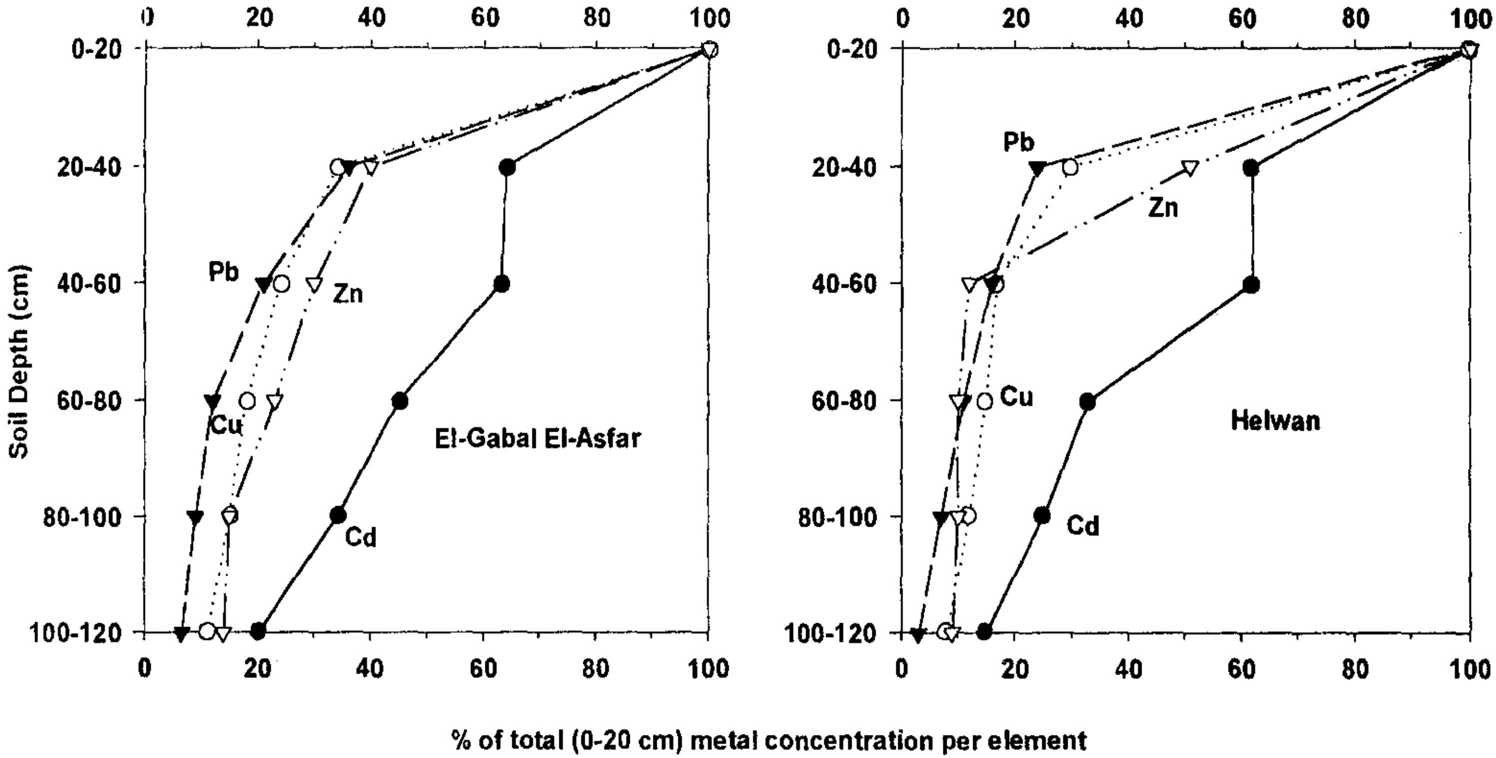

Fig.(2) Distrbution of total metal content with soil depth as a percent of surface layer content.

Oxides bound-metal ranging from 0.16 to 258.9 $mgkg^{-1}$ in different locations, of Cd, Cu, Pb and Zn exist in the oxides pool. The highest values were recorded for Zn, whereas the least ones belong to Cd. The values ranging approximatliy from 4.95 to 33.15% of the total. The highest percentages are recorded for Helwan soils followed by El Gabal El Asfar soils. This result could be attributed to high oxides which adsorbed Cd, Cu, Pb and Zn (Fig 1).

Organic bound-metal was the predominant form, ranging from 0.09 to 180.6 $mgkg^{-1}$ in different locations, of Cd, Cu, Pb and Zn exist in the organic pool. The highest values were recorded for Zn, whereas the least ones belong to Cd. The values ranging approximatliy from 6.27 to 52.48 % of the total. The highest percentages are recorded for Pb and Cu in El Gabal El Asfar followed by Helwan soils. These results attributed to high organic matter content (Fig 1). Thes result could be attributed to the high affinity of Pb and Cu to form complexes with organic substances. Bloom and McBride (1979) and Camobreco *et al.*(1996) estimated the relative preferential for some divalent cations of transition on H^+ - peat and HA, and obtained the following series; Cu > Pb >> Fe > Ni = Co = Zn > Mn = Ca.

The residual fraction, the metal exists in primary minerals and/or precipitated as phosphates, silicates, etc., is the second predominate form for all metals. In average of, 26.10 – 48.32 % of the total of the studied metals are exist in the residual fraction. The conditions of studied sandy soils; high pH, low contents of both total carbonates and clay; promote chemical precipitation of soluble metal burden in sewage effluent. Also, slow diffusion of metal into the interior lattice of soil minerals is possible according to Dowdy *et al.*(1991). They suggested that it is possible over 14-Yr period, some of the added Cd and Zn slowly diffused into interior of the mineral. Dowdy *et al.*, (1991) has observed adsorption of metals within the crystal interior of illite and smectite clay minerals varied percentages of each metal were associated with oxides, and carbonates- fractions.

The average percentage value of each particulate-bound metals species in all studied soils followed the order: residual (26.10 – 48.32 %) > organic-bound (6.27 to 52.48 %) > oxides-bound (4.95 to 33.15%) > carbonate-bound (0.67 to 22.05 %)> exchangeable (1 to 6 %) of the total present in the soils. These results can be considered as basic information for the metals status of soils (Ramos *et al.*, 1994; Onyatta and Huang, 1999).

In general, heavy metals burdened in sewage effluent and industrial wastes distributed among different soil chemical pools, with great affinity to residue in relatively less mobile forms such as residual, organic- and oxides-. These results mean that the soil has ability to minimize the immediate risk of the added heavy metal through decreasing its mobility, hence reducing photoavailability of these metals. But the question is how long these soil constituents will be able to sustain the continuous supply of such heavy metals?

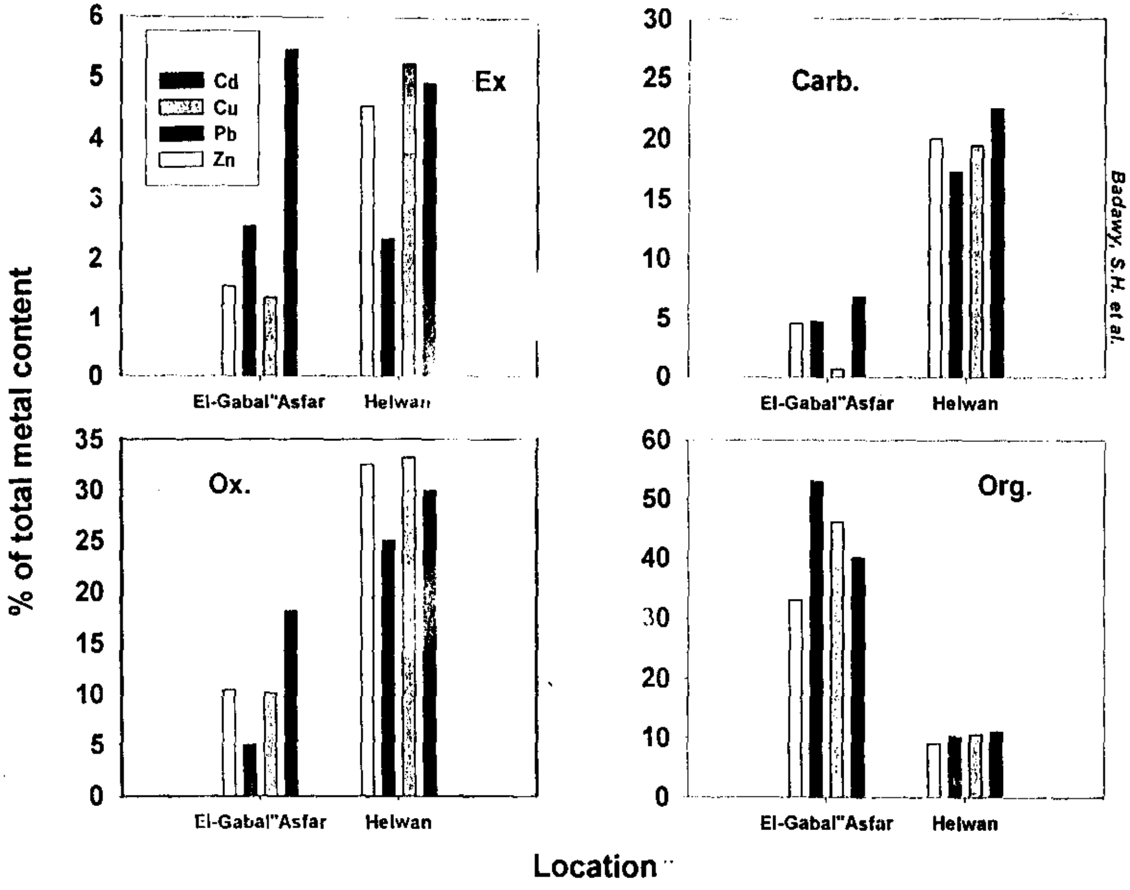

Fig. (1). distrbution of different fractions of studied metals as a percent of total.

3-Mobility of heavy metals in the soil profile:

Tables (2, 3, 4 and 5) show a high movement of studied heavy metals downward the soil profile. The relative distribution shows that the different metals (Cd, Cu, Pb and Zn) fractions decreased with increasing the depth. The percentage of distributed fractions from the surface layers showed that the deepest layer (100-120 cm) is amounted to approximately 20 % for Cd; 11% for Cu; 6% for Pb and 14% for Zn in El-Gabal El-Asfar soil which is higher than in Helwan soil which represents 15 % for Cd; 8.7 % for Cu; 3 % for Pb and 8% for Zn of their total contents in the surface layer (0-20 cm). Although, the results verifying high movement of the studied metals, Fig. (2) Show that Cd and Zn are more movable than Pb and Cu. Similar results were obtained by Li and Shuman (1996). They reported that, except for slight movement of Cd in the Clarendom soil profiles, there was no movement of Pb in the other two soil profiles (Fuquay and Dothan). Pb had accumulated in the topsoils because of their affinity with organic matter fraction.

These differences in metals mobility due to soil pH and $CaCO_3$ content. The high contents of $CaCO_3$ in calcareous soil (Helwan) minimized the mobility. This result agree with those reported by Ma and Lindsay,(1990). In contrast high movement of sewage- borne heavy metals, the sludge burden ones slightly moved out of the incorporation layer. Dowdy *et al.* (1991) suggested that small amounts of sludge- borne Cd and Zn moved out of the tillage zone into the subsoil after 14-Yr of massive sludge addition. Also, Dowdy and Volk (1983) found very little evidence of trace metals movement beyond the zone of incorporation. High movement of sewage effluent burden heavy metals could be attributed to; 1) Liquid nature of the effluent, 2) coarse texture and high permeability of the studied soil which facilitate the transport of the sewage sludge effluent carrying residence heavy metals, and 3) employed irrigation regime (flood irrigation) lead to magnifying the quantity of sewage effluent added to the soil that increases heavy metals load. The abovementioned knowledges are verifying high movement of Cd in El-Gabal El Asfar (sandy soils) than Helwan (calcareous soils) and Cu had accumulated in the topsoils because of their affinity with organic matter fraction. Similar results were obtained by Li and Shuman (1996).

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المفصولات الكيميائية للفلزات الثقيلة وحركتها في بعض الأراضي الملوثة

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أجريت الدراسة الحالية بهدف التعرف علي المفصولات المختلفة لعناصر الكادميوم ، الرصاص ، النحاس والزنك وحركتها في القطاع الأرضي تحت تأثيرمصادرمختلفة للتلوث . وقد جمعت عينات من القطاعات الأرضية محل الدراسة من ثلاثة مواقع من كل من الجبل الأصفر و حلوان والتي استقبلت مياه المجاري والنفايات الصناعية لفترات طويلة . وقد أوضحت النتائج المتحصل عليها حدوث انخفاض تدريجي في كل من رقم pH التربة والمحتوي الكلي من الكربونات بزيادة فترات الري في حين زاد المحتوي العضوي.

كم أظهرت النتائج أن متوسط قيم النسبة المئوية لكل مفصول من تلك المفصولات في جميع الأراضي تحت الدراسة تتبع الترتيب التالي : المتبقي (٢٦,١٠– ٤٨,٣٢%) > المرتبط عضويا (٦,٢٧–٥٢,٤٨%) > المرتبط بالأكاسيد (٤,٩٥– ٣٣,١٥ %) > المرتبط بالكربونات (٠,٦٧–٢٢,٠٥%) > المتبادل (١–٦%) من المحتوي الكلي في الأراضي تحت الدراسة.

وقد أوضحت الدراسة أن النسبة المئوية للمفصولات المختلفة في الطبقات السطحية مقارنة بأعمق الطبقات (١٠٠–١٢٠ سم) كانت تمثل ٢٠% للكادميوم ، ١١% للنحاس ، ٦% للرصاص و١٤% للزنك في أراضي الجبل الأصفر والتي كانت أعلي من منطقة حلوان التي والتي مثلت فيها المفصولات المختلفة القيم الاتية ١٥% للكادميوم ، ٨,٧ للنحاس ، ٣% للرصاص و ٨% للزنك من المحتوي الكلي لها في الطبقة السطحية (٠ – ٢٠ سم). وقد كان كل من الكادميوم والزنك اكثر حركة من الرصاص والنحاس.