

## Effect of Pollution Source on Distribution of Some Potential Toxic Elements in Different Soil Systems

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### ABSTRACT

Heavy metals found in soils are potentially toxic to human life and the environment. The bioavailability and the toxicity of metals depend on metal association and distribution in soil systems. The main aim of this work is to study the effect of source of pollution on the distribution of Pb, Ni, Cu and Zn in soils. Three groups of contaminated soil samples (G1, G2, and G3) represented by 21 soil samples for all groups, were collected from El-gabal El Asfar, Kafr El-Zayat and El-Saff areas to be tested in this work. According to American Soil Taxonomy, selected groups were classified under two great groups i.e. *Typic Torrerts* (G1 and G2) and *Typic Psammments* (G3). The selection of these groups of soils based on the source of pollution represented by the irrigation with sewage effluents in G1, irrigation with both industrial and sewage effluents polluted water (G2) for more than 50 years. In (G3), however, pollution created from the location of this group adjacent to cement factory. The obtained results indicated that source of pollution drastically influenced heavy metals distribution in all groups of soils. For example, in sewage soils (G1), except the residual form, organically bound Pb was the highest fraction compared to other fractions studied, in other groups; however, the same pollutant associated with Fe-Mn oxide was higher than organically bound form. Data also showed that in all soils, regardless the source of pollution, distribution of heavy metals arranged as follow: Readily available form (RAF) > moderately available form (MAF) > Hardly available form (HAF). Concerning the effect of soil properties in relation to pollutants distribution, data showed that clay contents of used soils, organic matter (OM) and in some cases pH and EC were the most dominant factors controlled heavy metals distribution under our experimental conditions. Different factors controlled heavy metals distributions in contaminated soils according to source were discussed.

**Key words:** heavy metals, distribution, source of pollution, soil properties

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### Introduction

Soil contamination with anthropogenic heavy metals, which mainly comes from industrial activity, atmospheric deposition and soil application of sewage sludge, has received much attention in recent years. The anthropogenic heavy metals are believed to be easily accumulated in the topsoil Samsøe-Petersen *et al.*, (2002). and Baker and Copper (1990), resulting in potential problems such as toxicity to plants and animals Ma, *et al.*, (2002) Berti and Jacobs (1996). accumulation in food chain, perturbation of the ecosystem and adverse health effects Forstner (1995) and Stalikas *et al.*, (1997)

Sequential fractionation techniques are being used increasingly to provide more useful assessments of soil heavy metal contamination than is possible with single extractions or total metal concentrations alone Anxiang *et al.*, (2005) In addition, heavy metals fractionation is a fairly widely used technique for understanding the mechanisms of heavy metals distribution in soils and to help assess bioavailability of trace metals in soils. Such assessment assumed that the metal bioavailability decreased with each successive extraction step in the procedure. Therefore metals in water soluble and exchangeable fractions would be readily bioavailable form to growing plants, whereas the metals in residual form would be more hardly available form.

In addition, it is well known that residence time directly relates to the bioavailability of heavy metals in soils Pedersen *et al.*, (2000), Joner *et al.*, (2002) and Alexander (2000). Generally bioavailability of heavy metals decreases with increasing residence time McLaughlin (2001). Such time effect is attributed to the reactions between metal ions and soils, which mainly include complexation, adsorption, and precipitation of metal ions in the soil particle surface or diffusion into the mesopores and micropores of soil. However, the source of pollution of soil system becomes more important factor in bioavailability of heavy metals in soil system since the distributions of such pollutants will be vary according to the source.

Accordingly, the primary objective of this study is to investigate the effect of source and residence time of soil exposed to contamination on distribution of Pb, Ni, Cu and Zn in some Egyptian contaminated soils. The results of this study may be a guide for selecting the suitable remediation strategy(s) should be applies according to conditions of pollution in these soils.

## Materials and Methods

### 2.1 Soil Types used:

Three sets of top soil samples were collected located in El-Gabal El-Asfar (G1), Kafr El-Zayat (G2) and El-Saff (G3) were analyzed in this work. The main sources of pollution in these soils are sewage effluents, mixture between sewage and industrial and industrial sources. Different soil properties were determined according to Cottenie *et al.*, (1982) and presented in table 1.

### 2.2 Heavy metals distribution:

Heavy metals distributions were conducted according to Ma and Rao (1997). In summary, one gram of each soil sample is weighted into a 40-ml polycarbonate centrifuge tube and the following fractionating steps were obtained:

**Step 1:** Water-soluble (WS): One gram soil sample extracted with 15 ml of de-ionized water for 2 h.

**Step 2:** Exchangeable (EXC): The residue from water-soluble fraction is extracted with 8 ml of 1M MgCl<sub>2</sub> (pH7.0) for 1h.

**Step 3:** Carbonate-Form (CA): The residue from exchangeable fraction is extracted with 8 ml of 1 M NaOAc (adjusted to pH 5.0 with HOAc) for 5h.

**Step 4:** Fe-Mn Oxides-Form (Fe-Mn): The residue from carbonate fraction is extracted with 0.04 M NH<sub>2</sub>OH.HCL in 25% (v/v) HOAc at 96 °C with occasional agitation for 6h.

**Step 5:** Organically Form (ORG): The residue from Fe-Mn oxide fraction is extracted with 3 ml of 0.02 M HNO<sub>3</sub> and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2 with HNO<sub>3</sub>). The mixture is heated to 85 °C for 2h, with occasional agitation. A second 3-ml aliquot of 30% H<sub>2</sub>O<sub>2</sub> (pH 2 with HNO<sub>3</sub>) is added and the mixture heated again to 85°C for 3h with intermittent agitation. After cooling, 5 ml of 3.2 M NH<sub>4</sub>OAc in 20% (v/v) HNO<sub>3</sub> is added and the samples diluted to 20 ml and agitated continuously for 30 min.

**Step 6:** Residual Fraction (RES): The residues from organic fraction are digested using HF-HCl/HNO<sub>3</sub>.

Generally, water soluble and exchangeable forms were considered to be the mobile and easily bioavailable, while residual form was considered to incorporate into crystalline lattice of soil minerals and appeared to be the most inactive.

**Table 1:** Some physical and chemical properties of soil samples collected from different areas based on air dried samples.

Location	Sample No.	pH	EC dS/m	OM %	CaCO <sub>3</sub> %	Particle size distribution %			Surface Area m <sup>2</sup> /g	Heavy metals total concentration ppm			
						Sand	Silt	Clay		Pb	Ni	Cu	Zn
El-gabal El Asfar (G1)	1	6.80	0.20	3.60	2.09	86.1	9.7	4.20	16.00	1.70	6.70	8.00	40.50
	2	7.93	0.60	3.00	1.74	85.8	4.2	10.00	32.00	1.10	17.00	25.40	88.00
	3	7.50	0.41	2.80	1.60	88.4	2.5	9.15	27.00	1.00	9.50	13.50	60.00
	4	8.32	0.45	2.30	1.35	92.4	0.1	7.47	20.00	1.00	9.50	8.00	45.50
	5	8.81	0.40	2.80	1.63	89.7	2.5	7.80	22.00	1.30	13.50	18.30	67.00
	6	8.88	0.45	2.00	1.16	89.2	0.1	10.60	30.00	2.50	16.00	19.10	77.50
	7	8.24	0.20	1.40	0.81	85.6	9.9	4.50	17.00	0.90	12.50	18.30	68.30
El-Saff (G2)	8	6.78	0.30	0.30	0.18	92.5	4.3	3.20	14.00	57.20	1.40	9.45	21.05
	9	6.39	0.20	1.20	0.70	94.1	2.7	3.20	13.00	54.35	14.00	13.30	45.55
	10	6.35	0.60	1.40	0.84	85.0	5.8	9.20	25.00	50.60	11.00	3.70	32.55
	11	6.50	0.10	0.40	0.26	85.6	9.6	4.60	20.00	47.20	14.00	2.45	9.60
	12	6.83	0.20	0.20	0.12	93.0	2.6	4.40	16.00	57.70	18.00	35.65	400.60
	13	6.28	0.80	1.90	2.85	90.2	6.2	3.60	15.00	63.20	14.00	33.50	94.55
	14	5.56	0.30	0.20	0.12	84.3	9.9	5.80	23.00	48.20	18.80	111.70	73.05
Kafr El-Zayat (G3)	15	7.60	0.40	1.72	0.65	14.5	35.1	50.40	230.00	8.40	8.03	11.50	190.00
	16	7.70	0.80	1.43	1.34	14.4	33.0	52.60	232.00	14.00	8.40	25.00	63.00
	17	7.93	2.00	1.80	1.56	15.5	32.1	52.40	229.00	12.00	8.00	8.40	160.00
	18	8.37	2.10	1.06	0.95	13.4	31.0	55.60	242.00	15.00	10.00	9.00	131.00
	19	8.16	2.60	2.30	0.65	13.7	32.0	54.30	235.60	16.00	9.50	6.00	180.00
	20	8.29	2.80	1.32	1.30	12.8	34.6	52.60	228.80	18.70	6.00	19.58	185.00
	21	8.16	2.10	1.96	0.72	14.7	34.1	51.20	229.50	25.80	15.00	42.90	149.00

### 2.3 Metal determination:

Metal concentrations in soil fractions were determined by inductively coupled plasma-mass spectrometry (ICP-MS; VG Plasma Quad 3, Fisons Instruments, UK) under optimized operating conditions. The total metal concentrations in soils were determined after digestion with HNO<sub>3</sub>-HF-HClO<sub>4</sub> (1:1:1) mixture under high

pressure conditions. The digestion procedure of soil samples and optimization of ICP-MS were documented by Zhang and Shan (1997).

#### 2.4 Statistical analysis:

Different statistical analysis such as relationships between heavy metal fractions and soil properties were evaluated by correlation coefficient which carried out taking into consideration all metal fractions with soil properties of the surface soil samples, according to SAS Institute, (1985).

### 3. Results:

The accumulation of metal ions and metalloids in different compartments of the biosphere and their possible mobilization under environmentally changing conditions induces a perturbation of both the structure and function of the ecosystem and might cause adverse health effects to biota. The distribution of Potential toxic element in soil system is an important tool in the bioavailability of such pollutants.

The total concentration of the pollutants range were as follows: In G1 (El Gabal El Asfar), the concentrations of PTEs were ranged in Pb between 131-166 ppm; Ni: 42-113 ppm; Cu: 53-99 ppm; Zn: 281-483 ppm. In G2, (El-Saff), the corresponding values were 170-180 ppm for Pb; Ni: 105-122 ppm; Cu: 89-110 ppm; Zn: 288-348 ppm. In G3 (Kafr El-Zayat), however, the concentrations of PTEs were 174-186 ppm for Pb, Ni: 66-76 ppm, Cu: 26 ppm and Zn: 118-125 ppm. The concentrations in this work were expressed as percentage for each fraction from the total to understand the actual bioavailable forms of the pollutants through the distribution of studied heavy metals.

#### 3.1 Heavy metals distribution in the contaminated soils as affected by source of pollution:

##### 3.1.1 Lead:

Data represented in table (2) and depicted in figure 1 showed that lead  $Pb^{+2}$  distribution in different sites, the readily available form represented by the sum of water soluble and exchangeable forms ranged between 6 and 16% in sewage farms (El-Gabal El-Asfar, decreased to be between 6-12% in the soils exposed to industrial effluents (El-Saff area) and from 4-11% in Kafr El-Zayat, the soils which exposed to both industrial and sewage effluents. It should be mentioned here that the high values were detected in sewage farms compared to other sites, more details about the reasons of this phenomenon will be documented in the discussion. Also, data showed that in almost all cases regardless the site, in WS form the highest value was observed in S7 and the lowest was in S5, the same trend was almost observed in the exchangeable form.

**Table 2:** Lead  $Pb^{+2}$  distribution in different soil groups as affected by source of pollution.

Sample No.	W S %	Exchang. %	Carbonate %	Fe-Mn %	Organic %	Residual %
El-gabal El Asfar (G1)						
S1	3.94	12.06	17.54	26.56	16.00	30.06
S2	3.73	10.97	15.06	16.75	17.02	36.50
S3	4.13	6.19	8.74	11.03	16.24	53.68
S4	4.35	6.22	8.08	10.92	18.06	52.36
S5	2.16	4.20	9.00	11.20	18.90	54.59
S6	2.71	8.60	16.25	17.25	18.70	43.81
S7	5.07	10.22	12.74	18.61	12.01	41.36
El-Saff (G1I)						
El-Saff						
S8	4.46	7.24	10.03	20.73	12.01	45.53
S9	4.47	4.71	15.42	18.84	11.24	45.32
S10	3.42	4.27	12.82	21.08	12.82	45.58
S11	3.12	3.69	8.22	15.93	12.36	56.69
S12	2.94	3.53	13.82	18.53	7.65	53.53
S13	2.03	6.45	12.18	15.74	5.74	57.87
S14	5.26	6.92	13.21	19.29	12.45	42.87
Kafr El-Zayat (G1II)						
S15	4.46	7.24	10.03	20.72	12.01	45.52
S16	4.47	4.71	15.42	18.83	11.24	45.32
S17	3.42	4.27	12.82	21.08	12.82	45.58
S18	3.12	3.68	8.22	15.93	12.36	56.69
S19	2.94	3.53	13.82	18.53	7.65	53.53
S20	2.03	6.45	12.18	15.74	5.74	57.87
S21	5.65	0.00	14.19	20.73	13.37	46.06

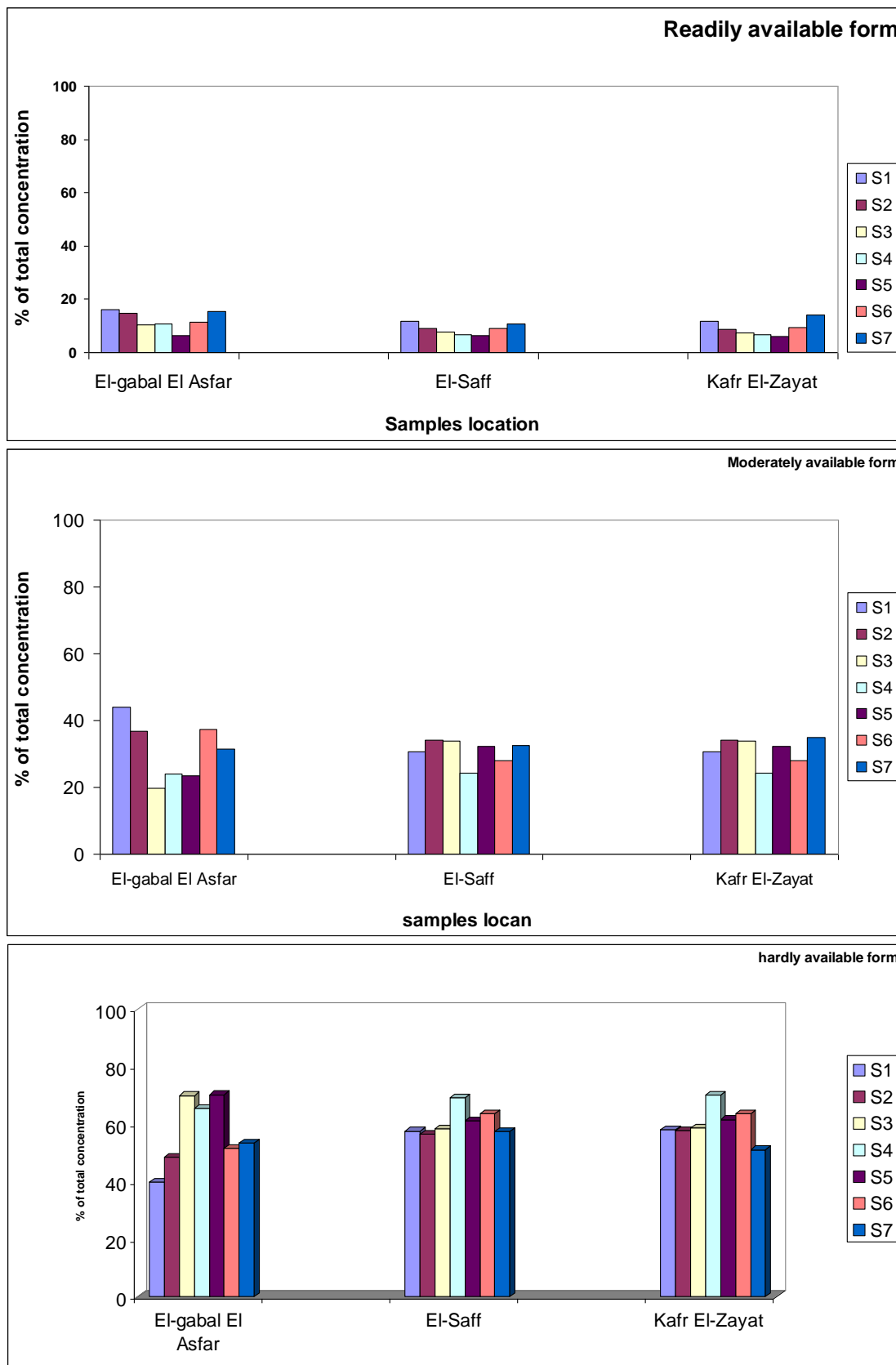


Fig. 1: Lead distribution in different forms in different studied regions.

According to the obtained data  $Pb^{2+}$  moderately available forms values were high in Kafr El-Zayat site ranged between 24-35 % of total concentration followed by El-Saff site 24-34% and the lowest values observed

in El-Gabal El-Asfar region with exception observed in one soil reached to 44% of total concentration. For the same form in all cases the Fe-Mn oxide fraction was higher than carbonate one in different soils used regardless the region selected, the greatest percentage observed in S1 and S3 in Kafr El-Zayat region.

The hardly available form of Pb, represented by the sum of both organic and residual fractions was the highest values in different sites compared to other forms studied. Data in table (2) showed that organic form in El-gabal El-Asfar was higher than that of El-Saff and Kafr El-Zayat regions. Numerically, organic form was ranged between 12-23% in El-Gabal El-Asfar meanwhile the corresponding values were ranged between 5-15 and 5-14 in both El-Saff and Kafr El-Zayat regions respectively. Worth to mention that reverse trend was observed in residual form of Pb in soil system.

### 3.1.2 Nickel:

Data in table (3) represented Ni distribution in different soils as affected by source of pollution. Like Pb, data showed that most of Ni retained in residual form (ranged between 21-43%). In sewage soils, data indicated that organic fraction reached to about 24% of total Ni in most cases, decreased to 10-12 % in almost all soils in industrial polluted soils of El-Saff region and 11-17% in Kafr El-Zayat soils. This result may declare the problem of sewage soils in retaining such pollutant. Some exceptions were observed as in S4 where the hardly available form reached to more than 65%, the same trend was observed in El-Saff soil (S11 and S15) which represents the mixture between sewage effluents and industrial contaminants.

In moderately available form, data showed that the Fe-Mn oxide form values in all soils regardless the source of pollution were significantly higher than the carbonate form, for example, in sewage soils ranged between 17-35% meanwhile it were 12-25% in Kafr El-Zayat soil, the same trend was also observed in El-saff soil samples. Regarding the comparison between different soils in the sites, in sewage soils the moderately available form reached to about 62% in S2 almost the same was observed in S9 from El-Saff industrial site and S16 from Kafr El-Zayate region. Nevertheless, in most cases regardless the source of pollution, this form ranged between 45-60% of total Ni found in soils.

Concerning the readily available form, data showed that almost no variation was between different sites collected, meanwhile a significant variation observed inside each site according to soil properties determined. In El-Gabal El-Asfar the readily available form in S3 was about 9% of total Ni, while it was 4.6 % in S6. It should be mentioned that almost the same values were observed in S9 and S19 in El-Saff industrial polluted soil and Kafr El-Zayate which represents the mixture between sewage and industrial polluted soils.

### 3.1.3 Copper distribution:

Data in table (4) indicated that most of Cu in these soils was found in residual fraction in most cases. In El-Gabal El-Asfar, the percentages of Cu in residual fraction were ranged between 37-80% from the total Cu content. The higher percent of Cu was pronounced in S6 and the lower one was in S4.

**Table 3:** Ni<sup>2+</sup> distribution in different soil groups as affected by source of pollution.

El-gabal El Asfar (G1)						
Sample No	WS%	EXCH%	carb%	fe-mn%	org%	res%
S1	0.46	4.92	12.31	19.08	22.46	40.77
S2	1.19	6.70	25.00	35.23	10.23	21.65
S3	1.09	7.92	16.83	24.55	15.84	33.76
S4	0.71	4.52	12.14	17.14	23.81	41.67
S5	1.28	3.51	15.14	30.14	17.57	32.36
S6	0.94	3.75	15.78	24.53	14.06	40.94
S7	1.06	3.54	17.26	23.19	11.50	43.45
El-Saff (G2)						
S8	0.92	5.38	15.38	22.77	9.85	45.69
S9	1.15	6.82	26.14	36.36	8.52	21.01
S10	1.49	7.90	17.33	23.76	11.88	37.64
S11	1.19	5.00	14.05	17.38	21.19	41.19
S12	1.51	3.38	15.68	30.41	14.19	34.84
S13	1.17	3.59	16.41	24.84	12.66	41.33
S14	1.12	3.72	18.67	22.12	10.88	43.49
Kafr El-Zayate (G3)						
S15	0.46	4.92	12.31	19.08	22.46	40.77
S16	1.19	6.70	25.00	35.23	10.23	21.65
S17	1.09	7.92	16.83	24.55	15.84	33.76
S18	0.71	4.52	12.14	17.14	23.81	41.67
S19	1.28	3.51	15.14	30.14	17.57	32.36
S20	0.94	3.75	15.78	24.53	14.06	40.94
S21	1.06	3.54	17.26	23.19	11.50	43.45

In G2, soil irrigated with effluent water and treated with sewage sludge for less than 10 years, the residual fraction percentages were ranged between 26-49% from the total content of Cu, the respective values for G3 were 51-36 % for S11 and S12 respectively. As a percent of total, most of non-residual fraction, Cu is concentrated in Fe-Mn oxide followed by that associated with carbonate fraction.

**Table 4:** Cu<sup>2+</sup> distribution in different soil groups as affected by source of pollution.

El-gabal El Asfar (G1)						
Sample No	WS%	EXCH%	carb%	Fe-mn%	org%	res%
S1	2.86	4.77	21.93	29.02	3.13	38.28
S2	1.26	4.81	26.20	29.06	6.86	31.81
S3	2.52	4.54	10.18	19.96	14.62	48.19
S4	2.08	6.67	15.14	21.25	17.64	37.22
S5	2.82	3.39	15.80	23.55	14.81	39.63
S6	2.08	7.95	24.24	31.25	15.34	19.13
S7	2.75	4.92	16.50	25.90	10.85	39.07
El-Saff (G2)						
S8	3.18	5.29	23.29	32.21	3.88	32.19
S9	1.28	4.87	25.98	29.47	6.96	31.44
S10	2.51	4.52	9.68	19.90	14.57	48.85
S11	2.27	7.26	17.56	23.15	19.21	30.50
S12	3.14	3.77	18.04	26.23	16.49	32.29
S13	2.18	8.33	27.96	32.72	16.06	12.77
S14	3.05	5.45	19.73	28.72	12.03	31.04
Kafr El-Zayat (G3)						
S15	2.86	4.77	21.93	29.01	3.13	38.28
S16	1.26	4.81	26.20	29.06	6.87	31.81
S17	2.52	4.54	10.18	19.96	14.62	48.19
S18	2.08	6.66	15.13	21.24	17.63	37.21
S19	2.82	3.39	15.80	23.56	14.81	39.64
S20	2.08	7.96	24.26	31.27	15.35	19.14

In these two forms, the obtained results indicated that more than 50 % of total Cu are associated with these two fractions in most cases of G2 soils. The percentages of organically bound Cu in the studied soil groups were observed to be the important fraction hold soil Cu after carbonated and Fe-Mn fractions in the case of decreasing their values. Worth to mention that the lowest percentage of Cu in all soils were detected for Exch. and WS forms in all groups of tested soils with some exceptions detected in both G1 and G3.

### 3.1.4 Zinc:

Results showed that residual fraction of Zn represented the higher form compared with other fractions (table 5). Results showed that (16-55%) of total Zn was retained in soils of G1, this ration was decreased in G2 to be (16-51%) and reached the maximum values in G3 (16-51 %).

Among the non-residual fraction, the Fe-Mn oxide form contained the greatest amount of Zn in most soils in the studied groups.

The dominating chemical form for Zn was varied between different groups according to source and time of receiving the pollutants. The Fe-Mn oxide-bound Zn represents 19-50 %, 19-50 % of total G2 and G3 respectively, which represent higher bound form with the carbonate-bound Zn.

The org. bound Zn in the studied group samples were potentially varied according to the source of pollutants and perhaps according to the soil components. Data showed that org-Zn ranged between 4 and 11% of total Zn in all groups.

### 3.2 Correlation analysis between soil properties of different groups and pollutants fractionation:

The correlation coefficient was estimated between the determined soil properties (table 1) and each of Pb, Ni, Cu and Zn fractions (tables 2-5).

The obtained values in tables 6 and 7 indicate that in most cases pH and EC did not give significant correlation with the fractions of the pollutants under consideration. However pH is highly positive correlated with org-pb and org-Cu.

While Ni- fractions have high positive values in G1 group (El-Gabal El-Asfar region) under sewage effluents for about 50 years. The positive correlation coefficient between O.M content and organically bound toxic elements ranged between 0.88\*\* - 0.92\*\* for Pb; 0.89\*\* - 0.93\*\* for Ni; 0.87\*\* - 0.88\*\* for Zn; 0.71\* - 0.76\* for Cu in the three groups of soils. Also O.M is highly positive correlated with Resid-Pb (0.86\*\*).

**Table 5:** Zn<sup>2+</sup> distribution in different soil systems as affected by source of pollution.

El-gabal El Asfar (G1)						
Sample No.	WS%	Exch%	Carb%	Fe-Mn%	org%	res%
S1	1.73	3.51	25.79	33.13	4.51	31.34
S2	1.07	7.32	23.59	32.27	7.81	27.93
S3	1.14	5.01	12.30	18.72	11.36	51.47
S4	0.97	3.95	18.70	21.86	6.32	48.20
S5	2.25	6.20	16.21	22.22	6.82	46.30
S6	1.06	5.05	23.47	49.97	4.29	16.15
S7	0.99	5.35	16.19	17.50	5.09	54.87
El-Saff (G2)						
S1	1.73	3.51	25.79	33.13	4.51	31.34
S2	1.07	7.32	23.59	32.27	7.82	27.93
S3	1.14	5.01	12.30	18.72	11.36	51.47
S4	0.97	3.95	18.70	21.86	6.32	48.20
S5	2.25	6.20	16.21	22.22	6.82	46.30
S6	1.06	5.05	23.47	49.97	4.29	16.15
S7	1.40	7.57	22.91	24.75	7.20	36.17
G3 Kafr El-Zayat (G3)						
S1	1.72	3.49	26.14	32.97	4.49	31.19
S2	1.07	7.33	23.63	32.26	7.81	27.92
S3	1.14	5.01	12.31	18.71	11.36	51.46
S4	0.97	4.58	18.58	21.72	6.28	47.88
S5	2.25	6.20	16.21	22.22	6.82	46.30
S6	1.06	5.25	23.42	49.87	4.28	16.12
S7	1.42	8.11	23.19	25.07	7.30	34.92

**Table 6:** Correlation analysis between some soil properties and distribution of Pb and Ni in the studied areas.

pb					Ni			
El-gabal El Asfar (G1)								
	OM	clay	pH	EC	OM	clay	pH	EC
WS	0.19	0.23	-0.32	-0.42	0.28	0.20	0.88**	0.18
EXCH	-0.87**	-0.79*	-0.49	-0.39	0.28	0.70*	0.92**	0.34
carb	-0.95**	-0.87**	-0.18	-0.27	0.70*	0.10	0.91**	0.29
Fe-Mn	-0.87**	-0.67	-0.21	-0.33	0.09	0.88**	0.82**	0.34
orgn	0.92**	0.91**	0.85**	0.07	0.80*	0.72*	0.85**	-0.06
res	0.91**	0.90**	0.59	0.19	0.26	0.23	0.94**	-0.36
Total	0.70*	0.86**	0.60	-0.13	0.24	0.14	0.90**	0.06
El-Saff (G2)								
WS	-0.56	0.23	0.21	0.46	0.26	0.57	0.45	0.22
EXCH	0.84**	0.62	0.17	0.53	0.06	0.53	0.32	0.21
carb	0.18	0.42	0.04	0.40	0.14	0.67	0.62	0.04
Fe-Mn	0.44	0.51	0.49	0.32	0.02	0.68	0.39	0.04
orgn	0.88**	0.13	0.01	0.37	0.59	0.62	0.55	0.11
res	0.26	0.02	0.45	0.38	0.07	0.25	0.80*	0.31
Total	0.11	0.21	0.57	0.54	0.05	0.59	0.70*	0.19
Kafr El-Zayat (G3)								
WS	0.56	0.23	-0.74*	-0.84	0.15	0.65	0.02	0.28
EXCH	0.44	0.47	-0.34	-0.29	0.05	0.53	0.31	-0.08
carb	0.18	-0.42	-0.27	0.08	0.12	0.69	0.19	-0.01
Fe-Mn	0.44	0.51	-0.74*	-0.50	0.02	0.69	0.15	0.10
orgn	0.91**	0.13	-0.44	-0.62	0.51	0.36	0.26	0.49
res	0.26	0.02	0.50	0.47	0.05	0.29	0.32	0.45
Total	-0.07	0.19	0.14	0.06	0.05	0.59	0.04	0.26

The clay content of the studied samples, as an important factor particularly in the group of G3 (where clay ranges between 50-56%), the estimated correlation showed that Org-and Res- fractions of Pb gave high and positive values. For Cu and Zn pollutants, most fractions have non-significant relationship with clay contents except the Org-Cu which has positively significant correlation coefficient (0.76\*).

Regarding silt content, only Fe,Mn-Ni, Carb-Cu and Exch- forms gave have highly significant correlation. Also the surface area, of the studied samples, gave high positive correlation with Org. and Residual forms (0.81\*\*-0.83\*\*).

**Table 7:** Correlation analysis between some soil properties and distribution of Cu and Zn in the studied areas.

Cu				Zn				
El-gabal El Asfar (G1)								
	OM	clay	pH	EC	OM	clay	pH	EC
WS	0.53	0.43	-0.50	-0.59	0.30	0.45	0.38	-0.05
EXCH	0.01	-0.19	-0.17	0.43	0.14	0.25	0.71*	0.45
carb	-0.71*	-0.70*	-0.30	0.41	-0.59	-0.39	0.49	0.29
Fe-Mn	-0.51	-0.62	-0.59	0.24	-0.51	-0.49	0.52	0.35
orgn	0.91**	0.76*	0.86**	0.34	0.77*	0.63	0.75*	0.51
res	0.59	0.39	-0.54	-0.07	0.76*	0.91**	0.31	-0.24
Total	0.37	0.14	-0.56	0.23	0.32	0.53	0.90**	0.20
El-Saff (G2)								
WS	0.30	0.37	0.05	0.04	0.30	0.45	0.52	-0.26
EXCH	-0.30	-0.32	-0.22	0.47	0.14	0.25	-0.02	-0.17
carb	-0.88**	-0.77*	-0.02	0.14	0.59	-0.39	0.22	-0.03
Fe-Mn	-0.95**	-0.87**	-0.06	0.28	0.51	-0.49	0.14	0.52
orgn	0.73*	0.69	0.81**	0.21	0.72*	0.63	0.78*	-0.14
res	0.56	0.35	0.07	-0.16	0.86**	0.91**	0.43	-0.48
Total	0.04	-0.29	-0.08	0.48	0.32	0.41	0.51	-0.10
Kafr El-Zayat (G3)								
WS	0.53	0.43	-0.23	-0.06	0.30	-0.01	0.13	0.31
EXCH	0.01	-0.19	0.09	-0.09	0.17	0.61	0.34	0.46
carb	-0.71*	-0.70*	-0.69*	-0.73*	-0.61	0.69*	0.14	0.05
Fe-Mn	-0.51	-0.62	-0.90**	-0.81**	-0.51	0.57	0.24	0.31
orgn	0.91**	0.76*	0.88**	0.65	0.71*	-0.29	0.73*	0.32
res	0.59	0.39	-0.37	-0.25	0.86**	-0.45	0.34	0.35
Total	0.37	0.14	-0.54	-0.42	0.31	0.19	0.49	0.56

- \*means significance at 0.05 level
- \*\* means significance at 0.01 level
- Other numbers did not gave any significance

#### 4. Discussion:

Metal pollution in soil can be created from different sources such as sewage effluents applied through the irrigation with low quality water, heavy application of fertilizers, and location of soils beside source of pollution like factories...etc. The graduations in distribution of elements were explained by Ma *et al.*, (1997). they documented that WS and Exchangeable fractions will be readily bioavailable to the environment, meanwhile heavy metals in residual fraction are highly bound and wouldn't be released under natural conditions, worth to mention that the same result was reported by Xian (1989). The other determined fractions i.e. Carbonate, Fe-Mn oxides and organically bound forms considered as a reserve source, replenished the decreasing of heavy metals concentrations in soil system Clevenger and Mullins (1982).

As an important result in this study, the two main forms (residual and non residual) distribution were controlled by the type of pollutant(s) studied, soil properties and source of pollution. Specifically, the main form of pollutants in sewage soils, as referred by Soad El-Ashry *et al.*, (2011), is the organic one for all pollutants studied compared to other forms.

In some cases, data showed that Pb<sup>2+</sup> distributed in non-residual form was in Fe-Mn oxide fraction as shown in groups G1 and G2, the same result was reported by Carmen and Murray (2001). Under increasing of organic matter in G1 (1.3-3.6%), the same pollutant was found in organic fraction, similar result was reported by Sposito *et al.*, (1982). The decreasing order of different non-residual fractions of Pb according to the mean value in groups G1 and G2 are: Fe-Mn > Carb > Org. > Exch. > WS, the respective arrangement of pollutants in G3 was Org > Carb > Fe-Mn > Exch > WS.

As mentioned above, the type of pollutant becomes a very important factor in heavy metal distribution in soil system. Tipping *et al.*, (1985) and McGrath and Cegarra (1992). found that adsorption of Pb to Mn oxides was approximately 40 times greater than that of Fe oxides. The high concentration of Pb in group G3 (Kafr El Zayat area) compared to other groups of soils could be attributed to the vicinity close to the highways; the same observation was mentioned by Harrison *et al.*, (1985) and Scanlon (1991)

Nickel pollutant mainly associated with Fe-Mn oxide fraction followed by carbonate and organic form in the soils of G1. In group G3, although the increase of clay content and applying organic fertilizers, org-Ni comes in the third category after Fe-Mn and organic forms, this result may be due to the concentration of pollutant competed to other PTEs found in soil system. The decreasing order of Ni distribution in the three groups of soils could be arranged as: Fe-Mn > org. = Carb > Exch > Ws in G1, G2 and org > Fe-Mn = carb > Exch > Ws for G3.

Results of Cu distribution showed that organically bound Cu was the dominant fraction in the soils of groups G2 and G3. The increase of organic matter in soil would help in reducing the metal ions form associated with exchangeable sites and acidic conditions take place according to the increase of OM content could bind more metals in organic fraction.



Correlation analysis between soil parameters and pollutants fractionation emphasized that organic matter content, in the studied samples, is highly correlated at 0.01 level with Pb, Ni and Zn at 0.05 level with organically bound fraction. The clay content and specific surface area of used soil were the most important soil parameters influencing distribution of the heavy metals in the studied groups. According to the obtained results, the relationship between soil parameters and pollutant fractions were complicated and varied in different soils, however, they were the main factors in distribution of heavy metals. It may also be the reason for the contradiction between different studies as reported by McLaren and Crawford (1973) Iyengar *et al.*, (1981). They mentioned that statistical relationship was observed between metal fractions and soil properties. In contrast, Miller and McFee (1983) found no significant relationship between the two factors. In other work, Ramos, *et al.* (1994). reported that distribution of metals to various chemical fractions mainly depended on total metal content of the soils.

It can be concluded that although the concentrations of heavy metals in soil system is very important parameter in their distribution, source of pollution and soil properties were also very important parameters controlled both the type of PTEs found in soils, distribution and subsequently bioavailability.

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