ISSN 1110-0419

Annals Of Agric. Sc., Moshtohor,
Vol. 45(3): 1259-1268, (2007).

ASSESSMENT OF SOME HEAVY METALS POLLUTION IN SOME SOILS OF EGYPT

BY

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ABSTRACT

The study represents an attempt to ascertain some of possible reactions of some heavy metals (Cd, Cu, Pb and Zn) in a sludge soil (Abu-Rawash farm), and an industrial contaminated soil, near to the Industrial Complex, Helwan City.

The obtained results of the present study indicate that soil –pH and total carbonate content (TCC) slightly decreased in the two tested soils. However, clay content and organic matter content were increased in the sludge soil due to the organic and sediment materials existed in the sewage effluents.

The results also reveal that the total content (through the profile) for the tested heavy metals in the sludge soils may be ranked descending as follows (in mg/kg) Zn (492.42), Cu (54.66) Pb (52.27) and Cd (5.48). Meanwhile in the industrial – contaminated soil they ranked as; (in mg/kg) Zn (102.08) Pb (85.9) Cu (45.66) and Cd (7.06) .

Also, the DTPA-extractable metals may be ranked in (mg/kg) as follows; Zn(12.59),Cu(12.55). Pb (0.84) and Cd (0.25). Meanwhile, in the industrial – contaminated soil, they ranked as follows: Cu(1.06), Zn(4.54), Pb (1.37), Cu(1.06) and Cd (0.19) mg/kg.

The results also indicate that the content of the tested metals may by arranged decendingly as; Cd > Pb > Cu > Zn and Pb > Cd = Cu > Zn in the sludge and the industrial – contaminated soil, respectively.

The studies of fractionation showed that residual (32.5%), organic fraction (29.06%) dominates the sludge soil followed by carbonate (19.31%) > oxide (12.06%) >exchangeable (6.15%) of their sum. Meanwhile, in the industrial- contaminated soils these fraction could be arranged according to their magnitudes as residual =oxide (27%)> carbonate (21.35%) >exchangeable = organic (11%).

On a mean basis, the results also indicated that the active portions of Cd^{2+} in the tested soil on a mean basis in (pM=-log Cd^{2+}) were; 8.534 and 8.093 in the sludge soil and the industrial contaminated soil, respectively .

The relatively high portion percent of Cd^{2+} in the former soil compared by Helwan soil, may be attributed to the lowering pH values of the former one as a result of sewage effluents.

Key words: Heavy metals- total content – activity – fractionation.

INTRODUCTION

Soil pollution with heavy metals has become an important social and environmental challenging problem. Heavy metals accumulation through both geogenic as well as anthropogenic sources as metal smelting industries, industrial effluent, sewage sludge, refuse, burning fossil fuel (Alloway, 1995).

Traditionally, assessment of metal pollution of soil is based on measurements of total metal content in soil system and its activity in soil solution concentrations, evaluation of the adsorbed and exchangeable fractions of total concentrations obtained though the use of various selective extractants .

Furthermore, (Aboulroos *et al.*, 1991; Badawy and Helal,2002; El-Gendi,2003) accepted that metal toxicity in soil is controlled manly by the free metal species more than the undissolved .

Also, the studies of Bell *et al.* (1991), Holm *et al.*,(1995), Sauve *et al.*, (1997) and Bipra (1997) demonstrated that the mobility and bioavailability of those metals can be more fully identified on the basis of the free species studies of that pollutant.

So, the main objectives of the present study are: to evaluate the content of Cd, Pb, Cu and Zn in tow polluted areas in Egypt (sludge and industrials and to assess the behavior of Cd in the tested soil (mobility, fractionation and the active specces of Cd^{2+}) in two sites in Egypt enduring of heavy metal contamination .

MATERIAL AND METHODS

Two polluted sites enduring of heavy metals contamination for a rather long time were selected from Cairo governorate, Egypt. These two sites are Abu-Rawash area which received sewage effluent as a solely source of irrigation and the second site from Helwan area characterized by industrial contamination. At each site, two soil profiles were dug to a depth of 150 cm as the following; one profile representing the contaminated area either sludge or industrial contaminates soils and the second profile was selected from uncultivated area and assumed to be uncontaminated(control). At each profile the soil was sampled at each 30 cm up to a depth of 150 cm. Three subsamples were taken from each soil sampled layer to make a composite sample for the relevant analysis.

The soil samples were air dried, sieved through a 2 mm screen for routine analysis, according to conventional methods as described by Black (1965).

DTPA extractable metals:

The tested soils were analyzed for the available fraction of (Pb, Cd, Cu & Zn) as described by Lindsay and Norvell (1978). The clear supernatants were analyzed for the tested heavy metals using Inductively Coupled Spectrometer Plasma (ICP), Model 400.

Total content of heavy metals:

Total contents of Cu, Cd, Pb, and Zn were determined in the tested soil samples as described by Tessier *et al.* (1979).

Cadmium fractionation:

The selected soil samples were fractionated sequentially according to Tessier *et al.* (1979) to the following Fractions:-

1) Exchangeable portion (1M NaOAC, pH 8.2)
2) Bound to carbonate (1M NaOAC, pH 5.0)
3) Bound to Fe & Mn oxides (0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAC).
4) Organically bounded metal (0.02 M HNO_3 and 5.0 ml of 30% H_2O_2, pH 2.0 with HNO_3) and
5) Residual fraction (concentrated HF and $HClO_4$).

Measurement of Cd^{2+} activities:

Measurements of Cd^{2+} of the selected soil samples were run using the competitive chelation method described by Workman and Lindsay (1990) and El-Falaky *et al.* (1991).

RESULTS AND DISCUSSION

General characteristics of the tested soils:

The routine analyses of both sludge and heavy metals contaminated soils (in tables 1 a, b) reveal the followings:

Abu-Rawash, sludge- amended soil; the mean pH value of the control varied from 7.67 at profile bottom layer (120-150 cm) being increased (almost gradually) upwards reaching 7.85 at the surface 30 cm soil layer. As for the sludge soil, on contrary, the soil pH (7.2) of the bottom profile layer was gradually upward reduced reaching 6.85 at the surface soil layer. Note was thy referring that the soil pH tendency to be reduced upwards could be attributed to added organic acids and acidified products found in the added sludge materials.

The general pattern of clay distribution in the control profile showed the highest clay contents two bottomed soil layers, the coarsest texture was observed at the surface 30 cm layer.

The Table also shows that the initial organic matter content of the soil of Abu- Rawash was very low, being only (0.07 %in the control) . This content increased up to 3.22% through 40 years of continuous sludge application. Data in the Table reveal that the total carbonate content (TCC) in the control soils ranged between (1.01 to 1.94%, x = 1.34%) and (8.20 to 9.14 %, x = 8.61%) in Abou –

Rawash and Helwan soil, respectively. The lowering TCC of the former soil compared to the latter one may be attributed to dissolution by the action of the organic acids present in the sewage effluent, e.g., humic and fulvic acids, and also to the nitrification of the nitrogen mineralized during organic matter decomposition (Badawy and Helal, 2002; El-Gendi, 2003)

Table (1 a): Some soil physical and chemical properties for Abu-Rawash area.

Depth (cm)	Control				Sludge			
	pH	Clay%	OM%	TCC	pH	Clay%	OM%	TCC
0-30	7.85	1.47	0.09	1.94	6.85	5.29	4.02	0.54
30-60	7.81	2.31	0.06	1.41	6.90	6.09	3.31	0.68
60-90	7.63	1.55	0.06	1.30	7.19	6.12	3.42	0.64
90-120	7.82	2.55	0.07	1.01	7.15	5.13	3.30	0.72
120-150	7.67	3.46	0.07	1.05	7.20	4.68	2.05	0.70

Table (1 b): Some soil physical and chemical properties for Helwan area.

Depth (cm)	Control				Containment			
	pH	Clay%	OM%	TCC	pH	Clay%	OM%	TCC
0-30	8.01	5.96	0.45	8.20	7.60	9.34	1.98	7.92
30-60	8.01	4.45	0.23	8.25	7.64	9.59	1.26	7.94
60-90	8.13	4.97	0.41	9.14	7.71	7.35	1.20	8.11
90-120	7.94	4.44	0.36	8.97	7.83	9.49	0.79	8.11
120-150	7.90	2.80	0.27	8.49	7.80	8.75	0.74	8.01

Total metal contents:

Total content of each of the tested heavy metals in the soil profile at Abu-Rawash are presented in Table (2 a). The values of total Cu, Zn, Pb and Cd in mg/kg) ranged between (17.4 – 113), (66.3 – 1136.9), (7.03 – 120.7) and (4.02 – 6.3), respectively. The highest increments apparent in the surface soil layer (0-30 cm) are reasonably due to the accumulation of organic matter in this layer as a result of continuous irrigation with sewage effluent.

Table (2 a): Total and available heavy metal contents in Abu-Rawash farm

Depth (cm)	Total Content $mg.kg^{-1}$				Available content $mg.kg^{-1}$			
	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
0-30	113	1136.9	120.7	6.30	55.6	21.2	1.83	0.36
30-60	95	592	62.84	6.28	4.61	21,09	0.96	0.26
60-90	29.5	480	50.95	5.41	1.35	15.36	0.84	0.23
90-120	18.4	186.9	19.84	5.39	0.62	4.12	0.31	0.23
120-150	17.4	66.3	7.03	4.02	0.57	1.19	0.26	0.17
Mean	54.66	492.42	52.27	5.48	12.55	12.59	0.84	0.25
Control	19	34	3	0.51	2.19	4.56	0.12	0.09

The content of Cu of the surface layer was 6 times of those of the control. The level of Cu in the polluted soil still within the normal range of the maximum permitted Cu loading in soil establishes by the USEPA, regulation (1993), but higher than the limits described by Germany and Ontario, scientists (50-140 mg kg-1), McBride (1995). With respect to Zn data shown in table (2a) declare that the Level of total Zn in the profile surface layer was about 33 folds of its concentration (34 mg Kg^{-1}) in the control soil. Also, the level of total Pb and Cd in profile surface layer was about 40 and 11 folds of its concentration (3 and 0.51 mg /Kg for Pb and Cd, respectively) in the control soil.

Table (2 b): Total and available heavy metal contents in Helwan area

Depth (cm)	Total Content $mg.kg^{-1}$				Available content $mg.kg^{-1}$			
	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
0-30	51.9	476.3	94.8	8.0	1.34	12.50	1.29	0.27
30-60	54.2	180.5	86.5	7.94	1.40	4.02	1.12	0.20
60-90	51.6	103.6	84.4	7.82	1.08	2.62	1.45	0.19
90-120	38.1	76.8	81.9	6.54	0.76	1.63	1.99	0.15
120-150	32.5	73.2	81.9	5.02	0.70	1.95	0.99	0.17
Mean	45.66	102.08	85.9	7.06	1.06	4.54	1.37	0.19
Control.	27	75	9	1	0.13	2.48	0.1	0.05

Total (Cu, Zn, Pb and Cd) concentrations for Helwan area, contaminated by industrial wastes are also presented in Table (2b). The values of heavy metals are found in highest concentrations in the surface layer and decreasing with depth, except only for Cu at the (30-60 cm) soil layer, the values of Cu ranged from 32.5 to 51.9, Zn from 73.2 to 476.3, Pb from 81.9 to 94.8 and Cd from 5.02 to 8.0 mg /kg. The data reveal that Cu and Zn still within the normal range compared with the maximum permitted Cu and Zn loading established by USEPA (1993) regulation .Meanwhile, Pb and Cd are in the permissible level in the maximum values of permitted loading are (150 and 20 $mgkg^{-1}$) for Pb and Cd established by USEPA (1993) regulation. They were higher than those described by McBride (1995).

Heavy metals bioavailability:

Data in the Table (2a and b) show that the level of DTPA-extractable Cd, Cu, Pb and Zn in the control soils were in sequence as follows: 0.09, 2.19, 0.12 and 4.56 mg/Kg in Abu –Rawash soil and 0.05,0.13,0.10 and 2.48 mg/kg in Helwan soil . Due to sludge application these metals increased. The highest values were recorded for Zn (12.59, followed by Cu (12.55), > Pb (0.84) and Cd (0.25). The same observations were also recorded for Helwan soils, however the accumulation of the tested metals may be arranged descendingly (in ppm) as follows; Zn (4.54),Pb (1.37), Cu (1.06) and Cd (0.19) .

Movement of the tested heavy metals:

Fig. (1a and b) shows that contents of Zn, Cu, Pb and Cd in the deepest layer (120-150) amounted to 6,6, 15, 30 and 64% respectively for Abu Rawash and 15, 63, 86 and 63% respectively for Helwan area, of their contents in the surface layer. Consequently, the tested metals could be arranged according to their mobility as follows: Cd> Pb>Cu>Zn for the sewage pollution (Abu-Rawash), and Pb>Cd = Cu>Zn for industrial pollution (Helwan).

The varied leach ability of the testes metals could be attributed to their chemical forms presented in sewage or industrial wastes, at a higher degree and to the movable form of each metals.

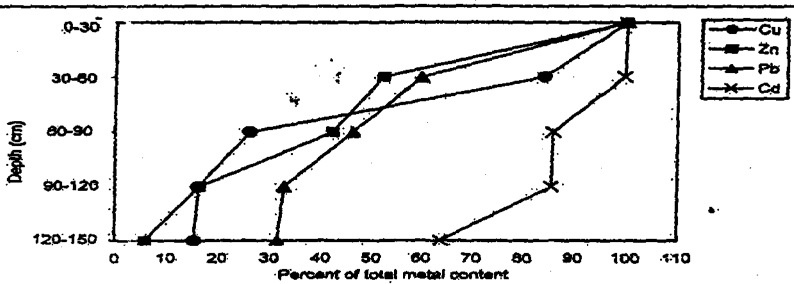

Fig. : Distribution of totals metal content with depth as a percent of surface layer content at Abu Rawash

Fig. (1 a): Distribution of totals metal content with depth as a percent of surface layer content at Abu Rawash.

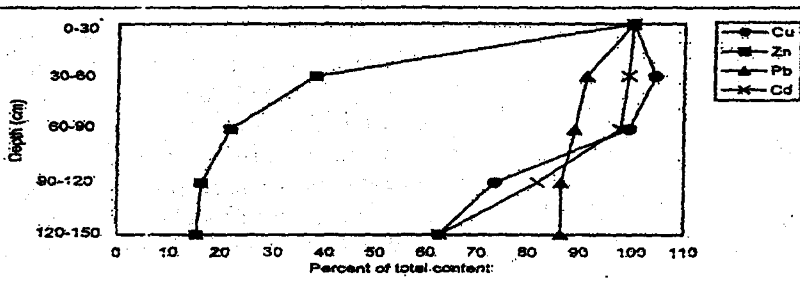

Fig. : Distribution of total metals content with depth as a percent of surface layer content at Helwan

Fig. (1 b): Distribution of totals metal content with depth as a percent of surface layer content at Helwan.

Fractionation of soil Cd:

Fig. (2a,b) illustrate the various fractions of Cd extracted sequentially expressed as percentage of their sums in the tested soils. It's obvious from the figures that Cd-exchangeable fraction constituted the least amount of Cd in Abu – Rawash soil; it is varied from 3.77 to 9.06 as percentage of the sum of the all extracted Cd fractions, (mean 6.15%). Meanwhile, this fraction amounted 12.90% of the sum of fractions in Helwan soil. The lowest value of this portion in the first soil may be due to the negative correlation between pH value and the amount of exchangeable form of Cd as mentioned by Aboulroos *et al.*, (1991), Onyatta and Huang (1999) and Badawy and Helal (2002).

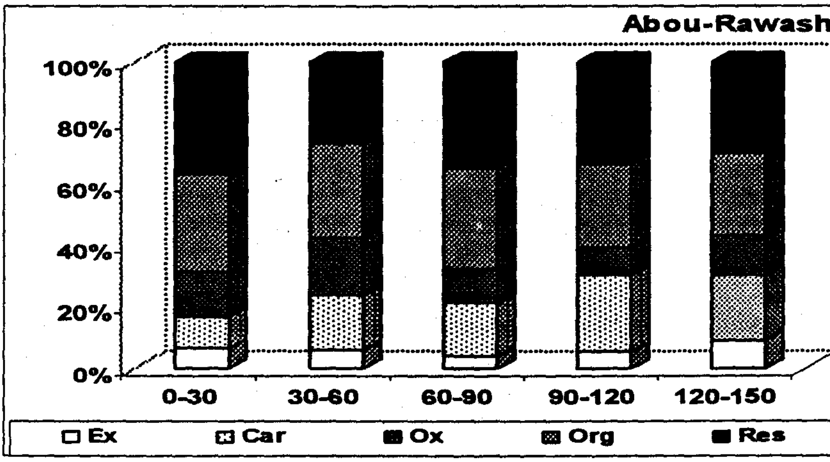

Fig. (2 a): Cd fraction in Abo-Rawash soil samples expressed as % of their sum

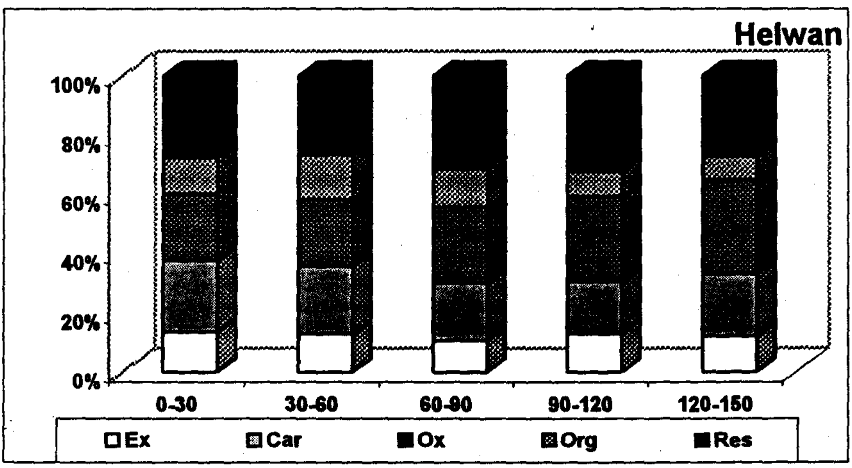

Fig.(2 b): Cd fraction in Helwan soil samples expressed as % of their sum

Also, the figure (2a, b) showed that Cd-Carbonate fraction averaged of 19.31% and 21.35% of their sum in Abu – Rawash and Helwan soil, respectively . The relative high portion of carbonate fraction in the former soil may be due to the high content of $CaCO_3$ in that soil.

Also, the Figures showed that Cd-Oxides fraction constituted relatively high portion of total (average of 7.441 $mgkg^{-1}$, equal to 23.2% of total) in Helwan soil samples .Meanwhile, it constituted only 12.06% in the Abu-Rawash soil samples. This highest portion of Cd –oxide in Helwan soil may be related to the Al-, Fe-, and Mn–oxides in the soils. Simillar conclusions were also observed by El-Sokkary, (1979); Aboulroos *et al.* (1991), El- Gendi *et al.* (1997), Badawy and Helal(2002) and El-Gendi (2003).

The present data show that the Cd-organic fraction is the dominant fraction in Abu –Rawash soil (average 1.35 $mgkg^{-1}$ or 29.06% of total). Whereas, it is amounted only 11.32% in Helwan soil. The high Cd – organic bounded portion in the first soil may be related to the high content of organic carbon content in the soil.

The data also reveal that Cd-residual fraction constituted the highest portion of the soil. It averaged around 32.50% and 27.02 % in Abu –Rawash and Helwan soil, respectively. This fraction can be considered as the primary form of native Cd in these soils.

On an aware basis It be concluded from the previous results that the extracted various fractions may be arranged descendingly as follows:

In Abu–Rawash soil: Residual (32.5%) > Organic (29.06%) > Carbonate (19.31%) > Oxide (12.06) > Exchangeable fraction (6.15).

In Helwan soil: Cd fractions may arranged as follows; residual = oxide (ca. 27 %) > carbonate (21.35%)> exchangeable =organic (ca. 11%)

Measurement of Cd^{2+} activities in the tested soils:

The data of Table 3 show that *p* Cd^{2+} activities in Abu-Rawash soils varied from (7.804 to 8.311) with mean of (8.534), whereas in Helwan soils it ranged from (8.446 to 8.678), with a mean value of (8.093) .

The data of the Table (3) also indicate that $Cd2^{+}$ in Abu-Rawash soil is higher than that in Helwan soil by (34%). These findings may due to amending the former soil with sludge for long time, consequently leading to decrease soil pH, wheares the latter soil has been contaminated by industrial wastes which was characterized with high pH.

Table (3): The equilibrium mole fraction, equilibrium pH and the calculated Cd^{2+} of the tested soils.

Location	Soil depth(cm)	Eq(pH)	Eq CdL/ CdL+pbL	P Cd^{2+}
Abu-Rawash	0-30	7.23	0.067	7.80393
	30-60	7.30	0.068	7.93749
	60-90	7.36	0.051	8.18243
	90-120	7.39	0.052	8.234
	120-150	7.42	0.05	8.31103
	Mean			8.534016
Helwan	0-30	7.50	0.053	8.44572
	30-60	7.53	0.047	8.5579
	60-90	7.51	0.049	8.4998
	90-120	7.50	0.048	8.48876
	120-150	7.59	0.047	8.6779
	Mean			8.09378

$P=-\log M^{2+}$

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تأثير التلوث ببعض الفلزات الثقيلة فى بعض الأراضى في مصر

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هذه الدراسة توضح صورة للتفاعلات في بعض الفلزات الثقيلة (النحاس-الزنك-الرصاص-الكادميوم) وذلك في الأراضي الملوثة بمصدرين من التلوث وهما: الأراضي الملوثة بمخلفات الصرف الصحي (مزرعة أبورواش)، الأراضي الملوثة بمخلفات الصرف الصناعي (منطقة حلوان القريبة من المصانع). وأوضحت النتائج أن قيمة الـ (pH) وأيضاً نسبة الكربونات الكلية (TCC) حدث بها نقص طفيف في كلاً من الموقعين.بينما حدثت زيادة في نسبة المادة العضوية والطين في الأراضي الملوثه بمخلفات الصرف الصحي وهذا يعزي إلى لوجود المواد المرسبة في مياه الصرف الصحي.

كان المحتوى الكلي من العناصر في الأراضى الملوثه بمخلفات الصرف الصحي (٤٩٢,٤٢) مللجم / كجم في الزنك – (٥٤,٦٦) مللجم / كجم في النحاس – (٥٢,٢٧) مللجم / كجم في الرصاص – (٥,٤٨) مللجم / كجم في الكادميوم بينما الأراضي الملوثه بمخلفات الصرف الصناعي كانت الكميه الكلية من الفلزات كالأتى الزنك (١٠٢,٠٨) مللجم / كجم – الرصاص (٨٥,٩) مللجم / كجم – النحاس (٤٥,٦٦) مللجم / كجم – الكادميوم (٧,٠٦) مللجم / كجم. أما تقدير الميسر من العناصر وذلك باستخدام مستخلص الـ (DTPA) كانت متوسط تركيز الفلزات (بمللجم / كجم) هي الزنك (١٢,٥٩) – النحاس (١٢,٥٥) – الرصاص (٠,٨٤) – الكادميوم (٠,٢٥) وذلك في الأراضي الملوثه بمخلفات الصرف الصحي. أما في الأراضي الملوثه بمخلفات الصرف الصناعى كان التركيز هو الزنك (٤,٥٤) مللجم / كجم و الرصاص (١,٣٧) مللجم / كجم و (١,٠٦) مللجم / كجم في النحاس و الكادميوم(٠,١٩) مللجم / كجم.

وفي دراسة الصور الكيميائية المختلفة لفلزالكادميوم. أوضحت النتائج أنه فى الأراضى الملوثة بمخلفات الصرف الصحى كانت الصورة التبقيه (٣٢,٥%) الصورة العضوية (٢٩%) والصورة المرتبطة بالكربونات بنسبة (١٩,٣١%) وتليها الصورة المرتبطة بالأكاسيد (١٢,٠٦%). أما تركيز الصورة المتبادلة فكان (٦,١٥ %).

أما فى في الأراضي الملوثه بمخلفات الصرف الصناعي كانت الصورة المتبقية = الصورة المرتبطة بالأكاسيد (٢٧%) وكانت نسبة الصورة المرتبطة بالكربونات (٢١,٣٥%) والصورة المرتبطة بالمادة العضوية = الصورة المتبادلة (١١ %).

وأوضحت النتائج أن نشاط عنصر (cd)+2 أعلى في الأراضي الملوثه بمخلفات الصرف الصحي عنها في الأراضي الملوثه بالصرف الصناعي وذلك لانخفاض قيمة الـ (pH).