

# STUDIES ON SOME HEAVY METALS CONTENT IN POLLUTED SOILS AND THEIR ACCUMULATION IN PLANTS

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## ABSTRACT

The present study was conducted to investigate the accumulation of some heavy metals (Cd, Cu, Pb and Zn) in soils and plants with different sources of pollution. The soil samples were collected from 3 sites from each of El-Gabal EL-Asfar, Abou-Rawash, and Helwan areas which received sewage sludge and sewage effluent for a long time. Also, one soil sample from Helwan was collected to represent the contamination by industrial waste. The plant samples were taken from the same location of soil samples.

Soil pH and total carbonate content (TCC) are slightly decreased as the irrigation period increased. However, organic matter increased. Total, bioavailable contents of Cd, Cu, Pb, and Zn of soils, increased as the irrigation period increased. Total contents exceeded, in many cases, and/ or reached, in some ones, the maximum permitted loadings.

DTPA-extractable Cd, Cu, Pb and Zn increased continuously in the studied areas which received sewage sludge, sewage effluent and industrial materials for a long time. Bioavailable portions were found to represent a great deal of the total contents. The low percentage of total extracted by DTPA is due to its precipitation as CaCO<sub>3</sub>. These results give an evidence of high availability of sewage effluent burden-metals to plants. There are negative correlation confections between DTPA extractable -Cd and each of pH and CaCO<sub>3</sub>; and a positive correlation confections with total, organic matter and clay contents.

The concentrations of Cd, Cu, Pb and Zn in different plant organs increased with increasing the irrigation time period of sewage effluent and both sewage sludge and industrial material applications to soils. The absolute values of these metals in plant organs are different from metal to another, depending on the sewage sludge content and the availability of these metals in the soil which are controlled by different soil parameters (CaCO<sub>3</sub>, pH, clay and organic matter). The values of these metals followed the order Cd < Pb < Cu < Zn. The obtained results indicate that the heavy metals accumulation in leaves or straw higher than edible parts (grains or seeds) of plants. This is due to the low translocations of these metals in plants.

**Keywords:** Sewage effluent, heavy metals, Cd, Cu, Pb, Zn, accumulation

## INTRODUCTION

The application of sewage sludge and sewage effluent to land is, in principal, an effective disposal method. Not only does it provide a solution to the sludge disposal problem, but also it can prove to be beneficial to soil fertility and hence agricultural productivity (Chang *et. al.*, 1978 and Higgins, 1984). When sludge addition ends, the lack of fresh organic matter and the decomposition of the organic matter previously added may result in large changes in binding of metals due to changes in their chemicals forms in soil.

Associated changes in bioavailability may then produce large increases or decreases in the risks of potentially toxic metals to crops, animals or man. It is very important to establish what might happen to the

chemical forms of metals present in such soils. Existing long-term field experiments can produce vital information at the present time as well as helping to determine what might be the picture in future. Considerable information is available on the effects after few years and little on chemical forms of metals in the long term when the upper permissible metal concentrations in soil have been reached at a given site. This may take 30 years or more when further sludge applications are then prohibited by law (DoE, UK, 1989).

The presence of heavy metals is the most critical long-term hazard when applying sludge to land (Logan and Chaney, 1983). Research on the possible adverse effects of heavy metals accumulation in agricultural soils has focused on the pools of heavy metals available to plants (Sposito et al., 1983; Alva, 1992; and Davis, 1994; Taylor *et. al.*, 1995). Heavy metals in soils may exist in forms that reflect their solubility and availability to plants. Previous studies have demonstrated that soils have substantial capacity to sorb heavy metals from solution, and metal concentrations in solutions are controlled by sorption-desorption reactions at the surface of both inorganic and organic soil colloidal materials (Swift and McLaren 1991). Colloidal Fe and Mn oxides are capable of sorbing large amounts of heavy metals (Mckenzie 1972, 1980; Zasoki and Burau 1988 and Backes et al. 1995). They are important metal sorbents in sandy soils, in addition to organic matter, since other organic colloidal minerals are generally not present. In many cases, metals are coprecipitated with Fe and Mn oxides.

The objective of this study is to: (I) investigate the contents of various heavy metal (Cd, Cu, Pb, and Zn) in soils differing widely in soil properties, which were treated with sewage effluent and industrial materials for a long time. (II) investigate the relationship between soil properties and the availability of studied heavy metals, and (III) investigate the accumulation of heavy metals in different plant types.

## **MATERIALS AND METHODS**

This study was carried out on four different locations in Egypt, which contaminated consequently by considerable amounts of toxic metals; 3 sites from El-Gabal El-Asfar, Abou-Rawash, and Helwan areas which received sewage sludge and sewage effluent for long time and one site from Helwan which contaminated by industrial waste. The description of these experiments is as follow:

### **El-Gabal El-Asfar area:**

The sandy soil of El-Gabal El-Asfar farm is located at north east of Cairo Governorate, which is irrigated with sewage effluent of Cairo city since 1911. Control soil content 3.1% clay, 0.07% organic matter, pH of 8.75, 3.89% of total carbonate content (TCC) and total contents 0.78, 12.36, 17.64, and 33.52 ug/g soil of Cd, Cu, Pb, and Zn, respectively. As general practice, the soil was initially treated with sewage sludge before put under cultivation and irrigated with sewage effluent carried out during the year 1986.

**Helwan area:**

Helwan area is one of urban area in Egypt, it is located at south – east of Cairo. The sludge experiment started in 1990 on a desertic (sandy) soil with 3.0% clay, 0.06% organic matter, pH of 8.43, 44.61% of TCC, and total contents 1.62, 7.51, 13.95, and 100.75 ug/g soil of Cd, Cu, Pb and Zn, respectively, which irrigated with sewage effluent of Cairo city and which comprises both municipal and industrial wastes. The soil was treated with sewage sludge at rates of 20- 40 ton/ha for 6 years (sewage sludges obtained from sewage of Helwan station).

**Industrial area:** This area endure of emissions of toxic metals from various industrial activities together with household sources. The control soil contains 25.23% clay, 0.32% organic matter, pH of 8.33, 23.55% of TCC, and total contents 1.67, 8.11, 14.93, and 108.8 ug/g soil of Cd, Cu, Pb and Zn, respectively. The industrial wastes are dumpes into El-Hagar canal.

**Abou-Rawash area:**

The soil samples were collected from Abou-Rawash area which located in east of Giza Governorate, Egypt. Control soil contains 1.27% clay, 0.07% organic matter, pH of 7.42, 3.46% of total carbonate content (TCC) and total contents 0.16, 0.66, 4.16, and 2.19 ug/g soil of Cd, Cu, Pb and Zn, respectively.

**Soil sampling and analysis:**

The soil samples were collected from 3 sites from each of El-Gabal El-Asfar, Abou-Rawash, and Helwan areas which received sewage sludge and sewage effluent for long time. Also, three sites from Helwan which contaminated by industrial wastes. 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) and Black (1965).

**Total Metal Content:**

One gram (dry weight) soil samples were digested using 12 ml of a mixture of HClO<sub>4</sub> and HF (5:1 v/v) in platinum crucible. The crucible was brought to near dryness, before adding a further 12 ml of the acid mixture, and again bringing to near dryness. Finally, 1ml of HClO<sub>4</sub> was added and the sample was evaporated until the appearance of white fumes. The residue was then dissolved in 5 ml of concentrated HCl before making up to 25 ml with deionised water. Copper, Pb and Zn were analyzed by Flame Atomic Absorption spectrophotometer and cadmium by Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS).

**DTPA-Extractable metal:**

'Available' Cd, Cu, Pb and Zn were determined for all samples using 0.005 M DTPA (diethylene triamine penta acetic acid) using the methods of Lindsay and Norvell (1978).

### Sewage sludge and sewage effluent samples and analysis:

Air dried sewage sludge samples were collected from El-Gabal El-Asfar farm, where sewage sludge from greater Cairo area has been disposed. Six samples were collected from different locations of different drying beds, then six subsamples were collected from each location and mixed to form a composite sample. The solid sewage sludge was air dried, and crushed to pass through a 2 mm sieve. The dried samples were stored for metal analysis. The general characteristics and total and available heavy metals of sewage sludge were determined using the same methods used in soils.

Sewage effluent samples were collected from different locations of El-Gabal El-Asfar farm. The sewage effluent samples were analyzed for pH, EC, and soluble Cu, Zn, Cd and Pb using the standard methods outlined by Dewis and Freites (1970) and Jackson (1967). The analysis of sewage effluent and sewage sludge shown in Table (1).

**Table (1): General characteristics and some heavy metals contents of sewage effluent and sewage sludge collected from different studied locations.**

Variables	Sewage sludge		
	Abu-Rawash	El-Gabal El-Asfar	Helwan
pH (1:2.5)	6.45	6.61	6.55
EC (dS/m) 1: 2.5	3.62	3.84	8.70
Organic matter %	46.8	45.3	44.8
Total-N %	2.13	2.35	2.31
Total-P%	0.87	0.52	0.85
Total-K%	0.16	0.19	0.31
Available-N (ppm)	989	550	620
Available- P (ppm)	113	168	151
Available- K (ppm)	250	288	344
Total metal content (ppm)			
Cd	8.43	4.89	25.27
Cu	386	398	1660
Pb	236	279	328
Zn	1187	741	1582
DTPA-extractable metal (ppm)			
Cd	0.53	0.59	0.88
Cu	26.8	32.5	75.0
Pb	1.19	1.27	5.92
Zn	55.9	47.8	70.9
Sewage effluent			
pH	6.95	6.89	7.34
EC (dS/m)	0.75	1.62	1.89
NO <sub>3</sub> <sup>-</sup> (ppm)	1.53	2.05	2.50
P <sup>-</sup> (ppm)	3.13	2.46	1.94
Soluble ions (meq/l)			
Ca <sup>++</sup>	1.20	0.75	0.91
Mg <sup>++</sup>	1.84	0.43	0.74
Na <sup>+</sup>	1.12	0.22	1.57
K <sup>+</sup>	0.20	0.20	0.60
Cl <sup>-</sup>	1.82	0.52	1.05
HCO <sub>3</sub> <sup>-</sup>	0.74	0.42	0.56
SO <sub>4</sub> <sup>-</sup>	1.82	0.52	1.67
Metal (ppm)			
Cd	0.05	0.04	0.05
Cu	0.01	0.02	0.01
Pb	0.34	0.35	0.35
Zn	0.16	0.16	0.18

**Plant sampling and analysis :**

Plant samples were collected from the same locations of soil samples. The samples comprise both leaves and edible parts of different plant species grown in the studied areas, corn (leaves and grains), alfalfa (tops), bean (leaves and seeds) and wheat (straw and grains).

The plant samples were washed by  $10^{-4}$  M HCl, dried, crushed, and stored for analysis. Plant samples were digested using acid digestion technique ( $\text{HNO}_3 - \text{H}_2\text{SO}_4 - \text{HClO}_4$ ) as described by Jackson (1967). Concentrations of Zn, Cu, Cd, and Pb were measured in acid extracts by an atomic absorption spectrophotometer (Perkin–Elmer). All analysis were done in duplicates.

**Statistical Analysis:**

Genstat 5 (1987) was used for all statistical procedures.

**RESULTS AND DISCUSSION****I- General characteristics of the soils:**

The general properties, pH, clay, organic matter, bulk density, and total carbonate content of the studied soils are given in Table (2). The results show that the pH range values in all locations varied from 7.4 to 8.8 the initial, nonpolluted, soils had the highest pH values. The pH values slightly decreased as the irrigation period increased. The reaction of the soils was alkali in the beginning and changed to slight acid ( 6.1- 6.9) as a general range of change in El-Gabal El Asfar soils, the lowest one In El-Gabal El Asfar farm which irrigated for 70 years with sewage effluent.

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. The fast initial drop in pH is expected in this coarse texture sandy soil having a very low buffering capacity. The accumulation of organic matter content of the soil after 15 years lessened further decrease in soil pH. The correlation coefficient between organic matter content and soil pH was highly significant in all the soils.

Data of Table (2) indicate that the total carbonate content (TCC) of the irrigated soils, ranging from 0.57 to 17% are markedly lower than those, ranging from 3.46 to 44.6 %, of the initial ones. TCC content of the soils decreased continuously with increasing periods of using sewage effluent in irrigation. These values decreased from 44.61 to 17% in Helwan area which irrigated with sewage effluent. The decrease in  $\text{CaCO}_3$  of the soil can 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. The correlation coefficient between soil organic matter contents and  $\text{CaCO}_3$  content was highly significant in all soils.

On the other hand data in Table (2) show the initial organic matter content of the soil of El-Gabal El-Asfar was very low, being only 0.07 %. This content increased continuously with years of sewage effluent utilization till it reached about 6.15% after 70 years. Also, the particles of the clay - size

fraction, are increasing with the irrigation period comparing with the background one.

Data in Table (2) show that the bulk density decreased with increasing years of sewage effluent utilization, this due to the high organic matter of sludge which improved the soil physical characteristics. This finding agrees with Peterson et al., 1979; Joost et al., 1981; Hinesly et al., 1982; Peterson et al., 1982 and Topper and Sabey, 1986.

**Table (2): Some physical chemical characteristics of studied soils.**

location	Years	Clay %	pH (1:5)	TCC%	OM%	Bd (g/cm <sup>3</sup> )
El-Gabal El-Asfar	Control	3.15	8.75	3.89	0.07	1.52
	15	19.79	6.56	3.00	3.79	1.24
	70	23.79	6.11	1.57	6.15	1.22
Abou- Rawash	Control	1.27	7.42	3.46	0.07	1.54
	7	7.44	6.95	1.84	3.35	1.25
	15	17.73	6.90	0.57	5.79	1.23
Hewlan1	Control	25.23	8.43	44.61	0.06	1.37
	7	36.04	7.46	30.50	2.66	1.37
	15	37.10	7.40	17.00	3.31	1.30
Helwan 2	Control	3.00	8.33	23.55	0.32	1.28
	15	14.39	7.68	11.60	0.79	1.21
	20	17.39	7.45	11.00	1.46	1.16

\* % of total content

## II- Total metal contents:

Total metal contents (Table 3) ranged from 0.15 to 0.67 within an average 0.43 mg/kg for Cd; from 0.66 to 8.11 within an average 4.27 mg/kg for Cu; from 4.10 to 17.6 within an average 12.7 mg/kg for Pb; from 22.5 to 109 within an average 66.4 mg/kg for Zn, respectively, of the non-polluted soil show that, except for Pb, the non-polluted soils are almost free of the studied heavy metals. The high level of Pb could be attributed to the pollution by vehicle exhaust, since the some of studied is nearly high way.

The results listed in Table (3) show drastic increase in heavy metals contents of the soil being irrigated with sewage effluent. As the period of irrigation increased, the total contents progressively increased. The contents of Cd, Cu, Pb and Zn of the soil irrigated with sewage effluent in El-Gabal El-Asfar for 15-Yr were 22, 121, 3, and 8 times higher than those of non-polluted soil, respectively. The contents of Cd, Cu, Pb and Zn of the soil irrigated with sewage effluent in Abou-Rawash for 15-Yr were 40, 83, 10 and 14 times higher than those of non-polluted soil, respectively. The contents of Cd, Cu, Pb and Zn of the soil irrigated with sewage effluent in Helwan1 for 15-Yr were 9.4, 12, 6, and 4 times higher than those of non-polluted soil, respectively. The contents of Cd, Cu, Pb and Zn of the soil irrigated with sewage effluent in Helwan2 for 15-Yr were 14, 20, 7, and 8 times higher than those of non-polluted soil, respectively.

Comparing with the maximum permitted metal loading in soil established by USEPA-503 regulation, McBride (1995), (Cd 20; Cu 750; Pb

150; Zn 1400 ppm) the level of Pb in the surface layer of the soil of the present work being irrigated for 15-Yr exceed the maximum permitted values set by all the above mentioned organization. Except for USEPA-503 values, Cd contents of the present study are higher than the maximum permitted values of all standards. Total content of Cu accumulated in the surface layer of being irrigated for 15-Yr was almost equal to the maximum values set Ontario, but, however, it was lower than the value of the Netherlands. (No value recorded for USEPA-503). But it is important to declare that these values were suggested for the use of sewage sludge in agricultural land they considered the adsorptive properties of sludge, which often prevent excessive uptake of many heavy metals into crop. Thereby these regulations permit concentrations of particular metal to increase locally in soil by a factor of hundred or more than present concentrations, McBride (1995). Thereby, we have to deal with the above mentioned standards as a guide-line only due to the high solubility and mobility of sewage- burden metals which, contradiction to sewage sludge, may facilitate uptake of heavy metals into crops. Hence the maximum permitted metal loading in soil may decrease upon dealing with untreated sewage effluent.

**Table (3): Total metals content (ppm) of the studied soils.**

location	Yraes	Cd	Cu	Pb	Zn
El-Gabal El-Asfar	Control	0.26	0.78	17.64	33.52
	15	5.65	94.91	49.00	252.3
	70	7.35	169.38	120.19	617.4
Abou- Rawash	Control	0.15	0.66	4.10	22.52
	7	3.98	32.17	19.58	127.8
	15	5.92	54.94	39.98	310.5
Hewlan1	Control	0.65	7.51	13.95	100.8
	7	5.68	80.12	31.91	205.2
	15	6.12	86.12	84.48	372.7
Helwan 2	Control	0.67	8.11	14.93	108.8
	15	7.99	153.9	66.48	525.0
	20	9.16	161.5	97.62	832.7

### III- Metal Bioavailability:

Data in Table (4) show that no detectable level of DTPA-extractable Cd, Cu, Pb and Zn was found in the control soils (uncontaminated).

However, with time the values increased continuously until it reached 0.33, 0.25, 0.15, and 0.19 ppm of El-Gabal El-Asfar, Abou-Rawash, and Helwan (SE) areas which received sewage sludge and sewage effluent for long time and Helwan (inds.) which contaminated by industrial waste, respectively. Comparison between the listed values and those reported for Cd by El-Sokkary and Lag (1980) and Aboulroos et al.(1996) for soils of Egypt, show a rapid accumulation of plant available form of studied metal as a result of using sewage effluent in irrigation. Also, the extracted values are increasing with time. Bioavailable portions were found to represent a great deal (from 2.1 to 4.5 %) of the total contents. Statistical analysis gave

correlations ( $r = 0.995^{**}$ ,  $0.822^{**}$ ,  $-0.755^{**}$ ,  $-0.511^{**}$ , and  $0.839^{**}$ ) between DTPA extractable -Cd and each of total and organic matter contents, pH,  $\text{CaCO}_3$ , and clay contents, respectively. In conclusion, these results prove the high mobility of sewage burden-heavy metals, which may enhance metal uptake by plant, and downward movement of metals and contamination of ground water.

Data in Table (4) show that the value of DTPA- extractable Cu increased with time continuously until it reached 6.15, 1.79, 2.24, and 4.55 ppm of El-Gabal El-Asfar, Abou-Rawash, and Helwan (SE) areas which received sewage sludge and sewage effluent for a long time and Helwan (inds.) which contaminated by industrial waste, respectively. Comparison between the listed values and those reported for Cu by El-Sokkary and Lag (1980) and Aboulroos et al.(1996) for soils of Egypt, show a rapid accumulation of plant available form of studied metal as a result of using sewage effluent in irrigation. Also, the extracted values are increasing with time. Bioavailable portions were found to represent a great deal (from 2.31 to 4.72 %) of the total contents. Statistical analysis gave correlations ( $r = 0.998^{**}$ ,  $0.720^{**}$ ,  $0.560^{**}$ ,  $0.296$ , and  $0.796^{**}$ ) between DTPA extractable - Cu and each of total and organic matter contents, pH,  $\text{CaCO}_3$ , and clay contents, respectively. In conclusion, these results prove the high mobility of sewage burden-heavy metals, which may enhance metal uptake by plant, and downward movement of metals and contamination of ground water.

Data in Table (4) show that the value of DTPA- extractable Pb increased with time continuously until it reached 2.26, 0.71, 1.61, and 1.82 ppm of El-Gabal El-Asfar, Abou-Rawash, and Helwan (SE) and Helwan (inds.) areas, respectively. Comparison between the listed values and those reported for Pb by El-Sokkary and Lag (1980) and Aboulroos et al.(1996) for soils of Egypt, show a rapid accumulation of plant available form of studied metal as a result of using sewage effluent in irrigation. Also, the extracted values are increasing with time. Bioavailable portions were found to represent a great deal (from 1.74 to 1.91 %) of the total contents. Statistical analysis gave correlations ( $r = 0.642^{**}$ ,  $0.486^{*}$ ,  $0.266$ ,  $0.084^{**}$ , and  $0.595^{**}$ ) between DTPA extractable-Pb and each of total and organic matter contents, pH,  $\text{CaCO}_3$ , and clay contents, respectively. In conclusion, these results prove the high mobility of sewage burden-heavy metals, which may enhance metal uptake by plant, and downward movement of metals and contamination of ground water.

Data in Table (4) show that the value of DTPA- extractable Zn increased with time continuously until it reached 19.23, 9.65, 11.64, and 18.96 ppm of El-Gabal El-Asfar, Abou-Rawash, and Helwan (SE) and Helwan (inds.) areas, respectively. Comparison between the listed values and those reported for Zn by El-Sokkary and Lag (1980) and Aboulroos et al.(1996) for soils of Egypt, show a rapid accumulation of plant available form of studied metal as a result of using sewage effluent in irrigation. Also, the extracted values are increasing with time. Bioavailable portions were found to represent a great deal (from 3.29 to 2.22 %) of the total contents. Statistical analysis gave correlations ( $r = 0.993^{**}$ ,  $0.569^{**}$ ,  $0.776^{**}$ ,  $0.655^{**}$ , and  $0.787^{**}$ ) between DTPA extractable-Zn and each of total and organic matter



contents, pH, CaCO<sub>3</sub>, and clay contents, respectively. In conclusion, these results prove the high mobility of sewage burden-heavy metals, which may enhance metal uptake by plant, and downward movement of metals and contamination of ground water.

**Table (4): DTPA-extractable metals (ppm) in the studied soils.**

location	Years	Cd		Cu		Pb		Zn	
		ppm	%*	ppm	%*	ppm	%*	ppm	%*
El-Gabal	Control	n.d	-	n.d	-	n.d	-	n.d	-
El-Asfar	15	0.25	4.4	3.40	3.58	0.90	1.84	8.30	3.29
	70	0.33	4.5	6.15	3.63	2.26	1.88	19.23	3.11
Abou-Rawash	Control	n.d	-	n.d	-	n.d	-	n.d	-
	7	0.18	4.5	1.54	4.72	0.36	1.84	4.16	3.26
	15	0.25	4.2	1.79	3.26	0.71	1.78	9.65	3.11
Hewlan1	Control	n.d	-	n.d	-	n.d	-	n.d	-
	7	0.12	2.1	1.84	2.31	0.61	1.91	6.25	3.05
	15	0.15	2.4	2.24	2.60	1.61	1.91	11.64	3.12
Helwan 2	Control	n.d	-	n.d	-	n.d	-	n.d	-
	15	0.18	2.2	3.82	2.48	1.16	1.74	11.65	2.22
	20	0.19	2.1	4.55	2.79	1.82	1.86	18.96	2.28

% of total content

The low percentage of total Cd, Cu, Pb and Zn extracted by DTPA is due to its precipitation as CaCO<sub>3</sub> ( Street et al., 1977). These results give an evidence of high availability of sewage effluent burden-metals to plants.

#### IV- Accumulation of some heavy metals in plants:

Contents of Cd, Cu, Pb and Zn in the leaves, straw and edible parts (grains, seeds) of the plants grown in the studied soils are given in Table (5). The results show that the concentrations of Cd, Cu, Pb and Zn in different plant organs increased with increasing the irrigation time of sewage effluent and both sewage sludge and industrial material applications to soils. The absolute values of these metals in plant organs are different from metal to another, depending on the sewage sludge content and the availability of these metals in the soil which are controlled by different soil parameters (CaCO<sub>3</sub>, pH,.....etc.). The values of these metals followed the order Cd < Pb < Cu < Zn. The same results were obtained by Maclean et al, (1969); Cox and Rains, (1972); Hardiman *et. al.*, (1984) and Adriano, (1986). They reported the reduction of Pb, Cd, Pb and Zn in plant tissue grown in soil amended with limestone or calcium carbonate. The obtained results indicate that the heavy metals accumulation in leaves or straw higher than edible parts (grains, seeds) of plants. This is due to the low translocations of these metals in plants.

The concentration of Cd in all plant samples ranged from 0.03 to 0.19 with an average of 0.12 ppm (alfalfa tops ranged from 0.14 to 0.19 ppm, corn ranged from 0.09 to 0.19 for leaves and from 0.07 to 0.17 for grains, Bean ranged from 0.13 to 0.19 for leaves and from 0.04 to 0.13 for seeds, and

wheat ranged from 0.09 to 0.19 for straw and from 0.03 to 0.18 for grains). The Cd content in all studied plants lies within the normal range comparing with the intermediate concentration of Cd reported by Adriano (1986) was <0.30 ppm and Huffman and Hodgson (1973), found that the levels of Cd were generally below 0.30 ppm (wheat = 0.20 ppm, grasses = 0.17 ppm). Bergman and Cumakov, (1977) found that the recommended levels are for Cd 0.05-0.2 ppm while toxic level of this element are 5-30 ppm.

A highly significant correlation coefficients were found between leaves of corn, bean, wheat, alfalfa tops and soils DTPA-extractable content of Cd (0.51\*, 0.57\*, 0.66\* and 0.56\*) respectively. Also, between wheat grains and DTPA-extractable content of Cd (0.55\*), respectively.

The concentrations of Cu in all plant samples ranged from 5.2 to 41 with an average 13 of ppm (alfalfa tops ranged from 16.8 to 41.2 ppm, corn ranged from 8.5 to 13.2 for leaves and from 5.9 to 10.3 for grains, Bean ranged from 9.55 to 38.5 for leaves and from 6.3 to 39 for seeds, and wheat ranged from 7.1 to 17.1 for straw and from 5.2 to 10.2 for grains). The Cu content in all studied plants lies within the normal range comparing with the intermediate concentration of Cu reported by; Adriano, 1986; Aboulroos *et. al.* 1996; Brown *et. al.* 1998). Also, Sillanpaa (1982) found an average concentration of 10.9 ppm Cu in ear leaf of corn (range from 5.6 to 15.6 ppm); the average value for wheat tops was lower being 8.3 ppm (range from 3.6 to 18.8 ppm).

A highly significant correlation coefficients were found between leaves of corn, bean, wheat, alfalfa tops and soils DTPA-extractable content of Cu (0.71\*\*, 0.75\*\*, 0.66\* and 0.69\*) respectively. Also, between corn gains, bean seeds, and DTPA-extractable content of Cu (0.71\*\* and 0.78\*\*), respectively.

The concentrations of Pb in all plant samples ranged from 2.9 to 13.7 with an average of 6.3 ppm (alfalfa tops ranged from 5.7 to 10.8 ppm, corn ranged from 4.4 to 8.8 for leaves and from 3.2 to 6.7 for grains, Bean ranged from 5.2 to 13.7 for leaves and from 2.9 to 9.6 for seeds, and wheat ranged from 3.6 to 10.6 for straw and from 3.2 to 8.2 for grains). The concentrations of Pb in plants in this study is higher than the normal range compared with plants grown in uncontaminated soil (6.3 ppm) as reported by Chapman (1975). But still lower than toxic range according to Bergman and Cumakov, (1977). They reported that the toxic level of Pb 30-300 ppm.

A highly significant correlation coefficients were found between leaves of corn, bean, wheat, alfalfa tops and soils DTPA-extractable content of Pb, (0.53\*, 0.91\*\*, 0.72\*\* and 0.91\*\*), respectively. Also, between corn grains, wheat grains and DTPA-extractable content of Pb (0.77\*\* and 0.54\* ), respectively.

The concentrations of Zn in all plant samples ranged from 34 to 173 with an average of 72 ppm (alfalfa tops ranged from 109 to 173 ppm, corn ranged from 43 to 97 for leaves and from 36 to 61 for grains, Bean ranged from 65 to 103 for leaves and from 42 to 82 for seeds, and wheat ranged from 63 to 131 for straw and from 34 to 60 for grains). The concentrations of Zn in plants in this study lies within the sufficiency range of Zn in plants. Sillanpaa (1982) found an average concentration of Zn levels in 200 samples of field grown corn and wheat collected from different locations in

Egypt varied from 15.1 to 49.8 ppm with an average value of 31.6 ppm for corn leaves, and from 7.9 to 71 ppm with an average of 31.1 ppm for wheat tops.

**Table (5): Heavy metals content in different parts of studied plants (ppm).**

Area	Period (year)	Plant	Orange	Metals				
				Zn	Cu	Cd	Pb	
El-Gabal El-Asfar	15	Alfalfa	Tops	135.42	20.44	0.14	7.57	
	70			173.15	41.20	0.18	10.75	
	15	Corn	Leaves	77.58	9.89	0.16	7.51	
	70		Grains	52.44	7.71	0.11	5.37	
		70	Leaves	Grains	96.75	11.90	0.19	8.75
				Grains	61.12	8.89	0.17	6.69
	15	Bean	Leaves	81.25	22.74	0.15	9.54	
	70		Seeds	65.81	16.23	0.10	6.95	
		70	Leaves	Seeds	102.56	38.47	0.19	13.69
				Seeds	82.02	22.83	0.13	9.55
	15	Wheat	Leaves	92.13	12.76	0.17	8.48	
	70		Grains	60.29	8.34	0.11	5.88	
	70	Leaves	Grains	131.00	17.12	0.19	10.55	
			Grains	65.99	10.15	0.18	8.20	
Abuo-Rawash (Sludged soil)	7	Alfalfa	Tops	108.85	16.89	0.14	5.73	
	14			133.27	18.41	0.17	7.63	
	7	Corn	Leaves	60.85	8.53	0.09	4.44	
	14		Grains	36.12	5.87	0.07	3.19	
		14	Leaves	Grains	71.15	8.95	0.10	5.16
				Grains	44.10	7.12	0.08	3.75
	7	Bean	Leaves	67.13	9.55	0.09	5.15	
	14		Seeds	42.22	6.31	0.04	2.89	
		14	Leaves	Seeds	65.31	17.44	0.10	5.45
				Seeds	44.18	7.98	0.04	2.99
	7	Wheat	Leaves	63.16	7.42	0.09	3.63	
	14		Grains	34.22	6.93	0.03	4.10	
	14	Leaves	Grains	69.24	7.62	0.09	4.86	
			Grains	42.12	7.19	0.08	4.89	
Helwan (Industrial soil)	15	Alfalfa	Tops	134.45	21.45	0.18	9.20	
	20			136.65	22.21	0.19	9.68	
	15	Corn	Leaves	46.45	12.98	0.14	6.27	
	20		Grains	41.86	10.13	0.09	6.38	
		20	Leaves	Grains	47.29	13.21	0.14	6.40
				Grains	42.61	10.31	0.09	6.52
	15	Bean	Leaves	74.49	15.32	0.13	8.25	
	20		Seeds	44.30	8.02	0.10	4.51	
		20	Leaves	Seeds	75.23	15.47	0.14	9.15
				Seeds	44.74	8.85	0.10	5.22
	15	Wheat	Leaves	75.60	9.29	0.14	5.67	
	20		Grains	55.67	6.72	0.08	3.89	
	20	Leaves	Grains	80.97	9.75	0.15	6.07	
			Grains	58.46	7.05	0.08	4.09	
Helwan (Sludged soil)	7	Alfalfa	Tops	129.10	18.99	0.17	8.30	
	15			134.32	21.43	0.18	9.15	
	7	Corn	Leaves	43.12	11.80	0.12	5.42	
	15		Grains	41.26	9.15	0.08	3.87	
		15	Leaves	Grains	46.31	12.94	0.14	6.25
				Grains	41.73	10.10	0.09	4.05
	7	Bean	Leaves	71.00	12.50	0.11	6.50	
	15		Seeds	43.50	6.82	0.09	3.25	
		15	Leaves	Seeds	74.19	15.26	0.13	8.15
				Seeds	44.12	7.99	0.10	4.42
	7	Wheat	Leaves	66.14	7.13	0.09	4.15	
	15		Grains	36.21	5.15	0.04	3.20	
	15	Leaves	Grains	75.00	9.22	0.13	5.60	
			Grains	55.23	6.61	0.08	3.86	

A highly significant correlation coefficients were found between leaves of bean, wheat, alfalfa tops and soils DTPA-extractable content of Zn, (0.69\*, 0.51\* and 0.79\*\*), respectively. Also, between corn grains, bean seeds, wheat grains and DTPA-extractable content of Zn (0.51\*, 0.48\*, and 0.79\*\*), respectively.

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### **REFERENCES**

- Aboulroos, S.A., Holah, Sh.Sh, and Badawy S.H.(1989). Influence of prolonged use of sewage effluent in irrigation on heavy metal accumulation in soils and plants.ZPflanzenernahr. Bodenk. 152: 51-55.
- Aboulroos, S.A., Holah, Sh.Sh., and Badawy, S.H. (1996). Background levels of some heavy metals in soils and corn in Egypt. Egypt. J. Soil Sci. 36: 83-97.
- Adriano, D.C. (1986). Trace elements in the terrestrial environment. Springer-verlage, New York.
- Alva, A.K. (1992). Micronutrients states of Florida soils under citrus production. Commun. Soil Sci. plant Anal. 23: 2493-2510.
- Backes, C.A., Mcleran, R.G., Rate, A.W., and Swift, R.S. (1995). Kinetics of cadmium and cobalt desorption from iron and manganese oxides. Soil Sci. Soc. Am. J. 59: 778-785.
- Bergman, W. and A. Cumakov. (1977). Diagnosis of nutrient requirement by Plants. G. Fisher veriag jen and priroda Bratihva, 295 (CZ)
- Black, C.A. (ed .) ( 1965). Methods of soil analysis. Part. (1) and Part (2) . Amer, Soc.of Agron. Madison, Wisconsin.
- Brown, S., Angle, J.S. and Jacobs L.(1998). Beneficial co-utilization of agricultural municipal and industrial by-products, Kluwer Academic Publishers, printed in the Netherlands.
- Chang, A.C., Page, A.L., Lund, L.J. Pratt, P.R., and Bradford, G.R. (1978). Land application of sewage sludge- A field demonstration. Final Report for Regional Waste Water Solids Program. Dep.of soil and Environ.Sci., Univ. of California, Riverside. CA.
- Chapman, H.D. (1975). Diagnostic criteria for plant and soils. Eurasia Publ. House (p) LTD. Ram Nagar, New Delhi-110055.
- Cox, W.J. and Rains, D.W. (1972). Effect of lime on lead uptake by five plant species. J. Environ. Qual., 1: 167-169.
- Davies, B.E. (1994). Trace elements in the human environment. Problems and risks. Environ. Geochem and Health. 16: 97-106.
- Dewis, J., and Freitas, F. (1970). Physical and chemical methods of soil & water Analysis. FAO. Rome. Soil Bulletin No. 10.

- DoE; Department of the Environment (1989). Code of practice for agricultural use sewage sludge, HMSO, London.
- El-Sokkary, I.H., and Lag, J. ( 1980 ). Status of some trace elements in Egyptian soils and in wheat grains. *Beitrage trop. Land wirtsch. Veterinarmed.*, 18: 35-47.
- Genstat 5 committee (1987). *Genstat 5 Reference Manual*. Clarendon, Oxford, UK.
- Hardiman, R.T., Banin A. and Jacoby, B. (1984) The effect of soil type and degree of Metal contamination upon uptake of Cd, Pb, and Zn in bush beans (*Phaseolus vulgaris* L.) *Plant and Soil* 31:3-15.
- Higgins, A.J. (1984). Land application of sewage sludge with regard to cropping systems and pollution potential. *J. Environ. Qual.* 13: 441-448.
- Hinesly, T.D. Alexander, D.E., Redborg, K.E. and Ziegler, E.L. (1982). Differential accumulation of Cadmium and Zinc by Corn hybrids grown on soil amended with sewage sludge. *Agron. J.* 74: 469-474.
- Huffman, E.W.D. and Hodgson J.F. (1973). Distribution of cadmium and zinc/cadmium ratio in crops from 19 states east of the Rocky mountains. *J. Environ. Qual.* 2: 289-291.
- Jackson, M.L. (1967). *Soil chemical analysis*. Prentice-Hall India Part. Ltd., New Delhi, India.
- Joost R.E., Jones J.H. and Olsen F.J. (1981). Physical and chemical properties of coal refuse as affected by deep incorporation of sewage sludge and/or limestone. In *proc. Symp. on Surface Mining Hydrol., Sedimentals, and Reclamation*, University of Kentucky, Lexington, pp. 307-312.
- Lindsay, W. L. , and Norvell, W. A. ( 1978 ). Development of DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Amer. J.* 42: 421 - 428.
- Logan, T.J., and Chaney, R.L. (1983) Metals. In: *Utilization of municipal wastewater and sludge on land*. Page, A.L. *et. al.*, eds. Univ. of California, Riverside. CA. pp. 235- 326.
- Maclean, A.J., Halstead R.L. and Finn, D.J. (1969) Extractability of added lead in soils and its concentration in plants. *Canadian Journal of Soil Science*, 49: 327-334.
- McBride, M.B. ( 1995). Toxic metal accumulation from agricultural use of sludge: Are USEPA Regulation protective ? . *J. Environ. Qual.*, 24: 5 - 18.
- Mckenzie, R.M. (1972). The sorption of some heavy metals by the lower oxides of manganese. *Geoderma*, 8: 29-35.
- Mckenzie, R.M. (1980). The adsorption of lead and other metals on oxides of manganese and iron. *Aust. J. Soil Res.* 18: 61-73.
- Peterson, J.R., Pietz R.I. and Lue-Hing C. (1979). Water, soil and crop quality of Illinois coal mine soils amended with sewage sludge. In: *Utilization of municipal sewage effluent and sludge on forest and disturbed land*, W.E. Sopper and S.N. Kerr, Eds. (University Park, PA: The Pennsylvania State university Press), pp. 359-368.

- Peterson, J.R., Lue-Hing C., Gschwind J., Pietz R.I. and Zenz D.R.(1982). Metropolitan Chicago's Fulton County Sludge Utilization Program. In: Land reclamation and biomass production with municipal wastewater and sludge, W.E. Sopper, E.M. Seaker, and R.K. Bastian, Eds., pp. 322-338.
- Sillanpaa, M. (1982). Micronutrients and the nutrient status of soils: A global study. FAO soils Bull. 48. Rome,
- Sposito, G., Levesque, C.S., Leclaire, J.P., and Chang, A.C. (1983) Trace metal chemistry in arid-zone field soils amended with sewage sludge. III. Effect of time on the extraction of trace metals. Soil Sci. Soc. Am. J. 47: 898-902.
- Sposito, G., Lund, I.J., and Chang, A.C. (1982). Trace metal chemistry in arid-zone field soils amended with sewage sludge. I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Sci. Soc. Am. J. 46: 260-264.
- Street, J.I.; Lindsay, W.T. and Saby B. R. (1977). Solubility and plant uptake of Cd in soils amended with cadmium and sewage sludge. J. Environ Qual 6. 72-77.
- Swift, R.S., and McLaren, R.G. (1991) Micronutrient adsorption by soils and soil colloids. In Interactions at the soil colloid-soil solution interface. Bolt, G.H., *et. al* (eds.). Kluwer Academic Publ., Dordrecht, The Netherlands, pp. 257-292.
- Taylor, B.W., Xiu, H., Mehadi, A.A., Shuford, J.W., and Tadesse. J.F. (1995). Fractionation of residual cadmium, copper, nickel, lead, and zinc in previously sludge-amended soil. Commun. Soil Sci. Plant Anal. 26: 2193-2204.
- Topper K.F. and Sabey B.R. (1986). Sewage sludge as a coal mine spoil amendment for revegetation in Colorado. J. Environ. Qual. 15: 44-49
- Zasoki, R.J., and Burau, R.G. (1988) Sorption and sportive interaction of cadmium and zinc on hydrous manganese oxide. Soil Sci. Soc. Am. J. 52: 81-87.

## دراسات على محتوى بعض الفلزات الثقيلة في الأراضي الملوثة وتراكمها في النباتات

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أجريت هذه الدراسة بهدف التعرف علي تراكم بعض الفلزات الثقيلة (الكاديوم، النحاس، الرصاص، الزنك) في كل من التربة والنبات النامي عليها تحت ظروف تلوث مختلفة وقد تم تجميع عينات التربة من ثلاثة مواقع مختلفة هي ( الجبل الأصفر- أبو رواش -حلوان) وقد تم تقسيم العينات التي أخذت من منطقة حلوان إلي قسمين الأول من مناطق تم ريها بسائل وحمأة المجاري لفترات طويلة والثاني من مناطق تعرضت للتلوث بالمخلفات الصناعية. كما تم أخذ عينات النباتات من نفس المواقع السابقة.

### وقد أوضحت النتائج الآتي:-

١. انخفاض في كل من قيم رقم حموضة التربة (pH) والكربونات الكلية (TCC) مع زيادة فترات الري. بينما ارتفع كل من محتوى المادة العضوية والكميات الميسرة من (الكاديوم-النحاس-الرصاص-الزنك) بزيادة فترات الري
٢. ارتفاع القيم المستخلصة بواسطة DTPA من تلك الفلزات (كاديوم-نحاس-رصاص-زنك) باستمرار في المناطق المدروسة والتي تعرضت لإضافات سائل وحمأة المجاري وكذلك تلك التي تعرضت للتلوث الصناعي لفترات طويلة. وقد شكلت الكميات الميسرة من هذه الفلزات نسبة كبيرة من المحتوى الكلي لها. وأعطت النتائج المتحصل عليها من هذه الدراسة صورة واضحة عن مدى الصلاحية العالية للعناصر الذائبة في سائل المجاري بالنسبة للنبات.
٣. بينت نتائج التحليل الإحصائي وجود ارتباط موجب عالي المعنوية بين كل من المحتوى الكلي والميسر للفلزات الثقيلة وكل من المادة العضوية ونسبة الطين في التربة وارتباط سالب عالي المعنوية بين كل من المحتوى الميسر من تلك الفلزات وبين رقم الـ pH وكل من المادة العضوية ونسبة الطين في التربة.
٤. أن تركيزات (الكاديوم-النحاس-الرصاص-الزنك) في أجزاء النبات المختلفة قد ارتفعت بزيادة فترة تعرض التربة للري بسائل وحمأة المجاري وكذلك بزيادة التعرض للملوثات الصناعية المضافة للتربة. وقد لعب كل من محتوى التربة من كربونات الكالسيوم ورقم حموضة التربة دورا هاما في التحكم في القيم النهائية وكذلك مدى صلاحية تلك العناصر الثقيلة في التربة.
٥. وقد وجد أن قيم المحتوى الكلي والميسر من هذه الفلزات الثقيلة في التربة تتبع الترتيب الآتي: زنك<نحاس<رصاص<كاديوم. وأن تراكم الفلزات الثقيلة في النبات كان أعلي في أوراق وقش النباتات عنه في البذور أو الحبوب ويرجع هذا إلي الانتقال البطيء لهذه العناصر داخل النبات.