IMPACT OF SOME HEAVY METALS ON SOILS IRRIGATED WITH WASTE WATER

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Heavy metals movement in soil profiles is of major environmental concern because even slow transport through the soil may eventually lead to deterioration of groundwater quality. In this study, four metal-contaminated soil profiles were selected from croplands where waste water from 10th of Ramadan City, henceforth named Ramadan city, had been applied annually for periods of 8 to 25 years. One uncontaminated soil from the same physiographic area was also sampled as a control.

The distribution and chemical fractionation of heavy metals retained in the soils were examined. Soil samples were collected in 30 cm increments from the surface to 120 cm depth. Total content of Mn, Cu, Zn, Pb, Co and Ni in the soil samples were determined. To better understand metal movement in relation to metal fractions in the soil profiles, soil samples were also extracted sequentially for exchangeable, adsorbed, organic, carbonate, and sulfide fractions.

The soils receiving waste water had significantly higher concentrations of total Mn, Cu, Zn, Pb, Co and Ni than the untreated soil. Concentrations declined significantly with soil depth.

The sequential extraction results from untreated and treated soils show that the major portion of Mn, Zn, Co and Ni was associated with the sulfide fraction, while the major portion of Cu and Pb was associated with the organic and carbonate fractions.

Addition of organic wastes leads to an increase of heavy metals concentrations in the growing plants with different values in roots and shoots, and period of organic wastes addition.

In recent decades, soils polluted by heavy metals have increased as a result of human activity. Heavy metals contamination has received much attention with regard to their accumulation in soils, uptake by plants, and contamination of waters. Environmental hazards derived from heavy metals are linked closely to their movement in soil profiles because even slow transport through soil and subsoil materials may eventually increase the content of heavy metals in the groundwater. To evaluate the environmental impact of a contaminated soil, knowledge on total amount of heavy metals in soils without considering their compounds is not sufficient. The compounds in which the metals have an exist in the soil control the fate of heavy metals in contaminated soils, and it is essential to understanding of the metal distribution in each soil fraction.

Metals are distributed throughout soil components and are associated with them in various ways including ion exchange, adsorption, precipitation and complexation (Czupyran and Levy, 1989). Ramos *et al.* (1994) considered that the speciation determines metal mobility and bioavailability when physico-chemical conditions are favorable. Metal speciation in soils is commonly partitioned into the following five species: exchangeable, bound to carbonate, bound to Fe/Mn oxides, bound to organic matter and residual, mainly bound to clay minerals, (Tessier *et al.*, 1979).

The toxicity of metals depends not only on their total concentration, but also on their mobility and reactivity with other components of the ecosystem. The most common way to study element mobility in soils is by treatment with extractants of different chemical properties (Nowak, 1995; and Rauret, 1998).

For over 30 years, the rural developing district (El-Shabab and El-Tawfik, Cooperative Society) has received waste water without treatment from Ramadan City. The content of heavy metals of such water was 0.20, 0.15, 0.13, 0.08, 0.11 and 0.12 mgl^{-1} for Mn, Cu, Zn, Pb, Co, and Ni, respectively. This waste water has been used as irrigation water, so high amounts of toxic substances have been deposited in the soils and sediments of this area, including heavy metals. Heavy metals are not biodegraded and persist in the environment for long time, so the goal of this study is to evaluate the bioavailable concentrations of six heavy metals (Mn, Cu, Zn, Pb, Co and Ni).

MATERIALS AND METHODS

Twenty soil samples were collected from five soil profiles selected from the croplands representing untreated soils and soils irrigated with waste water (industrial and domestic) from Ramadan city for 8, 13, 18 and 25 years.

The waste water application rates were not clear because of the lack of field records. These soils were planted with different types of vegetables and field crops, *i.e.*, pepper, eggplant, cabbage, bean, maize and alfalfa. An abnormality of the plant growth was visible as a result of the phytotoxicity of the studied metals that has been confirmed by plant tissue analysis.

Four representative sites were sampled. Samples were collected at 30 cm intervals from the surface down to 120 cm. All soil samples were air-dried, sieved (2.0 mm) and stored. Soil properties were determined by standard methods (Black 1982). Soil samples were digested with acids mixture of HNO_3-H_2SO_4-$HClO_4$, (Hesse, 1971) to determine the total content of Mn, Cu, Zn, Pb, Co, and Ni.

Soil samples (triplicate for each sample) were fractionated into the exchangeable, adsorbed, organic, carbonate and sulfide fractions. The sequential extraction procedure used in this study is done according to Stover *et al.* (1976). The sequential extraction consisted of placing 2.0 g samples (oven-dried basis) of soil into a polypropylene centrifuge tube and extracting sequentially according to the procedure outlined in table (1). The samples were equilibrated on a reciprocating shaker, centrifuged, decanted and filtered through Whatman No. 42 filter paper after each extraction. The supernatant liquids were analyzed by atomic absorption spectrophotometer (AAS, Unicam 929). Standard solutions were used to determine the background matrix. All values given are averages of triplicate samples.

With respect to plant analysis, shoot and roots were harvested, and digested by the mixture of acids ($HNO_3 . H_2SO_4$, $HClO_4$), then analyzed for the studied six elements using atomic absorption spectrophotometer (AAS, Unicam 929).

TABLE (1). Order of sequential extraction sequence and designated chemical form extracted.

Extractant	Concentration of extractant, mole	Equilibrating time on shaking, hours	Designated compound form extracted
KNO_3	0.5	16	Exchangeable
X-H_2O	55.5	2	Adsorbed
NaOH	0.5	16	Organically bound
Na_2-EDTA	0.05	6	Carbonate
HNO_3 (70-80°C)	4.0	16	Sulfide

RESULTS AND DISCUSSION

Table (2) shows the characteristics of the soils of this study. The organic matter content in all the treated soils decreased with depth, while pH increased with depth. EC values in the treated soils decreased with depth, while increased with depth in the untreated soils. The same trend is observed

for CEC. The decrease of O.M content, EC and the increase of pH with increasing soil depth may be due to the surface addition of the industrial and sewage sludge wastes. On the other hand, the decrease of CEC with increasing soil depth is due to the decrease of clay content with depth.

TABLE (2). Physical and chemical properties of treated and untreated soil profiles with waste water.

Profile No	Depth, cm	Particle size distribution			pH (1:2.5)	EC dS m^{-1}	CEC me100g^{-1} soil	O.M %
		Sand %	Silt %	Clay %				
Untreated soils								
1	0-30	83.10	10.40	6.50	8.41	0.26	4.51	0.01
	30-60	76.70	13.20	11.10	8.39	0.65	6.30	0.05
	60-90	74.60	14.50	10.90	8.40	0.71	5.55	0.03
	90-120	77.25	15.24	7.51	8.25	0.55	5.21	0.02
Soils treated for 8 years								
2	0-30	75.90	13.50	10.60	7.16	0.39	5.40	0.76
	30-60	73.90	15.10	11.00	7.76	0.24	5.73	0.24
	60-90	74.30	14.90	10.80	7.80	0.22	5.60	0.20
	90-120	71.45	16.35	12.20	7.85	0.25	5.71	0.18
Soils treated for 13 years								
3	0-30	58.80	25.10	16.10	6.96	0.40	8.30	1.17
	30-60	61.70	22.90	15.40	7.14	0.35	7.00	1.09
	60-90	68.70	19.20	12.10	7.17	0.31	6.33	0.89
	90-120	71.20	17.00	11.80	7.25	0.28	6.20	0.32
Soils treated for 18 years								
4	0-30	61.30	23.00	15.70	7.76	0.35	7.00	0.92
	30-60	72.70	16.50	10.80	7.87	0.33	5.70	0.55
	60-90	75.60	12.90	11.50	8.10	0.26	6.30	0.14
	90-120	78.70	12.40	8.90	8.15	0.23	5.15	0.10
Soils treated for 25 years								
5	0-30	31.20	30.70	38.10	6.56	3.24	39.25	3.49
	30-60	54.30	20.30	25.40	6.88	1.79	21.75	3.01
	60-90	38.30	40.10	21.60	7.11	1.65	17.20	2.90
	90-120	57.80	29.30	12.90	7.40	1.59	10.19	1.70

Heavy Metals Contents and Fractions in the Soil Profiles

Following the application of waste water, the distribution of solid-phase heavy metals (Mn, Cu, Zn, Pb, Co and Ni) in the waste water treated soils changes widely and considerably with length of waste water addition

period. Nevertheless, these changes varied with the total amount, fraction type, soil depth and nature of element. Data in table (3) indicate that the concentration of total Mn, Cu and Zn in the waste water treated soils is higher than the untreated one. However, the concentration of these elements in both the untreated and waste water treated soils decreased downwards to the subsoil. This could be attributed to the mobility of such elements that have been accelerated by the coarse to moderate texture of the soil matrix. The mobility of these elements may be due to the convertion of these elements to the soluble form as a result of the biodegradation of the organic wastes in the sludge which results in organic acids having functional groups that can complex the elements (Tan *et al.*, 1971 and Gamble *et al.*, 1984) where they give suitable condition for moving of the elements through the soil profile. Also, there are some factors that affect this mobility such as soil pH, elemental ph and organic matter content. The higher concentration of heavy metal in the top of waste water treated soils is mainly rendered to contamination from the continuous addition of waste water. The solid-phase chemical forms of each element in waste water treated soils exhibited widely different patterns of elements fractions as shown in table (3). Regardless of element examined, the majority of metals in waste water treated soils are recovered by EDTA (Car. fraction) and HNO_3-extraction (Sulf. fraction). Also, the NaOH-extracted fraction (Org. fraction) of Cu and Zn appeared to have high values relative to the summation of whole fractions. Generally, the amount of heavy metals fractions increased with increasing period of adding the waste water. It is clear that more than 85 % of total Mn content in the untreated soil is in the sulfide fraction, while being far less (50 %) in the soils treated for 25 years, and varied between 70 and 80 % in the other treated soils. On the other hand, the adsorbed and organic fractions are less than 1 % regardless of treatment, while the carbonate fraction increased considerably and ranged between 9 and 30 % of the total Mn content in the waste water treated soil and much less, about 5-12 % in the untreated ones. The exchangeable fraction in soils treated for 8, 13 and 25 years is generally higher than both adsorbed and organic fractions. Therefore, the order of Mn fractions contents is: Sulfide > Carbonate > Organic > (Exch. + Ads.). For Cu, a small amount of Cu is found in the (Exch. + Ads.) fractions due to the low content of fine fraction in soil (clay content 6.5 %). In the treated soils, Cu is found mainly in the Org. fraction in the topsoil treated for 13 and 18 years due to their higher organic matter content if compared with the other soils. A comparison of the sludge and soil percentage for the organically bound metal indicates that Cu has high affinity for organic matter (de Matos *et al.*, 1996 and 2001). The organic matter content decreased with increasing depth, and therefore Cu in the organic form decreased downward the soil profiles. Generally, the order of Cu fractions is: Sulfide > Organic > Carbonate > (Exch. + Ads.).

For Zn, it is noticed that the predominant fraction is the sulfide fraction followed by carbonate, organic and (Exch. + Ads.) fractions. Both exchangeable and adsorbed extractable fractions are very low and comprise less than 1 % of the summation fractions. Therefore, these two fractions are combined together.

Data presented in table (4) show that the concentrations of Pb, Co and Ni in the untreated and waste water treated soils are higher in the top layer and decreased with increasing the soil depth. It is noticed that the total amount of these elements are higher in the waste water treated soils compared with the untreated one, where they increased with increasing addition period of the wastes, exceptionally Pb content which show little values in the soil treated for 18 years especially deep down the first 30 cm (1 st soil depth). These data agreed with Pierzynski (1985), Kabata Pendias and Pendias (1992) and Li and Shuman (1996) for Co, Ni and Pb, respectively. Many studies have been made on the distribution of Ni in soil profiles with conflicting results. Depending on the origin of the soil and pedogenic processes, the surface or the sub-surface soil may be relatively enriched or have the same Ni concentrations (Adriano, 1986). In some soils, Ni likes Fe and Mn may accumulate in the B-horizon as mixed oxides, while Ni may build up in the surface litter and humus. Berrow and Reaves (1986) found that, on average, the organic debris accumulated in the surface 0-6 cm of Scottish soils had smaller concentrations of Ni than mineral soil, but below the 6 cm there are only small changes in the Ni concentration with depth.

Data tabulated in table (4) show that the predominant fraction of Pb is the Car. fraction followed by Sulf. fraction, whereas the Exch. and Ads. fractions are very low. The Org. fraction follows an irregular pattern in the entire soil profile. Opposite to Pb, Co shows different pattern where the predominant fraction is the Sulf. fraction followed by Car. fraction, while the Ads. fraction is the latest one. The high content of Co- Sulf. fraction indicates that Co present in soil is in a stable form, while the low value of Pb-Exch. fraction indicates the low potential of Pb mobility in these soils. Also, it is clear that Co is relatively high in the Org. fraction of the top layer of soils treated for 25 years. This demonstrated a high association of Co with organic matter and forms a stable compound that leads to minimize the mobility of Co through soil depth. Increasing organic matter content in the topsoil might be helpful in binding Co in non-leachable forms and reduce the Co movement within soil profile. It is worthy mentioning that increasing period of application of wastes increased the percentage of Ni in the Org. fraction, while that in the Sulf. fraction drops. It appears that the Org. fraction and, to some extent, Car. fraction of Ni are the principal chemical forms of Ni induced through in waste water application. However, in the soils treated for 13 and 18 years, the Sulf. fraction amounts to about half of

the total Ni content and the order of fractions content is: Sulf. > Car. > Org. > (Exch.+Ads.). These results are in agreement with those of Sposito *et al.*, (1982).

Factors Affecting Heavy Metals Fractions in Soil Profiles

To emphasize the relationship between trace elements and soil variables, correlation coefficients are computed. The obtained coefficients indicate that exchangeable, adsorbed and carbonate fractions of Mn are highly significant positively correlated with clay content, EC and soil organic matter content, while being highly significant negatively correlated with sand and pH. Also, the sulfide fraction shows significant positive and negative correlations with clay content and pH, respectively. For Cu, the exchangeable, organic, carbonate and sulfide fractions show highly significant negative correlation with sand content and pH, while being positively correlated with CEC, EC and soil organic matter content. For Zn, it is noticed that the exchangeable, adsorbed, organic, carbonate and sulfide fractions show significant positive correlation with clay and soil organic matter content, while being highly significant negatively correlated with soil pH. These data agreed with those reported by Aboulroos *et al.* (1991) for Mn; Schalscha *et al.*(1982) and Abou Seeda *et al.* (1992) for Cu; Xiang *et al.* (1995) and El-Demerdashe *et al.* (1995) for Zn. They reported that the predominant fraction of Cu is principally in the organic form, while being in sulfide form for Zn and Mn.

The regression analysis indicates that silt, clay and soil organic matter content are highly significant positively correlated with the organic, carbonate and sulfide fractions of Pb, while being highly significant negatively correlated with sand and soil pH. Also, the exchangeable fraction of Co is highly significant and significant positively correlated with silt and clay, respectively while being significant negatively correlated with soil pH and sand content. On the other hand, clay and organic matter contents are highly significantly correlated with the organic, carbonate and sulfide Co fractions, while sand content and soil pH are highly significant negatively correlated with the previous fractions. The exchangeable, organic, carbonate and sulfide Ni fractions are highly significant positively correlated with clay content, EC and organic matter content, while being highly significant negatively correlated with sand content and soil pH. In this respect, Kiekens(1983), Sanders *et al.*(1986) and Anderson and Christensen(1988) mentioned that the most important factor determining the distribution of Ni between the solid and solution phases would seen to be pH, while factors such as the clay content and the amount of hydrous Fe and Mn oxides in the soil are of secondary importance. They added that the mobility of Ni in soils increases as the pH and CEC decreases.

TABLE (3). Total, DTPA-extractable and fractions of Mn, Cu and Zn in soils of different length of waste water treatment periods.

Profile No.	Depth, cm	Total Mn Mg l⁻¹	DTPA-Mn mg l⁻¹	Mn fractions (% Of the total)					Total Cu mg l⁻¹	DTPA-Cu mg l⁻¹	Cu fractions (% Of the total)					Total Zn mg l⁻¹	DTPA-Zn mg l⁻¹	Zn fractions (% Of the total)				
				Exch	Ads	Org	Car	Sulf			Exch	Ads	Org	Car	Sulf			Exch	Ads	Org	Car	Sulf
									Untreated soil													
1	0-30	45.00	0.81	0.53	0.31	0.07	5.13	89.44	27.50	0.31	3.27	0.15	8.29	61.67	22.18	25.45	0.56	0.55	0.31	4.68	7.35	15.14
	30-60	39.10	0.64	0.36	0.72	0.03	8.85	86.21	13.10	0.29	8.24	0.23	5.73	38.40	43.66	24.40	0.35	0.25	0.08	2.70	6.42	15.94
	60-90	20.15	0.45	0.35	0.74	0.05	8.93	86.10	11.22	0.21	3.30	0.18	8.29	26.02	57.84	20.10	0.31	0.55	0.30	4.68	5.80	11.96
	90-120	15.25	0.38	0.39	0.92	0.13	11.87	85.38	9.15	0.14	2.73	0.33	8.20	14.21	65.36	15.45	0.23	0.39	0.19	4.21	5.10	8.21
Average		29.88	0.57	0.41	0.67	0.07	8.70	86.98	15.24	0.24	4.39	0.22	7.63	35.08	47.26	21.35	0.36	0.44	0.22	4.07	6.17	12.81
									Soil treated for 8 years													
2	0-30	60.60	3.80	3.91	0.45	0.63	12.59	74.75	55.15	1.42	7.54	0.15	24.88	24.61	34.94	50.45	4.76	0.12	0.06	10.86	7.10	34.02
	30-60	43.90	1.97	2.07	0.18	0.55	11.89	80.21	28.10	1.05	11.39	0.32	19.75	31.49	31.14	37.55	2.47	0.03	0.03	7.08	4.33	27.41
	60-90	30.70	1.80	3.94	0.39	0.68	12.51	73.94	20.90	0.87	7.56	0.14	24.88	24.59	34.93	14.10	2.22	0.14	0.07	10.85	1.98	9.51
	90-120	25.10	1.66	3.90	0.56	0.76	14.58	75.18	15.55	0.66	10.29	0.26	22.12	19.36	43.34	11.23	1.98	0.27	0.18	9.08	2.01	7.25
Average		40.08	2.31	3.46	0.40	0.66	12.89	76.02	29.93	1.00	9.20	0.22	22.91	25.01	36.09	28.33	2.86	0.14	0.09	9.47	3.86	19.55
									Soil treated for 13 years													
3	0-30	84.35	7.98	2.66	0.14	1.00	16.92	70.55	60.45	1.93	3.57	0.08	39.37	26.34	24.10	105.70	7.39	0.14	0.09	18.95	16.23	64.65
	30-60	58.10	6.54	3.68	0.15	0.59	14.39	74.91	55.60	1.08	3.40	1.98	39.15	27.90	23.17	86.45	4.27	0.09	0.01	21.63	18.34	45.37
	60-90	52.19	6.14	3.64	0.19	0.61	14.41	74.73	40.11	1.10	3.39	1.97	39.14	27.90	23.16	79.15	4.50	0.14	0.09	18.95	12.15	48.41
	90-120	37.11	5.39	2.67	0.13	0.94	16.95	70.60	35.09	0.92	3.39	1.97	39.13	27.90	23.14	50.10	3.10	0.10	0.04	21.64	10.63	26.29
Average		57.94	6.51	3.16	0.015	0.79	15.67	72.70	47.81	1.26	3.44	1.50	39.20	27.51	23.39	80.35	4.82	0.12	0.06	20.29	14.34	46.18
									Soil treated for 18 years													
4	0-30	61.65	7.11	1.95	0.18	0.41	11.27	80.42	53.30	3.41	4.86	0.11	39.91	27.43	27.67	75.10	6.60	0.08	0.04	14.03	10.26	51.70
	30-60	57.70	7.01	0.24	0.31	0.09	9.72	83.26	44.50	1.49	0.16	0.20	29.35	24.56	36.36	61.45	4.42	0.07	0.03	8.43	6.75	47.50
	60-90	49.50	6.78	0.22	0.26	0.06	9.01	83.84	42.40	0.98	0.19	0.24	25.40	28.77	44.43	55.13	3.01	0.05	0.02	2.09	4.58	44.71
	90-120	38.13	4.11	0.21	0.26	0.05	9.05	83.66	31.90	0.88	0.19	0.25	25.27	28.71	44.29	39.84	1.91	0.08	0.05	14.03	5.44	27.43
Average		51.75	6.25	0.66	0.25	0.15	9.76	82.80	28.03	1.69	1.35	0.20	29.98	27.37	38.19	57.88	3.99	0.07	0.04	9.65	6.76	42.84
									Soil treated for 25 years													
5	0-30	115.00	8.70	12.11	0.48	1.38	30.63	50.92	67.35	4.25	2.88	0.06	32.03	25.21	39.82	241.29	9.00	5.20	0.16	25.74	66.59	51.70
	30-60	80.11	5.47	12.11	0.47	1.39	30.63	50.92	63.65	3.98	1.87	0.14	45.33	33.67	18.93	202.20	7.73	0.91	0.08	25.50	56.09	47.50
	60-90	60.15	4.20	12.05	0.47	1.33	30.59	50.87	50.11	3.85	2.93	0.06	29.10	22.91	36.18	170.11	7.10	5.20	0.16	25.74	46.96	44.71
	90-120	38.75	3.93	12.00	0.46	1.29	30.58	50.84	35.90	2.05	3.15	0.03	31.14	24.48	38.69	157.90	5.13	0.91	0.08	25.50	43.80	27.43
Average		73.50	5.58	12.07	0.47	1.35	30.61	50.89	29.75	3.53	2.71	0.07	34.40	26.57	33.41	192.88	7.24	3.06	0.12	25.62	53.36	42.84

TABLE (4). Total, DTPA-extractable and fractions of Pb, Co and Ni in soils of different length of waste water treatment periods.

Profile No.	Depth, cm	Total Pb mg kg⁻¹	DTPA-Pb mg kg⁻¹	Pb fractions (% Of the total)					Total Co mgkg⁻¹	DTPA-Co mg kg⁻¹	Co fractions (% Of the total)					Total Ni mgkg⁻¹	DTPA-Ni mg kg⁻¹	Ni fractions (% Of the total)				
				Exch	Ads	Org	Car	Sulf			Exch	Ads	Org	Car	Sulf			Exch	Ads	Org	Car	Sulf
									Untreated soil													
1	0-30	2.11	0.56	5.69	2.37	2.37	66.35	17.54	1.50	0.09	6.00	2.00	3.33	8.67	71.33	13.55	0.09	9.59	11.00	7.38	11.81	52.47
	30-60	1.91	0.46	1.57	1.05	3.14	72.25	17.28	1.60	0.12	10.00	2.50	4.38	8.75	68.75	11.05	0.06	8.78	12.04	10.32	13.76	50.32
	60-90	1.79	0.42	8.38	2.23	4.47	65.92	15.08	1.25	0.08	10.40	3.20	4.80	8.80	68.80	6.10	0.04	9.67	10.98	7.38	11.80	52.46
	90-120	1.53	0.33	6.54	1.96	2.61	64.71	31.37	0.89	0.05	11.24	3.37	4.49	14.61	64.04	5.56	0.02	0.90	0.90	7.01	11.51	55.94
Average		1.84	0.44	5.55	1.90	3.15	67.31	20.32	1.31	0.09	9.41	2.77	4.25	10.21	68.23	9.07	0.05	7.24	8.82	8.02	12.22	52.80
									Soil treated for 8 years													
2	0-30	3.55	1.81	1.69	1.41	1.13	84.51	4.23	2.80	0.33	1.79	1.43	5.36	2.14	82.14	18.15	0.69	6.61	5.12	11.90	20.61	49.09
	30-60	2.35	0.75	3.40	6.38	12.77	53.19	17.87	2.20	0.29	24.09	2.73	0.91	10.00	55.91	7.25	0.52	7.72	8.00	10.07	15.72	53.66
	60-90	1.98	0.62	2.53	1.52	2.02	33.33	7.58	1.75	0.23	24.00	2.86	1.71	9.14	56.00	5.11	0.51	7.63	8.02	9.98	15.66	53.62
	90-120	1.75	0.59	3.43	3.43	1.71	32.00	42.86	1.15	0.15	30.43	3.48	3.48	11.30	48.70	3.87	0.41	8.01	9.82	13.44	17.83	35.14
Average		2.41	0.94	2.76	3.19	4.41	50.76	18.14	1.98	0.25	20.08	2.63	2.87	8.15	60.69	8.60	0.53	7.49	7.74	11.35	17.46	47.88
									Soil treated for 13 years													
3	0-30	14.00	2.19	0.71	0.36	8.86	47.86	33.57	6.75	0.97	37.63	2.67	3.85	4.89	49.48	25.70	2.83	4.55	4.79	18.21	23.66	42.02
	30-60	13.20	2.05	0.68	0.23	3.03	49.24	38.94	6.55	0.88	1.68	3.36	2.29	17.40	67.94	20.50	2.43	4.05	2.54	14.00	21.12	49.56
	60-90	11.91	1.99	0.67	0.25	3.02	57.77	39.04	4.35	0.74	1.61	3.45	2.53	17.70	67.82	14.75	1.62	4.07	2.51	14.03	21.15	49.56
	90-120	8.75	0.98	0.69	0.34	9.03	48.00	33.71	3.89	0.69	37.53	2.57	3.86	5.14	48.84	11.35	1.30	4.58	4.76	18.24	23.70	42.03
Average		11.97	1.80	0.69	0.30	5.99	50.72	36.32	5.39	0.82	19.61	3.01	3.13	11.28	58.52	18.08	2.05	4.31	3.65	16.12	22.41	45.79
									Soil treated for 18 years													
4	0-30	16.90	2.03	5.98	3.61	6.09	70.95	8.52	10.60	1.09	7.55	2.55	4.15	15.94	64.62	45.20	2.98	7.81	5.53	21.90	23.56	34.51
	30-60	11.24	1.95	5.52	0.27	7.21	49.56	31.14	8.50	0.98	3.76	0.94	12.24	9.41	65.88	13.50	1.84	4.89	6.96	19.70	13.19	48.15
	60-90	8.21	1.12	5.72	1.34	1.34	54.45	31.43	5.90	0.77	15.93	2.88	4.75	2.88	66.95	15.15	1.65	8.51	4.55	13.40	18.42	48.38
	90-120	5.81	0.97	5.68	1.55	2.07	54.22	31.67	3.21	0.65	15.89	3.12	4.67	2.80	65.42	13.92	1.06	8.55	4.53	13.43	18.39	48.35
Average		10.54	1.52	5.73	1.69	4.18	57.30	25.69	7.05	0.87	10.78	2.37	6.45	7.76	65.72	21.94	1.88	7.44	5.39	17.11	18.39	44.85
									Soil treated for 25 years													
5	0-30	26.85	2.65	0.37	0.30	3.69	57.77	34.12	15.80	1.35	10.51	0.19	33.29	13.99	41.14	56.20	3.38	6.48	0.75	22.70	23.35	44.59
	30-60	24.10	2.34	0.33	0.29	3.98	52.90	37.47	12.25	1.11	5.88	0.24	11.84	3.59	72.82	34.20	2.33	0.87	2.19	28.48	45.58	10.47
	60-90	15.90	1.96	0.31	0.25	4.09	53.02	37.55	8.13	0.99	5.66	0.25	11.56	3.81	72.57	30.19	1.09	0.86	2.15	28.42	45.54	10.47
	90-120	10.98	0.75	0.36	0.18	4.10	52.82	37.34	6.71	0.85	10.43	0.15	33.08	14.16	40.98	22.11	1.01	0.47	0.77	22.70	23.34	44.46
Average		19.46	1.93	0.34	0.26	3.97	54.13	36.62	10.72	1.08	8.12	0.12	22.44	8.89	56.88	35.68	1.95	0.67	1.47	25.58	34.45	27.50

It is important to mention that the low content of the studied heavy metals in the (Exch. + Ads.) fractions could signify the low availability of these elements to plants, since the readily soluble form of elements is often regarded as the most bioavailable. Schalscha et al.(1982) suggest that KNO_3 fraction of trace metals represented potential mobility extracted fractions such as the DTPA-extractable fraction may be better correlated with trace elements availability to plants (Dahdoh and El-Demerdashe, 1995).

It is evident that the application of waste water have changed the solid phases containing heavy metals in soils away from those extractable with more severe reagents such as 4 M HNO_3, to those extracted with milder reagents such as dilute NaOH and EDTA. This change suggests that the waste water application plants than the non-amended soils, only Cu and Pb are more extractable with less diluted solutions. Also, it is important to mention that the recovery % of the studied elements with the studied reagents (for determining the fractions) compared with the total form varied between 84.23 and 100 % depending on the soil depth, period of adding the organic wastes and the nature of element.

Distribution of Heavy Metals in Plant Parts

Data in table (5) show the distribution of the studied metals in the different parts of some plants grown in soils treated with waste water for 8, 13, 18 and 25 years. It is evident that increased levels of heavy metals in soils generally resulted in higher heavy metal concentration in the parts of the growing plants. However, the degree of increase varied with plant species, plant part, period of waste water addition and the type of the studied element. In all the studied plants, the concentrations of heavy metals in roots are significantly higher than in the above ground parts (shoots). The roots have been known as good absorptive sponge to heavy metals in soil and water. Metals absorbed or adsorbed by roots are often bound with the cell wall material or other macromolecules to prevent them from translocation to the above ground parts (Dahdoh et al., 1997; Gaber and Dahdoh, 1999 and El-Maghraby, 2002). This explained why growth of the growing plants is not inhibited even if treated with very strong waste water (Chen et al., 1995). When the total content of heavy metals increased, the defensive mechanism of root (as a barrier) might have been exhausted and more metals are found in the aerial plant parts. It is noticed that the mobility of metals in the different plant parts was in the decreasing order(in most cases): Zn > Mn > Ni > Cu > Co > Pb for above ground plant part, while being Pb > Co > Ni > Mn > Zn > Cu for plant roots. Therefore excess Zn and Mn were likely to move up from roots to aerial mobility more than potential bioavailability in sludge-amended soils. Other plant parts that treated with organic wastes than Co and Pb. In general, the relative ratio of heavy metals in root to shoot decreased as input heavy metals increased, since excess heavy metals might have been translocated to the above ground portions. It is important to

mention that the normal concentration (mgl⁻¹) of the studied elements as shown by Lockman (1996) are as follows: 50-150 (Mn), 20-50 (Zn), 7-20 (Cu), 5-10 (Pb) and 1.0-9.5 (Ni), while the toxic levels for Pb and Ni are (30-300) and (10-100), respectively (Bergmann and Cumakov, 1977 and Davis *et al.*, 1978).

TABLE (5). Heavy metals content in plants grown in waste water-treated soils (mgl⁻¹)

Period (years)	8		13		18		25	
Plant species	Alfalfa		Beet		Bean		Maize	
Plant parts	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root
Element								
Mn	34.8	49.5	74.3	121.3	33.0	44.3	24.0	35.5
Zn	104.0	251.8	39.3	60.8	91.8	135.5	58.0	100.5
Cu	21.3	32.8	85.3	165.3	30.3	33.5	16.0	65.8
Pb	4.0	15.0	5.0	6.5	17.0	22.5	15.3	22.5
Co	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Ni	19.0	49.0	12.3	17.3	23.0	43.0	24.0	35.3
Zn equivalent (ppm)	264.0	673.0	308.3	529.8	336.4	476.4	363.0	514.5

Accordingly, the concentration of Mn, Cu, Pb, Co and Ni in the current study is within the normal range and did not reach the toxic level, except for Cu (alfalfa) and Zn for studied plants.

Zinc, Cu and Ni differ in their toxicity of specific plants in specific soils. Generally, Cu is twice as toxic as Zn, and Ni is eight times as toxic as Zn. In this respect, Chumbley (1971) introduced ppm Zn + 2X mgl⁻¹ Cu + 8X mgl⁻¹ Ni, to take into account the differences among metals. He suggested no more than 250 mgl⁻¹ Zn (equivalent) to be added to the agricultural soils (with pH maintained > 6.5). With regard to the obtained data, it is noticed that Zn equivalent is more than 250 mgl⁻¹ with addition of organic wastes for all the studied plants. However, there is no appearance of any visual harmful observations on the grown plants, it is a must to take into consideration that these plants are not suitable for human feeding due to the Zn equivalent value as well as increasing Zn concentration and some other heavy metals. In conclusion, it is important to mention that treating waste water in this region before being used in agricultural purposes is important to control the concentrations of these heavy metals that have the ability to accumulate in soils.

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أثر بعض الفلزات الثقيلة علي الأراضي المروية بمخلفات المجاري

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تعتبر حركة الفلزات الثقيلة خلال القطاع الأرضي من الأمور الهامة في التلوث البيئي، فالحركة البطيئة لهذه الفلزات خلال التربة تؤدي إلي تراكمها في التربة وقد تؤدي في النهاية إلي تدهور صفات الماء الجوفي.

اختيرت أربعة قطاعات أرضية منزرعة يتم ريها بمخلفات المجاري (صرف صحي وصناعي) لمدينة العاشر من رمضان لفترات تراوحت ما بين ٨ ، ٢٥ عاما ، كما تم إختيار قطاع لم يتم ريه بهذه المياه من نفس المنطقة. تم دراسة توزيع فلزات المنجنيز ، النحاس ، الزنك ، الرصاص ، الكوبالت ، النيكل) وكذلك الصور المختلفة لها ، حيث تم جمع العينات كل ٣٠ سم لعمق ١٢٠ سم ، كما تم تقدير المحتوي الكلي والميسر وكذلك عمل إستخلاص متتالي للصور المختلفة لهذه العناصر وهي : الصورة المتبادلة ، المدمصة ، العضوية ، الكربونات ، الكبريتيد.

أوضحت النتائج أن المحتوي الكلي كان أكبر كثيرا في الأراضي المروية بمخلفات المجاري عنه في الأراضي الغير مروية ، كما أن التركيز قل كلما زاد العمق. كذلك أوضح الاستخلاص المتتالي أن الجزء الأكبر من المنجنيز ، الزنك ، الكوبالت ، النيكل كان في صورة الكبريتيد ، بينما الجزء الأكبر من النحاس ، والرصاص كان مرتبط بالصورة العضوية والكربونات علي التوالي وذلك في كل من الأراضي الغير معاملة والمعاملة ، كما أوضحت النتائج أن إضافة المخلفات العضوية أدت إلي زيادة تركيز العناصر الثقيلة في النباتات النامية بدرجات متفاوتة تبعا لنوع النبات والجزء المدروس وكذلك مدة إضافة المخلفات.