

IMPACT OF IRRIGATION WITH SEWAGE WATER ON CALCAREOUS SOIL:

II- HEAVY METAL SPECIATION IN SOIL.

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ABSTRACT

Soil samples were collected from experimental fields plots irrigated with raw sewage water for different periods (3, 10 and 30 years) to investigate the solid-phase speciation of Cu, Zn, Cd, Ni and Pb in calcareous soil. A sequential extraction procedure was used to fractionate heavy metal into designated forms of exchangeable (Exch.), sorbed (Sorb.), organically bound (Org.), precipitated (Prec.) and residual (Resi). The obtained results showed that the residue fraction was the most abundant fraction in the control soil for all studied metals, followed by the precipitated (carbonate) fraction, while in the waste water irrigated soil, the average highest metal fraction, as percentage of total, was recorded as follows: org-bound for Cu; preci.-bound for Pb and resid. form for Zn, Cd and Ni. The distribution of solid phase metals in the different fractions did not significantly change as a result of sewage water irrigation. In some cases, metals in soils irrigated with sewage water tended to shift from less to more soluble forms, according to the period of irrigation with sewage water.

INTRODUCTION

Heavy metals are potentially toxic to human and the environment. Metal toxicity depends on its chemical associations in soils. The bioavailability of heavy metals and their mobility in soils are largely determined by their distribution among the various solid-phase components. Heavy metals in soils amended with various wastes are redistributed and transferred with time from labile forms to the more stable forms.

Fresh water is considered a vital resource especially in arid countries exhibiting a high population growth such as Egypt. In different fields in Egypt, plants have been made to conserve fresh water using technological development. One of these fields is the reuse of wastewater in irrigation (Abo Soliman *et al.*, 2001). The use of sewage effluent in irrigation usually takes place on sandy soil which has no other source of irrigation water. Despite that raw sewage water is useful amendment for cropland (Wang *et al.*, 1997). Also, crops grown on soils irrigated with sewage water may accumulate heavy metals in excessive quantities which, in turn, may cause health problems in animal and human being.

The solubility and mobility of heavy metals soil depends on certain chemical properties such as chemical speciation of metal, soil pH and redox potential, and water movement (Bang and Hesterberg 2004). As a result of transformations of heavy metals that take place in sewage sludge loaded soil, metals continue to be released into solution for a long period after sludge application (Vulkan *et al.*, 2002). Other studies revealed that the solubility

(and hence mobility potential) of organic and metallic contaminants in soil tended to decrease over time (Alexander, 2000).

Heavy metal content of a soil usually provides little information on the processes and dynamics of the availability and mobility of the metal. more useful, since it is related to mobility and uptake by plants and extractability by chemical treatments (McBride, 1994). Selective sequential procedures have been commonly used for studying metal mobility and availability in soil (Ma and Rao 1997). Different extraction schemes for soils have been described in literature (Tessier *et al.*, 1979; Sposito *et al.*, 1982 ; and Elsokkary, 1992). The sequential selective dissolution method (SSD) has been developed to study the forms, availability, mobility and transformation of heavy metals in sludge-amended soils. This method is based on both the solubility of individual solid-phase components and the selectivity and specificity of chemical reagents. (Tessier *et al.*,1979 and Chang *et al.*, 1984). In the SSD procedures, the terms of all fractions are more likely to be defined operationally rather than chemically (Kheboian and Bauer, 1987). However, each extractant in the procedures effectively targets on major solid-phase component. It is recognized that no case can an extractant remove all of a targeted solid-phase component without any attack on other components. No selective dissolution scheme can be considered completely accurate in distinguishing between different forms of an element (Han *et al.*, 2001). In addition, there may be redistribution and readsorption during sequential dissolution extraction (Kheboia and Bauer, 1987). It was reported that readsorption of metals (Cd, Cu, Pb and Zn) during sequential extraction was minimal (Kim and Fergusson, 1991).

Despite these shortcomings common to any chemical extraction procedure, sequential dissolution techniques still furnish more useful information on metal binding, mobility, and availability than can be obtained with a single extractant.(Han *et al.*, 2001). The heavy metals fractionation results reflect contamination time on the heavy metal lability and bioavailability in the soils (Lim *et al.*, 2002). This study was carried out to investigate the solid-phase speciation of Cu, Zn, Cd, Ni and Pb in soils which were irrigated with sewage water or ground water (well water).

MATERIALS AND MEHCDS

Soil samples were collected from the experimental field plots irrigated with raw sewage water for different periods or with ground water and cultivated with different plant species (Abdel Salam *et al.*, 2004).

The soil samples were air-dried, ground to pass 2mm-sieve and stored in polyethylene bags for analysis. The main properties of the soils were determined (Abdel Salam *et al.*,2004) and the data obtained are given in Table 1.

Table (1): Some chemical and physical properties soils irrigated with ground or with raw sewage water.

Irrigation Period (years)	Irrigation water	Soil Depth(cm)	PH (1:2.5)	EC (dsm-1)	O.M. %	CEC meq100g	CaCO3 %	Sand %	Silt %	Clay%	Texture
3	SW	0-20	8.1	2.3	0.7	8.7	14.8	76.2	14.4	9.4	Loamy sand
		20-40	7.9	1.7	0.4	-	20.1	71.9	23.3	4.8	
	GW	0-20	8.1	4.3	0.3	7.7	21.3	72.6	21.7	5.7	Loamy sand
		20-40	7.9	3.9	0.2	-	22.7	73.7	20.2	6.1	
10	SW	0-20	7.8	0.2	1.4	10.5	21.7	73.2	19.4	7.4	Loamy sand
		20-40	7.9	0.3	0.8	-	21.2	80.6	13.6	5.8	
	GW	0-20	7.8	2.3	0.8	9.6	24.8	74.1	17.3	8.6	Loamy sand
		20-40	8.0	0.6	0.4	-	25.4	76.3	13.9	9.8	
30	SW	0-20	7.8	0.7	4.8	13.1	14.7	48.4	34.7	16.9	Sandy Loam
		20-40	7.9	0.8	1.4	-	21.4	53.1	33.2	13.7	
	GW	0-20	8.2	4.6	0.2	8.5	18.4	48.7	32.9	18.4	Sandy Loam
		20-40	8.1	3.7	0.1	-	20.1	52.4	32.8	14.8	

GW :Ground water irrigated soil
 SW :Sewage water irrigated soil

Metal Speciation:

A sequential extraction procedure described by Sposito *et al.* (1982) and Emmerich *et al.* (1982) was employed to partition the total metals contents of soil (Zn, Cu, Cd, Pb, and Ni) into readily soluble (exchangeable + sorbed), organically bound, inorganic precipitated (mainly carbonates) and residual forms.

Two grams soil were sequentially extracted with 25 ml 0.5M KNO₃ for 16h (exchangeable form) followed by three extractions, 2h each, with deionized water to obtain sorbed form, the exchangeable+ sorbed metal form, (Readily soluble: F1) ; 0.5M NaOH for 16 h (organically bound form: F2); 0.05M Na₂ EDTA for 6h (precipitate form, mainly carbonate form: F3); and 4M HNO₃ at 80 °C for 16 h (residual form: F4). During each extraction, the soil suspension was shaken reciprocally for the respective duration as shown above, centrifuged, and the supernatant solution was filtered through a Whatman No.42 filter paper. Calculations used to obtain the amount of metal in each fraction after its extraction and centrifugation step and an assumption that the mass of soil remained constant (Sposito *et al.* 1982). The contents of the five trace metals (Zn, Cu, Cd, Pb, and Ni) in the filtered solutions were determined by AAS, Perkin Elmer model 5000.

RESULTS AND DISCUSSION

Tables 2-6 show the distribution of Cu, Zn, Cd, Ni and Pb among the different fractions of the soils. The results showed that the summation of the amount of heavy metals extracted by the sequential extraction procedure were greater than those extracted by the one-step aqua regia method. Jeng and Bergseth (1992) found that, in general, the total metal contents derived by summation of all forms were slightly greater than those measured by aqua regia. Sposito *et al.* (1982) stated that these differences may have been the result of the 4 M HNO₃ (80°C) extraction in the sequential procedure (residual fraction, F4) which is being more effective than the aqua regia extraction to obtain the total metal content and also because of the preconditioning of the soil sample by the previous extractions with NaOH and EDTA in the sequential procedure. They also reported that this fractionation procedure was experimentally precise although the total metal content estimated by summation of the fractions was slightly higher than that obtained by digestion with 4M HNO₃ (80°C). These differences were within the experimental error. However, there was a high significant correlation ($r^2 = 0.94^{**}$) between the sum of the metal fractions and the amount extracted by aqua regia.

Heavy Metal Distribution Among Chemical Fractions:

Table 8 shows the percentage distribution of Cu, Zn, Cd, Ni and Pb among the sequentially extracted fractions of the surface soil samples (0-20 cm) irrigated with sewage water for different periods (0, 3, 10, 30 years). The distribution of solid-phase heavy metals showed that the residual fraction was the most abundant fraction followed by the precipitated fraction (mainly

carbonate). This was true for all studied metals with the exception of Cu. This result agrees with the findings of Chang *et al.* (1984) ; Singh *et al.* (1988) ; Dudka and Chlopecka (1990) and Chlopecka *et al.* (1996). This information has important implications for the long-term potential of leaching metals to groundwater. Although sulfide minerals are often considered to be insoluble, they will dissolve as it is oxidized to sulfate. Thus, the metals will be released slowly to soluble forms over extended periods of time (Abdel-Saheb *et al.* 1994). Other workers (Sposito *et al.*, 1982; Zhu and Alva, 1993; Flores *et al.*, 1997) found that the quantities of exchangeable and sorbed forms (read. sol.) of heavy metals represented a small fraction of the total metal contents. However, the relatively high values of both the exchangeable and sorbed (read. Sol.) for Cu, Cd, Pb, and Ni could occur as a result of one or more of the following reasons: (i) the lack of selectivity of the reagents used so this leads to an overestimation of some fractions and underestimation of the others (ii) the possibility that metals may redistribute between the different phases during the sequential extraction and has been put as a shortcoming of some procedure, and (iii) the system of classification of the fractions (Miller *et al.*, 1986; Kheboian and Bauer, 1987 and Kim and Fergusson, 1991). It is clear from Table 8 that the period of sewage water irrigation had no significant effects on the distribution of Cd, Ni and Pb among the various metal fraction.

The unchanged distribution of metal fractions in the ground water and sewage water irrigated soils indicates that metal accumulation and transformation was similar in all soils although they differed in sewage water irrigation periods. This illustrates that major changes in metal distribution resulting from irrigation of the calcareous soil with sewage water can occur in a short period of time and this agrees with many other results (Flores *et al.*, 1997 and Singh *et al.*, 1998).

Han and Banin (1999) showed that heavy metal distribution among the solid-phase components of the soil is strongly dependent on the soil properties. Because the area under study have the same soil chemical environmental conditions (highly calcareous), so sewage water application did not appear to play a significant role in determining metal fractionation. This might be attributed to the buffer capacity of carbonate.

Sewage water irrigation of the soils significantly altered the distribution of some heavy metals among some solid-phase fractions (Table 8). Generally, it could be concluded that irrigation with sewage water shifted the solid phases containing Zn, Cu, and Pb in the soils away from those extractable with more severe reagents such as 4 M HNO₃, (residual fraction, F4) to those extractable with milder reagents such as dilute NaOH (Organic fraction, F2) and EDTA (Precipitate fraction, F3). This shift suggests that sewage water irrigation would provide the metals in labile forms that could be more readily available to plants than in the case of ground water irrigated soils. Our findings also support the conclusion of Kabata-Pendias (1993) where trace metals from anthropogenic sources are potentially more mobile than those are ultimately inherited from the geological parent materials. However, it should be kept in mind that the different elements, in the same bonding form, show different solubilities. Also, changes of soil pH as a result

of sewage water irrigation may result in changes of the speciation distribution of heavy metals (Buykx *et al.*, 2002).

Solid-phase Speciation of Metals:

Copper: Table 2 shows the various fractions, summation of all forms, and % recovery of copper in the layers (0-20 and 20-40 cm) of soil irrigated with ground water and sewage water for different periods (3, 10, and 30 years). The total Cu content (sum) of the upper soil layer (0-20 cm) was 18.5, 30.5 and 51.8 mgkg⁻¹, respectively for different period of irrigation with sewage water. These values were higher than the values of ground water irrigated soil (control) which were 13.8, 19.7 and 18.1 mg kg⁻¹, respectively. These values fall within the range reported by others (Miller *et al.*, 1986 and Singh *et al.* 1988).

Table (2): The amounts of copper fractions in soil (mg kg⁻¹) irrigated with raw sewage water for periods of 3, 10 and 30 years or with ground water.

Irrigation water	Soil Depth,cm	Read. Sol.	Org.	Prec.	Resi.	Sum	Total Aq.Reg.	Recovery
3 years								
S. W.	2-20	4.60	9.00	4.90	5.30	23.80	18.5	128.6
	20-40	2.20	3.00	2.00	6.00	13.20	14.3	92.3
G. W.	0-20	4.30	0.20	3.30	2.40	10.20	13.8	73.9
	20-40	3.20	5.30	1.80	4.70	15.00	13.8	108.7
10 years								
S. W.	2-20	3.30	21.50	2.80	10.40	38.00	30.50	124.6
	20-40	4.00	12.80	2.00	1.60	20.40	15.90	128.3
G. W.	0-20	4.90	5.90	1.80	2.30	17.90	19.70	90.9
	20-40	3.50	3.20	1.90	4.20	12.80	12.00	106.7
30 years								
S. W.	2-20	2.90	13.10	2.30	6.90	25.20	51.80	101.2
	20-40	7.30	40.00	5.20	3.30	3.30	24.90	107.7
G. W.	0-20	6.80	2.80	6.90	5.80	22.30	18.10	123.2
	20-40	3.30	2.40	3.30	5.10	14.10	15.00	94.0

The order of Cu contents in the different fractions of the control soil (0-20cm) was Read. Sol. >Res.> Prec. > Org. (Table 8 and Fig.1). The Org. fraction of Cu in the control soil was not high (15.83%) probably due to the low organic matter content of these soils (Singh *et al.* 1988). In contrast, the highest concentrations of Cu were associated with the organic fraction, and the strong relationship between soil Cu and organic matter has been reported by Stumm and Morgan (1990); and Phillips and Chapple (1995).

Irrigation with the sewage water for 3, 10 and 30 years significantly increased the percentage of Cu- organic fraction from 15.83% (control) to 37.82, 56.58, and 51.98% in the surface soil layer, respectively. In contrast, read. Sol and preci- fractions decreased after 3, 10, and 30 years of sewage water irrigation (Table 8). This is evidently indicating that the efficiency of organic matter was more important than CaCO₃ for Cu binding (Flores *et al.*, 1997). Ma and Uren (1998) noted that there were low concentrations of Cu in

the carbonate bound fraction even though CaCO_3 was added to the soil. Also, Sposito *et al.* (1983) concluded that Cu shifts from the residual fraction in the non-amended calcareous soil to the organic fraction after liquid sludge amendment. In the sewage water irrigated soil for 30 years, the amount of Cu in each fraction followed the order Org. > Res. > Read. Sol. > Prec. (Table 8 and Fig 1). A similar distribution pattern was observed by Ramos *et al.* (1994).

Zinc: There were marked variations for total Zn in soil (0-20 cm) ranging from 17.6 to 34.5 mg kg^{-1} in the control soil, and from 41.6 to 291.0 mg kg^{-1} in the sewage water irrigated (Table 3). Lindsay (1972) reported that soil Zn can be ranged from 10 to 300 mg kg^{-1} . While normal range given by Kabata-Pendias and Pendias, (1992) was 5-100 ug g^{-1} .

Table 8 shows that in the control soil surface, the highest percentage of Zn (82.85 %) was in the residual fraction, followed by the precipitated fraction (10.41 %). This is likely because carbonate adsorbs considerable quantities of Zn (Singh *et al.*, 1988). This finding supports several statements about Ca-exchange sites with high selectivities for Zn (Kabata-Pendias and Pendias 1992 ; Shuman, 1988 and Jeng and Singh, 1993). A small proportion of Zn (1.58%) in the surface control soil (0-20 cm) was organically bound whereas the readily soluble (sorbed and exchangeable bound) Zn was around of 5% of total (Fig 1).

Irrigation with sewage water generally resulted in redistribution of soil Zn from the residual fraction into the precipitated and organic fractions. For example, as sewage water was used for 10 years, organic Zn fraction increased from 2 to 10% and the Zn-precipitated fraction increased from 10 to 40% while residual Zn decreased from 83 to 46% of the total sum of soil Zn (Table 8). Similar trends were noted by Sims and Kline (1991). However, the general distribution pattern did not change and the majority of Zn was found in a residual fraction. A highly significant relationships between DTPA-extractable zinc and each of the chemical forms were observed (Table 7).

Cadmium: The concentrations of Cd, within the individual fractions of the sequential extraction analysis, are given in Table 4 . Total Cd contents in the examined surface soils varied from 1.9 to 2.9 and 2.6 to 4.1 mg kg^{-1} in the control and sewage water treated soil, respectively. These concentrations are exceeding the normal range (0.01-2.7 ppm) in agricultural soils reported by Kabata-Pendias and Pendias (1992). Although the irrigation with sewage water increased soil total Cd, the distribution of Cd among the various fractions in the sewage water irrigated soil remain similar to that in the control soil (Table 8). Other researchers found similar results (Chang *et al.*, 1984a; and Han and Banin, 1999).

The distribution of Cd between the different fractions shows that the highest percentage was found in the residual fraction followed by the precipitated, readily soluble and organic forms. This trend was true for both the control and sewage water irrigated soils (Table 8 and Fig 1). This result agrees with the observations of Chlopecka (1993), Abdel-Saheb *et al.* (1994).and Flores *et al.* (1997).

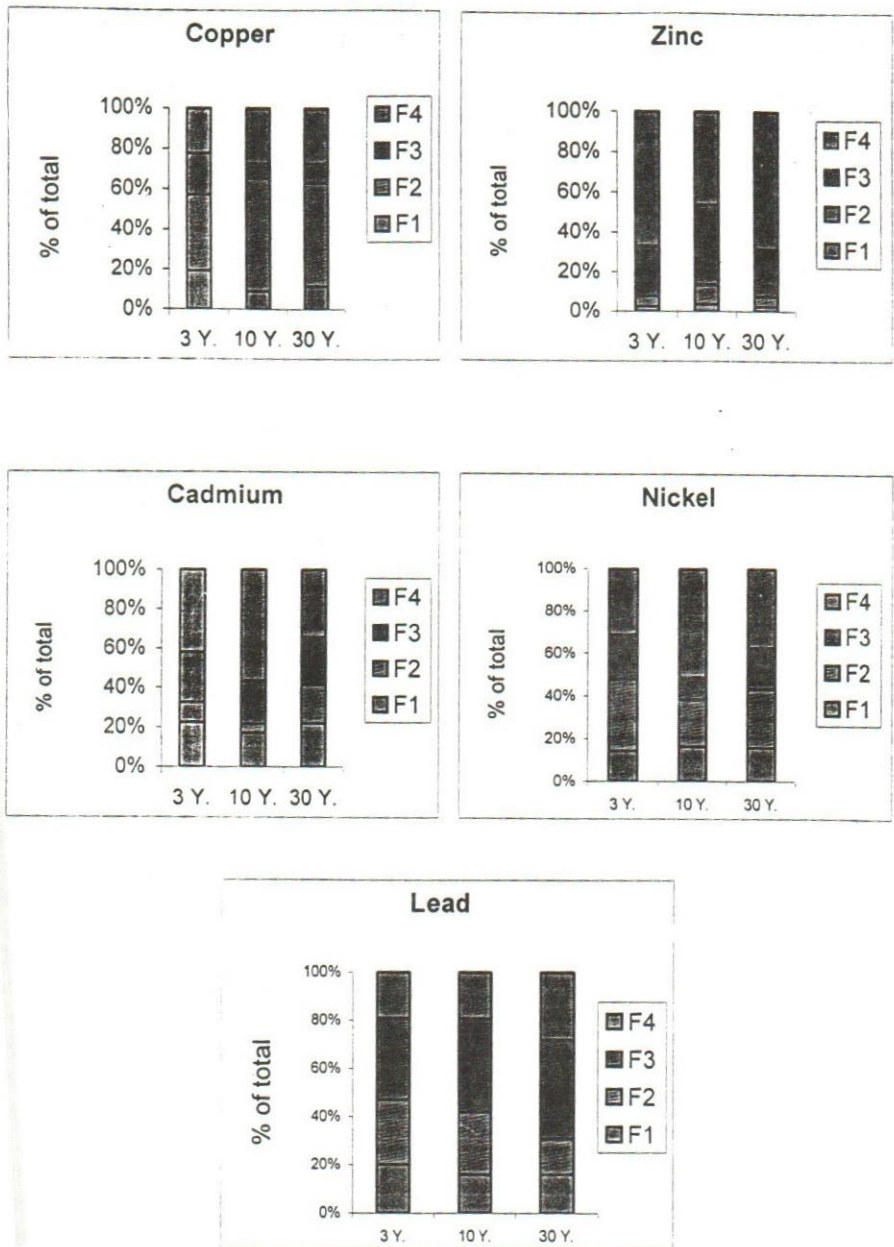


Fig. (1): Distribution of the Cu, Zn, Cd, Ni, Pb fractions in the surface soil layer (0 - 20 cm) at different sewage water application periods (3,10 and 30 years). Extracted fraction: F1 (Readily soluble) ; F2 (Organic); F3 (Precipitate); and F4 (Residual).

Table (3):The amounts of zinc fractions in soil (mg kg⁻¹) irrigated with raw sewage water for period of 3, 10 and 30 years or ground water.

Irrigation water	Soil depth,cm	Read. Sol.	Org.	Prec.	Resi.	Sum	Total Aq.Reg.	Recovery
3 years								
S. W.	0-20	1.40	2.80	13.70	35.80	53.70	41.60	129.1
	20-40	3.70	7.80	10.90	22.20	44.60	37.50	118.9
G. W.	0-20	1.40	0.10	3.00	24.50	29.00	34.50	84.1
	20-40	0.20	0.60	2.80	13.80	17.40	15.30	113.7
10 years								
S. W.	0-20	6.50	17.30	6.70	78.20	169.7	162.0	104.8
	20-40	6.40	6.00	8.90	10.10	31.40	29.50	106.5
G. W.	0-20	1.20	0.70	3.50	24.50	29.90	33.50	89.3
	20-40	0.20	1.10	8.10	5.20	13.60	12.00	113.3
30 years								
S. W.	0-20	7.40	14.90	72.20	205.0	299.5	291.0	102.9
	20-40	0.70	2.30	6.40	124.1	133.5	112.0	119.2
G. W.	0-20	1.30	0.40	1.80	16.10	19.6	17.60	111.4
	20-40	0.40	0.20	0.60	12.60	13.8	13.50	102.2

Table (4): The amounts of cadmium fractions in soil (mg kg⁻¹) irrigated with raw sewage water for periods of 3, 10 and 30 years or ground water.

Irrigation water	Soil Depth,cm	Read. Sol.	Org.	Prec.	Resi.	Sum	Total Aq.Reg.	Recovery
3 years								
S. W.	0-20	0.70	0.30	0.80	1.30	3.10	2.60	119.2
	20-40	0.30	0.20	1.30	2.30	4.10	3.80	107.9
G. W.	0-20	0.40	0.30	0.90	1.10	2.70	1.90	142.1
	20-40	0.20	0.40	0.40	1.70	2.70	2.60	103.8
10 years								
S. W.	0-20	0.40	0.10	0.50	1.30	2.30	3.20	109.4
	20-40	0.20	0.80	0.90	1.70	3.60	4.80	114.8
G. W.	0-20	0.50	0.30	0.90	1.80	3.50	2.10	109.5
	20-40	0.70	0.20	1.60	2.40	5.90	3.00	120.0
30 years								
S. W.	0-20	0.50	0.80	1.00	1.40	5.10	4.10	108.5
	20-40	0.90	0.30	1.00	2.20	4.00	4.00	102.6
G. W.	0-20	0.50	1.00	0.40	1.10	3.10	2.90	106.9
	20-40	0.40	0.30	0.60	1.50	2.80	2.40	116.7

The high percentage of readily soluble (Exch. + Sorb.) Cd in both of control and treated samples (Table 8) agrees with the findings reported in the literature (Elsokkary and La^og, 1978 and Ramos *et al.*, 1994). These results could be due to the low solubility of cadmium carbonate and the low

adsorption constant of the complex formed with the organic matter. The organic matter Cd fraction is being considered labile (Baron et al., 1990). Cadmium forms ionic complexes with humic and fulvic acids (Alloway, 1995) and they are less stable than those found with Cu and Pb. This behavior causes Cd becoming more concentrated in the carbonate fraction and the read. sol. (mainly exchangeable fraction) as shown in Table 4. Total Cd obtained by summation of the read. solu. and the carbonate fractions, were more than 39 and 48 % for the control and sewage water irrigated soil after 3 years, respectively. On the other hand, Cd-organic complexes are only loosely bound to soil particles and they are also easy to remove (Ramos et al., 1994). Cadmium associated with the non-residual fractions may be easily taken up by plants growing in the soils (Ramos et al., 1994). However, Sposito et al. (1982) stated that it is not possible to fractionate Cd successfully in the soils, particularly in the control soils, because the total metal contents were almost so small.

Nickel: The amounts of total Ni in the control and sewage water irrigated soils (0-20 cm) ranged from 20.5 to 22.0 mgkg⁻¹ and from 22.0 to 47.1 mg kg⁻¹, respectively (Table 5). Alloway (1995) reported that the average concentration of Ni in world soils is probably around 20 mgkg⁻¹. However, the upper level of Ni in the soils studied was within the normal ranges of this element (1-110 ppm) as given by Kabata-Pendias and Pendias, (1992).

Table (5): The amounts of nickel fractions in soil (mg kg⁻¹) irrigated with raw sewage water for period of 3, 10 and 30 years or ground water.

Irrigation Water	Soil depth,cm	Read. Sol.	Org.	Prec.	Resi.	Sum	Total Aq.Reg.	Recovery
3 years								
S. W.	0-20	3.50	8.20	5.20	7.60	24.50	22.00	111.4
	20-40	4.80	5.90	6.20	6.80	23.70	21.00	112.9
G. W.	0-20	3.60	6.00	5.20	6.40	21.20	21.00	101.0
	20-40	3.90	3.10	3.80	7.50	18.30	17.70	103.4
10 years								
S. W.	0-20	4.80	6.50	3.00	15.20	29.50	27.70	106.5
	20-40	1.50	4.70	5.20	12.10	23.50	21.60	108.8
G. W.	0-20	7.20	2.80	1.30	10.10	21.40	22.00	97.3
	20-40	0.90	1.00	3.30	7.80	13.00	13.80	94.2
30 years								
S. W.	0-20	7.50	12.90	19.10	17.60	47.10	47.10	108.3
	20-40	9.00	5.90	13.30	16.10	44.30	44.30	104.2
G. W.	0-20	2.50	1.20	7.80	7.70	19.20	20.50	93.7
	20-40	2.80	3.30	4.70	6.40	17.20	16.70	102.4

Table 5 reveals the different chemical fractions (mg kg⁻¹) of Ni as affected by ground water and sewage water irrigation for 3, 10 and 30 years. It is clear that irrigation with sewage water did not significantly change the percentage of metal fractions of the total sum (Table 8). Previous studies

showed that Ni fractions distribution departed from the original partition pattern of the control soil after addition of sludge but slowly returned towards the distribution characteristics of the non-amended soil (McGrath and Cegarra, 1992). However, the residual fraction was the dominant fraction (39.16%) for the control soil while this value reached 51.53% in the irrigated soil by sewage water for 10 years, followed by the precipitated fraction (23.74%) for control soil, and organic form (27.39%) for sewage water irrigated soil (Table 8 and Fig 1). It is found that over 50% of Ni in soils may be associated with the residual fraction and 20% in the Fe-Mn oxide fraction, with much of the carbonate fraction, and only a relatively small proportion in the exchangeable and organic fractions. Similar results were obtained by Hickey and Kittrick, (1984). In this study, the organic fraction represented about 16 and 33% of the Ni total summation Ni in the control and sewage water irrigated soils for 10 years, respectively. Using composted sewage sludge, Sims and Kline (1991) concluded that the organic fraction was the third largest fraction and increased from 5%, in the control soil, to 21% in the sludge amended soils. It noticed that the amount of exchangeable and sorbed Ni (>20%), was relatively higher than that of the previous studies. Also, a large proportion of Ni (16%), associated with the exchangeable fraction, was found by Hickey and Kittrick (1984). Other researchers (Sposito *et al.*, 1982 and Sims and Kline, 1991) concluded that the exchangeable and sorbed fractions combined were <7% of the total Ni. Sowder *et al.* (2003) showed that Ni was distributed across all operationally defined fractions, including substantial amounts in the labile fractions (4-15% in water-soluble+exchangeable), non crystalline and crystalline iron oxides (38-49%), and in the nonlabile residual fraction (25-34%).

Lead: The amounts of total Pb in the ground water and sewage water irrigated surface soil (0-20 cm) ranged from 17.7 to 25.3 and from 20.5 to 40.2 mg kg⁻¹, respectively (Table 6). These amounts are within the normal range (2.3-70.0 ppm) reported by Kapata-Pendias and Pendias (1992). Alloway (1995) stated that lead is present in uncontaminated soils at concentrations <20 mg/kg but much higher concentrations have been reported in many areas as a consequence of anthropogenic activities, often over many years.

Table 6 showed that different chemical species of Pb in the two soil surface layers (0-20 and 20-40 cm) irrigated with ground water and sewage water for 3, 10 30 years. The highest amount was found in the residual fraction followed by precipitated, and organic= read. Sol. (Table 8 and Fig. 1). This Pb distribution was similar to that found by Abdel-Saheb *et al.* (1994), Ramos *et al.* (1994), Phillips and Chapple (1995), Chlopecka *et al.* (1996), and Han and Banin (1999). The residual and precipitated fractions combined accounted for 61% of total sum Pb. Zhu and Alva (1993) reported that these two fractions represented the major proportion (71-95%) of total Pb in soils.

Relatively high percentage of Pb (19.40%) was found in the readily soluble fraction (mainly sorbed). This might be attributed to the high affinity of Pb to be adsorbed on the solid phase of soil (Abdel- Saheb *et al.*, 1994). Approximately 3.3% of the Pb extracted were associated with the

exchangeable phase. Chlopecka *et al.* (1996) noticed that relatively minor amounts of Pb are found in the exchangeable form.

Sewage water irrigated soils showed some differences in Pb species, since some amounts of Pb were transferred from the residual fraction into the precipitated fraction (Table 8).

Table (6): The amounts of lead fractions in soil (mg kg^{-1}) irrigated with raw sewage water for period of 3, 10 and 30 years or ground water.

Irrigation water	Soil depth, cm	Read. Sol.	Org.	Prec.	Resi.	Sum	Total Aq. Reg.	Recovery
3 years								
S. W.	0-20	4.60	6.10	7.70	4.40	22.80	20.50	111.2
	20-40	1.60	8.50	11.20	0.90	22.20	20.2	109.9
G. W.	0-20	3.70	2.80	2.90	6.30	15.70	17.70	91.8
	20-40	0.30	1.00	2.50	11.30	15.10	14.30	105.6
10 years								
S. W.	0-20	7.00	11.40	17.20	8.50	44.10	38.50	114.5
	20-40	4.20	9.80	11.20	1.50	26.70	24.00	111.3
G. W.	0-20	2.20	2.10	11.10	5.30	20.70	20.50	101.0
	20-40	1.80	0.70	4.00	3.50	10.00	10.70	93.5
30 years								
S. W.	0-20	5.00	4.60	12.90	8.80	31.30	40.20	77.9
	20-40	8.50	9.50	19.70	12.30	50.00	46.80	106.8
G. W.	0-20	7.20	9.00	1.80	12.00	30.00	25.30	118.6
	20-40	1.40	1.900	8.00	5.10	17.00	14.10	120.6

Table (7): Linear regression (r^2) between single form of extractable metal by sequential fractionation procedure and metal extracted by DTPA.

Metal	Read. Sol.	Org.	Preci.	Resi.
	r^2			
Cu	0.18	87.31**	29.42	71.77**
Zn	94.89**	97.36**	99.77**	72.10**
Cd	90.34**	1.03	64.56**	13.86
Ni	70.12**	78.99**	20.64	0.36
Pb	66.56**	26.75	48.64**	86.27**

Also, Table 8 reveals that the residual fraction decreased with sewage water irrigation. Therefore, Pb was transferred from less labile fraction (residual fraction) to the relatively more labile fraction (the carbonate and sorbed fractions). Sposito *et al.* (1982) concluded that the dominant fraction of Pb is the precipitated form regardless of sludge application and the organic fraction showed no significant change with sludge application rate, whereas the residual fraction may decrease slightly. Data obtained by Sposito *et al.* (1983) revealed that the predominant fraction of Pb in calcareous soil was the precipitated fraction. Another study by El-Gendy *et al.* (1999) showed that the highest organic fraction (55%) of Pb was obtained due to sewage effluent application.

Table (8): Fractions of sequentially extracted heavy metals of the surface (0-20cm) soils irrigated by raw sewage water for different periods as percent of total.

Element	irrigation period (years)	Fraction			
		Read. Sol.	Org.	Preci.	Resi.
Cu	0	33.34a	15.83b	24.45	26.38
	3	19.3b3	37.82ab	20.59	22.27
	10	8.7b	56.58a	7.37	27.28
	30	11.50b	51.98a	9.13	27.38
	ANOVA	**	**	N.S.	N.S.
Zn	0	5.16	1.58b	10.41b	82.85a
	3	2.61	5.21ab	25.51ab	66.67b
	10	3.83	10.19a	39.89a	46.08c
	30	2.47	4.97ab	24.11b	68.75b
	ANOVA	N.S.	N.S.	**	**
Cd	0	16.29	16.26	22.80	44.64
	3	22.58	9.68	25.81	41.93
	10	14.28	8.57	25.71	51.43
	30	21.95	19.51	24.39	34.15
	ANOVA	N. S.	N. S.	N.S.	N.S.
Ni	0	21.22	15.88	23.74	39.16
	3	14.28	33.47	21.22	31.02
	10	16.27	22.03	10.17	51.53
	30	15.92	27.39	19.32	37.37
	ANOVA	N. S.	N. S.	N. S.	N. S.
Pb	0	19.40	19.33	26.03	35.24a
	3	20.17	26.75	33.77	19.30b
	10	15.87	25.85	39.00	19.27b
	30	15.97	14.70	41.21	28.12ab
	ANOVA	N. S.	N. S.	N. S.	**

REFERENCES

- Abdel Salam, A. A.; H. M. El Sheemy and F. F. Minaisy. (2004). Impact of irrigation by sewage water on: I- Soil properties and heavy metals content in soils and plants(Under publication).
- Abdel-Saheb, I.; A. P. Schwab; M. K. Banks and B. A. Hetrick. (1994). Chemical characterization of heavy metal contaminated soil in southeast Kansas. *Water, Air and Soil Pollut.* 78: 73-82.
- Abo Soliman, M. S. ; M. M. Saied; H. A. Shams El-Din and M. A. Abo El-Soud (2001) Environmental impact of marginal water reuse II-Effect of marginal water on soil physical and chemical properties. *Zagazig J. Agric. Res.*, 28 (6) :1189-1207.
- Alexander, M. (2000). Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* 34: 4259-4265.
- Alloway, B. J. (1995). *Heavy Metals in Soils* 2nd edition. Chapman and Hall, London, UK.

- Bang, J. S., and D. Hesterberg. (2004). Dissolution of Trace Element Contaminants from Two Coastal Plain Soils as Affected by pH. *J. Environ. Qual.* 33: 891-901.
- Baron, J.; M. Legret and M. Astue. (1990). Study of interactions between heavy metals and sewage sludge. Determination of stability constants and complexation capacities of complexes formed with Cu and Cd. *Environ. Technol.* 11 : 151-162.
- Buykx, S. E., J. M. A. G. T. Van Hoop and J. P. G. Loch. 2002. Dissolution kinetics of heavy metals in Dutch carbonate- and sulfide-rich fresh water sediments. *J. Environ. Qual.* 31: 573-580.
- Chang, A. C.; A. L. Page; J. E. Warneke and E. Grgurevic. (1984). Sequential extraction of soil heavy metals following a sludge application. *J. Environ. Qual.* 13: 33-38.
- Chlopecka, A.; J. P. Bacon; M. J. Wilson and J. Kay. (1996). Forms of cadmium, lead and zinc in contaminated soils from southwest Poland. *J. Environ. Qual.* 25: 69-79.
- Dudka, S., and A. Chlopecka. (1990). Effect of solid-phase speciation on metal mobility and phytoavailability in sludge-amended soil. *Water, Air, and Soil Pollut.* 51: 153-160.
- El-Gendi-Somaya, S. A. ; A. H. M. Abu-Sinna and N. F. Kandil. (1999). Fractionation and accumulation of some heavy metals in soils and plants irrigated with sewage effluent. *Egypt. J. Soil Sci* 39 (2): 211-221.
- Elsokkary, I. H. (1992). Trace metals in sediments and water "Case study from Egypt, in *Impact of heavy metals on the environment*". Vernet, J. P. (Ed.) Elsevier Science Publishers. Netherlands pp. 355-379.
- Elsokkary, I. H. and J. La^og. 1978. Distribution of different fractions of Cd, Pb, Zn and Cu in industrially polluted and non-polluted soils of Odda Region, Norway. *Acta Agric. Scand.* 28: 262-268.
- Emmerich, W. E.; L. J. Lund; A. L. Page, and A. C. Chang. (1982). Solid phase forms of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.* 11: 178-181.
- Flores, L.; G. Blas; G. Hernandez and R. Alcala. 1997. Distribution and sequential extraction of some heavy metals from soils irrigated with wastewater from Mexico Coty. *Water, Air, and Soil Pollution* 8:105-117.
- Han, F. X., and A. Banin. 1999. Long-term transformation and redistribution of potentially toxic heavy metals in arid-zone soils: II. Incubation at the field capacity moisture content. *Water, Air, and Soil Pollution* 114: 221-250.
- Han, F. X.; W. L. Kingery and H. M. Selim (2001). Accumulation, Redistribution, Transport and Bioavailability of heavy metals in waste-amended soils. In "Trace Elements in soil" Iskander, I. K. and M. B. Kirkham. (Eds.) Lewis Publishers, Boca Raton, London. pp. 145-173.
- Hickey, M. G., and J. A. Kittrick. (1984). Chemicals partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.* 13:372-376.

- Jeng, A. S. and H. Bergseth. (1992). Chemical and mineralogical properties of Norwegian alum shale soils, with special emphasis on heavy metal content and availability. *Acta. Agric. Scand, Sect B, Soil Plant Sci.* 42: 88-93.
- Jeng, A. S., and B. R. Singh. (1993). Partitioning and distribution of cadmium and zinc in selected cultivated soils in Norway. *Soil Sci.* 156: 240-250.
- Kabata Pendias, A., and H. Pendias. (1992). Trace elements in soils and plants 2nd edition. CRC Press, Boca Raton, FL.
- Kabata Pendias, A. (1993). Behavioral properties of trace metals in soils. *Appl. Geochem. Suppl. Issue* 2:3-9.
- Kheboian, C., and C. F. Bauer. (1987). Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. *Anal. Chem.* 59: 1417-1423.
- Kim, N.D. and J.E. Fergusson. (1991). Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. *Sci. Total Environ.* 105: 191-209.
- Lim, T. T.; J. H. Tay and C. I. The. (2002). Contamination time effect on lead and cadmium fractionation in a tropical coastal clay. *J. Environ. Qual.* 31: 808-812.
- Lindsay, W. L. (1972). Zinc in soil and plant nutrition, *Adv. Agron.* 24: 186-197
- Ma, L. Q. and G.N. Rao. (1997). Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *J. Environ. Qual.* 26: 259-264.
- Ma, Y. B. and N. C. Uren. (1998). Transformations of heavy metals added to soil application of a new sequential extraction procedure. *Geoderma.* 84: 157-168.
- McBride, M. B. (1994). *Environmental Chemistry of Soils.* Oxford Univ. Press, New York.
- McGrath, S. P. and J. Cegarra. (1992). Chemical extractability of heavy metals during and after long application of sewage sludge. *J. Soil Sci.* 43: 313-321.
- Miller, W. P.; D., C. Martens, and L. W. Zelazny. (1986). Effect of sequence in extraction of trace metals from soils. *Soil Sci. Soc. Am. J.*: 598-601.
- Phillips, I and L. Chapple (1995). Assessment of a heavy metals contaminated site using sequential extraction, TCLP, and risk assessment techniques. *J. Soil Contami.* 4 (4): 311-325.
- Ramos, L.; L. M. Hernandez, and M. J. Gonzalez (1994). Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National Park. *J. Environ. Qual.* 23: 50-57.
- Sims, J. T., and J. S. Kline. (1991). Chemical fractionation and plant uptake of heavy metals in soils amended with co-composed sewage sludge. *J. Environ. Qual.* 20: 387-395.
- Singh, J. P.; S. P. S. Karwasra, and M. Singh. 1988. Distribution and forms of copper, iron, manganese and zinc in calcareous soils of India. *Soil Sci.* 146: 359-366.
- Singh, S. P.; F. M. Tack, and M. G. Verloo. (1998). Heavy metal fractionation and extractability in dredged sediment derived surface soils. *Water, Air, and Soil Pollut.* 102: 313-328.

- Sowder, A.G.; P.M. Bertsch, and P.J. Morris. (2003). Partitioning and availability of Uranium and Nickel in contaminated riparian sediments. *J. Environ. Qual.* 32:885-898.
- Sposito, G; L. J. Lund, and A. C. Chang. (1982). Trace metal chemistry in arid-zone Field soils amended with sewage sludge: 1. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Sci. Soc. Am. J.* 46: 260-264.
- Sposito, G. C. S., J. P. L. LeClaire, and A. C. Chang. (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
- Stumm, W. and J. J. Morgan. (1990). "Aquatic Chemistry". 2(ed.) New York, John Wiley & Sons.
- Tessier, A.; P. G. C. Cambell and M. Bisson. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51: 844-851.
- Vulkan, R.; U. Mingelgrin; J. Ben-An-Asher and H. Frenkel. 2002. Copper and zinc speciation in the solution of a soil-sludge mixture. *J. Environ. Qual.* 31: 193- 203.
- Wang, P.; Q. Erfu; Z. Li and L. M. Shuman (1997). Fractions and availability of nickel in loessial soil amended with sewage or sewage sludge. *J. Environ. Qual.* 26: 795-801.
- Zhu, B. and A. K. Alva. (1993). Distribution of trace metals in some sandy soils under citrus production. *Soil Sci. Soc. Am. J.* 57: 350-355.

تأثير الري بمياه الصرف الصحي على الارض الجيرية:

٢- الصور الكيميائية الارضية للعناصر الثقيلة بالارض

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جمعت عينات الارض من القطع التجريبية الحقلية والتي رويت بمياه الصرف الصحي الخام لمدد مختلفة (٣، ١٠، ٣٠ سنة) وذلك لتقييم وتقدير الصور الكيميائية الارضية (species) لكل من النحاس والزنك والكاديوم والرصاص. وقد استخدم لتحقيق ذلك طريقة الاستخلاص المتتابع لتقدير تلك الصور فى الارض والتي شملت كل من الصور المتبادلة، المدمصة، المرتبطة عضويا، والمترسبة، والمتبقية. اوضحت النتائج بصفة عامه أن الجزء المتبقى من العنصر هو الجزء السائد فى الاراضى المرورية بالمياه الجوفية (مياه ابار) ويلي ذلك الصورة المترسبة بينما فى الاراضى المرورية بمياه الصرف الصحي الخام فإن الصورة السائدة هي الصورة المرتبطة عضويا بالنسبة للنحاس، والمترسبة بالنسبة للرصاص ، والمتبقية بالنسبة لكل من الزنك والكاديوم والنيكل وقد اوضحت النتائج أن توزيع الصور الكيميائية الارضية لايتغير معنويا نتيجة للري بمياه الصرف الصحي الخام. وفى بعض الحالات فإن العناصر فى الاراضى المرورية بمياه الصرف الصحي تتحول من صورة اقل ذوبانا الى أخرى اكثر ذوبانا.