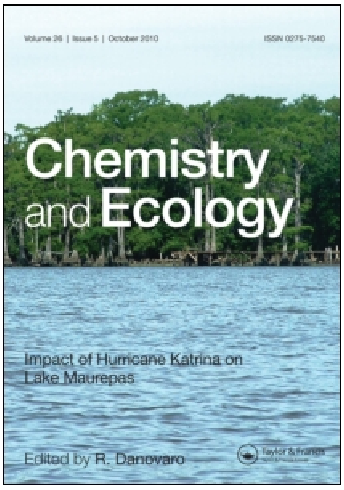

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Usman, Adel Rabie Ahmed and Ghallab, Ahmed(2006) 'Heavy-metal fractionation and distribution in soil profiles short-term-irrigated with sewage wastewater', Chemistry and Ecology, 22: 4, 267 — 278
To link to this Article: DOI: 10.1080/02757540600812859
URL: http://dx.doi.org/10.1080/02757540600812859

Chemistry and Ecology
Vol. 22, No. 4, August 2006, 267–278

Heavy-metal fractionation and distribution in soil profiles short-term-irrigated with sewage wastewater

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(Received 15 December 2005; in final form 28 April 2006)

Six soil profiles irrigated and non-irrigated with sewage wastewater were investigated for soil pH, electrical conductivity (EC), organic matter (OM), and $CaCO_3$. The distributions and chemical fractions of Cu, Zn, Cd, and Pb, and their lability were also studied. The results indicated that pH, EC, OM, and $CaCO_3$, as well as metal fractionation in soil profiles were affected by wastewater irrigation, especially in the surface layer. The surface layer (0–15 cm) irrigated with wastewater exhibited a 0.6 unit decrease in soil pH, a 40.6% decrease in $CaCO_3$, and a 200% increase in EC as compared with that of the non-irrigated soil. The soil OM increased from 0.04% to 0.35% in the surface layer. The irrigation of soil with wastewater resulted in transformation of metals from the carbonate fraction (CARB) towards the exchangeable (EXCH), Fe–Mn oxide (ERO), and organic (OM) fraction for Zn, towards the EXCH, the OM, and residual fraction for Cu, and towards the exchangeable (EXCH) fraction for Cd. It was concluded that the use of sewage wastewater led to salt accumulation and an increase in the readily labile fraction of Zn, Cu, and Cd in the surface layer. Therefore, this reason may limit the use of wastewater under arid and semi-arid conditions.

Keywords: Chemical fractions; Heavy metals; Sewage wastewater; Salt accumulation

1. Introduction

The shortage of water supply in arid and semi-arid regions requires the use of recycled sewage wastewater when possible. However, the application of untreated sewage water may cause problems in the soils [1]. One of the most limiting factors for land disposal and agriculture use of sewage wastewater is the presence of high levels of heavy metals. The feasibility of using sewage wastewater as a source of irrigation water depends upon its constituents, such as salts, nutrients, and trace contaminants, and the type and degree of wastewater treatment [2]. With repeated applications of wastewater, and particularly sludges, heavy metals could accumulate to toxic levels for plants [3] and soil organisms [4]. The toxicity and bioavailability of heavy metals depend upon their total concentrations and their chemical forms in the soil. Total concentrations of heavy metals may provide little indication of their specific bioavailability, mobility, and reactivity in soil [5, 6]. On the other hand, single-step and sequential extractions

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Chemistry and Ecology
ISSN 0275-7540 print/ISSN 1029-0370 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540600812859

have been widely used for determining availability and speciation of heavy metals in soil and the potential transfer of metals to plants and micro-organisms [7–12]. The reactions of heavy metals in soils include precipitation, dissolution, complexation–decomplexation, and adsorption–desorption processes. All of these processes are directly or indirectly affected by soil properties, such as pH, redox conditions, organic matter (OM), Fe oxides, $CaCO_3$, and clay mineral content [13]. The use of sewage wastewater, depending on its quality, may affect these processes as a result of its effect on chemical and biological soil properties, and therefore it affects heavy-metal redistribution among solid-phase components. Therefore, we aimed to study the changes in several chemical soil properties (pH, electrical conductivity (EC), OM, and $CaCO_3$), as well as distribution and chemical fractions of Zn, Cu, Cd, and Pb in soil profiles irrigated with sewage wastewater for 4 yr.

2. Materials and methods

2.1 *Soil sampling and analysis*

Three soil profiles were dug in a farm where soil irrigated for four years with sewage-wastewater. This farm located 6 km east of Edfu, Aswan, Egypt. The sewage-wastewater-irrigated farm was planted with *Khaya senegalensis*. Three other soil profiles were chosen to represent the nearby area, in which the soil has never been irrigated by sewage water. For all profiles irrigated and non-irrigated with sewage water, soil samples were collected from four different depths (0–15, 15–30, 30–60, and 60–90 cm). The classification of the soils studied is shown in table 1.

The soil samples were air-dried and ground to pass through a 2 mm sieve. The particle-size distribution was determined by the hydrometer method. Soil pH was measured using a glass elecrode in a 1:1 ratio (v/v) soil–water suspension, and then the EC of its extract was determined. Calcium carbonate content was determined using a calcimeter, and soil OM was determined using the modified Walkley method [14].

2.2 *Heavy metals fractionation*

Zinc, Cu, Cd, and Pb were extracted from soil samples following the sequential procedure [15–18] to recover the operationally defined fractions of exchangeable (EXCH), carbonate-bound (CARB), easily reducible oxide (ERO), organic-bound (OM), and residual (RES) forms.

One gram of soil sample was weighed and placed into a 50 ml polycarbonate centrifuge tube. The following extractions were carried out sequentially:

Table 1. Particle-size distribution (%) and classification of the studied soils.

Depth	Clay	Silt	Sand	Texture	Classification
Non-irrigated soils					
0–15	10.4	16.7	72.9	Sandy loam	Typic Torripsamments
15–30	8.3	12.4	79.3	Loamy sand	
30–60	4.5	16.0	78.5	Loamy sand	
60–90	3.3	12.4	84.3	Loamy sand	
Wastewater-irrigated soils					
0–15	15.0	14.2	70.8	Sandy loam	Typic Torripsamments
15–30	10.5	16.5	73.0	Sandy loam	
30–60	8.5	13.9	77.6	Loamy sand	
60–90	4.1	18.3	79.6	Loamy sand	

- (F1) Soluble plus EXCH: The sample was extracted by 1 M NH_4OAc, pH 7, for 2 h.
- (F2) CARB metals: The residue from (F1) was extracted by 1 M NaOAc, pH 5, for 2 h.
- (F3) ERO: The residue from (F2) was extracted by 0.04 M NH2OH.
- HCl in 25% HOAc for 6 h (water bath, 60 °C).
- (F4) OM-bound metals: The residue from (F3) was extracted by 30% H_2O_2 at pH 2 (adjusted with HNO_3) using a water bath at 80 °C for 5.5 h.
- (F5) Metals in the RES fraction: The residue from (F5) was digested by 4 M HNO_3. Digestion was conducted in a water bath at 80 °C for 16 h [18, 19].

Heavy metals in soil extractions were determined by atomic absorption spectrophotometer (AAS).

2.3 *Sewage-water analysis*

The water samples were filtered through a 0.45 mm membrane to remove suspended solids. Total soluble salts were determined using an electrical conductivity meter [20]. pH was measured using a glass electrode [21]. Sulphates were determined using the turbidimetry method, and sodium was measured using a flame photometer [14]. AAS was used to determine heavy-metal levels in wastewater.

2.4 *Statistical analysis*

A least significant differences (LSD) analysis (at $P = 0.05$) was used to compare the means.

3. Results and discussion

3.1 *Primary treated-sewage wastewater*

The results showed that the sewage wastewater contained Zn, Cu, Pb, and Cd (table 2). Ni was below the level by the AAS. The results further indicated that the heavy-metal concentrations were low. Thus, they were within the acceptable levels of irrigation water. These results agree with the findings of other researchers [2]. The sewage is probably not contaminated as the inputs in the sewage are introduced through domestic inputs and/or metals such as Cd, Cu, Pb, and Zn are removed substantially during the primary treatment.

Table 2. Chemical characteristics of wastewater.

Parameters	Value	Recommended maximum concentrations for irrigation [22]
pH	6.33	–
EC (dS m^{-1})	1.10	–
Sodium (mg l^{-1})	188.6	–
Chloride (mg l^{-1})	227.8	–
Sulphate (mg l^{-1})	131.5	–
Zn	0.32	2.0
Cd	0.01	0.01
Cu	0.10	0.2
Pb	0.03	5.0
Ni	BDL	0.2

Table 3. Average values of organic matter (OM), pH, $CaCO_3$, EC, and standard deviations in non-irrigated and sewage-wastewater-irrigated soil profiles.

	OM (%)		pH		$CaCO_3$		EC 1:1 (dS m^{-1})	
Depth (cm)	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil
0–15	0.04(0.04)	0.35 (0.20)	7.75 (0.08)	7.12 (0.05)	6.20 (0.9)	3.68 (0.4)	1.72 (0.4)	5.21 (1.5)
15–30	0.00	0.10 (0.06)	7.87 (0.04)	7.63 (0.08)	8.12 (0.7)	7.22 (1.0)	1.22 (0.2)	3.05 (0.9)
30–60	0.00	0.06 (0.04)	8.06 (0.09)	7.97 (0.08)	7.23 (1.1)	8.16 (0.5)	1.00 (0.4)	2.04 (0.6)
60–90	0.00	0.05 (0.05)	8.18 (0.06)	8.25 (0.07)	8.44 (1.8)	10.71 (1.2)	1.20 (0.6)	1.35 (0.5)

3.2 *Distribution of OM, pH, $CaCO_3$, and EC in soil profiles*

In the non-irrigated soil profile, the OM content was very low (0.04%) in the surface layer and was not detectable in subsoil layers. However, in wastewater-irrigated soil profiles, the OM ranged from 0.04 to 0.35% (table 3). The highest percentage of soil OM was found in the surface layer and decreased with depth. Many studies have shown that the use of sewage water in irrigating soils caused increases in the OM of these soils [23, 24].

For non-irrigated and wastewater-irrigated soils, the soil pH ranged from 7.12 to 8.25. The soil samples showed higher pH values in the subsurface layers than in the surface layer (table 3). In the 30 cm of the surface layer, the soil pH decreased significantly in response to irrigation with sewage wastewater. The highest pH changes were within 15 cm from the surface, where the pH dropped about 0.6 unit due to sewage-wastewater irrigation. This decrease in soil pH may be due to high inputs of nitrate and sulphate loads from wastewater, which decrease soil pH through the mineralization and nitrification processes [25].

The surface layer of the soil irrigated with sewage water had lower $CaCO_3$ levels compared with that of the non-irrigated soil (table 3). Calcium carbonate in the surface layer decreased from 6.20 to 3.68% due to wastewater irrigation. Similar results were reported by El-Desoky and Gameh [1]. The acidity of the sewage water may dissolve the calcium carbonate, resulting in a drop in soil pH. Moreover, organic acids and CO_2 produced from microbial activity due to wastewater irrigation may cause the soil pH to drop and $CaCO_3$ to dissolve.

The EC of the soil increased due to sewage wastewater irrigation (table 3). Effects of wastewater irrigation on EC of the soil profile were evident up to 60 cm depth. The highest increase in soil salinity was found in the 15 cm of the surface. The EC of the 15 cm of the surface layer increased from 1.72 to 5.21 dS m^{-1} due to wastewater irrigation. In fact, salt accumulation in the soil can lead to salinization and lower soil productivity [26]. In this connection, the current results showed that the use of sewage wastewater for irrigation can lead to salt accumulation in soil, which may limit its use under arid and semi-arid conditions.

3.3 *Metal fractionation and distribution with depth*

The distribution of different metal fractions (mean concentration and percentage) with depth for non-irrigated and wastewater-irrigated soils is shown in tables 4–6. The results indicated that metal fractions were affected by irrigation with sewage wastewater, especially in the surface layer.

Zinc (Zn) was mostly found in the residual fraction and followed by CARB, ERO, EXCH, and OM fractions (table 6). Ma and Rao [27] reported that Zn is strongly bound in the residual fraction. Our results showed that Zn bound to the RES fraction ranged from 60.2% (equivalent, 9.92 mg kg^{-1}) to 67.8% (equivalent, 14.3 mg kg^{-1}); Zn bound to the CARB fraction ranged

Table 4. Average concentrations (mg kg^{-1}) of Zn and Cu and standard deviations in different fractions of non-irrigated and wastewater-irrigated soil profiles.

	Cu		Zn	
	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil
EXCH				
0–15	0.34 (0.15)a	1.33 (0.52)b	0.33 (0.10)a	1.67 (0.60)b
15–30	0.23 (0.07)a	0.44 (0.06)b	0.13 (0.08)a	0.41 (0.09)b
30–60	0.20 (0.08)a	0.33 (0.14)a	0.12 (0.05)a	0.13 (0.11)a
60–90	0.20 (0.10)a	0.19 (0.13)a	0.09 (0.07)a	0.12 (0.04)a
CARB				
0–15	3.67 (1.2)a	1.83 (0.9)b	3.42 (1.5)a	0.67 (0.5)b
15–30	3.92 (2.0)a	4.00 (1.7)a	3.75 (1.8)a	3.58 (1.5)a
30–60	3.83 (1.2)a	5.75 (1.0)b	3.50 (2.5)a	3.25 (1.6)a
60–90	3.42 (1.6)a	4.33 (2.2)a	4.58 (1.7)a	3.92 (2.3)a
ERO				
0–15	1.92 (0.6)a	4.50 (1.1)b	1.67 (1.0)a	1.25 (1.1)a
15–30	2.08 (1.8)a	2.75 (1.4)a	2.25 (1.2)a	2.42 (2.1)a
30–60	3.08 (2.8)a	2.25 (0.9)a	2.33 (0.9)a	2.79 (1.4)a
60–90	3.17 (1.8)a	4.00 (2.9)a	2.50 (1.6)a	3.00 (2.0)a
OM				
0–15	BDL	0.43 (0.15)b	BDL	1.33 (0.63)b
15–30	BDL	BDL	BDL	0.28 (0.14)a
30–60	BDL	BDL	BDL	BDL
60–90	BDL	BDL	BDL	BDL
RES				
0–15	9.92 (5.0)a	14.00 (3.9)a	7.33 (2.3)a	10.92 (1.8)b
15–30	11.00 (4.4)a	10.83 (2.6)a	10.08 (4.4)a	8.00 (3.8)a
30–60	13.75 (5.5)a	14.67 (3.2)a	11.00 (2.9)a	10.42 (1.6)a
60–90	14.33 (3.9)a	15.75 (4.4)a	11.08 (4.0)a	12.25 (2.4)a

Note: BDL: below detection limit of AAS; values followed by a different letter are significantly different at $P = 0.05$.

from 15.8% (3.42 mg kg^{-1}) to 24.9% (3.67 mg kg^{-1}); and Zn bound to the ERO ranged from 12.2% (2.08 mg kg^{-1}) to 15.4% (3.17 mg kg^{-1}) in non-irrigated soils (tables 4 and 6). In general, the lowest percentage of Zn bound to RES fraction was found in the surface layer and tended to increase with depth. Moreover, the lowest percentage of Zn bound to ERO was recorded in the second layer (15–30 cm) and then tended to increase with depth. On the contrary, the highest percentage of Zn bound to the CARB fraction was recorded at the soil surface and tended to decrease with depth. This was observed for the organic fraction, in which the Zn concentration was too low to be detected.

Zinc fractionation and distribution were affected by irrigation with sewage wastewater. In the soil profiles irrigated with sewage wastewater, most of the Zn remained mainly in the residual fraction. The results showed that most of the changes in Zn transformation among solid-phase components occurred in the surface layer. Zinc was transformed from the CARB fraction to EXCH, ERO, and OM fractions due to irrigation with wastewater in the surface soil layer. The retention of Zn in the ERO fraction is explained by the high stability of Zn oxides and the ability of Zn to replace Mn on the oxide surface. Several other workers have also found that Zn was associated with Fe–Mn oxides [27–29]. Zinc bound to Fe–Mn oxides (ERO) could be remobilized if the soil drainage conditions deteriorate, causing Fe and Mn reduction. The results indicated also that Zn bound to the CARB fraction increased significantly in the third layer (30–60 cm depth) of the soil profile.

Table 5. Average concentrations (mg kg^{-1}) of Cd and Pb and standard deviations in different fractions of non-irrigated and wastewater-irrigated soil profiles.

	Cd		Pb	
	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil
EXCH				
0–15	BDL	0.03 (0.02)b	BDL	BDL
15–30	BDL	BDL	BDL	BDL
30–60	BDL	BDL	BDL	BDL
60–90	BDL	BDL	BDL	BDL
CARB				
0–15	0.14 (0.06)a	0.05 (0.02)b	2.25 (1.6)a	1.75 (1.3)a
15–30	0.10 (0.07)a	0.13 (0.11)a	2.92 (1.4)a	3.83 (1.6)a
30–60	0.13 (0.10)a	0.23 (0.14)a	2.67 (2.1)a	3.92 (1.7)a
60–90	0.18 (0.12)a	0.25 (0.09)a	2.17 (1.1)a	3.75 (2.1)a
ERO				
0–15	0.10 (0.08)a	0.15 (0.07)a	0.92 (0.6)a	2.42 (0.9)b
15–30	0.11 (0.09)a	0.15 (0.10)a	1.17 (0.8)a	1.92 (1.0)a
30–60	0.16 (0.08)a	0.18 (0.05)a	1.25 (1.0)a	1.50 (1.1)a
60–90	0.23 (0.11)a	0.21 (0.15)a	1.42 (0.7)a	1.58 (1.0)a
OM				
0–15	BDL	BDL	BDL	0.20 (0.07)b
15–30	BDL	BDL	BDL	BDL
30–60	BDL	BDL	BDL	BDL
60–90	BDL	BDL	BDL	BDL
RES				
0–15	0.15 (0.07)a	0.17 (0.05)a	1.83 (1.3)a	2.00 (1.6)a
15–30	0.10 (0.08)a	0.15 (0.07)a	2.42 (1.6)a	2.83 (1.1)a
30–60	0.15 (0.10)a	0.18 (0.08)a	2.83 (1.5)a	2.50 (1.8)a
60–90	0.18 (0.10)a	0.14 (0.06)a	2.67 (1.0)a	3.17 (1.5)a

BDL: below detection limit of AAS; values followed by a different letter are significantly different at $P = 0.05$.

Copper (Cu) was found mainly in the RES fraction (57.4–66.1%) of the non-irrigated soil profiles and 53.6–68.7% of total Cu of the wastewater-irrigated soil profiles (table 6). Other researchers [27, 30] also found that the majority of Cu in soils and sediments was associated with the RES fraction. In general, the highest percentage of Cu in the RES fraction was in the third layer of the soil profile (30–60 cm) of the non-irrigated soil, and this was found in the surface layer of the wastewater-irrigated soil (0–15 cm depth). High concentrations of Cu in the residual fraction were reported by Karathanasis and Pils [28] and were attributed to the Cu–Al substitution in the structure of alumino-silicate minerals. The carbonate and Fe–Mn oxide fractions were other contributors but with significantly lower concentrations compared with the residual fraction.

In the non-irrigated soil profile, Cu in the CARB fraction amounted to 19.5–26.7% of the total Cu, and in the ERO fraction, it was 13.3–13.7% of the total Cu. Copper in the EXCH fraction decreased with depth. The results showed that Cu fractionation among solid-phase components was affected by sewage-wastewater irrigation, especially in the surface layer. In the sewage-wastewater-irrigated surface layer, Cu decreased significantly in the CARB fraction from 3.42 mg kg^{-1} (26.7% of the total Cu) to 0.67 mg kg^{-1} (4.2% of the total Cu). However, it increased significantly from below the detection limit of ASS to 1.33 mg kg^{-1} (8.6% of the total Cu) in the OM fraction, from 7.33 mg kg^{-1} (57.4% of the total Cu) to 10.9 mg kg^{-1} (68.7% of the total Cu) in the RES fraction, and from 0.33 mg kg^{-1} (2.6% of the total Cu) to 1.67 mg kg^{-1} (10.4% of the total Cu) in the EXCH fraction (tables 5 and 7).

Table 6. Average percentage contribution (%) of each fraction to the total metal concentration (sum of all fractions).

	Zn		Cu		Cd		Pb	
	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil	Non-irrigated soil	Irrigated soil	Non-irrigated soil	irrigated soil
EXCH								
0–15	2.3	6.1	2.6	10.4	BDL	7.6	BDL	BDL
15–30	1.4	2.6	0.8	2.9	BDL	BDL	BDL	BDL
30–60	1.1	1.5	0.7	0.8	BDL	BDL	BDL	BDL
60–90	1.0	0.8	0.4	0.6	BDL	BDL	BDL	BDL
CARB								
0–15	24.9	8.6	26.7	4.2	36.7	12.5	42.8	26.7
15–30	23.0	21.6	25.6	23.8	37.0	26.8	45.3	43.7
30–60	19.6	25.4	19.5	19.6	32.5	37.7	37.9	49.4
60–90	15.8	18.0	25.0	19.2	27.6	44.0	33.1	42.2
ERO								
0–15	12.6	20.6	13.3	8.1	24.2	36.0	23.1	40.8
15–30	12.2	14.8	13.6	17.9	31.5	34.4	17.0	23.8
30–60	13.5	9.7	13.7	17.4	34.6	31.3	16.3	18.0
60–90	15.4	17.1	13.6	15.7	39.9	32.4	22.0	18.9
OM								
0–15	BDL	2.0	BDL	8.6	BDL	BDL	BDL	3.2
15–30	BDL	BDL	BDL	1.8	BDL	BDL	BDL	BDL
30–60	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
60–90	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
RES								
0–15	60.2	62.7	57.4	68.7	39.1	43.9	34.1	29.3
15–30	63.4	61.0	60.0	53.6	31.5	38.8	37.7	32.5
30–60	65.8	63.4	66.1	62.2	32.9	31.0	45.8	32.6
60–90	67.8	64.1	61.0	64.5	32.5	23.6	44.9	36.9

The significant increase in Cu in the OM fraction can be explained by its ability to form strong complexes with OM [31, 32]. Because of its similarity in ionic size to Fe and Mg, Cu is capable of substituting Fe and Mg in layer silicate minerals [18]. Therefore, the incorporation of Cu into the residual fraction had occurred.

Cadmium (Cd) was mostly found in the CARB, ERO, and RES fractions in non-irrigated soil profiles, making up as much as 100% of the total Cd (table 6). Cadmium may be adsorbed by clay minerals, carbonate, or hydrous oxides of iron and manganese or may be precipitated as Cd carbonate [13, 33]. The percentage of Cd bound to the CARB fraction ranged from 27.6% (0.18 mg kg^{-1}) to 37.0% of the total Cd (0.10 mg kg^{-1}) (tables 5 and 6). However, Cd bound to the ERO fraction ranged from 24.2% (0.10 mg kg^{-1}) to 39.9% of the total Cd (0.23 mg kg^{-1}). Moreover, Cd bound to the RES fraction varied from 31.5% (0.10 mg kg^{-1}) to 39.1% of the total Cd (0.15 mg kg^{-1}). In general, the highest percentage of Cd bound to the CARB fraction was found in the second layer (15–30 cm), and that of Cd bound to the RES fraction was in the first layer (0–15 cm). In contrast, the lowest percentage of Cd bound to ERO fraction was found in the surface soil and tended to increase with depth. The results showed also that Cd bound to the OM and EXCH fractions was below the detection limits of AAS.

Cadmium fractionation and distribution were affected by sewage wastewater irrigation. The results suggest that Cd might transform from the CARB fraction to the EXCH fraction due to the irrigation with wastewater in the surface layer (0–15 cm depth). In the surface soil irrigated with wastewater, Cd bound to the CARB fraction decreased from 36.7% (0.14 mg kg^{-1}) to 12.5% (0.05 mg kg^{-1}), but that bound to the EXCH fraction increased from below the detection limit of AAS to 7.6% (0.03 mg kg^{-1}). In addition, Cd bound to the CARB fraction tended to increase non-significantly in the third and fourth layer. The results also showed that Cd bound to the OM fraction was below the detection limit of ASS and was not affected after 4 yr of wastewater-irrigation. In the surface soil irrigated with wastewater, the Cd distribution followed the sequence of RES (43.9%) $>$ ERO (36.0%) $>$ CARB (12.5%) $>$ EXCH (7.6%) $>$ OM (below the detection limits of the AAS) fraction. However, the Cd distribution among solid phase components changed with depth. For example, at the lowest depth (60–90 cm), the Cd distribution followed the sequence of CARB (44.0%) $>$ ERO (32.4%) $>$ RES (23.6%) $>$ EXCH $=$ OM (below the detection limits of the AAS) fraction.

In all layers of the non-irrigated soil profile, Pb was mostly found in the CARB (33.1–45.3% of the total Pb) and/or RES (34.1–45.8% of the total Pb) fractions, followed by ERO (16.3–23.1% of the total Pb) (table 6). Other researchers [29] reported that up to 45% of Pb in the soils was bound to carbonate. The Pb distribution among the solid phase was changed in the soil surface layer due to sewage-wastewater irrigation. In sewage-wastewater-irrigated surface soil, Pb was mostly found in the ERO fraction (40.8%, equivalent to 2.42 mg kg^{-1}), followed by the RES fraction (29.3%, equivalent to 2.00 mg kg^{-1}), the CARB fraction (26.7%, equivalent to 1.75 mg kg^{-1}), and the OM fraction (3.2%, equivalent to 0.20 mg kg^{-1}) (tables 5 and 6). This result suggests that the Fe–Mn oxide can play a dominant role in Pb retention [34]. Oxides of Fe, Al, and Mn in soils were reported to have a high binding capacity for Pb [33]. The results showed that Pb bound to the OM fraction was below the detection limit of AAS in non-irrigated soil profiles. However, after 4 yr of sewage wastewater irrigation, the OM-bound Pb increased significantly only in the surface layer. Despite the reported affinity of Pb to the OM fraction [35, 36], the percentage of this fraction did not exceed 3.2% of total Pb in the surface layer. This can be explained by the low content of soil OM. In addition, Pb bound to the EXCH fraction was too low to be detected in irrigated and non-irrigated soils.

3.4 *Total concentrations of heavy metals in soil*

The total concentrations of selected heavy metals of the studied soil profiles expressed as the sum of all fractions are present in table 7. In non-irrigated and wastewater-irrigated soils, the total content of heavy metals (Zn, Cd, Cu, and Pb) can be considered normal for non-contaminated soil. Scheffer and Schachtschabel [33] gave the following values of heavy metals in non-contaminated soil: 10–80 ppm for Zn, 0.1–0.5 ppm for Cd, 2–40 ppm for Cu, and 2–60 ppm for Pb. The total contents of heavy metals were in the order of Zn $>$ Cu $>$ Pb $>$ Cd. The results showed that only the total concentration of Zn increased significantly in the surface layer due to irrigation with wastewater for 4 yr, but this was not critically high. The total concentration of Zn increased from 15.84 (non-irrigated) to 22.10 mg kg^{-1} (wastewater-irrigated) in the surface layer. Based on comparisons of the total concentration in the surface layer, Zn in the wastewater-irrigated soil increased at an estimated average rate of approximately 1.5 mg kg^{-1} yr^{-1}.

3.5 *Changes in lability of heavy metals in the soil*

The lability and mobility of metals in soil profiles may be assessed on the basis of absolute and relative content of metal fractions that are weakly bound to soil components. The heavy metals of solid-phase components were grouped into the readily labile, potentially labile, and non-labile groups [37, 38]. Metals of the exchangeable fraction are readily labile, whereas those of carbonate, easily reducible oxides, and organic fractions are potentially and highly dependent on soil properties and environmental factors (such as pH and Eh changes). Metals in the residual fractions are regarded as the non-labile fraction.

Table 7. Average total concentrations of heavy metals (sum of all fractions) and standard deviations in non-irrigated and sewage-wastewater-irrigated soil profiles.

Depth	Non-irrigated soil	Irrigated soil
Zn ($mg\,kg^{-1}$)		
0–15	15.84 (3.7)a	22.10 (2.4)b
15–30	17.23 (4.6)a	18.03 (4.4)a
30–60	20.87 (7.6)a	22.99 (3.0)a
60–90	21.12 (3.9)a	24.28 (2.7)a
Cu ($mg\,kg^{-1}$)		
0–15	12.74 (3.6)a	15.83 (1.5)a
15–30	16.22 (3.8)a	14.68 (3.5)a
30–60	16.95 (3.9)a	16.59 (1.8)a
60–90	18.26 (6.5)a	19.28 (3.7)a
Cd ($mg\,kg^{-1}$)		
0–15	0.39 (0.20)a	0.41 (0.06)a
15–30	0.31 (0.09)a	0.43 (0.30)a
30–60	0.44 (0.20)a	0.58 (0.11)a
60–90	0.58 (0.13)a	0.60 (0.24)a
Pb ($mg\,kg^{-1}$)		
0–15	5.00 (2.2)a	6.37 (1.3)a
15–30	6.50 (1.1)a	8.58 (2.5)a
30–60	6.75 (2.2)a	7.92 (2.3)a
60–90	6.25 (1.7)a	8.50 (0.9)a

Note: Values followed by a different letter are significantly different at $P = 0.05$.

In general, the overall lability of Zn and Cu in the studied soils was in the order of non-labile fraction > potential labile fractions > readily labile fraction. However, the overall lability of Cd and Pb was in the order of potential labile fraction > non-labile fraction > readily labile fraction (figure 1). Irrigation with sewage wastewater affected the lability of heavy metals in the soil, as a result of its influence on the heavy-metal distribution among the solid-phase components, especially in the surface layer. Irrigating the surface soil with sewage wastewater resulted in the movement of Zn, Cu, and Cd from the potentially labile fractions towards the readily labile fraction. Moreover, only the percentage of Cu increased significantly in the non-labile fraction. However, the order of overall lability of heavy metals in the irrigated soil was no different to that of the non-irrigated soil. The high values of the readily labile fraction have been interpreted as indices of relatively high lability and biological availability of heavy metals in the soil. The increase in the readily labile fraction may be mainly attributed to the decrease in pH of the surface layer. The pH is generally acknowledged to be a principle factor governing concentrations of soluble and plant-available metals [39, 40]. The solubility of heavy metals tends to increase at lower pH values and decrease at higher pH values [41]. The order of the readily labile fraction of heavy metals in the soil irrigated with wastewater for 4 yr was Cu (10.4%) > Cd (7.6%) > Zn (6.1%) > Pb (below the detection limit of the AAS). The highest lability for Cu can be attributed to its highly complexing nature with soluble organic fraction in the soil due to sewage-wastewater irrigation. It was observed that the readily labile fraction of Pb was too low to be detected in soil profiles. Lead is very immobile in soils and has a low solubility at pH >5 [33]. The elevated concentrations of Pb and Cd that were found in the potential labile fractions (especially as carbonate and Fe–Mn oxide forms) of this soil show an increased risk for potential toxicity problems, if significant acidification or deterioration in drainage conditions, causing Fe and Mn reduction, takes place.

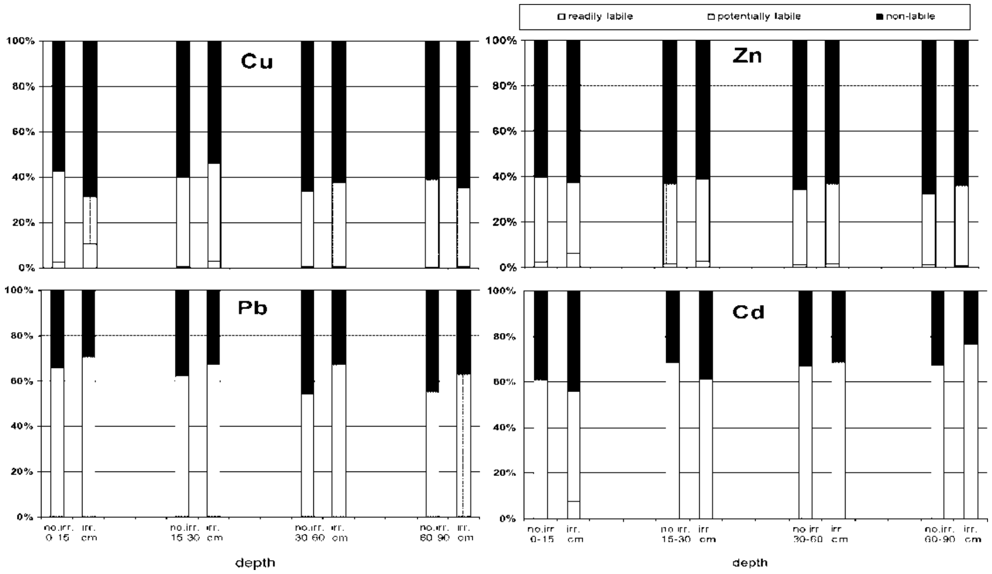

Figure 1. Effect of sewage-wastewater irrigation on the overall lability of heavy metals in the soil. no.irr.: non-irrigated soil; irr.: sewage-wastewater-irrigated soil.

4. Conclusion

This study has revealed that Cu, Zn, Cd, and Pb contents are low in the irrigation wastewater, while Ni was too low to be detected. Thus, the concentrations of heavy metals were within the acceptable ranges. The surface layer (0–15 cm) irrigated with sewage wastewater exhibited a 0.6 unit decrease in the soil pH, a 40.6% decrease in $CaCO_3$, and a 200% increase in EC compared with that of the non-irrigated soil. Moreover, the soil OM increased from 0.04% to 0.35% in the surface layer due to wastewater irrigation. Among all heavy metals, only total concentrations of Zn increased significantly in the surface layer due to irrigation with wastewater for 4 yr, but they were not critically high. Irrigation with sewage wastewater affected the lability of heavy metals in the surface layer, as a result of its influence on heavy-metal distribution among the solid-phase components. Irrigating the soil with sewage wastewater resulted in the transformation of metals from the potentially labile fraction towards the readily labile fraction for Zn, Cu, and Cd. However, the readily labile fraction of Pb was too low to be detected and was unaffected by sewage wastewater irrigation. The results showed that the use of sewage wastewater led to salt accumulation and an increase in the readily labile fraction of heavy metals in the surface layer. Therefore, this reason may limit the use of wastewater under arid and semi-arid conditions. Regular monitoring of irrigation wastewater and soil as well as appropriate management are needed to prevent any negative impacts of salt accumulations.

Acknowledgements

Gratitude is expressed to the Editor and the reviewers, who really helped to improve the manuscript.

References

[1] M.A. El-Desoky, M.A. Gameh. Heavy metal mobility and changes in properties of sandy soils irrigated with untreated sewage water at Assiut. *J. Agric. Sci. Mansoura Univ*., **23**, 4705 (1998).

[2] A.A. Aganga, S. Machacha, B. Sebolai, T. Thema, B.B. Marotsi. Minerals in soils and forages irrigated with secondary treated sewage water in Sebele, Botswana. *J. Appl. Sci*., **5**, 155 (2005).

[3] A.C. Chang, T.C. Granato, A.L. Page. A methodology for establishing phytotoxicity criteria for chromium, copper, nickel, and zinc in agricultural land application of municipal sewage sludge. *J. Environ. Qual*., **21**, 521 (1992).

[4] S.P. McGrath, A.C. Chang, A.L. Page, E. Witter, E. Land application of sewage sludge: Scientific perspectives of heavy metal loading limits in Europe and the United States. *Environ. Rev.*, **2**, 101 (1994).

[5] M.B. McBride. Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? *J. Environ. Qual.*, **24**, 5 (1995).

[6] Y.M. Luo, P. Christie. Bioavailability of copper and zinc in soils treated with alkaline stabilized sewage sledges. *J. Environ. Qual.*, **27**, 335 (1998).

[7] W.E. Emmerich, L.J. Lund, A.L. Page, A.C. Chang. Solid phase forms of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.*, **11**, 178 (1982).

[8] A.C. Chang, A.L Page, J.A. Warneke, E. Grgurevic. Sequential extraction of soil heavy metals following a sludge application. *J. Environ. Qual.*, **13**, 33 (1984).

[9] S.P. McGrath, J. Cegarra. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. *J. Soil Sci.*, **43**, 313 (1992).

[10] M.J. Mench, V.L. Didier, M. Löffler, A. Gomez, P. Masson. A mimicked in-situ remediation study of metal-contaminated soils with emphasis on cadmium and lead. *J. Environ. Qual.*, **23**, 58 (1994).

[11] C. Kabala, B.R. Singh. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *J. Environ. Qual.*, **30**, 485 (2001).

[12] A.R.A. Usman, Y. Kuzyakov, K. Stahr. Effect of clay minerals on extractability of heavy metals and sewage sludge mineralization in soil. *Chem. Ecol.*, **20**, 123 (2005).

[13] J.E. McLean, B.E. Bledsoe. Behaviour of metals in soils. *EPA Ground Water Issue, EPA 540-S-92-018*, p. 25 (1992).

[14] M.L. Jackson. *Soil Chemical Analysis*, pp. 966–1082, Prentice-Hall, Englewood Cliffs, NJ (1958).

[15] A. Tessier, P.G.C Campbell, M. Bisson. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, **51**, 844 (1979).

[16] B. Salbu, T. Krekling, D.H. Oughton. Characterization of radioactive particles in the environment. *Analyst*, **123**, 843 (1998).

[17] L.M. Shuman. Fractionation method for soil micronutrients. *Soil Sci.*, **140**, 11 (1985).

[18] F.X. Han, W.L. Kingery, H.M. Selmi, P.D. Gerard. Accumulation of heavy metals in a long-term poultry waste-amended soil. *Soil Sci.*, **165**, 260 (2000).

[19] G. Sposito, L.J. Lund, A.C. Chang. 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 (1982).

[20] M.L. Jackson. *Soil Chemical Analysis*, pp. 88–97, Prentice-Hall, Englewood Cliffs, NJ (1973).

[21] M.L. Jackson. *Soil Chemical Analysis*, Prentice-Hall, Englewood Cliffs, NJ (1967).

[22] FAO. *Wastewater Treatment and Use in Agriculture FAO Irrigation Paper 47*, Food and Agriculture Organization of the United Nations, Rome (1992).

[23] S.A. El-Gendy, S.H. Badawy, M.I.D. Helal. Mobility of some heavy metals nutrients in sandy soils irrigated with sewage sludge effluent. *J. Agric. Sci. Mansoura Univ.*, **22**, 3535 (1997).

[24] T.D. Hinsely, E.L. Ziegler, G.L Barrett. Residual effects of irrigation corn with digested sewage sludge. *J. Environ. Qual.*, **8**, 35 (1979).

[25] B.H. Shomar, G. Mueller, A. Yahya. Geochemical characterization of soil and water from wastewater treatment plant in Gaza. *Soil Sed. Contam.*, **14**, 309 (2005).

[26] X. Hao, C. Chang. Effect of 25 annual cattle manure application on soluble and exchangeable cations in soil. *Soil Sci.*, **167**, 126 (2002).

[27] L.Q. Ma, G.N. Rao. Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *J. Environ. Qual.*, **26**, 259 (1997).

[28] A.D. Karathanasis, J.R.V. Pils. Solid-phase chemical fractionation of selected trace metals in some Northern Kentucky soils. *Soil Sed. Contam.*, **14**, 293 (2005).

[29] L. Ramos, L.M. Hernandez, M.J. Gonzales. Sequential fractionation of copper, lead, cadmium and zinc in soils from Donana National Park. *J. Environ. Qual.*, **23**, 50 (1994).

[30] M.G. Hickey, J.A. Kittrick. Chemical partioning of cadmium, copper, nickel and zinc in soils and sediment containing high levels of heavy metals. *J. Environ. Qual.*, **13**, 372 (1984).

[31] M.B. McBride. Transition metal bonding in humic acid: an ESR study. *Soil Sci.*, **126**, 200 (1978).

[32] L.D. Tyler, M.B. McBride. Mobility and extractability of cadmium, copper, nickel, and zinc in organic and mineral soil columns. *Soil Sci.*, **134**, 198 (1982).

[33] F. Scheffer, P. Schachtschabel (Eds). *Lehrbuch der Bodenkunde*, 15. Auflage, p. 593, Spektrum Akademischer, Heidelberg, 2002.

[34] S. Schwertmann, R.M. Taylor. Iron oxides. In *Minerals and Soil Environments*, J.B. Dixon, S.B. Weed (Eds), pp. 379–438. ASA and SSSA, Madison, WI (1989).

[35] M. Mench, V. Vangronsveld, V. Didier, H. Clijsters. Evaluation of metal mobility, plant availability, and immobilization by chemical agents in a limed-silty soil. *Environ. Pollut.*, **86**, 279 (1994).

[36] M.A. Vile, R. Kelman Wieder, M. Novak. Mobility of Pb in *Sphagnum*-derived peat. *Biogeochemistry*, **45**, 35 (1999).

[37] F.X. Han, A. Banin. Long-term transformations of Cd, Co, Cu, Ni, Zn, V, Mn, and Fe in the native arid-zone soils under saturated condition. *Common. Soil Sci. Plant Anal.*, **31**, 943 (2000).

[38] F.X. Han, A. Banin, G.B. Triplett. Redistribution of heavy metals in arid-zone soils under a wetting–drying cycle soil moisture regime. *Soil Sci.*, **166**, 18 (2001).

[39] S. Brallier, R.B. Harrison, C.L. Henry, X. Dongsen. Liming effects on availability of Cd, Cu, Ni, and Zn in a soil amended with sewage sludge 16 years previously. *Water Air Soil Pollut.*, **86**, 195 (1996).

[40] J.S. Rieuwerts, I. Thornton, M.E. Farago, M.R Ashmore. Factors influencing metal bioavailability in soils: Preliminary investigations for the development of a critical loads approach for metals. *Chem. Spec. Bioavail.*, **10**, 61 (1998).

[41] M.C. Chuan, G.Y. Shu, J.C. Liu. Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH. *Water Air Soil Pollut.*, **90**, 543 (1996).