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RESEARCH ARTICLE

Fractionation and mobility of copper, cadmium, and lead in some soil irrigated with sewage water in Qena governorate, Upper Egypt.

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Abstract

This study was conducted to investigate the chemical fractionation and mobility of Cu, Cd and Pb in some soil irrigated with sewage water in Qena governorate, Upper Egypt. Sequential extraction results showed that in the treated soil, a major proportion of Cu, Pb, and Cd was associated with poorly crystalline iron oxide bound (PCFeOX), crystalline iron oxide – occluded (CFeOX) and a major proportion of Cu, Pb and Cd was associated with residual (RES) fractions. Based on relative percent. the results also show that The non-labile Cu, Cd and Pb in the non-irrigated soil partially transformed to the potentially labile Cu due to the irrigation with sewage water Also, a part of the readily labile and potentially labile Cu, Cd and Pb of the sewage water irrigated soils for short time transformed to the non-labile fraction with irrigation with same water for a long time. Higher mobility of metals in the soils irrigated with sewage water for short time represent a potential hazard for the redistribution and translocation of these metals into the food chain and leach to ground water.

Key words: Soil properties, Heavy metal fractions, mobility, sewage water

Introduction

The allout metal concentration does not provide a signal on the potential availability of elemental species and their possible mobility in an aquatic ecosystem. Thus, the assessment of essential speciation in the ecological compartment is a huge advance to comprehend the likely natural danger, portability and bioavailability of contaminations. The conduct of metals and their accessibility in the earth is an outcome of their chemical speciation. It is, therefore, indispensable to make available data on the probable availability of elemental species in the environment (Petruzzelli et al., 1989; Ianni et al., 1997; Osakwe et al., 2014). The chemical forms of a trace element decide its conduct in nature and its remobilization capacity. So, the use of extract solutions with a gradual increase from least aggressive to most aggressive provides gives extra data about trace element fractions that may be released from soil phase associations and become available for plant uptake when environmental factors change in the soil (Tessier et al., 1979; Ma and Rao, 1997; Abul Kashem et al., 2011). Heavy metals are related with different soil parts in various manners and these affiliations show their mobility and availability in soils (Ahumada et al., 1999; Abul Kashem et al., 2011). In recent years, there has been increased interest in the studies on speciation or chemical forms of heavy metals in polluted soils using sequential extraction techniques. Although they consume more time, these procedures provide

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knowledge and furnish detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals. The evaluation of elemental speciation in environmental compartment is a significant step to understand the potential environmental risk and mobility and bioavailability of pollutants (Petruzzelli et al., 1989; Kotoky et al., 2003; Osakwe et al., 2014). The dynamics of how elements move from one chemical form to another, in response to changing soil conditions can be also studied using fractionation techniques (Shuman, 1979; Roshdy, 2009).

The objectives of the present research was to investigate the irrigation with treated sewage water on the chemical forms and mobility of Cu, Cd and Pb, their distribution, bioavailability/mobility and transformation of these metals in soils, to predict their potential hazard, in some soil irrigated with sewage water in Qena governorate, upper Egypt.

Materials and Methods

Study Areas

The location lies in Qena governorate, upper Egypt, between Sohag governorate in the north and Luxor governorate in the south. It is considered a part of Al-Salihiyah sewage water management station that is located in the east of Qena city. It is situated between the latitude of 26°09’02.05" to 26° 09′23.04" N and the longitude of 32°46′33.37" to 32° 47′11.57" E. locations have some areas that are cultivated by forest plantations which use treated sewage waters.

Soil Sampling

Two study sites were selected on the basis of the differences in the period of irrigation with sewage water (2 and 15 years). Soils samples were taken at surface layer (0-30 cm) from these five places representing the soils that were irrigated with treated sewage waters. Other soil sample was taken at the same depth from another place in the study area, where the soil was not ever irrigated (a virgin soil). The collected soil samples were air-dried, crushed with a wooden roller, sieved to pass through a 2 mm sieve and kept for analysis.

Soil properties

The particle-size distribution was carried out by the pipette method (Richards, 1954; Jackson, 1969) and the corresponding textural class was determined from the USDA textural class triangle. The inorganic carbonate content of the soil samples was estimated by a Collins calcimeter according to Jackson (1973) and USDA (1996) The soil organic carbon content was determined according to the modified Walkely and Black method (USDA, 1996). The soil pH was measured by means of a digital pH meter in a 1: 1 ratio of the soil to water suspension and the electrical conductivity of the saturated soil paste extract (ECe) was estimated using an electrical conductivity meter (Jackson, 1973).

Soil chemical forms of heavy metals:

Tow grams of soil material were weighed and placed in 50 ml polycarbonate centrifuge tube Sequential extractions of heavy metals were carried out as follow:

a) Soluble and exchangeable form (S+Exch): The material of each soil in centrifuge tube was extracted using 20mL of 1.0M NH_4OAc at pH 7.0 and shaken for 2h. according to Kabala and Singh (2011).

b) Carbonate specifically sorbed form (carb-bound): The residue from the S+Exch extraction was treated with 30 mL of 1.0M NaOAc at pH 5.0, The slurry was shaken for

5h. in the centrifuge tube and then, centrifuged according to Ahnstrom and Parker (1999).

c) Mn oxide bound form (MnO-bound): The soil residue from the carb-bound extraction was treated with 20 mL of 0.1M $NH_2OH.HCl$ at pH 2.0 and shaken for 30 min. in the centrifuge tube. The sample was then centrifuged according to Sims et al (1986).

d) Organically bound form (O-bound): The soil residue from the MnO-bound step was treated with 4 mL of H_2O_2 (30%) and the sample in each centrifuge tube was evaporated on a steam bath to the original suspension level. After evaporation, the sample was cooled, treated with 20 mL of 1.0M NH_4OAc at pH 7.0, shaken for 2h. and then, centrifuged according to Shuman (1979).

e) Poorly crystalline Fe oxide bound form (PCFeOX-bound): The soil residue from the O-bound step was treated with 20 mL of a mixture of 0.2 M ammonium oxalate and 0.2 M oxalic acid at at pH 3.0. The sample in the centrifuge tube was shaken in the dark for 4h. and then, centrifuged according to Shuman (1979).

f) Crystalline Fe oxide bound from (CFeOX-bound): The soil residue from the PCFeOX-bound extraction was treated with 20 mL of citrate buffer (CB) solution. The sample in the tube was placed in a water bath at 80˚C. One gram of sodium dithionite was added, stirred for 15 min and then centrifuged. The extracts were placed in 50 mL volumetric flasks. The extraction was repeated another time and the extracts were placed in the same flasks and completed with (CB) solution to the volume (Kittric and Hope, 1963).

g) Total metals: A half gram of each studied soil material was digested using concentrated acids of HF, HNO_3 and HCl. according to Shuman (1979).

h) Residual form: This form was estimated by the difference between the total amount of a metal in the soil sample and the sum of the previous six extracted forms of this metal. Heavy metals concentrations in extracts were determined by a Buck Scientific INC 210 - Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

The results in Table 1 indicate that most of the soil samples in Qena location have a sandy texture. The organic matter (OM) content of the studied soils varies between 0.86 and 1.74 % in the soil irrigated with sewage water for a long time (15 years), between 0.29 and 1.39% with in the soils irrigated with sewage water for a short time (2 years), The lowest organic matter content is found in the surface and subsurface layers of the non-irrigated soil. It showed a scarcity in the plant and animal life. The calcium carbonate content of the studied soils varies between 0.31 and 5.22 % in the soils irrigated with sewage water for a long time (15 years), between 1.95 and 4.48% with an average value of 4.36% in the soils irrigated with sewage water for a short time (2 years)and 6.42% in the soil that has never been irrigated , Soil pH was between 6.83 and 7.38 in the soils irrigated with sewage water for a long time (15 years), between 7.31 and 7.61 in the soils irrigated with sewage water for a short time (2 years) and 8.05 in the soil that has never been irrigated. the use of sewage water in irrigation gives more decrease in the soil pH, me be attributed that Wastewater-irrigated soils contain high organic carbon and nitrogen contents, which could promote microorganism activity to break up organic nitrogen molecules into inorganic nitrogen and H+ ions Moreover, Dheri et al. (2007)

indicated that the production of organic acids due to the anaerobic decomposition of organic matter was a principal cause for the reduced pH in the soil irrigated with wastewater. The ECe values of the soils range from 1.94 to 2.78 dS/m in the soils irrigated with sewage water for a long time (15 years), from 2.24to 4.71 dS/m in the soils irrigated with sewage water for a short time (2 years) and 11.99 dS/m in the soil that has never been irrigated.

minimum and maximum air temperatures throughout the conduct of the study reached 24.70 ^{0}C and 28.79 ^{0}C, respectively. These were within the optimum requirements (20-35 ^{0}C) of upland rice for normal growth from planting to harvesting (Tuong and Bouman, 2003). Moreover, the mean relative humidity recorded at 82.21 % was sufficient for the growth of upland rice (Lafitte and Bennett, 2002).

Table 1. Characteristics of the soils used.

Used period of Sewage water In irrigation	Place No.	Particle-size distribution (%)			Soil texture	OM (%)	CaCO3 (%)	EC_e	pH (1:1)
		Sand	Silt	clay					
(2 years)	1	90.37	6.74	2.89	Sand	0.47	4.25	2.61	7.63
	2	91.71	5.00	3.28	Sand	0.29	1.95	2.24	7.31
	3	87.38	8.55	4.07	Sand	0.86	3.52	4.71	7.43
	4	88.82	7.78	3.41	Sand	1.39	2.95	2.78	7.38
	5	91.11	5.25	3.64	Sand	0.54	4.48	3.28	7.43
(15 years)	1	88.59	10.32	1.09	Sand	0.89	3.18	2.25	7.38
	2	94.93	1.53	3.54	Sand	1.30	0.31	1.94	7.11
	3	86.59	9.30	4.11	Sand	1.74	3.34	2.78	6.83
	4	88.30	5.78	5.92	Sand	0.95	0.49	2.28	7.14
	5	92.66	1.82	5.53	Sand	0.86	5.22	1.94	7.11
Non -irrigated soil		94.95	1.03	4.02	Sand	0.00	6.76	11.99	8.05

Fractionation and distribution of metals.

Copper (Cu)

The different forms of soil copper and their percentages of the total amount in the surface layer of studied soils are present in Tables 2 and 3, respectively. Generally, the soluble + exchangeable Cu form decreases in the order of sewage water shortly irrigated > sewage water prolonged irrigated > non-irrigated soils. The carbonate-bound form of the Cu in soils increases in the order of sewage water prolonged irrigated > sewage water shortly irrigated > non-irrigated soil. The MnOX bound form of Cu decreasing order of sewage water shortly irrigated > sewage water prolonged irrigated > non-irrigated soils. The organically bound Cu form can be ranked in the order of sewage water prolonged irrigated > sewage water shortly irrigated > non-irrigated soils. The PCFeOX Cu form of these soils decreases in the order of sewage water shortly irrigated > non-irrigated > sewage water prolonged irrigated soils. Copper occluded in the CFeOX form in the soils under study decreases in the order of non-irrigated > sewage water shortly irrigated > sewage water prolonged irrigated. Levels of the residual Cu decreases in the order of sewage water prolonged irrigated > sewage water shortly irrigated > non-irrigated soils.

Distribution of average of Cu forms (as percentages of the total Cu) in the surface layer of studied soils is illustrated in Table3 and Figure 1. Comparing Cu forms of the soils irrigated with sewage water with those of the non-irrigated one, it obvious that due to the irrigation with sewage water, there are increases in the residual, poorly crystalline iron oxide-bound, organically bound, Mn oxide-bound, carbonate-bound and S +Exch

Cu forms on the charge of decreases in the crystalline Fe oxide-occluded Cu form. The residual, organically bound, Mn oxide-bound, carbonate-bound and S+Exch Cu forms increased from 30.19, 1.56, 2.09, 1.91 and 1.38%, respectively in the non-irrigated soil to 34.10, 2.49, 12.96, 4.49 and 1.83%, respectively in the soils irrigated with sewage water for 2 years and to 42.96, 2.09, 10.97, 5.55 and 1.68% in the soils irrigated with sewage water for 15 years (Table 2 and fig. 1).

On the other hand, the crystalline Fe Oxide occluded Cu decreased from 44.96% in the non-irrigated soil to 22.44 and 18.98 % in the soils irrigated with sewage water for 2 and 15years, respectively. Also, a part of the crystalline Fe oxide occluded, poorly crystalline Fe oxide-bound, organically bound, Mn oxide-bound and S +Exch Cu forms in the soils irrigated with sewage water for a short time transformed to carbonate-bound and residual Cu forms in the soils irrigated with sewage water for a long time. So, the crystalline occluded, the poorly crystalline Fe oxide-bound, organically bound, Mn oxide-bound and S. +Exch Cu forms decreased from 22.44, 21.73, 2.49, 12.96 and 1.83%, respectively in the soils irrigated with sewage water for short time to 18.98, 17.78, 2.09, 10.67 and 1.68%, respectively in the soils irrigated with sewage water for a long time (Table 2 and fig. 1). On the other hand, the carbonate-bound and residual Cu forms increased from 4.49% and 34.10% respectively in the soils irrigated with sewage water for a short time to 5.55% and 42.96%, respectively, in the soils irrigated with sewage water for a long time.In general, the Cu forms in the surface layer of studied soils could be ranked in the order of Residual > CFeOX> PCFeOX > MnOX > Carb. > O-bound > S+Exch for the soils irrigated with sewage water for a short time, Residual > CFeOX > PCFeOX > O-bound. > S+Exch > Carb. > MnOX for the soils irrigated with sewage water for a long time, and CFeOX > Residual > PCFeOX > MnOX > Carb.> O-bound > S+Exch. for the non-irrigated soil.

Manganese oxide bound Cu is also available for plants and the copper in the organically bound form is conceded an important source of available Cu for plants (Liang et al., 1991). McKenzie (1978) reported that the manganese oxide does not affect Cu availability. However, the copper in the poorly crystalline Fe oxide- bound and the crystalline Fe oxide-occulted Cu forms are non-labile (Usman, 2004). Moreover, residual Cu is relatively unavailable to plants (McLaren and Crawford, 1973). Awad (2007) found that the distribution Cu forms in the soils irrigated with sewage water in the order of Residual > O-bound > PCFeOX > Carb. > CFeOX > S+Exch. > MnOX for El-Gabal El-Asfar soil and in the order of Residual > PCFeOX > CFeOX > O-bound > Carb. > MnOX > S+Exch. for El-Madabeg soil.

Lead

Levels of different soil Pb forms and their percentages of the total amount in the surface layer of studied soils are present in Tables 4 and 5, respectively. The results show that, the soluble + exchangeable Pb form in the surface layer of these soils can be ranked in the order of sewage water shortly irrigated > non-irrigated > sewage water prolonged irrigated soils.

Table2: Copper (Cu) forms (mg/kg) in the surface layer of studied soils.

Irrigation Source and System	Place No.	Cu (mg/Kg) S.+Exch	Carb.	Mn OX.	O-bound	PCFeOX	CFeOx	Residual	Total
	1	0.49	1.10	5.60	0.54	4.09	6.20	9.85	27.86
	2	0.34	2.19	2.63	0.68	5.15	5.87	4.80	21.67
	3	0.73	0.60	3.48	0.91	9.59	6.74	9.15	31.21
Sewage water	4	0.44	0.92	3.26	0.26	6.36	6.14	8.63	26.00
(2 years)	5	0.49	0.81	2.45	0.89	4.13	4.86	13.90	27.54
	Mean	0.50	1.12	3.48	0.66	5.87	5.96	9.27	26.86
	1	0.55	0.26	0.47	0.88	3.23	4.76	18.50	28.64
Sewage water	2	0.62	3.81	0.25	1.10	10.19	9.25	9.78	35.00
(15 years)	3	0.56	0.65	5.56	0.40	5.87	5.65	18.72	37.41
	4	0.25	4.52	6.21	0.27	5.77	6.11	14.16	37.29
	5	0.59	0.49	4.58	0.90	4.08	4.79	8.04	23.48
	Mean	0.52	1.95	3.41	0.71	5.83	6.11	13.84	32.37
Non -irrigated soil		0.23	0.32	0.35	0.26	3.00	7.52	5.04	16.72

Table3: Copper (Cu) forms (%) of the total content in the surface layer of studied soils

Irrigation Source and System	Place No.	Cu (%) S.+Exch	Carb.	Mn OX.	O-bound	PCFeOX	CFeOx	Residual
	1	1.74	3.95	20.08	2.49	14.69	22.24	35.36
Sewage water	2	1.59	10.09	12.15	2.19	23.79	27.09	22.13
(2 years)	3	2.35	1.93	11.15	3.52	30.72	21.60	29.32
	4	1.67	3.53	12.54	0.95	24.46	23.61	33.18
	5	1.79	2.96	8.91	3.30	15.01	17.64	50.48
	Mean	1.83	4.49	12.96	2.49	21.73	22.44	34.10
	1	1.92	0.92	1.63	2.51	11.27	16.62	64.58
Sewage water	2	1.78	10.90	0.71	2.93	29.10	26.42	27.96
(15 years)	3	1.50	1.73	14.87	1.08	15.70	15.10	50.04
	4	0.67	12.13	16.65	1.16	15.46	16.39	37.97
	5	2.53	2.08	19.50	2.79	17.38	20.40	34.26
	Mean	1.68	5.55	10.67	2.09	17.78	18.98	42.96
Non-irrigated soil		1.38	1.91	2.09	1.56	17.94	44.96	30.19

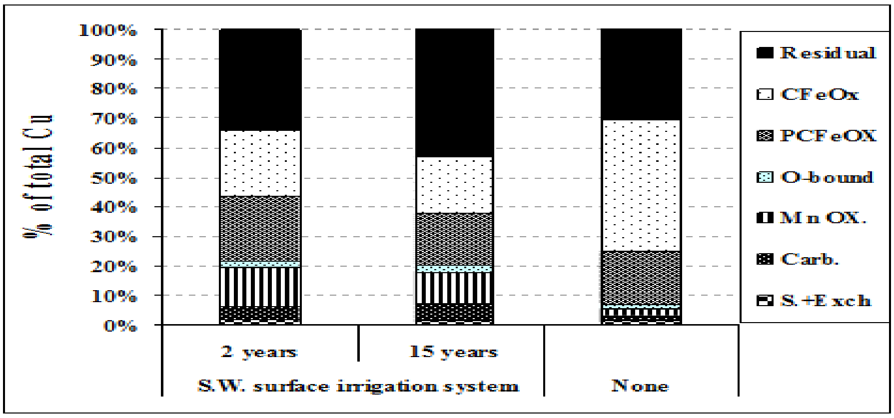

Figure 1: Distribution of average Cu forms (% of total content) in the surface layer of the soils irrigated with sewage water (S.W.), as well as of the non-irrigated one Non) in studied soils.

The carbonate-bound Pb form in the surface layer of these soils decreases in the order of sewage water prolonged irrigated > sewage water shortly irrigated > non-irrigated soils. Lead bound to Mn oxides form can be ranked in the order of sewage water shortly irrigated > non-irrigated > sewage water prolonged irrigated soils. The organically bound Pb in the surface layer of these studied soils extends from 0.10 to 0.14 mg/kg (0. 26 to 0.39 % of the total Pb) with an average of 0.12 mg/kg (0.32%) in the soils irrigated with sewage water for 15 years. However, it does not have detectable values in the soils irrigated with sewage water for 2 years or non-irrigated one. In general, the poorly crystalline Fe oxide bound Pb form be ranked in the order of sewage water prolonged irrigated > sewage water shortly irrigated > non-irrigated soils. Lead occluded in the crystalline Fe oxides in the surface layer of these soils decreases in the order of sewage water shortly irrigated > sewage water prolonged irrigated > non-irrigated soils . The Pb residual form can be ranked in the order of non-irrigated soils > sewage water prolonged irrigated > sewage water shortly irrigated soils.

The average Pb forms, as percentages of the total Pb, in the surface layer of studied soils are illustrated in Figure 2. The irrigation with sewage increased in the soluble + exchangeable, carbonate-bound, Mn oxide–bound, poorly crystalline Fe oxide-bound and crystalline Fe oxide-occluded Pb forms in the surface layer on the expense of decreases in the residual Pb form compared to those of the non-irrigated soil. Thus, the soluble + exchangeable, carbonate-bound, Mn oxide–bound, the poorly crystalline Fe oxide-bound and crystalline Fe oxide-occluded Pb forms increased from 3.75, 0, 6.76, 4.82 and 19.30%, respectively in the non-irrigated soil to 8.76, 9.72, 9.84, 14.46 and 40.39%, respectively, in the soils irrigated with sewage water for 2 years.On the other hand, the residual Pb form decreased from 65.37% in the non-irrigated soil to 16.83 and 14.09% in the soils irrigated with sewage water for 2 years and ground water, respectively.

Table4: Lead (Pb) forms (mg/kg) in the surface layer of studied soils.

Irrigation Source and System	Place No.	Pb (mg/Kg)							
		S.+Exch	Carb.	Mn OX.	O-bound	PCFeOX	CFeOx	Residual	Total
Sewage water (2 years)	1	0.70	3.07	1.11	0.00	1.48	8.03	2.49	16.88
	2	2.50	0.00	2.80	0.00	1.46	7.55	1.93	16.24
	3	1.07	1.82	1.00	0.00	7.49	7.07	5.94	24.39
	4	2.57	1.67	2.56	0.00	2.46	6.01	1.62	16.88
	5	0.79	2.21	1.04	0.00	1.57	7.33	3.98	16.92
	Mean	1.53	1.75	1.70	0.00	2.89	7.20	3.19	18.26
Sewage water (15 years)	1	2.95	1.15	1.22	0.12	9.13	11.22	14.14	39.92
	2	1.05	3.49	1.02	0.14	12.46	14.34	21.22	53.72
	3	0.90	2.84	1.18	0.11	8.20	11.12	6.06	30.40
	4	0.00	6.74	1.13	0.12	6.85	2.29	13.53	30.66
	5	1.37	3.25	1.07	0.10	9.22	11.30	9.69	35.99
	Mean	1.25	3.49	1.07	0.12	9.17	10.06	12.93	38.09
Non-irrigated soil		1.14	0.00	2.05	0.00	1.46	5.85	19.82	30.32

Table5: Lead (Pb) forms (%) of the total content in the surface layer of studied soils.

Irrigation Source and System	Place No.	Pb (%)						
		S.+Exch	Carb.	Mn OX.	O-bound	PCFeOX	CFeOx	Residual
Sewage water (2 years)	1	4.17	18.18	6.59	0.00	8.76	47.56	14.75
	2	15.38	0.00	17.25	0.00	8.97	46.49	11.91
	3	4.40	7.45	4.10	0.00	30.73	28.97	24.36
	4	15.22	9.89	15.15	0.00	14.56	35.61	9.57
	5	4.64	13.08	6.13	0.00	9.28	43.32	23.54
	Mean	8.76	9.72	9.84	0.00	14.46	40.39	16.83
Sewage water (15 years)	1	7.38	2.87	3.06	0.30	22.87	28.10	35.42
	2	1.95	6.50	1.90	0.26	23.19	26.70	39.50
	3	2.95	9.33	3.87	0.36	26.98	36.59	19.93
	4	0.00	21.97	3.67	0.39	22.35	7.48	44.14
	5	3.80	9.02	2.97	0.28	25.60	31.40	26.93
	Mean	3.22	9.94	3.09	0.32	24.20	26.05	33.18
Non-irrigated soil		3.75	0.00	6.76	0.00	4.82	19.30	65.37

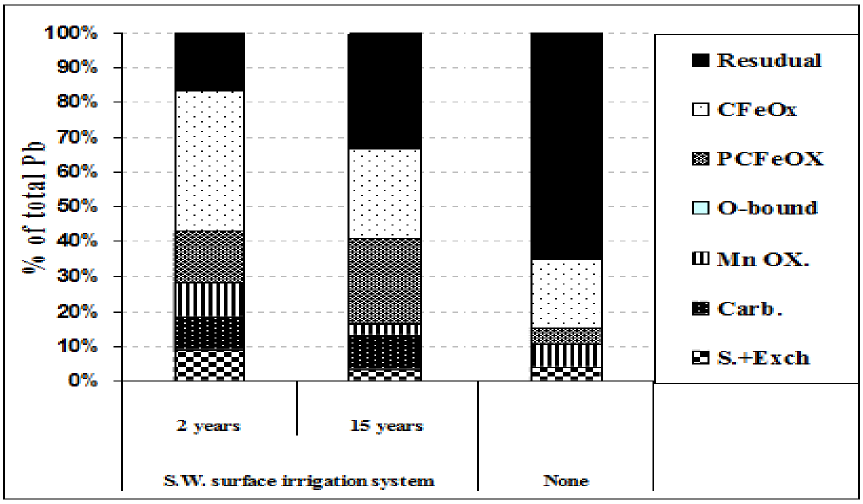

Figure 2: Distribution of average Pb forms (% of total content) in the surface layer of the soils irrigated with sewage water (S.W.), as well as of the non-irrigated one (Non) in studied soils.

However, irrigation these soils with sewage water for 15 years increased the carbonate-bound, organically bound, poorly crystalline Fe oxide-bound and crystalline Fe oxide-occluded Pb forms on the charge of reducing the soluble + exchangeable, Mn oxide–bound and residual Pb forms compared to those of the non-irrigated soil (Tables 5 and Fig. 2).Also, a part of the soluble + exchangeable, Mn oxide-bound and crystalline Fe oxide-occluded Pb forms in the soils irrigated with sewage water for 2 years transformed to the carbonate-bound, organically-bound and the poorly crystalline Fe oxide-bound and residual Pb forms in the soils irrigated with sewage water for 15 years. So, soluble + exchangeable, Mn oxide-bound and crystalline Fe oxide-occluded Pb forms decreased from 8.76, 9.84 and 40.39%, respectively in the soils irrigated with sewage water for short time to 3.22, 3.09 and 26.05%, respectively in the soils irrigated with sewage water for 15 years. On the other hand, carbonate-bound, organically-bound, poorly crystalline Fe oxide-bound and residual Pb forms increased from 9.72, 0, 14.46 and

16.83% respectively in the soils irrigated with sewage water for 2 years to 9.94, 0.32, 24.20 and 33.18%, respectively in the soils irrigated with sewage water for 15 years.

In general, the Pb forms in the surface layer of studied soils could be arranged in the order of CFeOX > Residual >PCFeOX > MnOX> Carb. > S. +Exch. for the soils irrigated with sewage water for 2 years, Residual > CFeOX > PCFeOX > Carb. > S. +Exch. > MnOX > O-bound for the soils irrigated with sewage water for 15 years and Residual > CFeOX > MnOX > PCFeOX > S. +Exch. for the non-irrigated soil.

Usman and Ghallab (2006) found that in soils irrigated with sewage water for 4 years; Pb was mostly found in the easily reducible oxide fraction (40.8%), followed by the residual fraction (29.3%), the carbonate fraction (26.7%) and the organic fraction (3.2%). Badawy and El-Motaium (2003) showed that the distribution of Pb forms of the sandy soils amended with sewage sludge had the order of residual > O-bound > Carb. > ExchangeableThe Fe and Mn oxides in the soils were reported to have a high binding capacity for Pb (Scheffer and Schachtschabel, 2002). In the soils irrigated with sewage water for more than 50 years and in the soils irrigated with Nile water, Pb forms of the soils had the order of CFeOX > Residual > PCFeOX > Carb. > O-bound > S. +Exch. > MnOX and CFeOX > Residual > S. +Exch. > O-bound > Carb. > PCFeOX > MnOX in the non-irrigated soils (Roshdy, 2009). Awad (2007) found that the distribution of Pb forms in soils irrigated with sewage water in the order of Residual > PCFeOX > Carb. > CFeOX > S. +Exch. > MnOX > O-bound in El-Gabal El-Aafar soil and in the order of Residual > PCFeOX > Carb. > MnOX > O-bound > CFeOX > S. +Exch. in El-Madageg soil.

Cadmium

Levels of different soil Cd forms and their percentage of the total amount of Cd in the surface layer of studied soils are shown in Tables 6 and 7 respectively. The data in the tables 6and 7 showed that, The Cd in the soluble + exchangeable and the carbonate bound form in the surface layer of these soils decreases in the order of sewage water shortly irrigated > sewage water prolonged irrigated > non irrigated soils .

Cadmium in MnOX form in the surface layer of the soils irrigated with sewage water for a long time ranged from 0.00 to 0.02 mg/kg with an average of 0.004 mg/kg which it represents 0.00 to 0.89% with an average of 0.18% of total. However, it does not have detectable levels in the soils irrigated with sewage water for a short time and non-irrigated soils. In all studied sites, the Cd in the organic form and bound to poorly crystalline Fe oxides is not detectable. It means that these forms in these soils could be neglected (Tables 6 and 7). Moreover, Cd in the residual form decreases in the order of sewage water irrigated soils for a long time > non irrigated soil > sewage water irrigated soils for a short time, in the surface layer of these soils.

The average Cd forms, as percentages of the total Cd, in the surface layer of studied soils are illustrated in Figure 3. The soluble + exchangeable, carbonate-bound and crystalline Fe oxide-occluded Cd forms in the surface layer of the soils irrigated with sewage water for 2 years increased on the charge of decreasing in the residual Cd form compared to those of the non-irrigated soil. So, the soluble + exchangeable, carbonate-bound and crystalline Fe oxide-occluded Cd forms increased from 0, 0 and 59.71%, respectively, in the non-irrigated soil to 8.29, 13.65 and 64.61%, respectively in the soils irrigated with sewage water for 2 years (Table 7 and Fig.3). On the other hand, the residual Cd form decreased from 47.96% in the non-irrigated soils to 13.45% in the soils irrigated with sewage water for 2 years.

Moreover, the irrigation with sewage water for 15 years, increased the soluble + exchangeable, carbonate-bound, Mn oxide bound and residual Cd forms in the surface layer on the expense of decreasing in the crystalline Fe oxide-occluded Cd form compared to those of the non-irrigated soil. So, the soluble + exchangeable, carbonate-bound, Mn oxide bound and residual Cd forms increased from 0, 0, 0 and 47.96%, respectively, in the non-irrigated soil to 2.19, 3.96, 0.18 and 51.68%, respectively in the soils irrigated with sewage water for 15 years (Table 7 and Fig.3). On the contrary, the crystalline Fe oxide-occluded Cd form decreased from 52.04% in the non- irrigated soil to 41.99% in the soils irrigated with sewage water for 15 years. Also, a part of the soluble + exchangeable, carbonate-bound and crystalline Fe oxide-occluded Cd forms in the soils irrigated with sewage water for 2 years

Table 6: Cadmium (Cd) forms (mg/kg) in the surface layer of studied soils.

Irrigation Source	Place No.	Cd (mg/Kg)							
		S.+Exch	Carb.	Mn OX.	O-bound	PCFeOX	CFeOx	Residual	Total
Sewage water (2 years)	1	0.07	0.17	0.00	0.00	0.00	0.52	0.12	0.88
	2	0.00	0.00	0.00	0.00	0.00	0.25	0.06	0.31
	3	0.06	0.10	0.00	0.00	0.00	0.10	0.00	0.26
	4	0.00	0.00	0.00	0.00	0.00	0.25	0.11	0.36
	5	0.06	0.05	0.00	0.00	0.00	0.33	0.02	0.45
	Mean	0.04	0.06	0.00	0.00	0.00	0.29	0.06	0.45
Sewage water (15 years)	1	0.18	0.12	0.00	0.00	0.00	1.02	2.52	3.84
	2	0.00	0.00	0.00	0.00	0.00	1.99	0.95	2.94
	3	0.10	0.21	0.02	0.00	0.00	1.02	0.97	2.32
	4	0.00	0.00	0.00	0.00	0.00	1.22	2.54	3.76
	5	0.06	0.24	0.00	0.00	0.00	1.22	1.60	3.12
	Mean	0.07	0.11	0.00	0.00	0.00	1.29	1.71	3.19
Non -irrigated soil		0.00	0.00	0.00	0.00	0.00	0.51	0.47	0.98

Table 7: Cadmium (Cd) forms (%) of the total content in the surface layer of studied soils.

Irrigation Source	Place No.	Cd (%)						
		S.+Exch	Carb.	Mn OX.	O-bound	PCFeOX	CFeOx	Residual
Sewage water (2 years)	1	7.67	19.18	0.00	0.00	0.00	59.71	13.45
	2	0.00	0.00	0.00	0.00	0.00	80.86	19.14
	3	21.49	39.10	0.00	0.00	0.00	38.81	0.60
	4	0.00	0.00	0.00	0.00	0.00	70.47	29.53
	5	12.28	9.98	0.00	0.00	0.00	73.19	4.55
	Mean	8.29	13.65	0.00	0.00	0.00	64.61	13.45
Sewage water (15 years)	1	4.75	3.06	0.00	0.00	0.00	26.57	65.62
	2	0.00	0.00	0.00	0.00	0.00	67.72	32.28
	3	4.29	9.12	0.89	0.00	0.00	44.07	41.62
	4	0.00	0.00	0.00	0.00	0.00	32.44	67.56
	5	1.91	7.63	0.00	0.00	0.00	39.14	51.33
	Mean	2.19	3.96	0.18	0.00	0.00	41.99	51.68
Non -irrigated soil		0.00	0.00	0.00	0.00	0.00	52.04	47.96

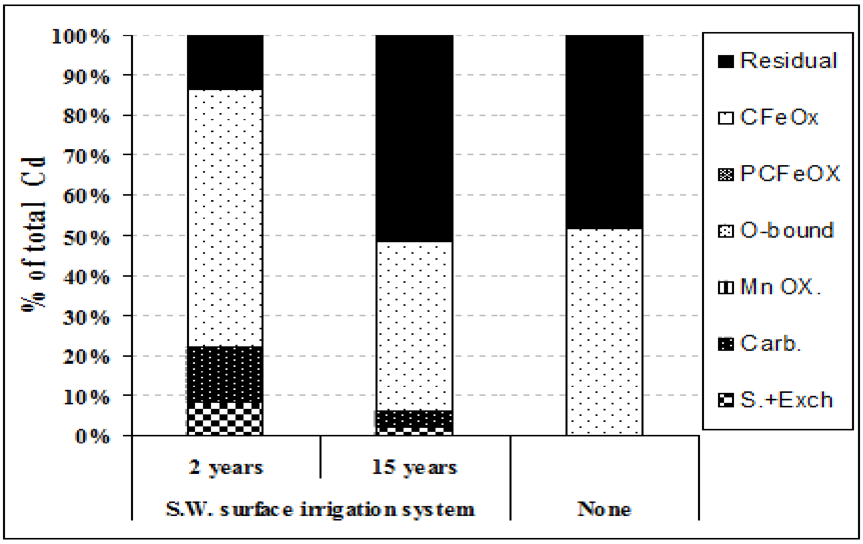

Figure 3: Distribution of average Cd forms (% of total content) in the surface layer of the soils irrigated with sewage water (S.W.), as well as of the non-irrigated one (Non) in studied soils.

transformed to the Mn oxide-bound and residual Cd forms in the sewage water irrigated soils for 15 years . So, the soluble + exchangeable, carbonate-bound and crystalline Fe oxide-occluded Cd forms decreased from 8.29 , 13.65 and 64.61%, respectively in the soils irrigated with sewage water for 2 years to 2.19, 3.96 and 41.99%, respectively in the soils irrigated with sewage water for 15 years (Table 7 and Fig.3). On the other hand, the Mn oxide-bound and residual Cd forms increased from 0 and 13.55%, respectively, in the soils irrigated with sewage water for 2 years to 0.18 and 51.68%, respectively, the in the soils irrigated with sewage water for 15 years.

The distribution of Cd forms in the surface layer of soils irrigated with sewage water and with Nile water was reported to be arranged in the order of MnOX > Residual > Carb > O-bound > S. +Exch> CFeOX > PCFeOX and Carb > MnOX > Residual > O-bound > CFeOX > PCFeOX > S. +Exch for the non-irrigated soils (Roshdy, 2009). Cadmium in sandy soils irrigated with sewage water for 5 years was reported to be in the carbonate, easily reducible oxides and residual forms; The Cd distribution in the surface layer in these soils followed sequence of residual > easily reducible oxides > carbonate > exchangeable> the organic matter (Usman and Ghallab, 2006). Badawy and El-Motaium (2003) showed that Cd in sandy soils amended with sewage sludge had the distribution of residual > organic > oxides > carbonate > exchangeable.

Heavy Metal Overall Lability:

The soil metal forms could be grouped into three fractions of readily labile, potentially labile and non-labile (Han and Banin, 2000; Han et al; 2001; Usman and Ghallab, 2006; Roshdy, 2009). The readily labile fraction includes the soluble and exchangeable forms that are mobile and bioavailable for plants (Cottenie et al 1982; El-Desoky, 1989 ; Roshdy, 2009). Metals associated with Fe-Mn oxides (reducible fraction) have a medium mobility that may change under reducing conditions to cause a release the metals. Metals associated with organic matter (oxidizable fraction) have a medium to low mobility (Katana et al., 2013).

Cupper.

Figures 4 illustrate the distribution of average readily labile, potentially labile and non-labile Cu fractions in the surface layer of the studied soils

The irrigation of the soils with sewage water caused the non-labile Cu fraction to transform to the potentially labile one. Apart of non-labile Cu fraction in the non-irrigated soil transformed to the potentially labile fraction with the irrigation using sewage water. So the non- labile Cu fraction decreased from 75.15% in the non-irrigated soil to 56.54 and 61.94% in the sewage water irrigated soils for a short and a long time, respectively, (Figure 4). On the other hand, the potentially labile Cu fraction increased from 23.50% in the non-irrigated soil to 41.67 and 36.09 % in the sewage water irrigated soils for a short time and long a time, respectively

Also, a part of the readily and potentially labile Cu fraction in the sewage water irrigated soils water for a short time transformed to the non-labile fraction in the with sewage water irrigated soils for a long time. So, the readily and potentially labile fractions decreased from 1.83 and 41.67%, respectively, in the sewage water irrigated soils for a short time to 1.68 and 36.09 %, respectively, in the sewage water irrigated soils for a long time (Figure 4). On the contrary, the non-labile Cu fraction increased from 56.54% in the sewage water irrigated soils for a short time to 61.94% in those irrigated with sewage water for a long time.

Lead

Figure5 illustrates the distribution of the average readily labile, potentially labile and non-labile Pb fractions in the surface layer of the studied soils. It is clear that irrigating soils with sewage water caused the non-labile Pb fraction to partially transform to the potentially labile one. Therefore, the no labile Pb decreased from 84.67% in the non-irrigated soil to 57.22 and 59.23% in soils irrigated with sewage water for a short time and sewage water for a long time, respectively. On the contrary, the potentially labile Pb increased from 11.58% in the non-irrigated soil to 34.02 and 37.55% in the soils irrigated with sewage water for a short time and sewage water for a long time, respectively.

Moreover, the readily labile Pb in the sewage water irrigated soils for a short time partially transformed to both non-labile and potentially labile Pb due the irrigation with this water for a long time. Thus, the readily labile fraction Pb decreased from 8.76% in the sewage water irrigated soils for a short time to 3.22 % in the sewage water irrigated soils for a long time. However, both the non-labile Pb and potentially labile Pb increased from 57.22 and 34.02 %, respectively, in the sewage water irrigated soils for a short time to 59.55 and 37.55% in those irrigated with sewage water for a long time.

Cadmium

There are changes in the lability of Cd fractions due to the irrigation with sewage water. The non-labile Cd in the non-irrigated soil partially transformed to both readily labile and potentially labile Cd due to using sewage water in the irrigation (Fig. 6). Thus, the non-labile Cd decreased from 100% in the non-irrigated soil to 78.19% and 94.19% in the soils irrigated with sewage water for a short time and a long time respectively. On the other hand, the readily labile Cd increased 0% in the non-irrigated soil to 7.89 and 2.14% in the soils irrigated with sewage water for a short time and a long time, respectively. Moreover, the potentially labile Cd increased from 0% in the non-irrigated soil to 13.92 and 3.68% in the soils irrigated with sewage water for a short time and a long time respectively. Also, both readily labile and potentially labile Cd fractions in the soils irrigated with sewage water for a short time partially transformed to the non-labile Cd one when they were irrigated with this water for long time (Fig. 6) So, the readily labile Cd and potentially labile Cd decreased from7.89 and 13.92%, respectively, in the soils irrigated with sewage water for a short time to 2.14 and 3.68%, respectively, in the soils irrigated with sewage water for a long time. However, the non-labile Cd increased from 78.19% in the soils irrigated with sewage water for a short time to 94.19% in the soils irrigated with sewage water for a long time.

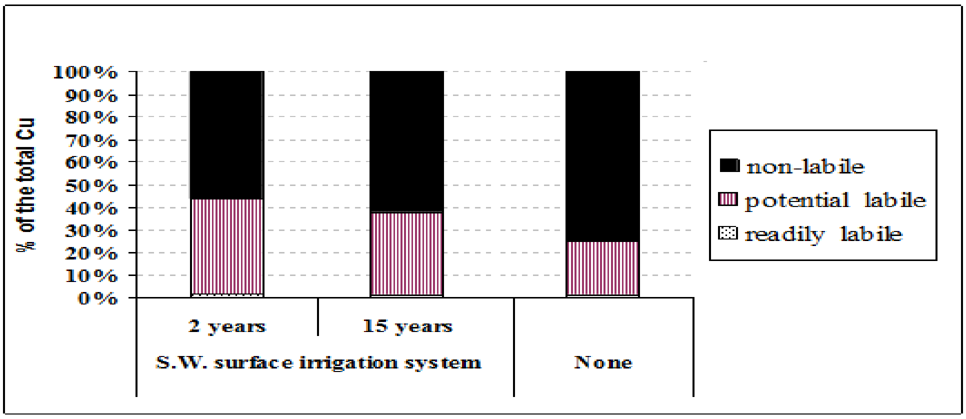

Figure:4 Distribution of average readily labile, potentially labile and non-labile Cu fractions (% of the total content) in the surface layer of the soils irrigated with sewage water (S.W.), as well as of the non-irrigated one (None) in studied soils.

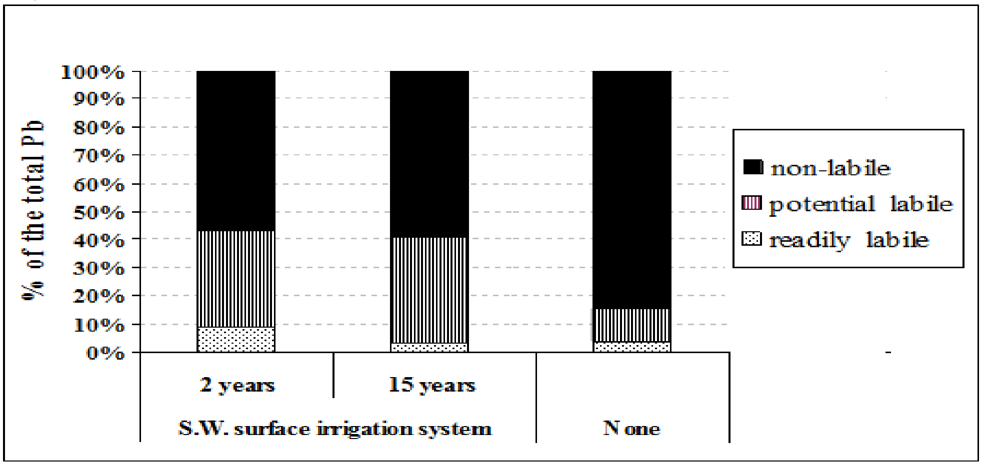

Figure:5 Distribution of average readily labile, potentially labile and non-labile Pb fractions (% of the total content) in the surface layer of the soils irrigated with sewage water (S.W.), as well as of the non-irrigated one (None) in studied soils.

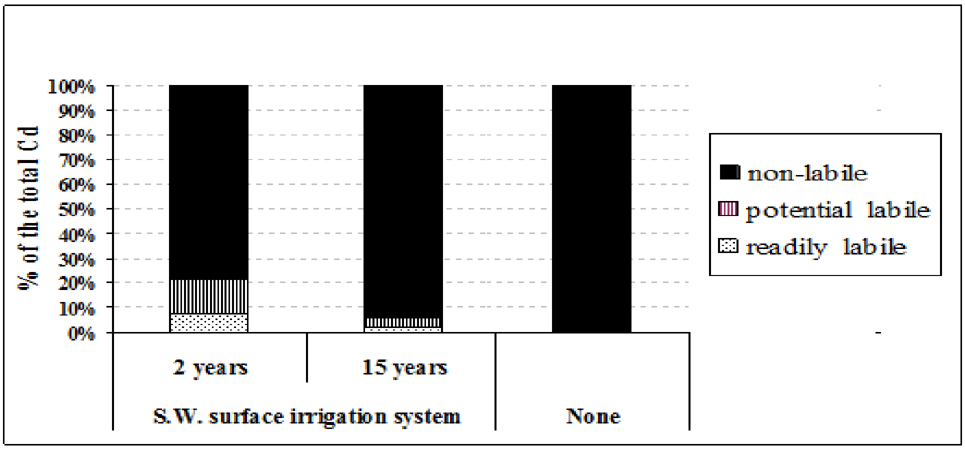

Figure:6 Distribution of average readily labile, potentially labile and non-labile Pb fractions (% of the total content) in the surface layer of the soils irrigated with sewage water (S.W.), as well as of the non-irrigated one (None) in studied soils.

Conclusions

The non-labile Cu in the non-irrigated soil partially transformed to the potentially labile Cu due to the irrigation with sewage water. Also, a part of the readily labile Cu and potentially labile Cu of the sewage water irrigated soils for short time transformed to the non-labile fraction with irrigation with same water for a long time. Also, a part of the non-labile Pb fraction of the non-irrigated soil transformed to the potentially labile Pb fraction with using sewage water in irrigation. Moreover, the readily labile Pb of the sewage water irrigation soils for a short time partially transformed to the non-labile and potentially labile Pb fractions using this water in the irrigation for a long time. The use of sewage water in irrigation caused, the non-labile Cd of the non-irrigated soil to transform partially to the readily labile and potentially labile Cd fractions. Also, a part of the readily labile and potentially labile Cd of the sewage water irrigated soils for a short time transformed to the non-labile Pb fraction with keeping the irrigation with this water for a long time.

REFERENCES

Abul Kashem, Md., Singh, B.R., Imamul Huq, S. M. and Kawai1, S. (2011) “Fractionation and mobility of cadmium lead and zinc in some contaminated and non- contaminated soils of Japan", Journal of soil science and environmental management3(9): pp. 241-249.

Ahnstorm, Z. S. and Parker, D. R. (1999) "Development and assessment of a sequential procedure for the fractionation of soil cadium”, Soil Science Society of America Journal 63: pp.1650-1658.

Ahumada, I., Mendoza, J. and. Ascar, L. (1999) "Sequential extraction of heavy metals in soils irrigated with wastewater", Communications Soil Science Plant Analysis. 30: pp.1507–1519.

Awad, M.Y.M. (2007) "Mobility of heavy metals in some contaminated Egyptian soils treated with certain organic materials”, Ph.D. The University of Assiut, Egypt.

Badawy, S.H. and EL-Motaium, R.A. (2003) "Fate of same heavy metals in a sandy soil amended with sewage water sludge and their accumulation in plants", Egyptian Journal of Soil Science 43 (1): pp. 1- 16.

Cottenie, A., Verloo, M., G. and Kiekens, L. (1982) Biological and analytical aspects of soil pollution. Laboratory of analytical and Agrochemistry. State Univ., Ghent-Belgium.

El-Desoky, M.A. (1989) 'Iron oxide forms and heavy metal transformations in Sulfaquepts in Baltimore Harbor dredged materials. Ph.D. Dissertation, Univ. Maryland, College Park, MD, USA.

Han, F.X. and Banin, A. (2000) "Long-term transformations of Cd, Co, Cu, Ni, Zn, V, Mn and Fe in the native arid-zone soils under saturated condition" Communications in Soil Science and Plant Analysis 31: pp. 943-957.

Han, F.X., Banin A. and Triplett, G.B. (2001) "Redistribution of heavy metals in arid-zone soils under a wetting–drying cycle soil moisture regime". Soil Science . 166: pp. 18-28.

Ianni, C., Ruggieri, N., Rivaro, P. and Frache, R. 1997. "Evaluation and comparison of two selective extraction procedures for heavy metal speciation in sediments" Analytical Sciences Journal 17: pp. 1273– 1278.

Jackson, M.L. (1969) Soil chemical analysis-advanced course" Published by author, Soil Science Department, Wisconsin University, Madison, USA.

Jackson, M.L. (1973) "Soil chemical analysis" Prentice-Hall, Inc., Englewood Cliffs. NJ, USA.

Kabala, C. and B.R. Singh. (2001) "Fractionation and mobility of copper, leadand zinc in soil profiles in the vicinity of a copper smelter". Journal of Environmental Quality, 30: pp. 485-492.

Katana, C., Jane, M. and M. Harun. (2013) "Speciation of Chromium and Nickel in Open-Air Automobile Mechanic Workshop Soils in Ngara" Nairobi, Kenya. World Environment, 3(5): pp. 143-154.

Kittric, J.A. and Hope, E.W. (1963) "A procedure for the particle-size separation of soils for X-ray diffraction analysis". Soil Science, 69: pp. 319-325.

Kotoky, P., Bora, B.J., Baruah, N.K., Baruah, P., Baruah J. and Borah, G.C. (2003) "Chemical fractionation of heavy metals in soils around oil installation, Assam" Chemical Speciation and Bioavailability 15(4): pp. 115-125.

Liang, J., Stewart J.W.B. and Karamanos, R.E. (1991) "Distribution and plant availability of soil copper fractions in Saskatchewan" Canadian Journal of Soil Science 71: pp. 89-99.

Ma L.Q. and Rao, G.N. (1997) "Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils". Journal of Environmental Quality 26: pp. 259-264.

McKenzie, R.M. (1978) "The effect of two manganese dioxides on the uptake of lead, nickel, copper and zinc by subterranean clover". Australian Journal of Soil Research 16: 209-214.

McLaren, R.G. and D.V. Crawford. (1973) Studies on soil copper. I. “The fractionation of copper in soils”. Journal of Soil Science 24: pp. 172-181.

Osakwe, J.O., and Adowei, P. and Jnr, M.H. (2014) Evaluation of Heavy Metal Species in Bottom Sediments from Imo River System, Southeastern Nigeria. Research Journal of Chemical Sciences 4(6), pp. 23-30.

Petruzzelli G., Lubrano L. and Guidi, G. 1989. “Uptake by corn and chemical extractability of heavy metals from four years compost treated soil” journal of plant and soil science, 16, 23 – 27.

Richards, L.A. (1954) “Diagnosis and improvement of saline and alkali soils” USDA. Handbook, Washington, USA.

Roshdy, Nadia, M.K. (2009) "Distribution and forms of some heavy metals in a contaminated soil at Assuit " Ph.D The University of Assiut, Egypt.

Scheffer, F. and Schachtschael, P. (2002) “Lehrebuch der Bodenunde. 15. Auflage. Spektrum Akademischer Verlag Heidelberg. Berlin

Shuman, L.M. (1979)“Zinc, manganese and copper in soil fractions”. Soil Science Journal 127: pp. 10-17.

Sims, R., Sorensen, D., Sims, J., Mamood, J., Dupont, R., Jurinak, J. and Wagner, K. (1986) “Contaminated surface soils in place treatment techniques”. Noyes Publisher, Park Ridge, NJ, USA.

Tessier A, P.G.C. Campbell and M. Bisson 1979. “Sequential extraction procedure for the speciation of particulate trace metals”. Anal. Chem., 51: pp. 844-851.

USDA, (United States, Department of Agriculture). (1996) “Soil Survey Investigations. Soil Survey Laboratory Methods Manual”. Report No.42, V.3, Washington, D. C.

Usman, A.R. A. (2004) “Soil reclamation and conservation: Evaluation of several additives for remediation and quality improvement of soil”. Ph.D.Thesis, Institute of Soil Science and Land Evaluation, Hohenheim University .,Stuttgart, Germany.

Usman, A.R.A. and Ghallab, A. (2006). “Heavy metal transformation and distribution in soil profiles short-term-irrigated with sewage waste water”. Journal of Chemical Ecology 22 (2): pp. 267-278.