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Research Paper

Effect of periodic application of wastewater on chemical forms of zinc and copper in soil depths

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Abstract: The current study was carried out in order to investigate the effect of periodic application of wastewater on some soil chemical properties and distribution and migration of copper (Cu) and Zinc (Zn) in soil profile. Application of wastewater on the soil properties showed that, irrigation with wastewater decreased soil pH and CCE, and on the other hand, increased Ec, SAR and OM, compared with non irrigated soils. The change of Zn and Cu fractions with depth for non-irrigated soil showed that Zn and Cu are strongly associated with the residual fraction. Chemical forms (Total forms) of Cu and Zn tendency to decrease with depth. Increased wastewater after 6 and 12 months caused increases in all chemical forms of Zn (except Carbonate form), especially in the surface layer. The mobility factor of Zn was reduced in three layers after 6 months of irrigation. In contrast, after 12 months of irrigating with wastewater resulted in the transformation of metals from the non mobile fraction towards the mobile fraction and finally mobility factor of Zn was increased in three layers. The result showed higher concentrations of chemical forms of Cu in the surface layers than sub surfaces. In irrigated soil, concentration of Chemical forms of Cu tendency to decrease with depth. The mobility factor of Cu was increased in three layers after 6 and 12 months of irrigation. Generally, application of wastewater caused increase in chemical forms of Zn and Cu and finally mobility factor, however, these factors were below of very mobile range.

Keywords: Chemical forms, Fractionation, wastewater, Copper, Zinc

Introduction

In arid and semi-arid conditions, because of limited water resources, municipal wastewater could be used for irrigation plants (Liu et al. 2005, Ghanbari et al, 2007). Long-term effects of wastewater irrigation might include contamination of soil, plant, and ground water with heavy metals (Sharma et al. 2007; Nouri et al., 2008). In soils, heavy metals of interest exist in several different chemical fractions and are linked with a range of components (Saffari et al, 2009b). The dynamism of heavy metals depends on their chemical forms. The mobility, transport and partitioning of heavy metals in soils are dependent on various soil chemical properties (Saffari et al, 2009b). The application of wastewater has led to changes in some soil properties; therefore, wastewater can play an important role in metal mobility. In recent times, fractionation studies of heavy metals in soils using a sequential extraction method can provide an understanding of its chemical forms and potential mobility. Generally, the fractions considered are as follows: exchangeable, carbonate bound, iron and manganese hydroxides bound, organically complexes and residual fractions (Kabala and Singh, 2001). Different fractions of soil metals vary significantly in their chemical reactivity and mobility (Saffari et al, 2009a). The water-soluble, carbonate, and exchangeable forms of metals are considered to be the most mobile in soil (Shuman, 1991), and metals bound to organic matter are also found to be mobile in soil (Iyengar et al., 1981). There is little information available on the effect of the addition of wastewater on the chemical forms and mobility of heavy metals in various periods and different depths of soils. Flores et al (1997) showed that, the highest concentrations of soil Cu, Cd, Pb and Zn after application of wastewater were set up in the surface layers at all soil profiles. Sequential chemical fractionation indicated that the metals were predominantly associated with the organic fraction. Also, reported that chemical forms decrease with depth. Usman and Ghallab (2008) showed that, application of wastewater to soils had the greatest effect on fractions of exchangeable, iron and manganese hydroxides, and organic fraction for Zn and for Cu was in the exchangeable and residual fraction. Zhao et al (2010) reported that Cd, Cr, Ni, Zn and Cu in soils treated with wastewater irrigation were mainly in the residual fractions and small amounts were present in exchangeable and carbonate fractions. Haroun et al (2006) reported that Zn in soils treated with tannery sludge for 50-day was mainly in the residual fraction. Illera et al, (2000) reported that application of different types of municipal solid waste changed the distribution of Zn chemical forms. This change caused the relative amount of residual and organic bound to increase and the relative amount of oxides fractions to decrease. The objectives of this study were to (1) determine and evaluation the effect of periodic application of wastewater on the distribution and migration of Cu and Zn in soil profile (2) evaluate periodic application of wastewater on some chemical properties of soil.

Materials and Methods

Sampling location and Soil Characterization

In order to study the effects of irrigation with municipal wastewater on the distribution of chemical forms of Cu and Zn an experiment was conducted at wastewater treatment on plant and soil. The experimental site was located in research farm of Kerman University. The wastewater irrigated farm was planted with Pistachio. The experiment was a randomized complete block design with 3 replications. Our study was divided into three periods: the beginning time of treatment (T1), 6 (T2) and 12 (T3) months after irrigation by wastewater and fresh water, two zones: irrigated with wastewater and irrigated with fresh water, and three depths: 0-30, 30-60, and 60-90. Irrigation was conducted every 8 days by irrigating by wastewater and fresh water. Some characteristics of treated wastewater and fresh water are shown in Table 1. Soil samples were collected from three depths (0–30,

30–60, and 60–90 cm). The soil samples were air-dried and ground to pass through a 2mm sieve. Particle size analysis was performed using Hydrometer method (Day, 1965); pH was measured in saturated paste; cation exchange capacity (CEC) was determined using a method of Chapman (1965); percentage of calcium carbonate equivalent (CCE) was measured by acid neutralization (Salinity Laboratory Staff, 1954); organic matter (OM) content was determined using Walkley and Black (1934); plant-available fraction of Zn and Cu was determined by means of atomic absorption spectrophotometer (Lindsay and Norvell, 1978); Aqua regia (mixture of HF, $HClO_4$, HNO_3, and H_2SO_4) was used to determine the total contents of Zn and Cu (Ma and Uren, 1997). Some soil properties are presented in Table 2.

Table 1. Selected properties of the fresh water and wastewater

Parameters	unite	tab water	wastewater
TSS	mg L^{-1}	4.5	85
PH	-Log[H^+]	7.78	7.8
EC	ds m^{-1}	0.51	1.46
Na	me L^{-1}	0.8	10.2
SAR	-------	1.02	6.8
BOD	mg L^{-1}	-------	35

Table 2. Chemical properties of soils prior to experimentation

Depths (cm)	pH	EC	CEC	OM	CaCO3	SAR	Zn-DTPA	Cu-DTPA
		(dS m^{-1})	(cmol(+)kg^{-1})	(%)	(%)		mg kg^{-1}	mg kg^{-1}
0-30	7.93	2.9	25.2	1.1	27.2	2.23	0.54	1.2
30-60	7.75	1.4	10.5	0.7	34.6	1.9	0.31	0.9
60-90	7.61	1.3	8.1	0.5	31.8	1.9	0.2	0.6

Fractionation procedure

The procedure of Sposito et al. (1982), was used for this study, is designed to separate Zn and Cu into 5 operationally defined fractions: exchangeable (F1), sorbed (F2), organic (F3), carbonate (F4), and residual fractions (F5). A summary of the procedure is as follows:

- F1: Two grams of soil were weighted and placed in a 50-mL polycarbonate centrifuge tube, Sample extracted with 25 mL of 0.5 M KNO_3 for 16 h.
- F2: residue from exchangeable fraction extracted with 25 mL of deionized water for 2 h (three times).
- F3: residue from sorbed fraction extracted with 25 mL 0.5 M NaOH for 16 h.
  F4: residue from organic fraction extracted with 0.05 M Na_2EDTA for 2 h.
- F5: residue from carbonate fraction extracted with 4 M HNO_3 for 16 h in 80°C.

After each successive extraction, the extracted solution was separated by centrifuging at 3500 rpm for definite time. The supernatant was filtered for analysis of Zn and Cu by atomic absorption spectrometry (AAS) (Shimatzu AA-670G).

Mobility Factor of Cu and Zn

The mobility of Cu and Zn could be assessed by a "mobility factor" (Salbu et al, 1998) which could be calculated according to the equation as followed:

$$MF = \frac{F1 + F2 + F4}{F1 + F2 + F3 + F4 + F5} \times 100$$

Data Analysis

Duncan mean separation tests were used to separate treatment effects using SAS software (SAS Institute Inc. 2005).

Results

Effect on some soil properties

Variations of pH, EC, SAR, CCE, OM and CEC with soil depth, in different duration of wastewater irrigation are graphically shown in Fig. 1. Irrigation with wastewater after 6 and 12 months, decreased pH compared with beginning time of treatment. Before of irrigation, pH was 7.93, 7.75 and 7.61 in the 0–30, 30–60 and 60-90 cm layers, respectively. The pH was reduced to 7.74, 7.66 and 7.55 in the soil layers 0–30, 30–60 and 60–90 cm after 6 months, and to 7.58, 7.51 and 7.53 after 12 months of irrigation. In surface layer and subsoil layer (30-60 cm), the soil pH decreased significantly in response to irrigation with wastewater. Moderate pH change of the soil with increase wastewater irrigation might be due to lower pH of wastewater being used for irrigation and nitrification of ammonium (Mohammad and Mazahreh, 2003). Other researchers found that soil pH increased with wastewater irrigation due to higher pH of wastewater and high content of basic cations such as Ca, Mg and Na in the wastewater (Presley et al., 2004; and Qian and Mecham, 2005; Hu et al., 2006). It is well known that soil pH plays an important role in the mobility of metals as in their bioavailability for plants. The major reason of essential element deficiency in arid soils is high pH. Thus, by reducing the soil pH, the availability of nutrients for plants improved. Result showed that treated wastewater gave significant increases in EC and SAR in the soil. EC of soil prior to irrigation was 2.9, 1.4 and 1.3 dS m^{-1} in the soil layers 0–30, 30–60 and 60–90 cm, respectively. Twelve months later it had increased significantly to 4.5 dS m^{-1} in the top layer (0–30 cm) and to 2.5 dS m^{-1} in the 30–60 cm layer. The highest increase in soil salinity was found in the surface layer. The maximum soil salinity was obtained by T3. This finding supports that of Malla et al., 2007 and Galavi et al., 2010. The existence of Na, Mg and Ca in the wastewater (Ghanbari et al., 2007; Galavi et al., 2010) and transports high amounts of water soluble salts from the subsoil by capillary flow, especially in the arid regions, can increase EC of soil. The previous study has reported that elevated salinity levels could have increased the metal mobility in soils. This course of action is complete when some cations like

Na and K, replace with the heavy metal cations in the absorption places (Maldonado et al., 2008). Soil depth showed similar effects on the distribution of pH, Ec and SAR in the soil profile. Soil pH, Ec and SAR tendency decrease with depth. The treatments effect on CEC of soil was indistinctive. Wastewater application did not change CEC content. Galavi et al (2010) and Qishlaqi et al (2008) reported that irrigation with wastewater has significantly increased CEC of soil. CCE and OM content as affected by duration of wastewater application (months) and soil depth. Soil OM increased with increasing the period of application. This increase is attributed to the contents of the nutrients and organic compounds in the wastewater applied. This increase was the highest in the topsoil (0–30 cm) and for the longer period of wastewater application. Many studies have shown that the use of wastewater as irrigation water caused the increases of OM in the soils (Qian and Mecham, 2005; Galavi et al., 2010, Ramirez-Fuentes et al., 2002; Rusan et al., 2007). Vazquezmontiel et al (1996) found no positive effect on soil OM content by wastewater application. During the research CCE decreased gradually. The wastewater treated soil had lower CCE levels compared with the non-irrigated soil. CCE was 27.2, 34.6 and 31.8% in the 0–30, 30–60 and 60-90 cm soil layers, prior to application of wastewater. The final concentration of soil CCE after 12 months was 18.1, 24.3 and 27.3 %, respectively. Similar results were reported by El-Desoky and Gameh (1998) and Usman and Ghallab (2006). The acidity of the wastewater may dissolve the calcium carbonate, resulting in a go down in pH and CCE contents. Furthermore, organic acids and CO2 created as of microbial activity may cause the soil pH to decrease and calcium carbonate to dissolve (Usman and Ghallab, 2006).

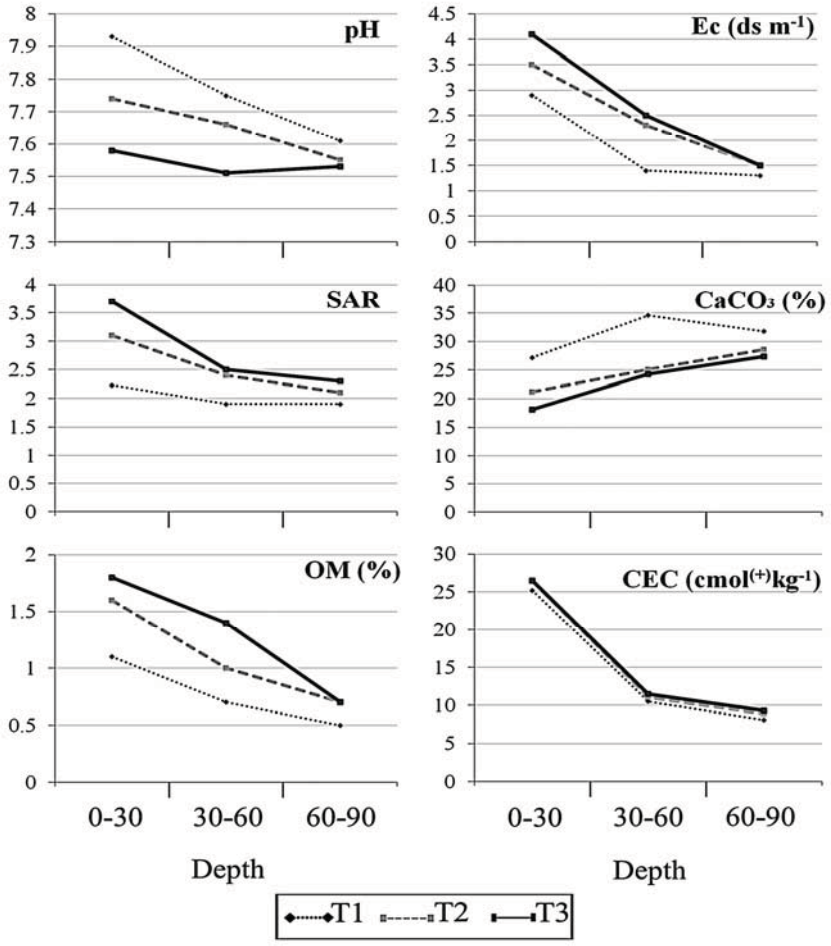

Figure 1. Variation of some chemical properties of soil with depths before and after 6 and 12 months irrigation with Wastewater

Distribution of the Zn and Cu fractions in non-irrigated soil

The Zn and Cu fractions with depth for non-irrigated soil in obtained by Sposito et al method are presented in Tables 1. Before of irrigation, total Zn was 77.41, 62.3 and 51.9 in the 0–30, 30–60 and 60-90 cm layers, respectively. The sequential extraction results show that Zn is strongly associated with the residual fraction, which agrees with the observation of many researchers (Abollino et al. 2006; Tapan and Rattan 2007; Saffari et al., 2009b). Zn associated with residual fraction in 0-30, 30-60, and 60-90cm layers of soil were 63.3 (81.8 %), 50.7 (81.4 %), and 43.5 µg g^{-1} (83.8 %), respectively. Zn fractions in non-irrigated soil at soil layers decreased in the following order: residual> carbonate> organic> exchangeable> Sorbed. This finding supports that of Saffari et al. (2009b). Dhane and Shukla (1995) reported that 95.9% of total zinc of soil belonged to residual fraction. Abollino et al. (2006) reported that Zn fractions in contaminated soil decreased in the following order: residual > manganese hydroxides > carbonate> organic> exchangeable. In the 0–30 and 30–60cm layers, Sorbed and exchangeable fractions were lower than the detection limit of AAS. The Sorbed and exchangeable fraction are of minor importance accounts for 1.3 and

0.5% of the total Zn in the soil, respectively. Similar fractionation of Zn in non-irrigated soil, residual fraction was the largest fraction of Cu, followed by the Carbonate fraction, organic fraction, then the sorbed fraction, and the smallest was the exchangeable fraction. Jalali and Khanlari (2007) reported that in natural and contaminated soils, the highest amounts of Cu are associated with the RES fraction. Adamo et al. (1996) and Mengel and Kirkby (2001) reported that Cu was strongly associated in carbonate fraction of calcareous soils. Graf et al (2007) studied the fractionation of Cu in young and old alluvial soils and found that greater proportion of Cu was associated with carbonate and Fe and Mn oxide fractions. Li et al. (2009) reported that around 90% of Cu was associated with the residual fraction of polluted soils. Before of irrigation, total Cu was 42.66, 36.3 and 19.8 in the 0–30, 30–60 and 60-90 cm layers, respectively. The concentration of total Cu decreases with increase in depth. Zn associated with residual fraction in 0-30, 30-60, and 60-90cm layers of soil were 29.8 (69.9 %), 26.4 (72.7 %), and 11.4 μg g^{-1} (42.2 %), respectively. Cu distribution pattern obtained by Sposito et al method follow the order residual >> carbonate > organic> exchangeable > sorbed. Chemical forms of cu tendency decrease with depth. The lowest proportion of Cu bound to 'sorbed' was recorded in the subsoil (60–90 cm) and then tended to decreases with depth.

Table 3. Concentration (μg g^{-1}) and relative percentage (%) of chemical forms of Zn and Cu Before irrigation with wastewater (each number is mean of 3 observations)

Chemical forms		F1	F2	F3	F4	F5	Total		F1	F2	F3	F4	F5	Total
Depths		Zn							Cu					
0-30	μg g^{-1}	0.98^{a}	0.35^{a}	4.58^{a}	8.2^{a}	63.3^{a}	77.41^{a}		2.38^{a}	0.5^{a}	3.98^{a}	6^{a}	29.8^{a}	42.66^{a}
	%	1.3	0.5	5.9	10.6	81.8			5.6	1.2	9.3	14.1	69.9	
30-60	μg g^{-1}	n.d.^{b}	n.d.^{a}	3.7^{b}	7.9^{a}	50.7^{b}	62.3b		2^{a}	0.2^{a}	3.4^{ab}	4.3^{b}	26.4^{b}	36.3^{b}
	%	0.0	0.0	5.9	12.7	81.4			5.5	0.6	9.4	11.8	72.7	
60-90	μg g^{-1}	n.d.^{b}	n.d.^{a}	2.8^{C}	5.6^{b}	43.5^{c}	51.9c		1.7^{a}	n.d.^{a}	3^{bc}	3.7^{b}	11.4^{c}	19.8^{c}
	%	0.0	0.0	5.4	10.8	83.8			8.6	0.0	15.2	18.7	57.6	

Different letters with in a column indicate significant differences by Duncan's multiple range test at $P<0.05$.

Distribution of Zn fractions as affected by wastewater

The results show that Zn fractions were affected by the duration of wastewater irrigation and soil depths (figure 2). Increased wastewater after 6 and 12 months caused increases in all chemical forms of Zn (except Carbonate form), especially in the 0-30 cm layer. Irrigation with wastewater in the surface layer after six months, Zn was mostly found in residual fraction (77.6%, equal to 66.6 μg g^{-1}), followed by the organic fraction (10.4%, equal to 8.966.6 μg g^{-1}), the carbonate fraction (9%, equal to 7.7 μg g^{-1}), the exchangeable fraction (2.1%, equal to 1.8 μg g^{-1}) and the sorbed fraction (0.9%, equivalent to 0.8 μg g-1). The percentage of Zn in the exchangeable, sorbed and organic fractions increased, while that in the residual and carbonate fractions decreased. The acidity of the wastewater dissolved large proportions of the calcium carbonate. The decreases in carbonate fraction were related with the losses of calcium carbonate (Saffari et al, 2009a) from the soil irrigated. Heavy metals mobility in soils is estimated by using an equation as described by Salbu et al. (1998). The rate of mobility factor for heavy metals provides information about their potential mobility in soils (Siddiqui and Khattak, 2010). The rate of mobility factor lower than 10% for heavy metals was considered to be highly immobile in soils (Torri and Lavado, 2008). For the ratio greater than 50% suggests that element is very mobile in soils (Ahumada et al., 1999). Before of irrigation, the mobility factor was 12.31% in the surface layer. The mobility factor was reduced to 12% in the soil layer after 6 months of irrigation. The application of wastewater in soil reduced the carbonate fraction and to increased the others fractions, especially organic form. Oluwatson et al. (2008) reported that mobility factor of Cd, Pb and Zn in the urban soils of North-West Nigeria varied from 13 to 30, 5 to 6, and 15 to 25%, respectively, in all soils. They concluded that Pb was highly stable in soils hence unavailable to plants. In the second and third layers of the soil, similar of surface soil layer, Zn fractionation and distribution were affected by irrigation with wastewater. In the second and third layers of the soil after six months of irrigation with wastewater, the concentration of Zn in soil components was to be in the following order: residual> organic> carbonate. In the subsoil layers irrigated with wastewater, most of the Zn remained mainly in the residual fraction.

Zn was changed from the residual form to organic, carbonate and exchangeable forms due to irrigation with wastewater in the subsoil layers. After application wastewater, the residual fraction decrease and Zn was transformed to the organic, carbonate and exchangeable fraction. The exchangeable fraction in 30-60 cm layer of soil after six month irrigation was very low. In these conditions, sorbed fraction was lower than the detection limit of AAS. Before of irrigation, the mobility factor was 12.68 and 10.79% in the 30-60 and 60-90cm layers, respectively. After six months of irrigation with wastewater, the mobility factor was reduced to 9.38 and 7.92% in the 30-60 and 60-90cm layers, respectively. Wastewater addition generally led to significant decrease in mobility and bioavailability of Zn in both layers.

Twelve months later of wastewater irrigation, concentration of total Zn had increased significantly in the top layer (0–30 cm) compared with that of to non irrigated soil. The surface layer (0–30 cm) irrigated with wastewater after twelve months, Zn was mostly found in residual fraction (75.2%, equal to 69.4 μg g^{-1}), followed by the carbonate fraction (10.7%, equal to 9.9 μg g^{-1}), the organic fraction (10.2%, equal to 9.4 μg g^{-1}), the exchangeable fraction (2.5%, equal to 2.3 μg g^{-1}) and the sorbed fraction (1.4%, equivalent to 1.3 μg g^{-1}). After 12 months of irrigating the top soil with wastewater resulted in the transformation of metals from the non mobile fraction towards the mobile fraction. The mobility factor of irrigated soil after 12 months was 14.63% in top layer.

In general, before and after irrigation in different periods, the highest (residual fraction) concentration of Zn fractions was found in the surface layer and tended to decrease with depth. Twelve months after applying wastewater in the 30-60 and 60-90cm of layer soil result showed that the residual fraction was transformed into carbonate and organic fractions. The dominant fraction of Zn in soil after twelve months of irrigation in the subsoil layers was residual fraction. In the wastewater treated soil in third layer (60-90cm), the fraction distribution of Zn were residual > organic > carbonate and residual > carbonate > organic for 6 and 12 months after irrigation, respectively. In this layer in two periods of irrigation, exchangeable and sorbed fractions were lower than the detection limit of AAS. After twelve months of irrigation with wastewater, the mobility factor was some increased to 12.23 and 10.23% in the 30-60 and 60-90cm layers, respectively.

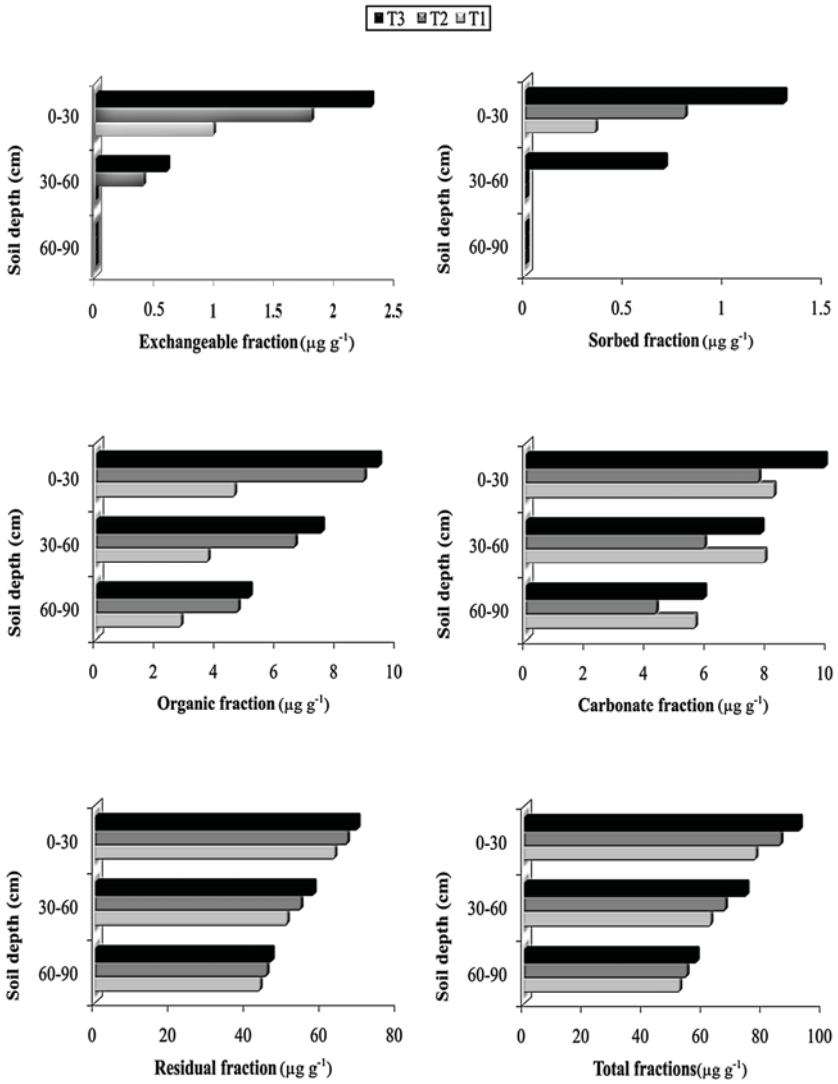

Figure 2. Chemical forms of Zn as affected by duration of wastewater application and soil depths

Distribution of Cu fractions as affected by wastewater

After irrigation with wastewater, the chemical distribution of Cu in soils receiving wastewater was different from that of the native soils (fig 3), indicating that irrigation with wastewater had large effect on Cu fractionation.

Chemical forms of Cu increased with wastewater irrigation after 6 and 12 months. The result showed higher concentrations of chemical forms of Cu in the surface layers (0–30 cm) than sub surfaces layers (30–60 cm and 60–90 cm). Six months after wastewater application, about 66.2% (32.1 µg g^{-1}) of the total Cu was associated with the residual fraction, and 16.1% (7.8 µg g^{-1}) resided in the carbonate fraction in the surface layer. In irrigated soil (T2), Concentrations of residual form, carbonate form, organic form, sorbed form and exchangeable fraction in surface layer (0–30 cm) were 7.7, 30, 8, 80, and 42 percent, respectively, higher than values obtained from non irrigated soil. Chemical forms of Cu in irrigated soil at surface layer after six months irrigation, decreased in the following order: residual>> carbonate> organic> exchangeable> Sorbed. In irrigated soil, concentration of Chemical forms of Cu tendency to decrease with depth. Although that in both deep layers, application of wastewater increased soil Cu in all chemical forms. In the second and third layers of the soil after six months of irrigation with wastewater, the concentration of Zn in soil components was to be in the following order: residual> organic> carbonate> exchangeable>sorbed. Before of irrigation, the mobility factor of Cu was 20.82% in the surface layer. The mobility factor was

increased to 24.95 in the soil layer after 6 months of irrigation. After six months of irrigation with wastewater, the mobility factor was increased to 25.89 and 38.94% in the 30-60 and 60-90cm layers, respectively. Twelve months later of wastewater irrigation, concentration of total Cu had increased significantly in all three layers (0–30, 30-60, 60-90 cm) compared with that of to non irrigated soil. The surface layer (0–30 cm) irrigated with wastewater after twelve months, Cu was mostly found in residual fraction (62.2%, equal to 35.2 µg g^{-1}), followed by the carbonate fraction (16.1%, equal to 9.1 µg g^{-1}), the organic fraction (12.5%, equal to 7.1 µg g^{-1}), the exchangeable fraction (6.9%, equal to 3.9 µg g^{-1}) and the sorbed fraction (2.3%, equivalent to 1.3 µg g^{-1}). The mobility factor was increased to 25.27% in the soil layer after 12 months of irrigation. After 12 months of irrigating the top soil with wastewater resulted in the transformation of metals from the non mobile fraction towards the mobile fraction. In the wastewater treated soil in second and third layers (30-60, 60-90 cm), the fraction distribution of Zn were residual > carbonate > organic > exchangeable > sorbed, for 12 months after irrigation. Twelve months after applying wastewater in the 30-60 and 60-90cm of layers soils result showed that the residual fraction was transformed into carbonate and organic fractions. After twelve months of irrigation with wastewater, the mobility factor was 25 and 34.04% in the 30-60 and 60-90cm layers, respectively.

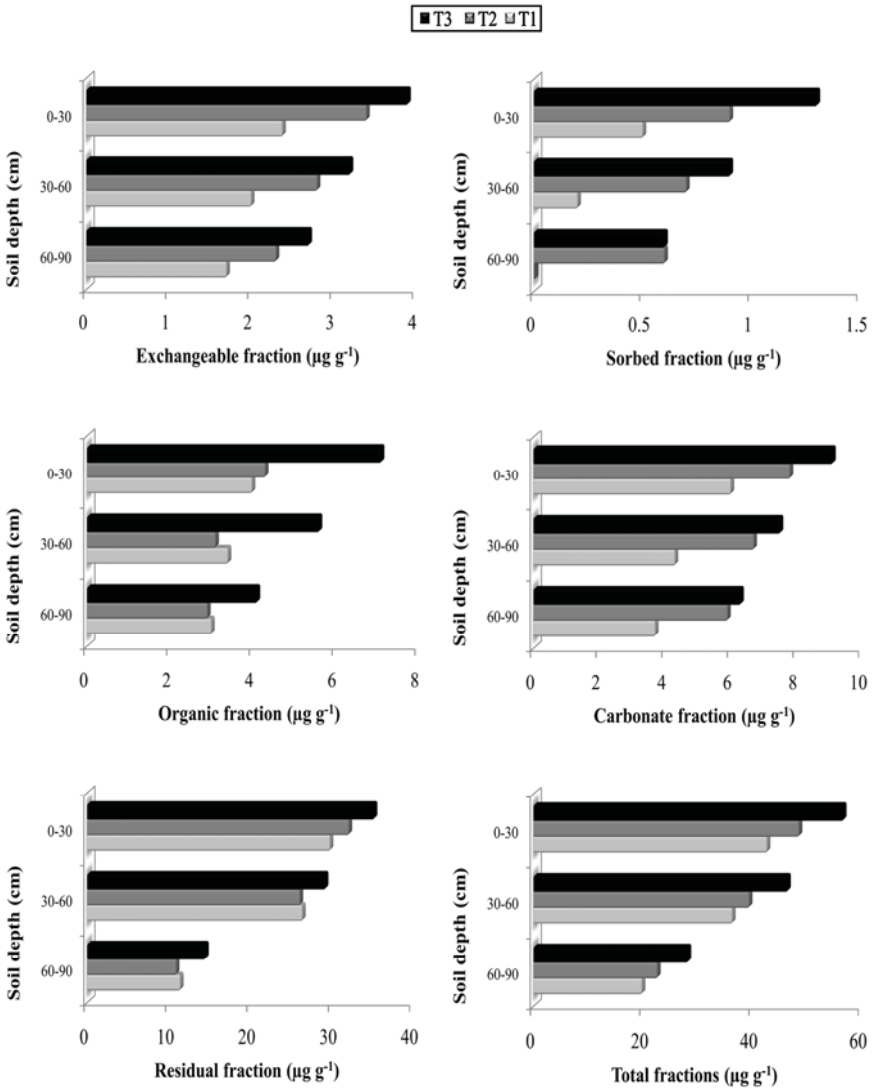

Figure 3. Chemical forms of Cu as affected by duration of wastewater application and soil depths

Conclusion

The effect of periodic application of wastewater on the soil properties showed that irrigation with wastewater (after 6 and 12 months) decreased soil pH and CCE compared with beginning time of treatment. On the other hands, application of wastewater increased Ec, SAR and OM compared with non irrigated soils. The CEC amount did not change after 2 periods of wastewater irrigation. Before and after irrigation, all of the chemical properties show that decreased with depth (expect CCE). The Zn and Cu fractions with depth for non-irrigated soil showed that Zn and Cu are strongly associated with the residual fraction. Zn fractions in non-irrigated soil at soil layers decreased in the following order: residual> carbonate> organic> exchangeable> Sorbed. Similar fractionation of Zn in non-irrigated soil, residual fraction was the largest fraction of Cu, followed by the Carbonate fraction, organic fraction, then the sorbed fraction, and the smallest was the exchangeable fraction. Chemical forms of cu and Zn tendency to decrease with depth. The results show that Zn and Cu fractions were affected by the duration of wastewater irrigation and soil depths. Increased wastewater after 6 and 12 months caused increases in all chemical forms of Zn (except Carbonate form),

especially in the 0-30 cm layer. Before of irrigation, the mobility factor was 12.31% in the surface layer. The mobility factor was reduced to 12% in the soil layer after 6 months of irrigation. The application of wastewater in soil reduced the carbonate fraction and to increased the others fractions, especially organic form. Also, before of irrigation, the mobility factor was 12.68 and 10.79% in the 30-60 and 60-90cm layers, respectively. After six months of irrigation with wastewater, the mobility factor was reduced to 9.38 and 7.92% in the 30-60 and 60-90cm layers, respectively. Wastewater addition generally led to significant decrease in mobility and bioavailability of Zn in both layers. Twelve months later of wastewater irrigation, concentration of total Zn had increased significantly in the top layer compared with that of to non irrigated soil. After 12 months of irrigating the top soil with wastewater resulted in the transformation of metals from the non mobile fraction towards the mobile fraction. The mobility factor of irrigated soil after 12 months was 14.63% in top layer. In general, before and after irrigation in different periods, the highest (residual fraction) concentration of Zn fractions was found in the surface layer and tended to decrease with depth. Twelve months after applying wastewater in the 30-60 and 60-90cm of layer soil result showed that the residual fraction was transformed into carbonate and organic fractions. After twelve months of irrigation with wastewater, the mobility factor was some increased to 12.23 and 10.23% in the 30-60 and 60-90cm layers, respectively. Chemical forms of Cu increased with wastewater irrigation after 6 and 12 months. The result showed higher concentrations of chemical forms of Cu in the surface layers than sub surfaces. In irrigated soil, concentration of Chemical forms of Cu tendency to decrease with depth. Although that in both deep layers, application of wastewater increased soil Cu in all chemical forms. Before of irrigation, the mobility factor of Cu was 20.82% in the surface layer. The mobility factor was increased to 24.95 in the soil layer after 6 months of irrigation. After six months of irrigation with wastewater, the mobility factor was increased to 25.89 and 38.94% in the 30-60 and 60-90cm layers, respectively. Twelve months later of wastewater irrigation, concentration of total Cu had increased significantly in all three layers (0–30, 30-60, 60-90 cm) compared with that of to non irrigated soil. The mobility factor was of Cu increased to 25.27% in the soil layer after 12 months of irrigation. After 12 months of irrigating the top soil with wastewater resulted in the transformation of metals from the non mobile fractions of Cu towards the mobile fractions of Cu.

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