



Chelate Induced Redistribution of Pb and Zn Fractions in Contaminated Soils and Implications on Phytoremediation



H. Abdelrahman

Soil Science Department, Faculty of Agriculture, Cairo University, Giza 12613, Egypt

LEAD and Zn contaminated soils, after sewage sludge (SS) or industrial wastes (IW) applications, were incubated with 5 and 10 mmol kg⁻¹ soil of diethylene triamine penta acetic acid (DTPA) and ethylene diamine tetraacetic acid (EDTA) or with 10 and 20 mmol kg⁻¹ soil of citric acid for up to 60 days. Consequently, *Amaranthus retroflexus* L. and *Chenopodium album* L. were tested in a chelate-assisted Pb and Zn phytoextraction greenhouse trial. In both incubated soils, the organic (Org) bound Pb increased over the incubation period, simultaneously, with a decrease in the oxide bound (Oxid) and carbonate bound (Carb) Pb fractions. Similar observations was found for Zn fractions during the incubation course of both contaminated soils. The EDTA was more effective in increasing the exchangeable Pb at 40 days of incubation in both soils whereas the DTPA was more effective in increasing the exchangeable Zn at 40 days of incubation. The pot experiment showed that *Amaranthus retroflexus* L. was more effective than *Chenopodium album* L. in the phytoextraction of Pb and Zn. The maximum amount of Pb and Zn *Amaranthus* phytoextracted in a 70-d growth period was 6.5 and 8.2 mg kg⁻¹ soil, respectively, whereas the maximum phytoextracted amounts of Pb and Zn by *Chenopodium* were 3.9 and 3.5 mg kg⁻¹ soil, respectively. Although EDTA and DTPA was more effective in redistributing metals among their fractions during incubation, higher removal of Pb and Zn was achieved after citric acid by *Amaranthus*. After environmental and economic evaluation, studied weed species can be used in chelate-assisted phytoremediation to decontaminate Pb- and Zn-contaminated soils.

Keywords Contaminated soils, Sewage sludge, Industrial wastes, *Amaranthus retroflexus* L., *Chenopodium album* L.

Introduction

Soil contamination by heavy metal has rapidly increased during the last few decades in both developed and developing countries (Yang et al., 2018) due to anthropogenic activities, which adversely affect the environment and ecosystem (Li et al., 2013 and Chen et al., 2015). In Egypt, the growing population, dictates increasing the cultivated area, however, limited water resources remain a limiting factor to agricultural production. Low quality water from non-conventional sources (e.g., agricultural drainage water and sewage effluent) has been used as an alternative source of irrigation water for more than 70 years.

Low quality water is often contaminated with heavy metals, organic pollutants, and pathogens (Suchkova et al., 2014) and applying such water in irrigation contaminates soil and increase health risks to people via food chain (Rai et al., 2019 and Suchkova et al., 2014).

Earlier works reported that many sites in Egypt have been contaminated due to anthropogenic activities. For example, Abouloos et al. (1989) studied the effect of prolonged use of sewage effluent in irrigation on the sandy soils of El-Gabal El-Asfar farm in Egypt and reported that the total content of heavy metals (i.e., Fe. Mn. Zn. Cu. Pb. Cd. Ni and Co) in soils irrigated with sewage

effluent increased with increasing years of using sewage effluent in irrigation. The contents of Zn, Pb and Co in soil irrigated with sewage effluent for 20 years were much higher than the suggested acceptable level (300, 100 and 50 mg kg⁻¹, respectively; Kabata-Pendias and Pendias, 1992).

Many conventional technologies such as solidification/stabilization and vitrification were used to immobilize pollutants, thereby minimizing their migration to other environments (Du et al., 2010). Conventional remediation technologies are either very expensive (such as vitrification) and are often harmful to soil properties (*i.e.*, texture, organic matter, microorganisms) that are desirable for the restoration of contaminated sites (Rulkens et al., 1995). Due to the high cost of many remediation technologies, it is necessary, in Egypt, to apply economically feasible, efficient and in-situ remediation methods/technologies. Phytoremediation could be a promising method to decontaminate sites, in Egypt, separately or combined with other cost-effective techniques. Phytoremediation of heavy metals contaminated soils has gained an increasing attention because of its cost effective and many environmental benefits (Kumar et al., 2013 and Stingu et al., 2012). For example, Nejatizadeh-Barandozi and Gholami-Borujeni (2014) reported that *Amaranthus retroflexus* L. had great potential in phytoremediation of contaminated soils. Also, Liu et al. (2002) proved in a field study that *Amaranthus retroflexus* L. can accumulate higher Cd amounts.

Phytoremediation has another advantage as the harvested plants containing heavy metal(s) can be ashed and valuable metal(s) can be extracted and recycled (Licht and Isebrands, 2005 and Anderson et al., 1998).

Combining chelates with phytoremediation has been considered effective in enhancing the remediation of contaminated soil (Bian et al., 2018). The application of chelates to heavy metals contaminated soil has resulted in increasing metal mobility, thereby enhancing phytoextraction (Chen et al., 2003 and Suman et al., 2018) and increasing the content of heavy metals in plant by > 40 and up to 200 fold (Huang & Cunningham, 1996 and Blaylock et al., 1997).

Many chelates, such as cyclohexylenedinitrilotetraacetic acid (CDTA), diethylene triamine penta acetic acid (DTPA), ethylene diamine disuccinate (EDDS), and ethylene diamine tetraacetic acid (EDTA) have

been studied for their ability to dissolve metals and enhance plants uptake of metals (Singh and Ma, 2007). Among these chelate, EDTA and DTPA have been found to be one of the most effective chelates to enhance heavy metal bioaccumulation. EDTA has shown greater ability to enhance the uptake of Pb compared to other chelates (Tandy et al., 2004). EDTA seems to have a linear relationship with metal removal from soils (Hong and Jiang, 2005). The use of EDTA as a chelate to soil was reported as the most efficient to enhance the phytoavailability of Pb, Hg and Cd (Nejatizadeh-Barandozi and Gholami-Borujeni, 2014).

The current work aimed to: i) test the effect of EDTA, DTPA and citric acid on the redistribution of Pb and Zn fractions in contaminated soils and ii) test the performance of *Amaranthus retroflexus* L. and *Chenopodium album* L. in chelate-assisted phytoextraction of Pb and Zn contaminated soils.

Materials and Methods

Site description and soil sampling

Soil samples were collected from two different locations in Egypt that were contaminated with heavy metals either because of sewage sludge/effluent applications (SS soil) or due to industrial wastes applications (IW soil). The SS location is in Al-Gabal Al-Asfar farm (30°13' N 31°23' E), which was established on a sandy loam soil and is being used for more than 70 years to dispose sewage sludge and effluents from the Wastewater Treatment Plant for Cairo Metropolitan. The IW location is in Al-Teppin area near the Iron and Steel Factory (29°45' N 31°18' E) where the nearby industrial activities are the main source of contamination either through air deposition or industrial effluents.

Soils samples were collected from the surface layer (0–30 cm) from different areas of each location. Samples were transported to laboratory, air dried, 2-mm sieved and stored properly for subsequent analyses and pot experiments.

Preliminary analysis

A preliminary metal analysis was carried out to determine metals content in the studied soils. Metal content was extracted by DTPA for the bioavailable form (Lindsay and Norvell 1978), and by a mixture H₂O₂ and H₂SO₄ for the total metal content and then detected by using atomic absorption spectrophotometer. The metal analysis showed that Pb and Zn were the most common (with higher content) in both soils. The relatively higher content of both metals is mainly related to the nature of the sewer system and the vicinity of industrial activities near the sampled sites. The

sewer system in Egypt does not separate house sewage from industrial sewage.

Work by Kamel and Khater (2004) reported different weed species that are able to accumulate higher concentrations of heavy metals in their shoots. Based on the availability and plant biomass, *Amaranthus retroflexus* L. (referred hereafter as Amaranthus) and *Chenopodium album* L. (referred hereafter as Chenopodium) were tested for their ability to phytoextract Pb and Zn from contaminated soils.

Chelate effects on metal distribution

The effects of two concentrations of EDTA, DTPA and citric acid (CA) on Pb and Zn redistribution among their fractions in both soils were tested. The chelate concentrations were 5 or 10 mmol kg⁻¹ soil of EDTA and DTPA and 10 or 20 mmol kg⁻¹ soil of CA. A 50 gram of 2-mm sieved soil samples were placed in a 250-mL glass bottles and 25 mL distilled water containing the assigned chelate concentration was added to samples. Bottles were covered with loose cardboard and placed in ventilated incubator at 40±2 °C for 20 or 40 or 60 days.

During the incubation, soil moisture was maintained at field capacity by frequent additions of distilled water when needed. Three replicates were used for each concentration of each chelate and each incubation period. After the designated time, related bottles were removed from the incubator, air-dried in air-ventilated space at room temperature and then finely ground. Afterward, samples were extracted according to the method described in Tessier et al. (1979) where metals are fractionated for the exchangeable (Exch), the carbonates-bound (Carb), the oxides-bound (Oxid), and the organic-bound (Org) fractions. The residual fraction was determined by difference from the total content of Pb or Zn as follows: residual = total metal content – (Exch + Carb + Oxid + Org).

Pot experiment

Seeds of *Amaranthus retroflexus* L. and *Chenopodium album* L. were collected from plants grown near the contaminated sites and preserved properly. A pot experiment was conducted in a greenhouse to determine the total removal of Pb and Zn by both plants. Each pot contained 1 kg of 2-mm sieved soils, and was sown with seeds to ensure the growth of five plants per pot. Chelate was added, with irrigation water, 10 days after germination and plants were harvested 70 days after germination. Amounts of chelates were calculated to provide the designated concentrations (5 and 10 mmol kg⁻¹ soil of EDTA or DTPA; 10 and 20 mmol kg⁻¹ soil of CA). Irrigation water amounts were added by

difference in pot weight where soil moisture were brought to field capacity. Distilled water was used for irrigation to avoid any possible contamination.

The transfer ratio of Pb and Zn from soils to Amaranthus and Chenopodium was calculated according to Cui et al. (2004) by dividing the metal concentration in plant tissue by the metal concentration in soil.

Statistical analysis

The reported data represent the mean values of three replicates with standard deviation. Data were tested for their normality of distribution and homogeneity of variance, and, when necessary, the data were transformed. Two-way ANOVA with repeated measures in one factor (time) was performed using Prism (Ver. 6, GraphPad Software, Inc.) to evaluate the statistical significance of the impact of chelate type, chelate concentration, incubation time and their interactions on Pb and Zn fractions. Two-way ANOVA was performed to evaluate the effect of plant, chelate, and their interactions on the removal of Pb and Zn from soils.

Results and Discussion

Soil characteristics

The SS treated soil had a slightly acidic pH (Table 1), EC of 1.0 mS cm⁻¹ and up to 5% soil organic matter (SOM) – uncommon for Egyptian soil – due to the historical input of organic matter. The SS treated soil, also, contained about 2% of CaCO₃ and was about 80% sand. DTPA extractable Pb and Zn were 98 and 89 mg kg⁻¹, respectively. The IW treated soil had a neutral pH (Table 1) and higher EC of 6.0 mS cm⁻¹. The IW soil contained 2% SOM, 4% CaCO₃ and was 78% sand. The DTPA extractable Pb and Zn in the IW soil were 118 and 40 mg kg⁻¹ soil for Pb and Zn, respectively.

Chelate induced redistribution of metal fractions in SS treated soil

Pb

The distribution of Pb, among its fractions, before chelates application was: Carb- (20%) > Org- (17%) > Oxid- (15%) > Exch-Pb (1.6%). The residual fraction was 46% of soil total Pb. As a general response to chelate application, the Org-Pb increased over the incubation period, simultaneously, with a decrease in the Oxid- and Carb-Pb fraction (Fig. 1a). The addition of chelates, especially EDTA, is known to increase the concentration of Pb in soil solution, at the expense of other Pb-bound fractions (see the review of Saifullah et al., 2009) however, few works investigated the effect of the chelates on the re-distribution of Pb among its fractions. For example, Kirkham (2000) found the addition of EDTA to increase the Exch-Pb and Carb-Pb in soil treated with sludge.

TABLE 1. Main Chemical and physical characteristics of the studied soils

Parameter	SS treated soil	IW treated soil
pH, 1:2.5 in H ₂ O	6.24	7.33
EC, mS cm ⁻¹	1.00	6.01
OM, g kg ⁻¹	56.3	19.6
CaCO ₃ , g kg ⁻¹	17.9	141
DTPA-Pb, mg kg ⁻¹	98.2	118
Total Pb, mg kg ⁻¹	334	996
DTPA-Zn, mg kg ⁻¹	87.5	39.5
Total Zn, mg kg ⁻¹	323	215
Sand, g kg ⁻¹	797	783
Silt, g kg ⁻¹	85.0	185
Clay, g kg ⁻¹	118	49.4
Texture class	Sandy Clay Loam	Sandy Loam

SS: Sewage sludge treated soils, IW: Industrial wastes contaminated soils.

The Exch-Pb fraction reached its maximum at 40 days then it decreased at 60 days of incubation, which might be due to the exchange reactions between chelated Pb and other soil divalent cations, such as Fe origination from soil (Komárek et al., 2007). At the end of the incubation period (60 d), the residual fraction, nearly in all cases, represented more than 40% of the total Pb content. Usually, the residual fraction accounts for about 50% of the total metal content in agricultural soils (Orroño & Lavado, 2009 and Aikpokpodion et al., 2013).

The 10 mmol EDTA kg⁻¹ soil was the most effective, at 40 days of incubation, in increasing the Exch-Pb followed by the 10 mmol kg⁻¹ DTPA (2.7% and 2.4%, respectively). Remarkably, large increases in the Org-Pb was observed, 60 days of incubation, with the higher concentration of the three tested chelates (Fig. 1a). The effect of the chelates on the increase of the Org-Pb fraction was clearly significant against the control treatment only at 40 and 60 days of incubations. On the other hand, the decrease in the Oxide-Pb was clear at 60 days of incubation with the EDTA and CA, with the lower concentration, which was statistically confirmed ($P < 0.05$) when compared to the initial conditions. In general, the overall fractional change (sum of changes in Exch-, Carb-, Oxide- and Org-Pb) ranged 1.1–7.7% increase,

indicating the mobilization of a proportion of the residual fraction.

The repeated measure analysis (RMA) showed that the addition of DTPA, EDTA and CA, at any concentration at 40 days of incubation, resulted in significantly different Pb fractions distribution compared to the untreated soils. It also showed that, at 20 days of incubation, only samples treated with the higher concentrations of the chelates were significantly different than the untreated soils, however, at 60 days of incubation, Pb contents after the DTPA and CA at any concentration were significantly different than Pb content in the untreated soils.

Zn

The distribution of Zn among its fractions, at the initial conditions, was as follow: Oxide (22%) > Carb (21%) > Org (14%) > Exch (3%) where the residual fraction made about 41% of the total Zn in the SS treated soil. The higher content of the Oxide-Zn is possibly due to the presence of high SOM content as suggested by Chahal et al. (2005) who reported a significant positive correlation between Oxide-Zn and organic carbon content in soils. The residual fraction, in most cases, was about 40% of total Zn, at 60 days of incubation. Generally, there was an increase in the Org-Zn fraction over the incubation period together with a gradual decrease in the Carb- and Oxide-Zn fraction (Fig. 1b).

Similar to Pb response to chelate additions, Exch-Zn reached its maximum concentration at 40 days of incubation then decreased except for the CA where the Exch-Zn continued to increase even at 60 days of incubation. The largest increase (5.7%) in the Exch-Zn occurred at 40 days of incubation with the 10 mmol kg⁻¹ soil of DTPA. Similar to the Org-Pb, the Org-Zn content increased during the incubation course, even at 60 days of incubation, where the largest increase (16%) was associated with the 10 mmol kg⁻¹ soil of CA (Fig. 1b), which is possibly due to the changes in soil pH and/or microbial activities that influenced the soluble/exchangeable Zn.

The decrease in the Oxide-Zn content was evident at 60 days of incubation especially after the 10 mmol DTPA kg⁻¹ soil. The total sum of changes in the fractions ranged -6.6% – 8.1%, which indicates no clear pattern of mobilization/immobilization of Zn from/to the residual fraction.

The RMA showed that incubation time and chelates application and their interaction had a significant effect ($P < 0.05$) on the redistribution of the Zn among its fractions. At 40 days of incubation, Zn content after DTPA, EDTA and CA at any concentration were significantly ($P < 0.05$) different than Zn content in the untreated soils. The RMA showed that only the 20 mmol kg⁻¹ soil of CA at 60 days had a significant effect on the Oxide-Zn, whereas at 40 days of incubation EDTA and CA at any concentration had a significant effect on the Zn-oxide fraction. Similar significant effect on Zn-Org was observed at 40 d and 60 days of incubation. Clearly, the effect of the chelates on the Org-Zn fraction was significant in comparison with the untreated soils at 40 d and 60 days of incubation.

Chelate induced redistribution of metal fractions in IW treated soil

Pb

The distribution of Pb among its fractions, at the initial conditions was: Oxide (20%) > Carb (14%) > Org (12%) > Exch (1%), whereas the residual fraction made about 49% of the total Pb in the IW treated soil. The chelates effect was generally seen in a slight increase in the Exch-Pb, especially at 40 days of incubation, followed by a decrease at 60 days and a very clear increase in the Org-Pb was very evident at 60 days of incubation. The Exch-Pb at 60 days of incubation was similar to the initial values before the incubation (Fig. 2a). As for the SS treated soil, the Carb- and Oxide-Pb decreased during the incubation course.

The largest increase (~2%) in the Exch-Zn occurred with the 10 mmol EDTA kg⁻¹ soil at 60 days of incubation, whereas the largest increase (18%) in the Org-Zn occurred with the 5 mmol DTPA kg⁻¹ soil at 60 days of incubation. The largest decreases in the Oxide-Zn was observed with either 10 mmol EDTA kg⁻¹ soil or 20 mmol CA (Fig. 2a). Li et al. (2018) showed that after EDTA application, the exchangeable Pb fraction increased significantly (17–90%) whereas the residual Pb fraction decreased (10–23%) suggesting that the complexation of EDTA and Pb is facilitated by Pb conversion from the residual fractions to exchangeable fractions, which then increased plant availability. In fact, the overall changes (sum of changes) in the Pb fractions (Exch, Carb, Oxide and Org) was around $\pm 12.1\%$ indicating mobilization/immobilization for a proportion of the residual Pb fraction but with no clear trend.

The RMA showed that all chelates affected significantly the Exch-Pb at 40 and 60 days of incubation. It also showed that the Carb- and Org-Pb were affected significantly by all the chelate at 60 days of incubation, however, at 40 days of incubation only the DTPA at any concentration affected significantly the Carb- and Org-Pb. Interestingly, The oxide-Pb was affected significantly only by the CA, at any concentration.

Zn

The distribution of Zn among its fractions before the incubation was as follow: Oxide (18%) = Carb (18%) > Org (13%) > Exch (2%) whereas the residual fraction accounted for 39% of the total Zn. A very large increase, up to 12%, in the Exch-Zn was found with DTPA at 40 d and 60 days of incubation (Fig. 2b). Both DTPA and EDTA had a significant effect ($p \leq 0.05$) on the Exch-Zn at 40 d and 60 days of incubation whereas the CA, at any concentration, did not significantly affect the Exch-Zn at any incubation time.

A decrease in the Carb-Zn was observed during the incubation course where the largest decrease (about 4%) was associated with the 10 mmol DTPA kg⁻¹ soil at 60 days of incubation. Moreover, a decrease in the Oxide-Zn was observed during the incubation course where the 10 mmol DTPA kg⁻¹ soil led to the largest decrease in the Oxide-Zn at 60 days of incubation. None of the studied chelates had a significant effect on the Carb-Zn at any concentration or at any incubation period when compared to the initial conditions.

The Org-Zn increased during the incubation course where the largest increase was associated with the 10 mmol EDTA kg⁻¹ soil at 60 days of incubation (Fig. 2b). Chelates application had a significant effect on the Org-Zn against the initial conditions at 40 d and 60 days of incubation. Similarly, the chelates had a significant effect on the Oxid-Zn against the initial conditions but only at 60 days of incubation. It seems that the CA was

the least effective in re-distributing Zn among its fractions in the IW treated soil, which might be attributed to the degradability of CA in comparison with relatively persistent EDTA or DTPA.

The total sum of changes (-0.9% – 16%) in the Zn fractions (Exch, Carb, Oxide and Org) was mainly positive, which indicates the mobilization of a proportion (up to 16%) of the residual Zn fraction.

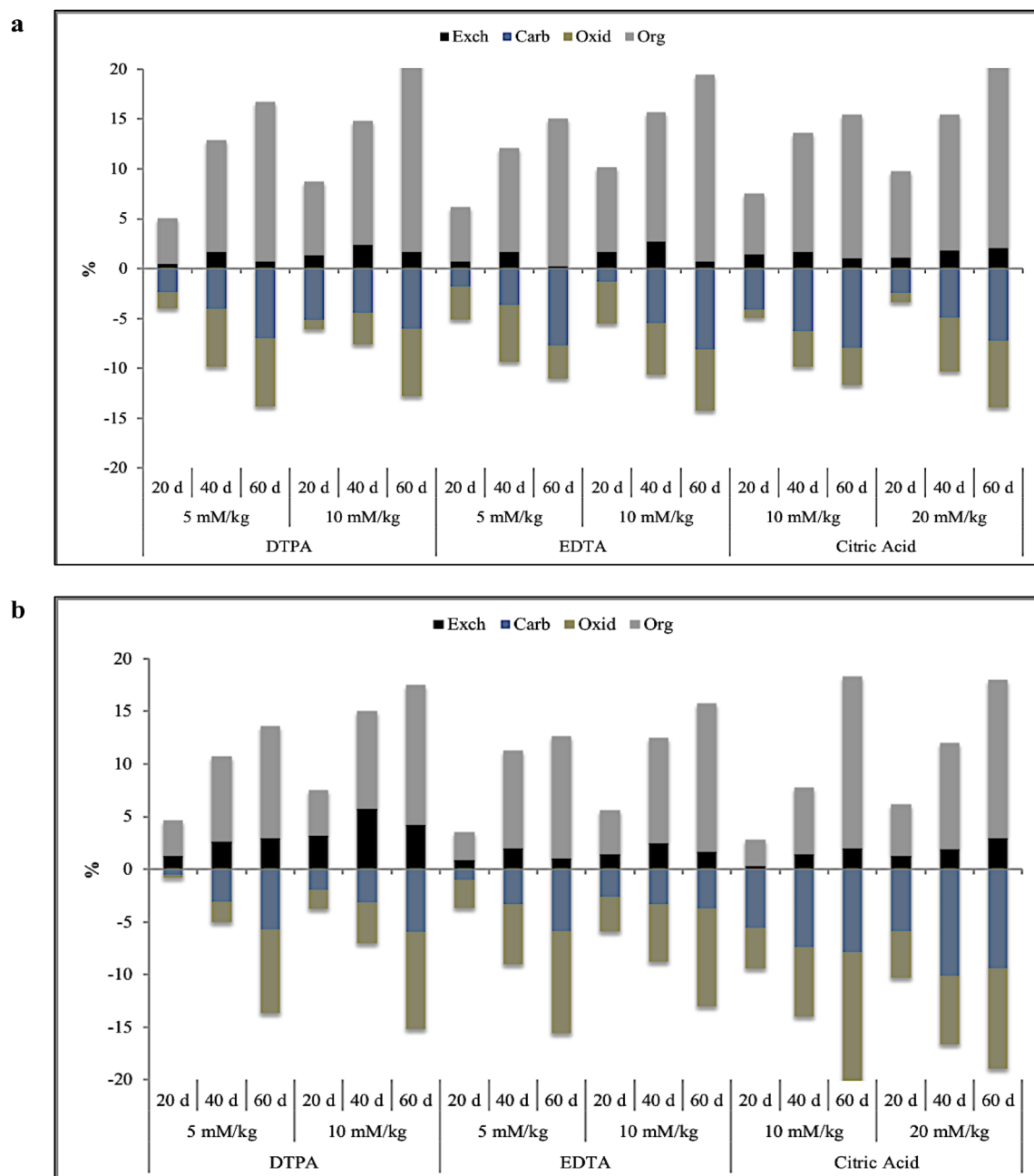


Fig. 1. Percentual changes in the exchangeable- (Exch), carbonate- (Carb), oxides- (Oxid), organic- (Org) Pb (a) and -Zn (b) fractions at 20, 40 and 60 days of incubation with different concentrations (mmol kg⁻¹ soil) of diethylene triamine penta acetic acid (DTPA), ethylene diamine tetraacetic acid (EDTA) and citric acid with different concentration in sewage sludge treated soil

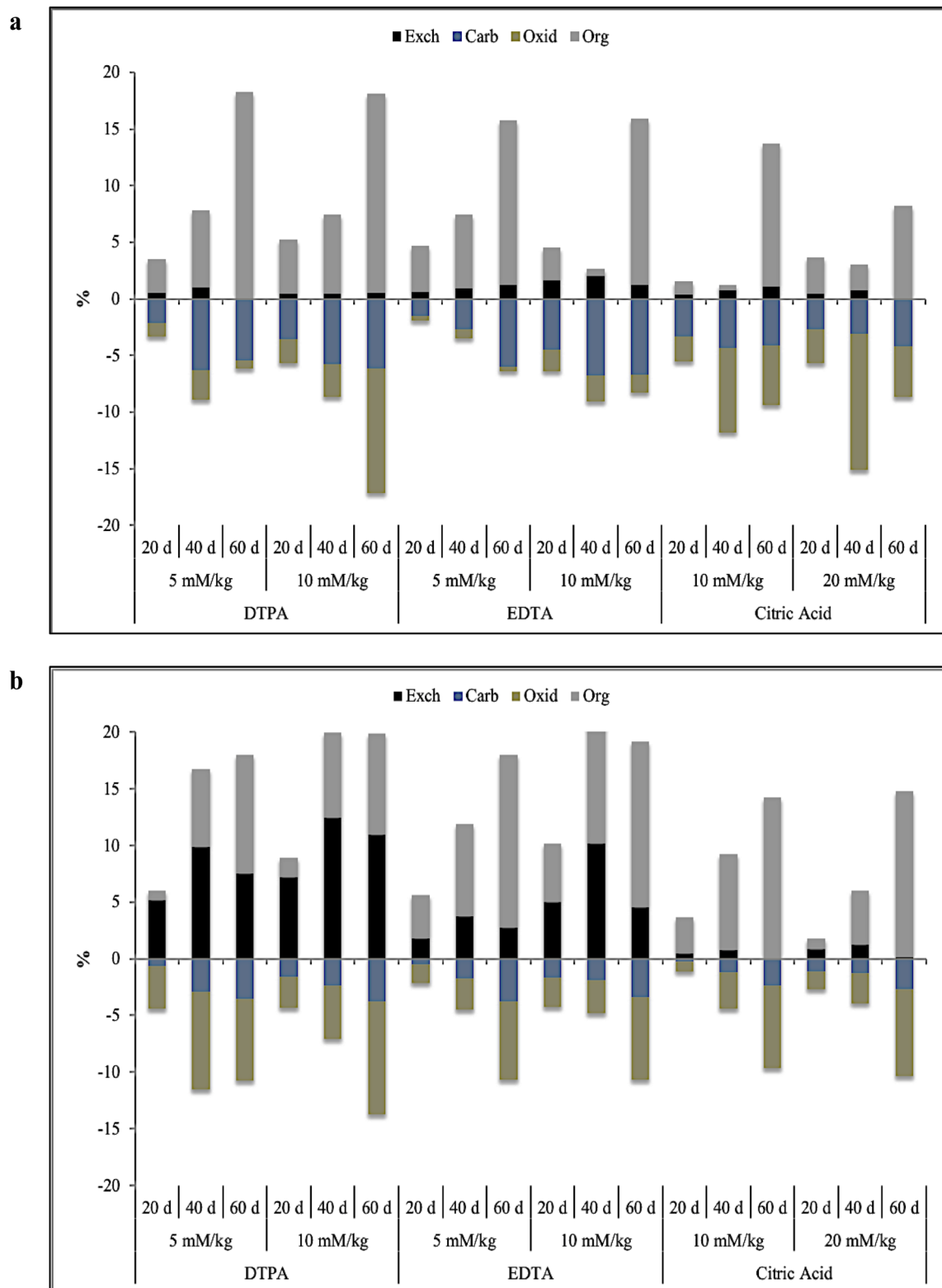


Fig. 2. Percent changes in the exchangeable- (Exch), carbonate- (Carb), oxides- (Oxid), organic- (Org) Pb (a) and -Zn (b) fractions at 20, 40 or 60 days of incubation with different concentrations (mmol kg⁻¹ soil) of diethylene triamine penta acetic acid (DTPA), ethylene diamine tetraacetic acid (EDTA), or citric acid with different concentration in soil contaminated by industrial wastes

Chelate-assisted Phytoextraction of Pb and Zn

The pot experiment showed that, in the SS treated soil, *Amaranthus* was more effective than *Chenopodium* in the phytoextraction of Pb and Zn (Fig. 3). The maximum amounts of Pb and Zn phytoextracted by *Amaranthus* in a 70-d growth period were 6.5 and 8.2 mg kg⁻¹ soil, respectively, whereas the maximum phytoextracted amounts of Pb and Zn by *Chenopodium* were 3.9 and 3.5 mg kg⁻¹ soil, respectively (Fig. 3). Results showed that higher removal of Pb and Zn was obtained by *Amaranthus* after CA, where the removal of Zn was higher than the removal of Pb (8.2 g vs 6.5 mg; Fig. 3), which might be possibly due to the toxic effect of EDTA and DTPA on plant roots. However, CA did not have the same effect with *Chenopodium* as the higher removal of Pb and Zn was observed after EDTA. The uptake of Pb and Zn by *Chenopodium* was similar, whereas *Amaranthus* uptake of Zn was more than for Pb in all cases (Fig. 3).

In the IW soil, *Amaranthus* was not much more efficient than *Chenopodium* in phytoextracting

Pb from the IW contaminated soil (Fig. 4) as it showed in the SS treated soil, however, the largest removal of Pb (2 mg kg⁻¹ soil) was observed with *Amaranthus* assisted with 5 mmol EDTA kg⁻¹ soil. *Chenopodium* extracted less Pb than did *Amaranthus* where the largest (1.5 mg) Pb phytoextraction by *Chenopodium* was observed after EDTA (Fig. 4). *Amaranthus* and *Chenopodium* phytoextracted similar amounts of Zn, specifically 2.2 and 2.5 mg Zn kg⁻¹ soil after EDTA for *Amaranthus* and *Chenopodium*, respectively (Fig. 4).

Amaranthus and *Chenopodium* showed high transfer factor for Pb and Zn from the SS treated soil than from the IW treated soil. The maximum transfer factor for Pb in the SS treated soil was associated with *Amaranthus* treated with EDTA and CA whereas in the IW treated soil the maximum transfer factor was associated with DTPA (Table 2). *Amaranthus* transferred more Zn than did *Chenopodium* with any chelate, yet, the Zn transfer factor was higher with DTPA than with other chelates for both plants.

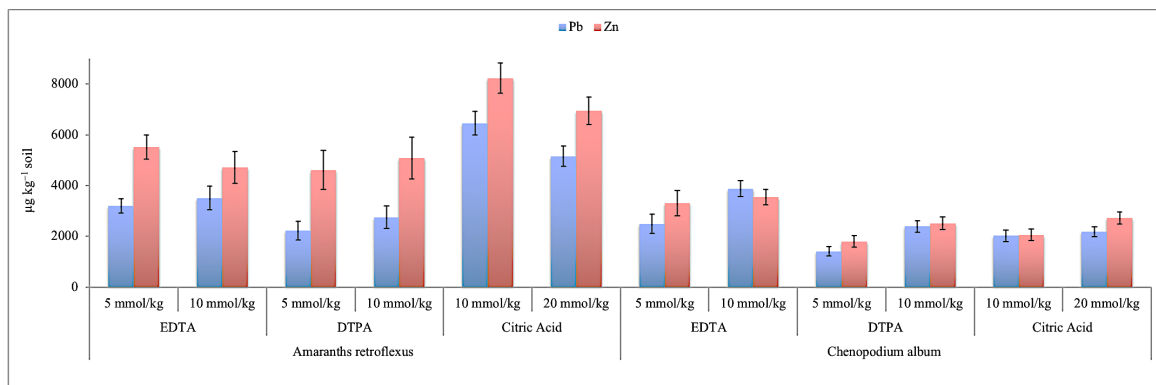


Fig. 3. Total removal of Pb and Zn from sewage sludge treated soil by *Amaranthus retroflexus* L. and *Chenopodium album* L. after treatment with diethylene triamine penta acetic acid (DTPA), ethylene diamine tetraacetic acid (EDTA), and citric acid

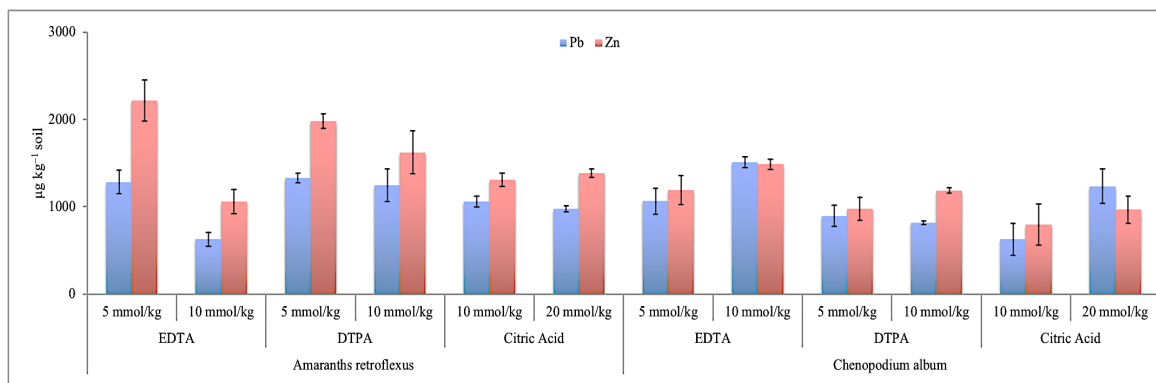


Fig. 4. Total removal of Pb and Zn from industrial waste treated soil by *Amaranthus retroflexus* L. and *Chenopodium album* L. after treatment with diethylene triamine penta acetic acid (DTPA), ethylene diamine tetraacetic acid (EDTA), and citric acid

TABLE 2. The transfer factor of Pb and Zn in plants calculated by dividing the metal concentration in plant tissue by the metal concentration in soil

Chelate	Conc. mmol kg ⁻¹ soil	<i>Amaranthus retroflexus</i> L.		<i>Chenopodium album</i> L.	
		Pb	Zn	Pb	Zn
SS treated soil					
EDTA	5	4	11	3	7
	10	6	11	5	7
DTPA	5	4	12	3	6
	10	4	12	5	8
CA	10	6	11	3	5
	20	5	10	4	7
IW treated soil					
EDTA	5	2	5	2	3
	10	2	5	4	5
DTPA	5	2	5	2	3
	10	4	6	2	4
CA	10	3	4	1	2
	20	2	4	3	3

EDTA: ethylene diamine tetraacetic acid; DTPA: diethylenetriaminepentaacetic acid; CA: citric acid; SS: Sewage sludge treated soils; IW: Industrial wastes contaminated soils.

Amaranthus and *Chenopodium* showed a transfer factor >1 which suggests both plants as a phytostabilizer as was suggested by Garba et al. (2012) for plants with a transfer factor >1. *Amaranthus* showed remarkably higher (up to 12) transfer factor for Zn from SS treated soils.

Conclusion and prospective implications

The study revealed that EDTA and DTPA can be used to change the distribution of Pb and Zn among their fractions in contaminated soils, which might be significant for phytoremediation of Pb and Zn contaminated soils. Chelates were able to remarkably increase the organic bound Pb and exchangeable Zn in sewage sludge- and industrial wastes treated soils. Studied weed species can be used, with chelates, to phytoextract Pb and Zn from contaminated soils. The use of these weed species for phytoremediation should not interrupt the crop production cycles in the studied areas, however, further studies should be performed to estimate the relative obtainable yield in response to associating weed and crop growth during the growing seasons. However, the effect of EDTA and DTPA on the grown crop should be assessed together with the fate of the chelates in the environment, as these chelates are known to have low rates of biodegradation.

Acknowledgement

Elena Vialykh, with the University of Calgary, is acknowledged for performing the statistical repeated measure analysis. Author is thankful for reviewers for their constructive comments and improvements of the manuscript.

References

- Aboulroos, S., Holah, Sh., and Badawy, S. (1989) Influence of prolonged use of sewage effluent in irrigation on heavy metal accumulation in soils and plants. *Z. Pflanzenernahr. Bodenk.*, **152**, 51-5.
- Aikpokpotion, P.E., Lajide, L., and Aiyesanmi, A.F. (2013) Characterization of Heavy Metal Fractions in Agricultural Soils Using Sequential Extraction Technique. *World J. Agr. Sci.*, **9** (1), 45-52.
- Anderson, C., Brooks, R., Stewart, R. and Simcock, R. (1998) *Harvesting a crop of gold in plants. Nature*, **395**, 553-554.
- Bian, X., Cui, J., Tang, B., Yang, L. (2018) Chelant-Induced Phytoextraction of Heavy Metals from Contaminated Soils: A Review. *Polish J. Environ. Stud.*, **27**, 2417-2424.
- Blaylock, M., Salt, D., Dushenkov, S., Zakharova, O., Gussman, C., Kapulnik, Y., Ensley, B., and Raskin, *Egypt. J. Soil. Sci.* **59**, No. 2 (2019)

- I. (1997) Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environ. Sci. Technol.*, **31**, 860 - 865.
- Chahal, D.S., Sharma, B.D., and Singh P.K. (2005) Distribution of forms of zinc and their association with soil properties and uptake in different soil orders in semi-arid soils of Punjab, India. *Commun Soil Sci Plant Anal.*, **36**, 2857-2874.
- Chen, X., Tsz-Fung Wong, J., Mo, W., Man, Y., Wang-Wai Ng, C., and Wong, M. (2015) Ecological Performance of the Restored South East New Territories (SENT) Landfill in Hong Kong (2000–2012). *Land Degrad. Dev.*, **1**, 1-13.
- Chen, Y., Lin, Q., Luo, Y., He, Y., Zhen, S., Yu, Y., Tian, G. and Wong, M. (2003) The role of citric acid on the phytoremediation of heavy metal contaminated soil. *Chemosphere*, **50**, 807-811.
- Cui, Y., Zhu, Y., Zhai, R., Chen, D., Huang, Y., Qui, Y., and Lian, J. (2004) Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. *Env. Int.*, **30**, 785-791.
- Du, Y.J., Liu, S.Y., Liu, Z.B., Chen, L., Zhang, F., Jin, F. (2010) An overview of stabilization/solidification technique for heavy metals contaminated soils. In: Chen Y., Zhan L., Tang X. (Ed.) *Advances in Environmental Geotechnics*. pp. 760-766, Springer, Berlin, Heidelberg.
- Garba, S.T., Santuraki, A.H., Barminas, J.T., Kamai, N. (2012) Ethylenediaminetetraacetic acid (EDTA) assisted phytoextraction of the metals; Cu, Cd, Cr, Ni and Zn by crowfoot grass (*dactyloctenium aegyptium*). *Int. J. Environ. Sci.*, **1**, 1-10.
- Hong, P. and Jiang, W. (2005) Factors in the selection of chelating agents for extraction of lead from contaminated soil: effectiveness, selectivity and recoverability. In: Nowack, B., van Briesen, J. (Ed.), *Biogeochemistry of Chelating Agents, ACS Symposium Series*, vol. **910**. American Chemical Society, pp. 421-431.
- Huang, J. and Cunningham, S. (1996) Lead phytoextraction: species variation in lead uptake and translocation. *New Phytol.*, **134**, 75-84.
- Kabata-Pendias, A., and Pendias H. (1992) Trace Elements in Soils and Plants. Boca Raton, FL, CRC Pres.
- Kamel, M.M., and Khater, H.A. (2004) Studies on some hyperaccumulator plants in Egypt. *Bull. Fac. Agric., Cairo Univ.*, **55**, 661-671.
- Egypt. J. Soil. Sci. **59**, No. 2 (2019)
- Kirkham, M.B., (2000) EDTA-facilitated phytoremediation of soil with heavy metals from sewage sludge. *Int. J. Phytoremediat.*, **2**, 159–172.
- Komárek M., Tlustoš P., Száková J, Chrastný V., and Ettler V. (2007) The use of maize and poplar in chelant-enhanced phytoextraction of lead from contaminated agricultural soils. *Chemosphere*, **67**, 640-651.
- Kumar, N., Bauddha, K., Kumara, S., Dwivedia, N., Singha, D. and Barmanb, S. (2013) Accumulation of metals in weed species grown on the soil contaminated with industrial waste and their phytoremediation potential. *Ecological Engineering*, **61**, 491-495.
- Li, X., Gao, J., Brierley, G., Qiao, Y., Zhang, J. and Yang, Y. (2013) Rangeland degradation on the Qinghai–Tibet Plateau: implications for rehabilitation, Land Degrad. Dev., **24**, 72-80.
- Li, Y., Luo, J., Yu, J., Xia, L., Zhou, C., Cai, L. and Ma, X. (2018) Improvement of the phytoremediation efficiency of *Neyraudia reynaudiana* for lead-zinc mine-contaminated soil under the interactive effect of earthworms and EDTA. *Sci. Reports*, **8**, 6417.
- Licht, L.A., and Isebrands, J.G. (2005) Linking phytoremediated pollutant removal to biomass economic opportunities. *Biomass Bioenergy*, **28**, 203-218.
- Lindsay, W.L, and Norvell, W.A. (1978) Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* **42**, 421-428.
- Liu, X., Nie, J. and Wang, Q. (2002) Research on Lead Uptake and Tolerance in Six Plants. *Acta Phyto.* **26**, 533-537.
- Nejatzadeh-Barandozi, F., and Gholami-Borujeni F. (2014) Effectiveness of Phytoremediation Technologies to Clean Up of Metalloids Using Three Plant Species in Iran. *Water Env. Res.*, **86**, 43-47.
- Orroño D.I., and Lavado R.S. (2009) Distribution of extractable heavy metals in different soil fractions. *Chem. Speciation & Bioavailability*, **21**, 193-198.
- Rai, P.K., Lee, S.S., Zhang, M., Tsang, Y.F., Kim, K-H. (2019) Heavy metals in food crops: Health risks, fate, mechanisms, and management, *Env. Int.*, **125**, 365-385.
- Rulkens, W., Grotenhuis, J. and Tichy, R. (1995) Methods of cleaning contaminated soils and sediments. In: Salomons, W., Förstner, U., Mader, P. (Ed.), *Heavy Metals*. Springer, Berlin, pp. 151-191.

- Saifullah, Meers, E., Qadir, M., de Caritat, P., Tack, F.M., Du Laing, G, Zia M.H. (2009) EDTA-assisted Pb phytoextraction. *Chemosphere*, **74** (10), 1279-1291.
- Singh, N., Ma, L.Q. (2007) Assessing Plants for Phytoremediation of Arsenic-Contaminated Soils. In: Willey N. (eds) *Phytoremediation. Methods in Biotechnology*, vol **23**. Humana Press.
- Stingu, A., Volf, I., Popa, V.I. and Gostin, I., (2012) New approaches concerning the utilization of natural amendments in cadmium phytoremediation. *Ind. Crops Prod.* **35**, 53-60.
- Suchkova, N., Tsiripidis, I., Alifragkis, D., Ganoulis, J., Darakas, E. and Sawidis, Th. (2014) Assessment of phytoremediation potential of native plants during the reclamation of an area affected by sewage sludge. *Ecological Engineering*, **69**, 160-169.
- Suman, J., Uhlak, O., Viktorova, J., and Macek, T. (2018) Phytoextraction of Heavy Metals: A Promising Tool for Clean-Up of Polluted Environment. *Front. Plant Sci.*, **16**, 1476.
- Tandy, S., Bossart, K., Mueller, R., Ritschel, J., Hauser, L., Schulin, R. and Nowack, B. (2004) Extraction of heavy metals from soils using biodegradable chelating agents. *Environ. Sci. Technol.*, **38**, 937-944.
- Tessier, A., Campbell, P.G.C., and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals *Anal. Chem.*, **51** (7), 844-851.
- Yang, Q., Li, Z., Lu, X., Duan, Q., Huang, L., Bi, J. (2018) A review of soil heavy metal pollution from industrial and agricultural regions in China: Pollution and risk assessment, *Sci. Total Environ.* **642**, 690-700.

إعادة توزيع مفصولات الرصاص والزنك، المحفز بالمخليات، في الأراضي الملوثة وتأثيره علي معالجتها

حماده عبدالرحمن

قسم الأراضي - كلية الزراعة - جامعة القاهرة - الجيزة - مصر

أجريت تجربة تم فيها تحضين الأراضي الملوثة لمدة تصل الي ٦٠ يوما مع ٥ او ١٠ ملليمول/كجم تربة من EDTA و DTPA أو ١٠ او ٢٠ ملليمول/كجم تربة من حامض الستريك ثم تم استخدام عرف الديك والزربيح الأخضر في تجربة أصص بالصوبة لاستخلاص الرصاص والزنك من الأراضي الملوثة بهما. أوضحت النتائج ازدياد المفصول العضوي من الرصاص خلال فترة التحضين مع المخليات في كلا من نوعي التربة قيد الدراسة وقد صاحب ذلك تناقص في مفصول الرصاص المرتبط بالأكاسيد والكربونات. وأوضحت النتائج تغيرات مماثلة في مفصولات الزنك في كلا من نوعي التربة خلال فترة التحضين. كانت الـ EDTA أكثر فاعلية في زياده الرصاص المتبادل عند ٤٠ يوما من التحضين بنوعي التربة محل الدراسة كما وجد أن الـ DTPA كانت أكثر فاعلية في زيادة الزنك المتبادل عند ٤٠ يوما من التحضين. وقد بينت تجربة الأصص أن نبات عرف الديك كان أكثر كفاءة من نبات الزربيح الأخضر في استخلاص الرصاص والزنك من الأراضي الملوثة بهما حيث وصلت الكمية المستخلصة من الرصاص والزنك بواسطة نبات عرف الديك الي ٦,٥ و ٨,٥ مجم/كجم تربة، علي التوالي في حين وصلت الكمية المستخلصة بواسطة نبات الزربيح الاخضر الي ٣,٩ و ٣,٥ مجم/كجم تربة من الرصاص والزنك، علي التوالي. علي الرغم من أن EDTA و DTPA كانتا أكثر كفاءة في إعادة توزيع مفصولات الرصاص والزنك خلال فترة التحضين، كان استخدام حامض الستريك أكثر فاعلية في استخلاص الرصاص والزنك بواسطة نبات عرف الديك. مع مراعاة البعد البيئي والاقتصادي يمكن التوصية باستخدام النباتات والمخليات قيد الدراسة لإزالة الرصاص والزنك من الأراضي الملوثة بهما.