Zinc desorption kinetics in wheat (*Triticum Aestivum* L.) rhizosphere in some sewage sludge amended soils

H.R. Motaghian[1*], A.R. Hosseinpur[1]

[1] Department of Soil Science, College of Agriculture, Shahrekord University, Shahrekord, Iran. *Corresponding author: hrm_61@ yahoo.com

Abstract

The objectives of this study were to determine Zn desorption characteristics and the correlation of these parameters with Zn extracted by DTPA-TEA method in bulk and rhizosphere amended soils with sewage sludge under greenhouse conditions by using a rhizobox. For amended soils 10 g of sewage sludge was added to 1 kg of 10 soil samples. The kinetics of Zn desorption in bulk and rhizosphere was determined by successive extraction with DTPA-TEA in a period of 1 to 504 h at 25 ± 1 ^{0}C. The results showed that Zn extracted using successive extraction in the rhizosphere were significantly ($p<0.01$) higher than in the bulk amended soils. The best model for describing extraction data for bulk and rhizosphere soils was the power function equation. The results indicated that Zn desorption rate in the wheat rhizosphere soils more than bulk soils. The results showed that significant correlation ($p<0.05$) between Zn desorption characteristics and DTPA-TEA-Zn were found in the bulk and rhizosphere soils. The results of this research revealed that Zn desorption characteristics that are help to estimate the Zn supplying power of soils in the wheat rhizosphere, are quite different than bulk amended with sewage sludge.

Keywords: Calcareous soils, DTPA-TEA, power function, rhizosphere, successive extraction

1. Introduction

Chemical extractive schemes have been largely proposed for assessing the pools of metal such as zinc (Zn) in the soil solid phase (Young *et al.*, 2006). Single extraction provides a simple approach for estimating the mobile pool (Mocko and Waclawek, 2004; Young *et al.*, 2006; Manouchehri and Bermond, 2009). Two chelating agents, DTPA (Diethylene three aminepenta aceticacid) and EDTA (ethylene diaminetetra aceticacid), routinely used to estimate available-Zn in soil (Lindsay and Cox, 1985) provide only a static measure of Zn availability

to plants. Since DTPA and EDTA chelate Zn, and maintain low Zn ion concentrations in soil solution, thus to an extent simulating Zn adsorption by roots of growing plants, the rate of Zn desorption from soil by DTPA or EDTA should provide a measure of a rate factor of Zn availability (Dang *et al.*,1994). This is especially important in calcareous soils, which generally contain quite large quantities of total Zn, but have only very small quantities of Zn in soil solution (Reyhanitabar and Gilkes, 2010), and thus the rate of

Zn release in the soil largely determines Zn availability to plants. Moreover, in most of these methods, the metal concentration is measured at equilibrium whereas natural systems are generally subject to changing conditions and are practically never at the equilibrium. Indeed, for these dynamic systems, the metal availability may be believed to be controlled by kinetic factors (Errecalde *et al.*, 1998; Ma *et al.*, 1999; Slaveykova *et al.*, 2003).

Reyhanitabar and Gilkes (2010) studded the kinetics of Zn extraction by DTPA from 12 calcareous soils of Iran for 0.25 to 192 h. They reported that the best model for describing extraction data for all soils was the exponential rate equation. However, other equations have been proposed for describing release kinetics and they may provide better descriptions of Zn extraction from soil (Sparks 1986).

The rhizosphere is defined as volume of soil affected by the presence of the roots of growing plants (Uren, 2007). The conditions at the rhizosphere are considerably different from those existing some distance from root system (Nye, 1981). Plants have the ability to transform metal fractions for easier uptake through root exudation or pH changes in the rhizosphere (Hinsinger, 2001; Wang *et al*., 2002). The soil properties, metal fractions, plant species and especially soil - plant interactions determine the bioavailability of metals in soils (Ehlken and Kirchner, 2002). Low-molecular-weight organic acids are exudates by plant roots and products of fungi and bacteria activity which desorption in the rhizosphere. Furthermore, there is increasing evidence that low-molecular-weight organic acids play an important role in supplying metals to roots, especially in metal deficient soils, and enhancing the uptake of metals by plants (Shan *et al.*, 2002). Therefore, study of kinetics desorption Zn in soils especially in the rhizosphere that is important environmental zone with quite different chemical properties gives information about potential of soils to supplying Zn for plant uptake.   Sewage sludge have been increasingly used in numerous countries around the world as fertilizers on farm lands because of their high content of organic matter and essential nutrients that favor crop growth (Renoux *et al.*, 2007). Sewage sludge is an important source of nutrients such as Zn. When soil is amended with sewage sludge a new source of heavy metals has been introduced. Therefore, it is necessary to determine the kinetics of Zn desorption in amended soils with sewage sludge to understand how it may influence soil Zn availability.

Study of kinetics Zn desorption in the rhizosphere amended soils with sewage sludge hasn't been carried out. Therefore, the objectives of the present study were (i) to evaluate the Zn desorption from bulk and rhizosphere soils amended with sewage sludge (ii) to evaluate different mathematical models for describing Zn desorption and (iii) to examine the relationship of Zn desorption rate obtained in the kinetics studies with conventional soil test method.

2. Materials and Methods

Ten soil samples used in this study were collected from the surface soils (0-30 cm) of Chaharmahal-Va-Bakhtiari province, in Central Iran. The soil samples were air dried and ground to pass through a 2 mm sieve for laboratory analysis. Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). Electrical conductivity (EC) was determined in 1 to 2, soil to water ratio by conductivity meter (Rhoades, 1996) and pH was measured in a soil to water ratio of 1:2 (Thomas, 1996). Organic carbon was determined by wet oxidation (Nelson and Sommers, 1996), equivalent calcium carbonate was determined by titration (Loeppert and Suarez 1996) and cation exchange capacity of the soils were determined by the 1 M NaOAC, at pH 7 (Sumner and Miller, 1996). Total Zn was determined using 4 M HNO_3 (Sposito *et al.*, 1982).

Solid sewage sludge was used from the refinery of Shahrekord city, central Iran. Sewage sludge were air-dried and ground to pass through a 1 mm sieve.
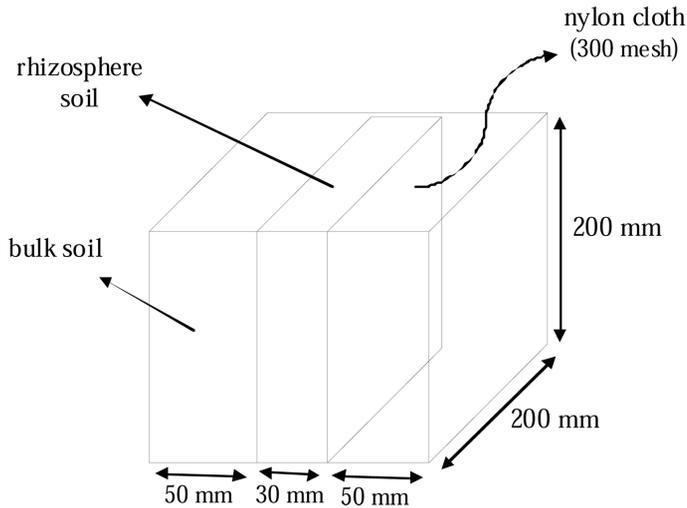
Figure 1. Sketch of a rhizobox used in this study

Properties of sewage sludge such as pH (soil to water suspension ratio of 1:5) (Thomas, 1996) and electrical conductivity (1 to 5, soil to water by conductivity meter), (Rhoades, 1996) were determined. Total and available Zn were determined using 4 M HNO_3 (Sposito *et al.*, 1982) and DTPA-TEA (Lindsay and Norvell, 1978), respectively.

A homemade rhizobox (Figure 1) (Wang *et al.* 2002) was used to plant wheat. The dimension of the rhizobox was 200mm × 130mm × 200mm (length × width × height). The rhizobox was divided into three sections: a central zone or rhizosphere zone (30mm in length), which was surround by nylon cloth (300 mesh), and left and right nonrhizosphere zones (bulk soil) (50 mm in length).

For amended soils, 1% (w/w) of sewage sludge was added to soils, and then soil samples were incubated at field capacity, for 1 month. After incubation, soils were air-dried. Wheat (*Triticum aestivum* L.) seeds were thoroughly rinsed with water and surface-sterilized by soaking in a mixture of NaClO (3%), and germinated on a filter paper. After the wheat seeds were germinated

for 24 h at 20 ^{0}C in the dark, uniformly germinated seeds with radical emerged were sown in the soil, which had been left in the rhizobox to equilibrate overnight. A total of 5 seeds were sown per rhizosphere zone and subsequently thinned to 3 plants. Plants were grown under greenhouse conditions. The temperature ranged from 20 to 25 ^{0}C during the day and 15 to 20 ^{0}C during the night. Plants were harvested 8 weeks after germination. The aboveground parts of the plants were first harvested as shoots. The rhizobox was then dismantled. The roots were found completely in the central zone. The rhizosphere soil was sieved gently to remove the roots by keeping the root mass intact as much as possible. Rootlets that passed through the sieve were subsequently removed with a pair of tweezers. The soils taken from two rhizosphere zone and a bulk soil (zones of the left and right) were mixed separately for further analysis.

For bulk soil and rhizosphere soil samples analyses were triplicated. The DTPA- TEA method (Lindsay and Norvell, 1978) was used for Zn extraction in the bulk and rhizosphere amended soils. Then concentrations of Zn were determined using an

atomic absorption spectrophotometer (model G.B.C. 932). Dissolved organic carbon (DOC) was extracted from the fresh soil samples using double-deionized water with a soil to water ratio of 1:2 (Corre *et al.*, 1999). The suspensions were shaken for 2 h at room temperature and then centrifuged at 2500g for 5 min. The extracts were filtered on nylon 0.45 μm filters. Finally, the DOC content was assayed using Walkley and Black method (Nelson and Sommers, 1996). Soil microbial biomass carbon was estimated by the chloroform-fumigation incubation method, adapted from Jenkinson and Powlson (1976).

Kinetics of Zn desorption was studied by successive extraction with DTPA-TEA solution. Two grams of the bulk and rhizosphere soils, in triplicate, suspended in 20 ml of DTPA-TEA solution were equilibrated at $25 \pm 10C$ for 1, 8, 24, 48, 72, 96, 120, 144, 168, 336 and 504 h by shaking for 15 min. before incubation and 15 min. before the suspensions were centrifuged. The supernatant liquid was measured for Zn by an atomic absorption spectrophotometer (model G.B.C 932). Zn desorption with time was fitted by using different equations (Table 1).

Table 1. Kinetic models used in this study

Kinetic equation	Expression form [a]	Reference(s)
Zero-order reaction	$(Zn_0 - Zn_t) = a - K_0 \, t$	Martin and Sparks,1983
First-order reaction	$\ln (Zn_0 - Zn_t) = a - K_1 \, t$	Martin and Sparks,1983
Parabolic diffusion	$Zn_t = a + R \, t^{0.5}$	Havlin *et al.* 1985; Sparks,1985;
Power function	$\ln Zn_t = \ln a + b \, \ln t$	Havlin *et al.* 1985
Simplified Elovich	$Zn_t = a + 1/\beta \, \ln t$	Havlin *et al.* 1985; Sparks 1985;

[a] Zn_0: amount of Zn (mg kg^{-1}) desorption at 504 h., Zn_t: amount of Zn (mg kg^{-1}) desorption at time t (h) and a and K_0, K_1, R,
[b]   and $1/\beta$ are constants.

Five models were tested by the least-square regression analysis to determine which equation described better the Zn desorption from the soils. Standard error of the estimate (SE) was calculated by:

$$SE = \left[\frac{\sum (Zn - Zn^*)^2}{(n-2)} \right]^{0.5}$$

where Zn and Zn* represent the measured and calculated amounts of Zn in soil at time t, respectively, and n is the number of data points evaluated.

The rate constant of Zn desorption from soils were calculated on the basis of these models.

The significant differences of dissolved organic carbon, microbial biomass carbon, extracted Zn and amount Zn desorption between rhizosphere and bulk soils were determined by using paired-samples t-test. The Pearson's correlation between concentrations of available-Zn and amount of Zn desorption and Zn desorption characteristics were determined. Statistical analysis of the data was performed using SPSS 17.0.

3. Results and Discussion

Properties of the soils are presented in Table 2. This results show that there was a wide variation in the selected chemical and physical properties of the soils. The mean of clay contents was 44 g kg^{-1}. The soils were alkaline and low in EC and organic matter. The pH

ranged from 7.6 to 8.1. The EC ranged from 0.12 to 0.25 dS m^{-1}. The OC ranged from 3.0 to 11.9 g kg^{-1}. The equivalent calcium carbonate contents varied from 113 to 410 g kg^{-1}. The CEC ranged from 11.5 to 22.5 cmol$_c$ kg^{-1}. The total Zn in all soils ranged from 34 to 58 mg kg^{-1}. Amount of Zn extracted using DTPA-TEA ranged from 0.28-1.39 mg kg^{-1}.

Table 2. Selected properties of soils

Soil no.	clay	silt	CaCO$_3$	OC	pH	EC (dS m^{-1})	CEC (cmol$_c$ kg^{-1})	Total Zn (mg kg^{-1})	DTPA-TEA- Zn (mg kg^{-1})
			(g kg^{-1})						
1	550	400	287	7.2	7.8	0.13	20.9	57	0.50
2	530	440	356	3.0	8.1	0.13	19.3	54	0.45
3	490	390	294	5.1	7.9	0.12	22.5	45	0.28
4	460	420	264	7.1	7.8	0.14	21.6	45	0.57
5	410	420	322	5.4	8.1	0.13	16.0	37	0.47
6	370	440	325	8.0	7.6	0.16	15.6	44	0.60
7	250	330	410	4.7	7.7	0.21	11.5	34	0.69
8	380	550	231	11.9	8.1	0.24	17.9	58	0.81
9	480	460	113	11.6	7.8	0.25	18.5	54	1.39
10	490	460	148	9.7	7.9	0.23	17.9	56	0.56

Value of pH of solid sewage sludge was 7.5. Electrical conductivity was 2.25 dS m^{-1}. Also, the available and total concentrations of Zn were 558 and 1321 mg kg^{-1}, respectively.

The DOC and MBC in the wheat rhizosphere compare to the bulk soils were increased significantly ($p<0.05$) with respect to the bulk in each soil (Table 2). The DOC ranged from 47-106 mg C L^{-1} in the wheat rhizosphere, while it ranged from 32-91 mg C L^{-1} in the bulk soils. In the wheat rhizosphere the MBC ranged from 333-940 mg C kg^{-1}, while it ranged from 235-735 mg C kg^{-1} in the bulk soils. The R/S ratio of DOC ranged from 6-67% and R/S ratio of MBC ranged from 13-104%.

The results illustrated that properties of rhizosphere soils was different camper to bulk soils. Irrespective of soil type there was a significant ($p< 0.01$) increase in DOC in the rhizosphere. The concentration of DOC in the rhizosphere can be affected by both plant root exudates and microbial activities. The results showed that in the rhizosphere soils correlation between DOC and MBC was significant (r= 0.69*), its correlation wasn't significant in the bulk soils (r=0.59, $p> 0.05$).

The overall effect of plant-microbe interaction is an increase in microbial biomass in the rhizosphere, owing to the high supply of organic carbon by roots and soils (Lynch and Whipps, 1990). Kim *et al.* (2010)

reported that bacterial populations and DOC were higher in the rhizosphere soils than that in bulk soils. They stated that DOC increase in the rhizosphere could be due to both plant root exudates and microbial populations. Also, they reported that correlation between number of bacterial colony and concentration of DOC in the rhizosphere after plant culture was significant ($p< 0.01$). Plant roots release a considerable amount of organic materials, including water soluble exudates (sugars, organic acids, and amino acids) and water insoluble materials such as cell walls, sloughed material and mucilage into soil. Many of these materials are readily degraded by soil microorganisms, but their continuous release maintains the organic matter concentration at higher levels than in bulk soil (Lombi *et al.*, 2001). It is well known that the root exudates serve as carbon source to heterotrophic microbial populations. Results of table 3 showed that Zn extracted using DTPA-TEA in the rhizosphere were significantly ($p<0.05$) higher than in the bulk soils. The Zn extracted using DTPA-TEA in the rhizosphere and bulk soils ranged from 3.29-5.51 and 3.23-4.84 mg kg^{-1} respectively.

Table 3. DOC, MBC and extracted Zn by DTPA-TEA determined in the rhizosphere and bulk soils

Soil	DOC (mg C L^{-1})			MBC (mg C kg^{-1})			DTPA-TEA-Zn (mg kg^{-1})	
No.	rhizosphere	bulk	R/S (%)	rhizosphere	bulk	R/S (%)	rhizosphere	bulk
1	71a	65b	9	686a	416b	65	3.64a	3.62a
2	54a	32b	69	333a	294b	13	3.76a	3.23b
3	47a	36b	31	480a	235b	104	3.29a	3.09a
4	102a	88b	16	784a	490b	60	3.92a	3.81a
5	55a	33b	67	549a	323b	70	4.04a	3.82b
6	57a	41b	39	578a	460b	26	4.30a	4.27a
7	53a	50b	6	696a	343b	103	5.16a	4.68b
8	106a	83b	28	715a	431b	66	5.31a	4.20b
9	104a	91b	14	940a	735b	28	5.51a	4.84b
10	99a	86b	15	584a	277b	111	4.61a	4.05b
mean	74A	61B	21	703A	449B	57	4.35A	3.98B

R/S (%): (amount of property in the rhizosphere to the bulk)-1 × 100 Means in each row and final row for different properties followed by the different letters are significantly different ($p<0.05$).

The pattern of successive extraction of Zn from the bulk and rhizosphere of soil no. 2 and 9 in DTPA-TEA solution is presented in Figure 2. Also, other soils show same trend similar to soil no. 2 and 9. Amounts of Zn desorption from the bulk and rhizosphere soils are given in Table 4. The results of this table showed that Zn extracted using successive extraction in the wheat rhizosphere were significantly ($p<0.01$) higher than bulk soils. The amounts of Zn desorption after 504 h of extraction period ranged from 14.29 (no. 3) to 18.66 (no. 9) mg kg^{-1} in the bulk soils, and ranged from 14.59 (no. 3) to 22.11 (no. 9) mg kg^{-1} in the rhizosphere soils. The soil no. 9 has CaCO$_3$ equivalent of 11.3% that may be accounted for the increase in Zn desorption compared to other studied soils. A possible explanation for the increase of extracted Zn in the rhizosphere could be the complex Zn with soluble exudates in the rhizosphere soils (Bernal and McGrath, 1994). Moreover, microbial growth in the rhizosphere might be stimulated by the continual input of readily assimilable organic substrates from the root which account, at least partly, for the increase of extractable Zn.

Different mathematical models (Table 1) were tested for their suitability to describe the Zn desorption from different soils including bulk and rhizosphere soils. Comparisons of R^2 and SE values (Table 5) indicated that the power function, parabolic diffusion, simplified Elovich and first order equations were described the reaction rates fairy well, as evidenced by the high coefficients of determination values and low standard error of the estimate. The regression relationships between Zn desorption and the time for the bulk and rhizosphere soil no. 9 as described by the simplified Elovich, parabolic diffusion, power function and first order equations are shown in Figure 3. In the bulk amended soils power function ($R^2=0.994$, SE=0.288 mg kg^{-1}) had the highest determination coefficients and the lowest standard error of the estimate and could describe Zn desorption. Also, parabolic diffusion ($R^2=0.950$, SE=0.661 mg kg^{-1}), simplified Elovich ($R^2=0.950$, SE=0.731 mg kg^{-1}) and first order ($R^2=0.960$, SE=1.005 mg kg^{-1}) models could well describe Zn desorption. In the rhizosphere amended soils power

function ($R^2=0.994$, SE=0.291 mg kg^{-1}) had the highest determination coefficients and the lowest standard error of the estimate and could describe Zn desorption. Also, parabolic diffusion ($R^2=0.956$, SE=0.723 mg kg^{-1}), simplified Elovich ($R^2=0.948$, SE=0.886 mg kg^{-1}) models could well describe Zn desorption. Therefore, the best model to describe the Zn desorption of bulk and rhizosphere soils was the power function equation. Also, Reyhanitabar and Gilkes (2010) reported that the best model for describing release Zn using DTPA-TEA was the exponential rate equation. Dang *et al*. (1994) tested different kinetics models to describe Zn desorption from Vertisols. Among the used models power function, parabolic diffusion and Elovich were chosen as the suitable models while the first, second, and the third order kinetics showed weaker fitness for the data. Pavlatou and Polyzopoulos (1988) proposed that the Elovich equation applies to desorption reactions, which are kinetically controlled by diffusion. This is evidenced by the close relationship between overall diffusion constants. Some of researcher reported that a parabolic diffusion model well described the interactions of metals with soils and soils constituents, the weathering of feldspars and the interactions of pesticides in soil (Garcia-Rodja and Gil-stores 1997).

There was a wide variation in the Zn desorption characteristics between bulk and rhizosphere soils. Desorption rate constants and intercept of Zn for four models are given in Table 6. In the bulk soils the fit of the data to power function yielded a straight line. The constant b ranged from 0.192 (soil 7) to 0.236 (soil 2) (mg kg^{-1})$^{-1}$. The constant a ranged from 3.35 (soil 2) to 5.00 (soil 7) mg kg^{-1} h^{-1}. Cumulative Zn desorption was fitted to parabolic diffusion equation. The Zn desorption rates (R) range from 0.519 (soil 3) to 0.728 (soil 9) mg kg^{-1} h$^{-1/2}$ in DTPA-TEA solution. Cumulative Zn desorption was fitted to the simplified Elovich equation. The constant $1/\beta$ ranged from 1.41 (soil 1) to 2.12 (soil 9) mg kg^{-1} h^{-1}. In bulk amended soils fit of the data to first order equation yielded a straight line. The constant K1 ranged from 53.31×10-4 (soil 3) to 61.96×10-4 (soil 9) (mgkg^{-1})$^{-1}$.
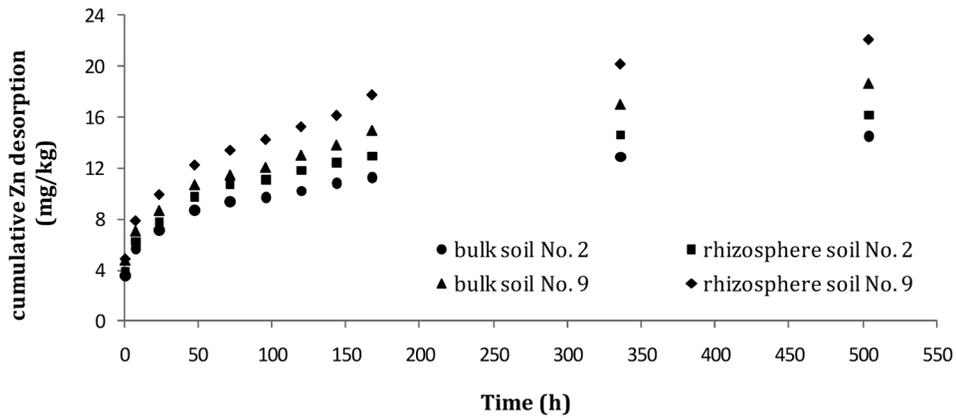
Figure 2. Cumulative amount of Zn desorption with time in soil No. 2 and 9 by successive extractions with DTPA-TEA.

Table 4. Concentration of Zn desorption (mg/kg) the bulk and the rhizosphere soils

Soil no.	Bulk	Rhizosphere
1	14.34b	15.51a
2	14.51b	16.16a
3	14.29b	14.59a
4	15.47b	15.83a
5	15.07b	15.27a
6	15.83b	16.58a
7	17.03b	17.95a
8	18.20b	19.25a
9	18.66b	22.11a
10	17.42b	18.56a
mean	15.97 B	17.18 A

Means in final row followed by the different letters are significantly different ($p<0.01$).
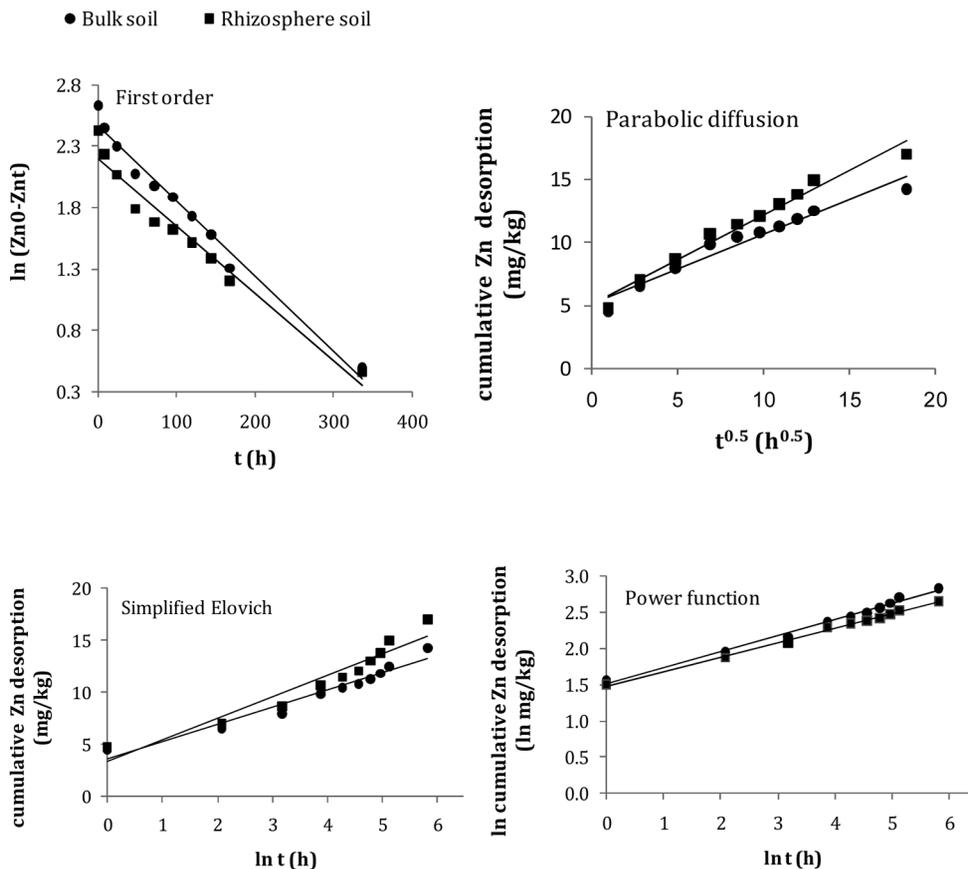
Figure 3. Cumulative Zn desorption (mg kg^{-1}) described by the four mathematical models for soil 9.

In the rhizosphere soils the fit of the data to power function yielded a straight line. The constant b ranged from 0.184 (soil 7) to 0.234 (soil 2) (mg kg^{-1})[-1]. The constant a can ranged from 3.69 (soil 3) to 5.54 (soil 7) mg kg^{-1} h^{-1}. Cumulative Zn desorption was fitted to parabolic diffusion equation. The Zn desorption rates range from 0.522 (soil 3) to 0.863 (soil 9) mg kg^{-1} h[-1/2] in DTPA-TEA solution. Cumulative Zn desorption was fitted to the simplified Elovich equation. The constant b ranged from 1.56 (soil 1) to 2.50 (soil 9) mg kg^{-1} h^{-1}.

The constant K1 ranged from 53.14×10^{-4} (soil 3) to 62.39×10^{-4} (soil 9) (mg kg^{-1})[-1]. The difference between Desorption rate constants indicates that Zn supplying power of the amended soils is different in the rhizosphere and bulk soils. The values of constants a and b vary widely for different soil types. The constant b in simplified Elovich, parabolic diffusion and first order equations has been introduced an index of Zn desorption rates in soils. These results showed that Zn desorption rate in the wheat rhizosphere soils more than bulk soils.

Table 5. Coefficient of determination (R^2) and standard error of the estimate (SE) of various kinetic models for Zn desorption in studied soils

soil		Zero-order		First-order		Parabolic diffusion		Simplified Elovich		Power function	
		range	mean	range	mean	range	mean	range	mean	range	mean
Bulk	R^2	0.699-0.858	0.768	0.922-0.979	0.960	0.919-0.972	0.950	0.922-0.977	0.950	0.987-0.997	0.994
	SE	1.363-2.890	1.738	0.467-2.220	1.005	0.501-0.742	0.661	0.388-1.082	0.731	0.195-0.430	0.288
Rhizosphere	R^2	0.731-0.848	0.779	0.948-0.982	0.964	0.939-0.976	0.956	0.914-0.964	0.948	0.986-0.998	0.994
	SE	1.508-7.700	2.928	0.690-7.226	2.423	0.550-0.858	0.723	0.564-1.736	0.886	0.150-0.601	0.291

SE, mg kg^{-1}. All coefficients of determination (R^2) are significant at the 0.01 level.

The parameter b in power function was less than 1 in all bulk and rhizosphere soils, indicating the Zn desorption rates were decreasing with time. Reyhanitabar and Gilkes (2010) stated that the constant a in the power function may indicate the number of surface sites available for desorption of Zn. Also, the constant b is a measure of the affinity of Zn for these sites with increasing affinity of sites being indicated by the value of 1/b. On the other word, an increase in the value of a decrease in the value of b probably indicates an increase in the rate of Zn desorption from the soils with DTPA (Dang *et al.* 1994). In the wheat rhizosphere soils the constant a increased and b constant decreased than bulk soils (Table 6). Therefore the initial Zn desorption rate in the wheat rhizosphere soils was more than bulk soils. Dang *et al.* (1994) reported that the b values ≤ 0.25 indicate more than a single diffusion rate of Zn, as suggested by the applicability of the parabolic double diffusion equation. Therefore in the bulk and rhizosphere soils

with sewage sludge one diffusion mechanism were involved. Dang *et al.* (1994) concluded that more than one diffusion mechanism such as diffusion from macroaggregates and microaggregates can be involved, or that the energies of Zn desorption increase exponentially or as a power function as Zn is desorbed by DTPA from soil solids and diffuses into the soil solution.

The different chemical and biological conditions of the rhizosphere with respect to the bulk soil can change metal fractions and therefore bioavailability of metals (Dessureault-Rompre *et al.*, 2008; Tao *et al.*, 2003). Moreover, low-molecular-weight organic acids produced by plant roots exudation and bacterial metabolism are involved in many processes operating in the rhizosphere, including nutrient acquisition, metal detoxification, and alleviation of anaerobic stress in roots (Jones, 1998). Through their acidification, chelating and oxidation-reduction reaction in the rhizosphere, they can affect the

speciation and transportation of Zn in the rhizosphere soil. Qin *et al*. (2004) demonstrated that various low-molecular-weight organic acids were able to influence the rate of heavy metals from different soils and increase the solubility of heavy metals through the formation of metal - organic complexes. Due to the effect of low-molecular-weight organic acids in the rhizosphere, the bioavailability of Zn in the rhizosphere is different from that in the bulk soil. Moreover citric acid is very common in natural environments, especially in the rhizosphere soils, and usually ranges from 10-5 to 10-3 M (Robert and Berthelin, 1986). The presence of citrate ligands during the formation of Fe oxides can significantly modify the structural and surface properties of the Fe oxides formed. These surface properties include surface area, surface porosity, surface charge, and surface geometry (Liu and Huang, 2003). The surface of Fe oxides is the region of their interaction with the soil solution and with other solid

phases, plant roots, and the soil biota (Schwertmann and Taylor, 1989). Correlations between the Zn desorption characteristics with Zn extracted using DTPATEA are shown in Table 7. The results of this Table showed that in the bulk and rhizosphere soils correlation between the rate constant values of parabolic diffusion, simplified Elovich and first order equations and $a \times b$ in power function with Zn extracted using DTPA-TEA were significantly. Also, significant correlation between the a value in power function and first order equations with extracted Zn using DTPA-TEA were found. Probably the best supporting evidence for any equation used to describe the kinetics of Zn desorption is the investigation of relation between the constants of any equation with extracted Zn by routine extractant. Therefore, Zn desorption characteristics including constants of equations can be used to evaluate the Zn supplying power of amended soils.

Table 6. Parameters of models used to describe desorption kinetics of Zn in bulk and rhizosphere soils

Soil no.	First-order		Simplified Elovich		Parabolic diffusion		power function	
	a $mg\ kg^{-1}\ h$	$K1 \times 10^{-4}$ $(mg\ kg^{-1})^{-1}$	a $mg\ kg^{-1}$	$1/\beta$ $mg\ kg^{-1}\ h^{-1}$	a $mg\ kg^{-1}$	R $mg\ kg^{-1}\ h^{-1/2}$	a $mg\ kg^{-1}\ h^{-1}$	b $(mg\ kg^{-1})^{-1}$
				Bulk				
1	1.94	53.41	3.15	1.41	4.58	0.457	3.75	0.202
2	2.13	53.51	2.57	1.64	4.18	0.536	3.35	0.236
3	2.13	53.31	2.61	1.52	4.14	0.519	3.38	0.230
4	2.19	54.65	3.39	1.61	4.85	0.541	4.20	0.201
5	2.19	57.12	2.86	1.68	4.43	0.557	3.71	0.223
6	2.25	57.36	3.02	1.73	4.56	0.585	3.97	0.217
7	2.53	58.21	4.14	1.77	5.77	0.593	5.00	0.192
8	2.41	60.25	3.27	2.06	5.14	0.689	4.36	0.228
9	2.48	61.96	3.05	2.12	4.84	0.728	4.34	0.230
10	2.36	59.32	3.46	1.89	5.13	0.640	4.48	0.213
				Rhizosphere				
1	2.16	53.90	3.53	1.62	5.05	0.539	4.31	0.199
2	2.24	58.40	2.88	1.87	4.68	0.618	3.85	0.234
3	2.15	53.14	2.92	1.56	4.39	0.522	3.69	0.215
4	2.20	54.85	3.58	1.66	5.11	0.552	4.38	0.200
5	2.17	57.10	3.92	1.69	4.82	0.549	4.12	0.207
6	2.23	60.21	3.21	1.81	4.78	0.616	4.20	0.215
7	2.28	58.57	4.70	1.83	6.40	0.608	5.54	0.184
8	2.44	61.63	3.76	2.15	5.69	0.724	4.93	0.217
9	2.66	62.39	3.58	2.50	5.64	0.863	5.12	0.229
10	2.39	59.42	3.91	2.01	5.71	0.676	4.95	0.208

Table 7. Correlation between the Zn desorption characteristics with Zn extracted using DTPA-TEA

models		Zn-DTPA-TEA	
		Bulk	Rhizosphere
Power function	a	0.85**	0.89**
	b	-0.29 ns	-0.30 ns
	a×b	0.85**	0.95**
Parabolic diffusion	a	0.75*	0.85**
	R	0.75*	0.84**
Simplified Elovich	a	0.65*	0.60ns
	1/β	0.72*	0.84**
First-order	a	0.84**	0.84**
	K_1	0.89**	0.86**
Zn desorption		0.82**	0.92**

** Significant at the 0.01 level, * Significant at the 0.05 level, and ns Not significant.

Conclusion

In this study Zn desorption characteristics and the correlation of these parameters with Zn extracted by DTPA-TEA in the bulk and rhizosphere amended soils with sewage sludge in greenhouse conditions were determined. The results showed that Zn extracted using DTPA-TEA in the rhizosphere were significantly higher than Zn extracted using this extractant in the bulk soils. The results showed that Zn extracted using successive extraction in the wheat rhizosphere were significantly higher than bulk soils. The best models for describing extraction data for all soils were the power function, parabolic diffusion, simplified Elovich equations in bulk and rhizosphere amended soils. The results indicated Zn desorption rate in the wheat rhizosphere soils more than the bulk soils. In bulk and rhizosphere soils significant correlation between determine Zn desorption characteristics and Zn desorption with extracted Zn using DTPA-TEA were found. Result indicated that after plant growth the soil which related to root is changed. So, this part of soil is different from others and must be considered in soil fertility studies.

References

Bernal M.P., McGrath S.P. 1994. Effects of pH and heavy metal concentrations in solution culture on the proton release, growth and elemental composition of Alyssum murale and *Raphanus sativus* L. Plant Soil. 166, 83-92.

Corre, M.D., Schnabel, R.R., Shaffer, J.A. 1999. Evaluation of soil organic carbon under forests, cool-season and warm-season grasses in the northeastern US. Soil. Biol. Biochem. 31,1531-1539.

Dang, Y.P., Dalal, R.S., Edwards, D.G., Tiller, K.G. 1994. Kinetics of zinc desorption from Vertisols. Soil Sci. Soc. Am. J. 58, 1392-1399.

Dessureault-Rompre, J., Nowack, B., Schulin, R., Tercier-Waeber, M.L., Luster, J. 2008. Metal solubility and speciation in the rhizosphere of *Lupinus albus* cluster roots. Environ. Sci. Technol. 42, 7146-7151.

Ehlken, S., Kirchner, G. 2002. Environmental processes affecting plant root uptake of radioactive trace elements and variability of transfer factor data. A review. J. Environ. Radioactiv. 58, 97-112.

Errecalde, O., Seidl, M., Campbell, P.G.C. 1998. Influence of a low molecular weight metabolite (citrate) on the toxicity of cadmium and zinc to the unicellular green alga *Selenastrum Capricornutum*: an exception to the free ion model. Water Res. 32(2), 419-429.

Garcia-Rodja, I., Gil-Stores, I.F. 1997. Prediction of parameters describing phosphorus-desorption kinetics in soils of Galicia (Northwest Spain). Environ. Qual. 26, 1363-1369.

Gee, G.W., Bauder, J.W. 1986. Particle size analysis, In: A. Klute, (ed). Methods of Soil Analysis. Part 1. 2nd edition. Agron. Monogr. 9. ASA and SSSA, Madison, WI. pp. 404-407.

Havlin, J.L., Westfall, D.G., Olsen, S.R. 1985. Mathematical models for potassium release kinetics in calcareous soils. Soil Sci. Soc. Am. J. 49, 371-376.

Hinsinger, P. 2001. Bioavailability of trace elements as related to root-induced chemical changes in the rhizosphere. In: G. R. Gobran, W. W. Wenzel, E. Lomb, (eds). Trace Elements in the Rhizosphere. CRC Press, Boca Raton. pp. 25-40.

Jenkinson, D.S., Powlson, D.S. 1976. The effects of biocidal treatments on metabolism in soil. I. Fumigation with chloroform. Soil Biol. Biochem. 8, 209-213.

Jones, D.L. 1998. Organic acids in the rhizosphere e a critical review. Plant Soil 205, 25-44.

Kim, K.R., Owens, G., Kwon, S.I. 2010. Influence of Indian mustard (*Brassica juncea*) on rhizosphere soil solution chemistry in long-term contaminated soils: A rhizobox study. J. Environ. Sci. 22(1), 98-105.

Lindsay, W.L., Norvell, W.A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. 42, 421-428.

Lindsay, W.L., Cox, F.R. 1985. Micronutrient soil testing for the tropics. Fertilizer Research. 7, 169-200.

Liu, C., Huang, P. M. 2003. Kinetics of lead adsorption by iron oxides formed under the influence of citrate. Geochimica et Cosmochimica Acta 67(5), 1045-1054.

Loeppert, R. H., Suarez, D.L. 1996. Carbonate and gypsum. In: D. L. Sparks, (ed). Methods of Soil Analysis, Soil Science Society of America Journal, Madison. pp. 437-474.

Lombi, E., Wenzel, W.W., Gobran, G.R., Adriano, D.C. 2001. Dependency of phytoavailability of metals on indigenous and induced rhizosphere processes: a review. In: G.R. Gobran, W.W. Wenzel, E. Lombi, (eds). Trace Elements in the Rhizosphere. CRC Press LLC. pp. 3-24.

Lynch, J.M., Whipps, J.M. 1990. Substrate flow in the rhizosphere. Plant Soil 129, 1-10.

Manouchehri, N., Bermond, A. 2009. EDTA in soil science. a review of its application in soil trace metal investigations. Terrestrial Aquat. Environ. Toxicol. 3, 1-15

Martin, H.W., Sparks, D.L. 1983. Kinetics of nonexchangeable potassium release from two coastal plain soils. Soil Sci. Soc. Am. J. 47, 883-887.

Mocko, A., Waclawek, W. 2004. Three-step extraction procedure for determination of heavy metals availability to vegetables. Anal. Bioanal. Chem. 380(5-6), 813-817.

Nelson, D. W., Sommers, L. E. 1996. Carbon, organic carbon, and organic matter. In: D. L. Sparks, (ed.). Methods of Soil Analysis, Soil Science Society of America Journal, Madison. pp. 961-1010.

Nye, P. H. 1981. Changes of pH across the rhizosphere induced by roots. Plant Soil 61, 7-26.

Pavlatou, A., Polyzopoulos, N.A. 1988. The role of diffusion in the kinetics of phosphate desorption: The relevance of the Elovich equation. J. Soil Sci. 39, 425-436.

Qin, F., Shan, X. Q., Wen, B. 2004. Effects of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils. Chemosphere. 57, 253-263.

Renoux, A.Y., Rocheleau, S., Sarrazin, M., Sunahara, G.I., Blais, J.F. 2007. Assessment of a sewage sludge treatment on cadmium, copper and zinc bioavailability in barley, ryegrass and earthworms. Environ. Pollut. 145, 41-50.

Reyhanitabar, A., Gilkes, R. J. 2010. Kinetics of DTPA extraction of zinc from calcareous soils. Geoderma 154, 289-293.

Rhoades, J.D. 1996. Salinity: electrical conductivity and total dissolved solids. In: D. L. Sparks, (ed). Methods of Soil Analysis. Soil Science Society of America Journal, Madison. pp. 417-435.

Robert, M., Berthelin, J. 1986. Role of biological and biochemical factors in soil mineral weathering. In: P.M. Huang, M. Schnitzer (eds). Interactions of Soil Minerals with Natural Organics and Microbes. SSSA Spec. Pub. no. 17. SSSA, Madison, Wis. pp. 453-496.

Schwertmann, U., Taylor, R.M. 1989. Iron oxides. In: J. B. Dixon, S. B. Weed, (eds). Minerals in Soil Environments. SSSA Book Series no.1. SSSA, Madison, Wis. pp. 379-438.

Shan, X.Q., Lian, J., Wen, B. 2002. Effect of organic acids on adsorption and desorption of rare earth elements. Chemosphere. 47, 701-710.

Slaveykova, V.I., Wilkinson, K.J., Ceresa, A., Pretsch, E. 2003. Role of fulvic acid on lead bioaccumulation by *Chlorella kesslerii*. Environ. Sci. Technol. 37, 1114-1121.

Sparks, D.L. 1986. Kinetics of reactions in pure and mixed systems. In: D. L. Sparks, (ed). Soil Physical Chemistry. CRC Press, Boca Raton, FL, pp. 83-145.

Sparks, D.L. 1985. Kinetics of ionic reaction in clay minerals and soil. Advances in Agronomy. 38, 231-266.

Sposito, G., Lund, L.J., Chang, A. 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge. I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Sci. Soc. Am. J. 46, 260-264.

Sumner, M.E., Miller, P.M. 1996. Cation exchange capacity and exchange coefficient. In: D. L. Sparks, (ed). Methods of Soil Analysis. Soil Science Society of America Journal, Madison. pp. 1201-1230.

Tao, S., Chen, Y.J., Xu, F.L., Cao, J., Li, B.G. 2003. Changes of copper speciation in maize rhizosphere soil. Environ. Pollut. 122, 447-454.

Thomas, G.W. 1996. Soil pH and soil acidity. In: D L. Sparks, (ed). Methods of Soil Analysis. Soil Science Society of America Journal, Madison. pp. 475-490.

Uren, N.C. 2007. Types, amounts, and possible functions of compounds released into the rhizosphere by soil-grown plants. In: R. Pinton, Z. Varanini, P. Nannipieri, (eds). The Rhizosphere. 2th edition. CRC Press. Taylor & Francis Group. pp. 1-22.

Wang, Z., Shan, X.Q., Zhang, S. 2002. Comparison between fractionation and bioavailability of trace elements in rhizosphere and bulk soils. Chemosphere. 46(8), 1163-1171.

Young, S.D., Zhang, H., Tye, A.M., Maxted, A., Thums, C., Thornton, I. 2006. Characterizing the availability of metals in contaminated soils. I. The solid phase: sequential extraction and isotopic dilution. Soil Use Manage. 21, 450-458.