

Full Length Research Paper

Investigation of zinc release patterns in different soil orders using mathematical models

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Time dependent Zn extraction with diethylenetriaminepentaacetic acid (DTPA) extractant from five soil orders were studied for shaking periods of 1 min to 24 h. Zinc release rate from the studied soils was initially fast followed by a much slower rate trend. Power function was the best model describing Zn release data, followed by Elovich and parabolic diffusion models, respectively. Significant correlation coefficients between Zn extracted at 120 min with those of previous shaking periods such as 1 min suggested that lower shaking periods might be relevant in DTPA soil test for Zn in the studied soils which may lead to quicker Zn extraction methods. Results showed that the rate values of the best fitted models for the studied soils were in the order: Histosols > Mollisols > Vertisols > Inceptisols > Alfisols. The above order well shows the higher potential of Inceptisols and Alfisols for Zn deficiency in comparison with the other soils studied. On the other hand, the organic soils studied are not likely to be Zn deficient. Positive correlations of clay and organic matter (OM) with the rate constants of the best fitted models suggest that clay and OM are most likely the main sites of Zn release in the studied soils.

Key words: Zinc, extraction, soil orders, diethylenetriaminepentaacetic acid (DTPA).

INTRODUCTION

Our information on the Zinc (Zn) status of soils is important from plant and human nutrition standpoint (Cakmak et al., 1999). There are differences in the value and pattern of Zn release among different soils. Singh et al. (2006) believed that such differences are related to different capacity of soils in supplying Zn to the soil solution. According to the findings of Singh et al. (1997), such differences are probably due to differences in the amount of labile sorbed Zn, types and quantities of soil components by which the Zn is retained, and other soil properties such as pH and cation exchange capacity (CEC).

Strawn and Sparks (2000) believed that three main processes which control metal bioavailability are (1) removal of metals from soil solution by sorption, (2)

release of metals from solid phase to soil solution, and (3) precipitation-dissolution of metal. The major reason for the common constraint of Zn deficiency is low availability of Zn to plant roots rather than low content of this nutrient in soils (Kalayci et al., 1999). A diethylenetriaminepentaacetic acid (DTPA) soil test has been adopted by many soil laboratories as a reliable method to extract available cationic micronutrients including Zn in calcareous soils (Havlin and Soltanpour, 1981) which provides a static measure of nutrient to plant. Study of kinetic models is, however, useful to describe the changes in nutrient availability with time and hence is required to assess the ability of soil to supply nutrient to continuous process of absorption by plants.

Patterns of Zn release from different soils have been described by different mathematical models. Reyhanitabar and Gilkes (2010) reported that Zn release from calcareous soils conformed to power function model. Dang et al. (1994) reported that Zn release from

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Vertisols coincided with parabolic double diffusion, two constant rate (power function), and simple Elovich models.

Cationic micronutrients deficiencies are common in some calcareous soils of southern Iran. Release characteristics of Cu (Ghasemi-Fasaei et al., 2006) and Mn (Ghasemi-Fasaei et al., 2009) have been studied in calcareous soils of southern Iran. However, data on Zn release behavior of different soil orders is limited. The main objectives of this present study were (1) to study and compare release characteristics of Zn in different soil orders and (2) to find out soil properties controlling Zn release from the studied soils.

MATERIALS AND METHODS

The experiment was conducted on ten soils including two samples from each of five orders Alfisols, Histosols, Inceptisols, Mollisols and Vertisols. Samples were collected from surface soils (0 to 30 cm) of different fields of Fars Province located in southern Iran. This study area lies between longitudes 50° 30' to 55° 38' E and latitudes 27° 3' to 42° 31' N. The soils were air dried, crushed, and sieved. Some physical and chemical properties of the soil including particle size distribution, calcium carbonate equivalent (CCE), organic matter (OM), electrical conductivity (EC), cation exchange capacity (CEC), and pH were determined using standard methods (Sparks et al., 1996). The classification of soils was also determined using standard procedure (Soil Survey Staff, 2003). Ten grams of each soil samples, in duplicate, was extracted with 20 ml DTPA extractant (Lindsay and Norvell, 1978) for shaking periods of 1, 10, 30, 60, 120, 240, 480, and 1440 min at $25 \pm 2^\circ\text{C}$. The extractant consists of 0.005 M DTPA (diethylenetriaminepentaacetic acid), 0.1 M TEA (triethanolamine), and 0.01 M CaCl_2 , with a pH of 7.3. Then samples were immediately centrifuged at 2500 rpm for 10 min. The supernatants were filtered and the filtrates analyzed for Zn using an atomic absorption spectrophotometer (AAS; PG 990, PG Instruments Ltd. UK). Five mathematical models commonly used in nutrient release study were used to assess the patterns of Zn release from the soils as follows:

zero-order ($q_t = q_0 - k_0t$), first-order ($\ln q_t = \ln q_0 - k_1t$), Elovich ($q_t = 1/\beta_s \ln \alpha_s \beta_s + 1/\beta_s \ln t$), parabolic diffusion ($q_t = q_0 + Kp t^{0.5}$), power function ($q_t = a t^b$)

where k_0 is zero-order rate constant ($\text{mg Zn kg}^{-1}\text{s}^{-1}$), k_1 is first-order rate constant (s^{-1}), kp is diffusion rate constant [$(\text{mg Zn kg}^{-1})^{0.5}$], α_s is initial Zn release rate ($\text{mg Zn kg}^{-1}\text{s}^{-1}$), β_s is Zn release constant [$(\text{mg Zn kg}^{-1})^{-1}$], a is initial Zn release rate constant ($\text{mg Zn kg}^{-1}\text{s}^{-1}$)^b, b is release rate coefficient [$(\text{mg Zn kg}^{-1})^{-1}$], q_t and q_0 are the amount of soil Zn released (mg Zn kg^{-1}) after t (s) period of extraction and at $t = 0$, respectively. A relatively high values of coefficient of determination (R^2) and low values of standard error of estimate (SE) were used as criteria for the selection of the best fitted models. Standard errors of estimate were calculated as follows:

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

where q and q^* represent the measured and predicted Zn released, respectively and n is the number of observations. Coefficients values of the best fitted models were calculated for the studied soils. Correlation coefficients between these values and soil properties were also determined. Data were analyzed using SPSS and Excel software packages.

RESULTS AND DISCUSSION

The soil orders were highly different from the view of physical and chemical properties. Organic matter (OM), clay content, and calcium carbonate equivalent (CCE) ranged from 1.3 to 7.9%, 19 to 75%, and 3 to 61%, respectively (Table 1). Cation exchange capacity (CEC) and electrical conductivity (EC) ranged from 10 to 35 $\text{cmol}_{(+)}\text{kg}^{-1}$ and 0.4 to 1.8 dSm^{-1} , respectively.

Coefficients of determination (R^2) and standard errors of estimate (SE) for five kinetic models were shown in Table 2. Power function was the best model describing zinc release data followed by Elovich and parabolic diffusion models, respectively. Zinc release data from different soil orders, however, were not adequately fitted to zero- or first-order models. Reyhanitabar and Gilkes (2010) reported that the power function was the best model describing Zn extraction data in calcareous soils. They observed that the ordered models were not fitted to Zn release data. The conformity of Zn release data to the both parabolic diffusion and Elovich models suggests that Zn release from the studied soils is probably controlled by diffusion. Aharoni et al. (1991) reported that conformity of release data to the Elovich equation could suggest a heterogeneous diffusion process. Also according to the results of Havlin et al. (1985) when both parabolic diffusion and power function models describe the rates of release process, the latter represents slow diffusion which is probably related to nutrient desorption from inside binding sites to external surfaces and subsequently to the soil solution (Dang et al., 1994).

Zinc release rate from the studied soils was initially fast and followed by a much slower rate trend (Figure 1) which is in agreement with the findings of Dang et al. (1994) in Vertisols. Relatively similar trends have been observed in our previous experiments on Cu desorption (Ghasemi-Fasaei et al., 2006) and Mn release (Ghasemi-Fasaei et al., 2009) in calcareous soils of Fars Province. A plot of the amounts of Zn release vs. $t^{0.5}$ (linear form of parabolic diffusion model) showed that there are considerable differences in Zn release rates between Histosols and other soil orders (Figure 1). Likewise, the results of Table 3 showed that mean q_0 (the amounts of Zn released at $t = 0$) and Kp (Zn diffusion rate constant) values for the studied soils was in the order: Histosols > Mollisols > Vertisols > Inceptisols > Alfisols. Two Histosols with the highest clay contents showed the highest q_0 and Kp values among studied soils (Tables 1 and 3). Above order well shows the higher potential of Zn deficiency in Inceptisols and Alfisols in comparison with other soils studied. On the other hand, the organic soils studied are not likely to be Zn deficient. According to the results of Dalal (1985), ab value derived from the power function model may be taken as initial rate of soil nutrient. In this present study, mean ab value was the highest in Histosols (Table 3), demonstrating higher mean initial release rates of Zn in the organic soil order than those of

Table 1. Classification and some physical and chemical properties of the studied soils.

Soil number	Classification	CEC (cmol _c kg ⁻¹)	EC (dSm ⁻¹)	pH saturated paste	CCE	OM	Sand	Silt	Clay
					%				
1	Typic Haploxererts	35	0.5	7.43	7	2.0	7	44	49
2	Typic Haploxererts	32	0.5	7.40	3	3.0	13	46	41
3	Typic Haploxerepts	20	0.9	7.23	38	2.9	37	30	33
4	Typic Calcixerepts	27	0.6	7.13	30	4.4	25	34	41
5	Calcic Haploxeralfs	10	1.6	7.62	42	1.5	22	45	33
6	Calcic Haploxeralfs	15	0.4	7.64	28	1.3	21	56	23
7	Entic Haploxerolls	21	1.3	7.97	61	7.2	37	37	26
8	Typic Haploxerolls	20	1.8	7.95	57	7.9	33	48	19
9	Hydric Haplofibrists	33	0.7	7.22	49	6.9	12	17	71
10	Hydric Haplofibrists	30	0.6	7.55	61	7.0	10	15	75

Table 2. Coefficient of determination (R²) and standard error of the estimate (SE) for different kinetic models.

Soil number	Zero order		First order		Parabolic diffusion		Elovich		Power function	
	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE
1	0.647	0.117	0.411	0.485	0.860	0.074	0.958	0.040	0.971	0.107
2	0.609	0.225	0.356	0.691	0.846	0.141	0.962	0.070	0.965	0.161
3	0.677	0.123	0.483	0.410	0.886	0.073	0.935	0.055	0.983	0.074
4	0.987	0.120	0.382	0.492	0.812	0.079	0.968	0.033	0.975	0.099
5	0.806	0.075	0.551	0.391	0.949	0.038	0.895	0.055	0.985	0.071
6	0.709	0.040	0.596	0.282	0.901	0.024	0.846	0.029	0.912	0.132
7	0.676	0.895	0.393	0.869	0.891	0.520	0.900	0.498	0.949	0.253
8	0.624	0.102	0.395	0.484	0.821	0.070	0.928	0.045	0.939	0.154
9	0.423	2.480	0.254	1.118	0.686	1.831	0.901	1.027	0.904	0.401
10	0.348	1.153	0.203	0.983	0.602	0.901	0.927	0.385	0.856	0.418
Mean	0.651	0.533	0.403	0.621	0.825	0.375	0.922	0.224	0.944	0.187

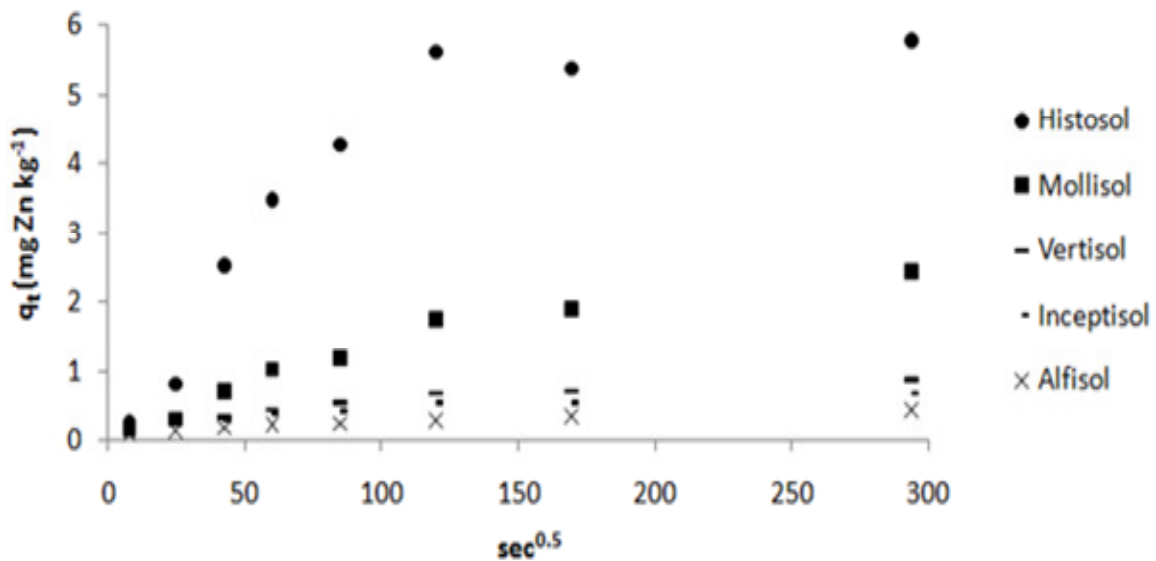


Figure 1. Kinetic of Zn release from five soil orders as described by linear form of parabolic diffusion model (Means of two soils for each soil order).

Table 3. Coefficients values of the best fitted models.

Soil order	Parabolic diffusion		Power function			Elovich	
	q_0 (mg kg^{-1})	K_p ($\text{mg kg}^{-1} \text{S}^{0.5}$)	a ($\text{mg kg}^{-1} \text{S}^{-1}$) ^b	b ($\text{mg kg}^{-1} \text{S}^{-1}$) ^b	ab ($\text{mg kg}^{-1} \text{S}^{-1}$) ^b	α_s ($\text{mg kg}^{-1} \text{S}^{-1}$)	β_s (mg kg^{-1}) ⁻¹
Vertisol	0.210	0.0018	0.043	0.250	0.011	0.0030	12.9
Vertisol	0.264	0.0032	0.029	0.340	0.010	0.0023	7.07
Inceptisol	0.232	0.0020	0.059	0.227	0.013	0.0037	11.9
Inceptisol	0.206	0.0016	0.042	0.248	0.010	0.0030	13.8
Alfisol	0.157	0.0016	0.041	0.233	0.010	0.0023	15.5
Alfisol	0.101	0.0007	0.039	0.170	0.007	0.0033	36.1
Mollisol	0.572	0.0146	0.039	0.436	0.017	0.0045	1.67
Mollisol	0.187	0.0015	0.040	0.242	0.010	0.0030	15.6
Histosol	1.920	0.0266	0.051	0.494	0.025	0.0125	0.80
Histosol	1.352	0.0109	0.062	0.409	0.025	0.0117	1.81

Table 4. Correlation coefficients between the values of Zn extracted at different extraction periods.

	Z-10	Z-30	Z-60	Z-120	Z-240	Z-480	Z-1440
Z-1	0.877**	0.897**	0.925**	0.905**	0.920**	0.939**	0.952**
Z-1440	0.924**	0.948**	0.976**	0.977**	0.991**	0.996**	
Z-480	0.947**	0.969**	0.989**	0.992**	0.997**		
Z-240	0.937**	0.960**	0.982**	0.993**			
Z-120	0.969**	0.985**	0.994**				
Z-60	0.981**	0.994**					
Z-30	0.991**						

Z-1 to Z-1440: Zn extracted throughout 1 to 1440 min, respectively. **: Significant at $p \leq 0.01$.

Table 5. Correlation coefficients between rate constants of the best fitted models.

Constant rate	q_0	a	ab	b	α_s	β_s
k_p	0.918**	0.314	0.864**	0.915**	0.831**	-0.662*
β_s	-0.640*	-0.306	-0.755*	-0.852**	-0.551	
α_s	0.975**	0.656*	0.950**	0.762*		
b	0.853**	0.223	0.869**			
ab	0.950**	0.655*				
a	0.532					

* and **: Significant at $p \leq 0.05$ and $p \leq 0.01$, respectively.

the four mineral soil orders studied. Differences in the amount and pattern of Zn release among different soils have been also reported by Singh et al. (2006). They believed that such differences are related to different capacity of soils in supplying Zn to the soil solution. According to the findings of Singh et al. (1997), such differences are probably due to differences in the amount of labile sorbed Zn, types and quantities of soil components by which the Zn is retained, and other soil properties such as pH and CEC. Significant correlation coefficients were found between the amounts of Zn extracted at different shaking periods (Table 4). Lindsay

and Norvell (1978) proposed a 120 min shaking period for extracting metal micronutrients with DTPA extractant. Significant correlation coefficients between Zn extracted at 120 min (Z-120) with those of previous shaking periods such as 1 min (Z-1) suggest that lower shaking periods might be relevant in DTPA soil test for Zn in the studied soils. These results show the necessity of paying more attention to lower shaking periods which may lead to quicker Zn extraction methods.

Correlation coefficients between rate constants of the best fitted models are given in Table 5. Rate constants of power function model (b and ab) were significantly

Table 6. Correlation coefficients between rate constants of the best fitted models and soil properties.

Coefficient	CCE	CEC	EC	OM	pH	Sand	Silt	Clay
q_0	0.461	0.483	-0.192	0.591	-0.209	-0.398	-0.839**	0.823**
K_p	0.473	0.390	-0.065	0.611	-0.070	-0.191	-0.702*	0.605
α_s	0.509	0.438	-0.233	0.574	-0.191	-0.400	-0.855**	0.835**
β_s	-0.321	-0.556	-0.089	-0.620	0.110	0.123	0.743*	-0.594
ab	0.567	0.451	-0.111	0.649*	-0.118	-0.278	-0.912**	0.803**
b	0.410	0.522	-0.065	0.680*	0.002	-0.236	-0.711*	0.638*
a	0.486	0.120	-0.110	0.262	-0.309	-0.029	-0.780**	0.565

* and **: Significant at $p \leq 0.05$ and $p \leq 0.01$, respectively.

correlated with those of parabolic diffusion models (k_p and q_0). There were also significant correlations between rate constants of Elovich (α_s and β_s) with those of parabolic diffusion models (k_p and q_0) which is in agreement with the findings of Pavlatou and Polyzopoulos (1988) who reported that the Elovich equation applies to the reactions that are controlled by diffusion mechanism.

Correlation coefficients between soil properties and the constant values of the best fitted models were shown in Table 6. Most of the rate constants were negatively correlated with silt content and positively correlated with clay content of the studied soils. The constant values of power function model (b and ab) were positively correlated with soil OM. It is, therefore, concluded that clay, silt, and OM contents are the most influential soil properties controlling Zn release from the studied soils. Positive correlations of clay and OM with the constant values of the best fitted models suggest that clay and OM are most likely the main sites of Zn release in the studied soils.

Conclusion

Zinc release rate from the studied soils was initially fast and followed by a much slower rate trend. Power function was the best model describing Zn release data followed by Elovich and parabolic diffusion models, respectively. Significant correlation coefficients between Zn extracted at 120 min with those of previous shaking periods such as 1 min suggest that lower shaking periods might be relevant in DTPA soil test for Zn in the studied soils which may lead to quicker Zn extraction methods. Results showed that the rate values of the best fitted models for the studied soils were in the order: Histosols > Mollisols > Vertisols > Inceptisols > Alfisols. Above order well shows the higher potential of Inceptisols and Alfisols for Zn deficiency in comparison with the other soils studied. On the other hand, the organic soils studied are not likely to be Zn deficient. Positive correlations of clay and OM with the rate constants of the best fitted models suggest that clay and OM are most likely the main sites of Zn release in the studied soils.

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REFERENCES

- Aharoni C, Sparks DL, Levinson S, Revina I (1991). Kinetics of soil chemical reactions: Relationship between empirical equations and diffusion models. *Soil Sci. Soc. Am. J.* 55:1307-1312.
- Cakmak I, Kalayci M, Ekiz H, Braun HJ, Kilinc Y, Yilmaz A (1999). Zinc deficiency as a practical problem in plant and human nutrition in Turkey: A NATO-science for stability project. *Field Crops Res.* 60:175-188.
- Dang YP, Dalal R, Edwards DG, Tiller KG (1994). Kinetics of zinc desorption from Vertisols. *Soil Sci. Soc. Am. J.* 58:1392-1399.
- Dalal RC (1985). Comparative prediction of yield response and phosphate uptake from soil using anion and cation-anion exchange resins. *Soil Sci.* 139:227-231.
- Ghasemi-Fasaei R, Maftoun M, Ronaghi A, Karimian N, Yasrebi J, Assad MT, Ippolito JA (2006). Kinetics of copper desorption from highly calcareous soils. *Commun. Soil Sci. Plant Anal.* 37:797-809.
- Ghasemi-Fasaei R, Maftoun M, Olama V, Molazem B, Tavajoh M (2009). Manganese-release characteristics of highly calcareous soils. *Commun. Soil Sci. Plant Anal.* 40:1171-1182.
- Havlin JL, Soltanpour PN (1981). Evaluation of the NH_4HCO_3 -DTPA soil test for iron and zinc. *Soil Sci. Soc. Am. J.* 45:70-75.
- Havlin JL, Westfall DG, Olsen SR (1985). Mathematical models for potassium release kinetics in calcareous soils. *Soil Sci. Soc. Am. J.* 49:371-376.
- Kalayci M, Torun B, Eker S, Aydin M, Ozturk L, Cakmak I (1999). Grain yield, zinc efficiency, and zinc concentration of wheat cultivars grown in a zinc-deficient calcareous soil in field and greenhouse. *Field Crops Res.* 63:87-98.
- Lindsay WL, Norvell WA (1978). Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42:421-428.
- Pavlatou A, Polyzopoulos NA (1988). The role of diffusion in the kinetics of phosphate desorption: The relevance of the Elovich equation. *J. Soil Sci.* 39:425-436.
- Reyhanitabar A, Gilkes RJ (2010). Kinetics of DTPA extraction of zinc from calcareous soils. *Geoderma* 154:289-293.
- Singh D, McLaren RG, Cameron KC (2006). Zinc sorption-desorption by soils: Effect of concentration and length of contact period. *Geoderma* 137:117-125.
- Singh D, McLaren RG, Cameron KC (1997). Desorption of native and added zinc from a range of New Zealand soils in relation to soil properties. *Aust. J. Soil Res.* 35:1253-1266.
- Soil Survey Staff (2003). *Keys to soil taxonomy*, 9th ed. Washington, D.C.: U.S. Government Printing Office.

Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Sumner ME (1996). *Methods of soil analysis*, part 2 and 3, 3rd ed. Madison, Wisc: American Society of Agronomy.

Strawn DG, Sparks DL (2000). Effect of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. *Soil Sci.Soc. Am. J.* 64:144-156.