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Kinetics of Zinc Ageing in Typic Torriorthent and Typic Haplocalcid Soils

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THIS STUDY aimed at investigating the kinetics of Zn-ageing in two arid soils of Egypt. It also introduced the curve-analysis models, beside of the commonly used adsorption-isotherm models for describing Zn-retention data of these soils. To reach these goals, samples of Typic Torriorthent and Typic Haplocalcid soils, with or without Fe and/or Zn salts, were incubated under the laboratory conditions for 28 days. AB-DTPA-Zn was determined in soils during different time periods through out the experiment. Cumulative Zn-retention data were calculated and fitted using different kinetic models. Another sorption experiment was conducted by shaking soil portions with a series of standard Zn solutions and the obtained supernatants were analyzed for Zn. The retention data were calculated and fitted using curve analysis models and adsorption isotherm models. The results show that application of Fe singly or in combination with Zn increased AB-DTPA-Zn significantly. This occurred up to 24 hr after application and decreased afterwards. Parabololic diffusion seemed to be the rate limiting step in the Typic Torriorthent soil up to 336 hr afterwards simple Elovich function was the best fitting model, while the first order model was the best fitting model in the Typic Haplocalcid soil. Curve-analysis suggests that Zn retained in Typic Torriorthent soil probably occurred due to specific and non-specific adsorption on heterogeneous sites; whereas Zn retained in Typic Haplocalcid soil probably occurred due to adsorption followed by precipitation reactions. Finally, curve analysis models could successfully explain Zn-sorption isotherms acting together in soil, while further calculations are needed for explaining the consecutive Zn-sorption isotherms.

Keywords: Zn retention, Kinetics, Adsorption isotherms, Sorption, Curve analysis.

Zinc deficiency is a widespread health problem (Prasad, 2012), representing nearly half of the world population (Welch and Graham, 2004 and Cakmak,

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2009) and is mainly related to the inadequate daily intake of Zn in human diet (Guilbert, 2002). Accordingly excessive transfer of Zn to the food chain is needed to maintain its level within the international permissible limits (Dudka and Miller, 1999). Application of Zn- fertilizers to the agricultural soils could serve rapidly in increasing Zn availability and uptake by the grown plants (Welch, 2002). Thus, rising above the deficiency problems of Zn in human diet (Cakmak, 2010). However, Zn bioavailability in soil might be affected with the application of other micronutrient fertilizers. There is a little information available in this concern. Also, the availability of Zn is expected to decline rapidly in soil after the applications of Zn fertilizers (Singh *et al.,* 2006). The term “ageing” refers to the effect of the time of soil contact on lessening the bioavailability of Zn in soil (Donner *et al.,* 2012). The interpretation of Zn aging data is of high significance to understand the kinetics of Zn retention in soil (Reyhanitabar and Gilkes, 2010). For this purpose, Zn aging data were fitted to theoretical and empirical models and the best-fitting-model introduces the proposed mechanism of Zn accumulation and sorption on solid surfaces (Gupta and Bhattacharyya, 2011).

It is worthy to mention that Zn retention in soil arises mainly through precipitation, strong sorption and physical entrapment in the mineral lattice of clay colloids (Puls and Bohn, 1988, Rashid and Ryan, 2004, Kumpiene *et al.,* 2008 and Priadi *et al.,* 2012). In spite of that, many researchers used only simple adsorption isotherm models for describing Zn retention data in soil (Reyhanitabar and Gilkes, 2010), yet describing Zn retention in soil should be considered more complicated than even using adsorption fitting models.

The current study aimed at investigating the kinetics of Zn ageing in two arid soils of Egypt, *i.e.,* Typic Torriorthent and Typic Haplocalcid soils. Also, it aims at throwing some light on the effects that might occur upon adding Fe and/or Zn salts to soils on Zn ageing at different periods following addition. Introducing the curve-analysis models beside of the commonly used adsorption isotherm models for describing Zn retention data in two soils of Egypt was also a matter of concern.

Material and Methods

Soils of study

The soil samples used in the current study were collected from the 0-30-cm surface layer of a Typic Torriorthent soil from Moshtohor village - El-Kaliobia Governorate and a Typic Haplocalcid one from El-Nubarie City, Bohera Governorate. Theses soil samples were air dried, sieved to pass through a 2mm sieve and analyzed for their chemical and physical properties using the standard methods described by Page *et al.* (1982) and Klute (1986) and results of analysis are presented in Table 1.

TABLE 1. Chemical and physical properties of the studied soils.

Soil parameter		Typic Torriort-hent	Typic Haploc-alcid	Soil parameter		Typic Torrior-thent	Typic Haplocalcid
pH		7.81	8.04	SP	%	73.40	23.30
OM	g kg^{-1}	26.31	7.03	Coarse sand	%	6.34	33.16
$CaCO_3$	g kg^{-1}	11.70	227.00	Fine sand	%	18.79	31.12
CEC	$cmol_c$ kg^{-1}	49.70	17.80	Silt	%	22.23	11.68
AB-DTPA Zn	µg g^{-1}	2.88	0.60	Clay	%	52.64	24.04
EC	dSm^{-1}	2.10	4.60	Textural class		Clay	Sandy Clay loam

pH: in 1:2.5 soil: water suspension; EC: in saturated paste extract.

The experimental work

1. Effects of ageing and applying Fe and/or Zn salts on Zn availability in the soils of study

Effect of ageing and amending soil with Fe and/or Zn using $FeSO_4.7H_2O$ and/or $ZnSO_4.7H_2O$ on Zn availability was a matter of concern in this study. Portions of 200 g each were packed uniformly in PVC pots (6 cm diameter ×7.5 cm depth) together with one of the following treatments: no addition of Fe or Zn (control treatment, T1), 100 µg Fe g^{-1} soil (T2), 100 µg Zn g^{-1} soil (T3) and 100 µg Fe + 100 µg Zn g^{-1} soil (T4) forming a set of 27 pots per treatment for every soil type (9 time periods × 3 replicates) . All treatments were incubated under the laboratory conditions at 30±8°C in a completely randomized design. During the experimental period, soil moisture was maintained gravimetrically at a constant moisture content of about 70% of the field capacity using deionized water and the different investigated treatments were sampled at the following time periods 1, 3, 7, 10, 14, 18, 21, 24 and 28 days.

2. The sorption experiment

A stock solution of 1000 µg Zn mL^{-1} was prepared from $ZnSO_4.7H_2O$, followed by a series of dilutions to bring up a set of Zn standard solutions of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 µg mL^{-1}. Six sets were taken from every standard concentration (25 mL each) and placed into 50mL centrifuge reaction tubes together with a 0.25g soil portion taken from each soil in three replicates (2sites×3 replicates=6 standard solutions). The centrifuge tubes were then shaken for 30 min and centrifuged at 3000 rpm and the supernatants were filtered using Whatman filter paper No. 42.

The chemical analysis

Soils were extracted with ammonium bicarbonate-DTPA (AB-DTPA) according to Soltanpour (1985) and analyzed for Zn using Atomic Absorption Spectrophotometer (Perkin Elemer, Model 969AA). All the chemicals used in this study were of analytical reagent grade obtained from Sigma-Aldrich Chemical Company Inc.

Data analyses

1. Analysis of variance

The obtained data were statistically analyzed using the Minitab program through analysis of variance (ANOVA) and least significant difference (LSD) at 0.05 probability level.

2. Fitting the retention data to curve analysis models

Zn retention data in relation to the total applied Zn concentrations were fitted using four curve analysis models as outlined by Abbas and Ismael (2010). These models are: (i) One-site saturation model (OSS, $y = \frac{ax}{b+x}$) which implies Zn sorption. (ii) One site saturation plus a linear component model (OSSL, $y = \frac{ax}{b+x} + ex$) which implies both Zn sorption and precipitation. (iii) Two-site saturation model (TSS, $y = \frac{ax}{b+x} + \frac{cx}{d+x}$) which implies sorption and specific sorption followed by physical entrapment in the mineral lattice of clay colloids. (iv) Two-site saturation plus a linear component model (TSSL, $y = \frac{ax}{b+x} + \frac{cx}{d+x} + ex$) which implies sorption and specific sorption followed by physical entrapment of Zn in clay colloids in addition to Zn precipitation in soil, where, “x” and “y” are the applied Zn concentrations and the cumulative retention of Zn, respectively. “a” and “c” are the calculated capacity parameters, “b” and “d” are the affinity parameters and “e” is the linear component parameter.

Zn retention data in relation to Zn concentration at the equilibrium solutions were fitted to both *Langmuir* and *Van Bemmelen- Freundlich* adsorption isotherms (the commonly used adsorption isotherms). The general forms of Langmuir and Freundlich adsorption isotherms as outlined by Sposito (2008) are:

$$Q_e = \frac{abC_e}{1 + bC_e}$$ Eq.: 1: *Langmuir* adsorption isotherm

where Q_e is the amount of Zn adsorbed at the equilibrium, the parameter (a) refers to the capacity coefficient, C_e is the concentration of Zn at equilibrium and b is the affinity coefficient.

$Q_e = kC_e^{\frac{1}{n}}$ Eq. 2: *Van Bemmelen- Freundlich* adsorption isotherm

where Qe and Ce are the same as in Eq. (1) and k and n are constants related to the capacity and affinity coefficients, respectively.

3. Fitting the time dependent sorption data to the different kinetic models

The cumulative retention of Zn (CRZ) was calculated as outlined by Abbas and Salem (2011) by subtracting AB-DTPA-extractable Zn obtained at each time period from the corresponding AB-DTPA-extractable Zn obtained at the first day of incubation which represents the highest AB-DTPA-extractable Zn values. The calculated values of CZR were plotted graphically against time of sampling and the obtained relations were fitted to zero order $Q_t = Q_0 - k_0 t$ and first Order: $\ln Q_t = \ln Q_0 - k_1 t$) (Wolt, 1994), power function $Q_t = at^b$ and simple Elovich $Q_t = \frac{1}{\beta}\ln(\alpha\beta) + (\frac{1}{\beta})\ln t$) (Dang *et al.*, 1994) besides the parabolic diffusion $Q_t = Q_0 + K_p t^{1/2}$ (Reyhanitabar and Gilkes, 2010), where "*t"* is the time elapsed after addition of Zn (*h*), "k_0"(zero order rate constant $(\mu g Zn.g^{-1}h^{-1})$), "k_1" (first-order rate constant (h^{-1})), "α" (initial sorption rate $(\mu g Zn.g^{-1}h^{-1})$), "β" (sorption rate constant $(\mu g Zn.g^{-1})^{-1}$), "a" (initial sorption rate constant $(\mu g Zn.g^{-1}h^{-1})^b$), "$b$" (sorption rate coefficient $(\mu g Zn.g^{-1})^{-1}$) and "K_p" (diffusion rate constant $(\mu g Zn.g^{-1})^{0.5}$). The used symbols Q_0 and Q_t refer to the amounts of CZR (µg Zn g^{-1}) calculated at time t (hour) and at t=zero, respectively.

The standard error of estimate (S.E.) was calculated according to Shariatmadari (2006) as follows

$$SE = [\sum (Q_t - Q_t^{\prime})^2 / (n-2)]^{1/2}$$

Where Q_t and $Q_t^{\prime}$ are the measured and predicted amounts of the AB-DTPA-Zn obtained at time t, respectively and n is the number of measurements.

Results and Discussion

Extractability of AB-DTPA- Zn in soil as affected by Zn-Fe interaction

Sole applications of Zn [T3] showed no significant effect on AB-DTPA –extractable Zn in both soils (Table 2). This indicates that the applied Zn took less than one day to be sorbed in soil. On the other hand, applications of Fe singly [T2] or in combination with Zn [T4] increased significantly the amount of AB-DTPA-extractable Zn in both soils. This is probably because Fe displaced Zn partially on the sorption sites of soil and consequently Zn released into soil solution. Thus, it can be deduced that fertilization of soil with Fe might improve Zn availability in soil. This finding stands in agreement with the results of Lohan *et al.* (2005) who found increase in Zn bioavailability owing to Fe applications. It is worthy to mention that the recorded increases in AB-DTPA-Zn owing to the combined application of Fe+ Zn (T4) were significantly lower than those attained upon application of Fe solely [T2].

TABLE 2. Main effects of Zn-Fe interactions on AB- DTPA-extractable Zn in µg Zn kg^{-1} soil.

Soil classification	T1	T2	T3	T4
Typic Torriorth	3.43 ± 0.53^{c}	92.58 ± 4.85^{a}	3.18±0.	84.74 ± 3.00^{b}
Typic Haplocal	0.80 ± 0.14^{c}	74.67 ± 5.09^{a}	0.80±0.3	65.63 ± 6.14^{b}

Control Treatment (T1), Fe-Treatment (T2), Zn-Treatment (T3) and Fe + Zn Treatment(T4) .

Effect of ageing on AB-DTPA- Zn in soil

The results shown in Fig.1a and 1b reveal that the treatments T2 (Fe-Treatment) and T4 (Fe+Zn –treatment) resulted in the highest concentrations of AB-DTPA-extractable Zn during the first day of application in both soils beyond which values of AB-DTPA-Zn decreased significantly. On the other hand, no significant changes occurred in AB-DTPA-extractable-Zn owing to T1 (control treatment) or T3 (Zn-treatment). Such a finding was more obvious in the Typic Haplocalcid soil than in the Typic Torriorthent one. Probably, $CaCO_3$ in the former soil tightly retained Zn (Mesquita and Vieira e Silva, 1996 and Wang & Harrell, 2005) and thus Zn retention in the Typic Haplocalcid soil exceeded Zn retention in the Typic Torriorthent one. The cumulative amounts of retained Zn (CRZ) were calculated for both T2 and T4 treatments, then the results were represented graphically in relation to the time of contact (Fig.1c and 1d). These relationships were fitted using different kinetic models to explore the kinetics of Zn retention in soil.

The calculated coefficients of determination (r^2) and the standard error of estimate (S.E.) are presented in Table 3. Based on the highest values of coefficient of determination and the lowest values of standard error of estimate (S.E.), the parabolic diffusion (t<336 hr) and simple. Elovich function (t>336 hr) are thought to be the best fitting models to describe Zn ageing kinetics in the Typic Torriorthent soil. This indicates that Zn diffusion is probably the rate limiting step of Zn retention in soil up to 336 hr (14 days), afterwards chemisorption became the rate limiting one. On the other hand, the first order model seemed to be the most fitting model for describing the kinetics of Zn ageing in Typic Haplocalcid soil.

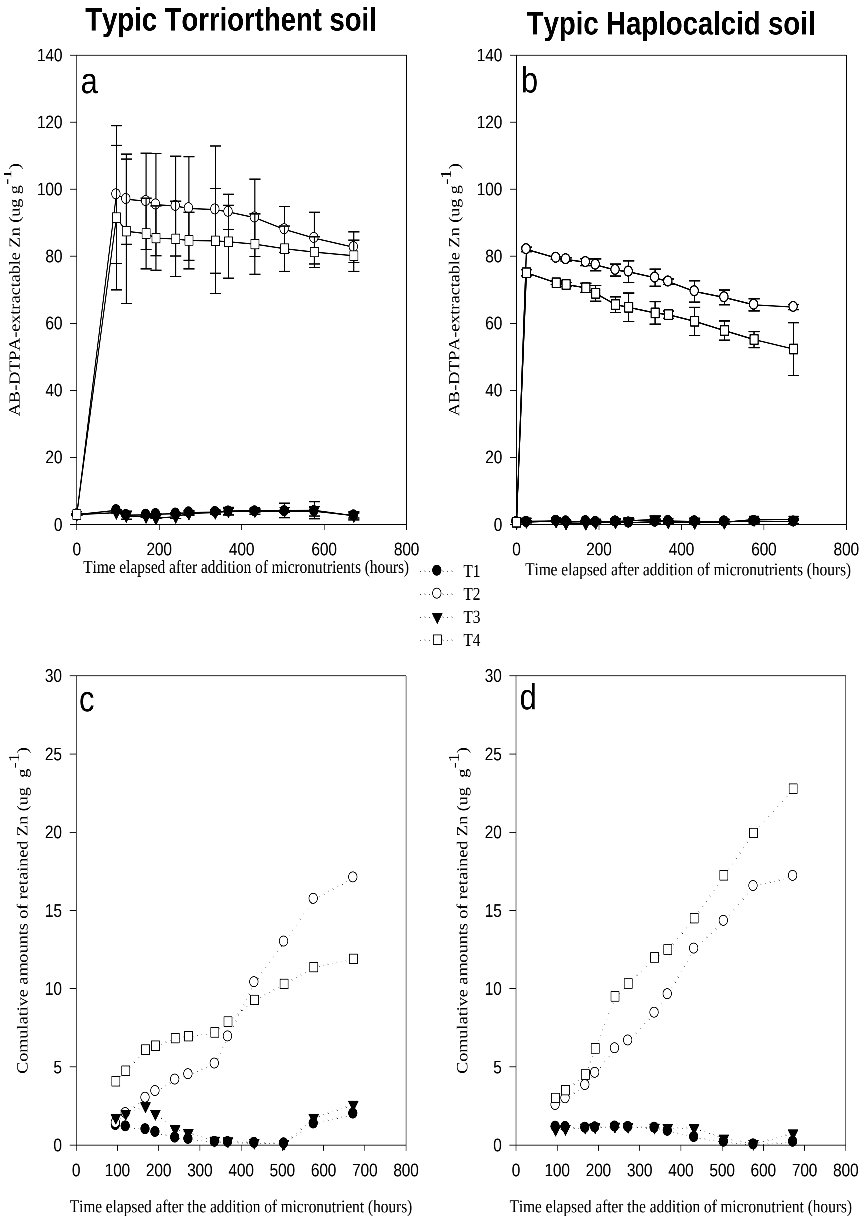

Fig. 1. AB-DTPA-extractable-Zn and cumulative amounts of retained Zn in soil as affected by the contact time. Rate of application of each Fe and Zn = 100 µg g^{-1}.

TABLE 3. Values of coefficient of determination (r^2) and standard error of estimation (S.E.) for the equations used to describe Zn sorption kinetics in Typic Torriorthent and Typic Haplocalcid soils.

Soil classification			Zero order		First order		Power function		Simple Elovich		Parabolic diffusion	
			r^2	S.E.	r^2	S.E.	r^2	S.E.	r^2	S.E.	r^2	S.E.
Typic Torriorthent	<336 h	T_2	0.958	0.828	0.888	0.148	0.961	0.767	0.977	0.451	0.998	0.023
		T_4	0.910	0.624	0.806	0.054	0.946	0.374	0.972	0.192	0.964	0.375
	>336 h	T_2	0.960	4.503	0.896	0.055	0.940	6.835	0.988	1.337	0.960	4.504
		T_4	0.959	0.726	0.983	0.008	0.969	0.547	0.988	0.216	0.959	0.547
Typic Haplocalcid		T_2	0.986	4.277	0.935	0.314	0.985	4.473	0.916	25.568	0.970	8.957
		T_4	0.989	5.107	0.885	0.579	0.989	5.226	0.944	25.817	0.985	7.085

Fe-Treatment (T2) and Fe + Zn Treatment(T4).

Modeling Zn retention data in Typic Torriorthent and Typic Haplocalcid soils

1. Effect of initial and equilibrium Zn concentrations on Zn retention on the Typic Torriorthent soil

The results shown in Table 4 reveal that neither the One site saturation + linear model (OSSL) nor the two site saturation + linear model (TSSL) could succeed in describing Zn retention data of this soil as their values were negative indicating desorption fittings rather than retention ones. The two site saturation model (TSS) seemed to be the most suitable model for describing Zn retention data of this soil as this model recorded the highest calculated r^2 values. Accordingly, the curve analysis of Zn retention data in the Typic Torriorthent soil proposed two adsorption isotherm fittings acting together affecting Zn retention in soil. The first one was more effective at the low concentrations of Zn and showed high affinity for Zn, probably indicating specific adsorption of Zn followed by physical entrapment in the mineral lattice of the clay colloids , while on the other hand, the second one was more effective at the high concentrations of Zn and revealed low affinity for Zn, probably indicating Zn adsorption on the surface negative charge of the soil. These results agree with those of Tiller *et al.* (1984) who found that Zn sorption in soil is characterized by initial rapid specifically sorption followed by slower non-specifically sites.

The retention data of Zn were then graphically represented as affected by equilibrium Zn concentrations and the obtained relations were fitted to Langmuir and Freiundlich isotherms. Based on the highest r^2 values and the least S.E. values, the results shown in Fig.3 and Table 5 reveal that Freundlich isotherm seemed to be the more suitable fitting for describing Zn sorption data on this soil and this relation became more pronounced after excluding the high affinity sorption curve. These results implied that the low affinity Zn-adsorption fitting took place through heterogeneous adsorption sites on soil particles. Baeyens and Bradbury (1997) suggested cation exchange on the permanent charge sites and surface complexation on the pH dependent surface hydroxyl groups for Zn sorption in soil.

TABLE 4. Fitting the data of zinc sorption on the Typic Torriorthent and Haplocalcid soils for the different curve analysis models.

Soil Classification	One site saturation + linear model (OSSL)				Two-site saturation model (TSS)				
	a	b	e	r^2	a	b	c	d	r^2
Typic Torriorthent	0.24	-7.94	0.08	0.998	48.31	1.06×10^3	189.20	5.42×10^3	0.997
Typic Haplocalcid	0.418	12.10	0.041	0.996	1.46×10^7	3.56×10^8	0.42	12.10	0.996
Soil Classification	One-site saturation model(OSS)				Two-site saturation+ linear model (TSSL)				
	a	b		r^2	a	b	c	d	e	r^2
Typic Torriorthent	1.35×10^2	1.68×10^3		0.995	-0.36	3.66	-25.30	-351.80	-1.16	0.999
Typic Haplocalcid	11.95	210.00		0.995	0.210	12.10	0.21	12.10	0.04	0.996

"a" and "c" are the calculated capacity parameters, "b" and "d" are the affinity parameters and "e" is the linear component parameter.

TABLE 5. The calculated parameters and coefficients of determination for the used adsorption isotherms .

Soil Class		Langmuir Isotherm parameters				Freundlich Isotherm parameters			
		A	B	r^2	S.E.	k	n	r^2	S.E.
Typic Torriorthent	Total	0.461	0.031	0.902	0.864	0.601	0.765	0.923	0.678
	-high affinity	0.194	0.230	0.929	0.129	0.246	0.802	0.943	0.103
Typic Haplocalcid	Total (A)	6.037	0.024	0.984	0.083	0.211	1.346	0.987	0.068
	+linear (B)	4.885	0.033	0.997	0.007	0.199	1.284	0.993	0.012
	-linear (C)	0.123	40.87	0.984	0.082	0.209	1.351	0.987	0.067

b : affinity coefficient , a : capacity coefficient, k: affinity coefficient, n: capacity coefficient .

2 .Effect of the initial and equilibrium Zn concentrations on Zn retention on the Typic Haplocalcid soil

Table 4 reveals that the calculated parameters of the TSS model, *i.e.,* "a" and "b" which relate to the capacity and affinity coefficients, respectively are too high to confirm this model. Also, the calculated capacity parameters ("a" and "c") and the affinity parameters ("b" and "d") of the TSSL model were nearly the same and therefore this model was rejected too. On the other hand, the OSS and OSSL can be considered the best fitting models for describing Zn retention in soil because of their high r^2 values; however, Zn sorption on this soil components is thought to be more complicated to conform only an adsorption isotherm model (Fig. 2). Adsorption isotherm is likely to be the main fitting model for Zn retention in soil up to 25 µg Zn mL^{-1} (initial Zn concentration); thereafter a linear relation suggesting Zn precipitation, became the dominant model. The beginning of this linear model, Zn precipitation, is of high importance since it may occur either at the same time with

Zn adsorption or as a succeeding step to Zn adsorption. The curve analysis model can not identify the beginning of the linear relation and therefore its results on the Typic Haplocalcid soil are confusing. Accordingly, Zn retention data in relation to the concentrations of Zn in the equilibrium solution were represented graphically in Fig. 2d and the obtained relations fitted to the Langmuir and Freundlich adsorption isotherms. The coefficient of determination value " r^2" and the standard error of estimates "S.E." value of Zn sorption data of the soil were calculated within the range of 0-50 µg Zn mL^{-1} (A), at the low range (< 25 µg Zn mL^{-1}) without excluding the linear relation (B) and at the low range (< 25 µg Zn mL^{-1}) after subtracting the linear relation (C). Based on the highest r^2 values, the Langmuir isotherm model seems more suitable for description of the Zn adsorption data at low concentrations of Zn (< 25 µg Zn mL^{-1}) without excluding the linear component (Fig. 4 and Table 5). These results indicate that Zn sorption in soil took place probably through two consecutive steps; the first one is adsorption in monolayer followed by precipitation.

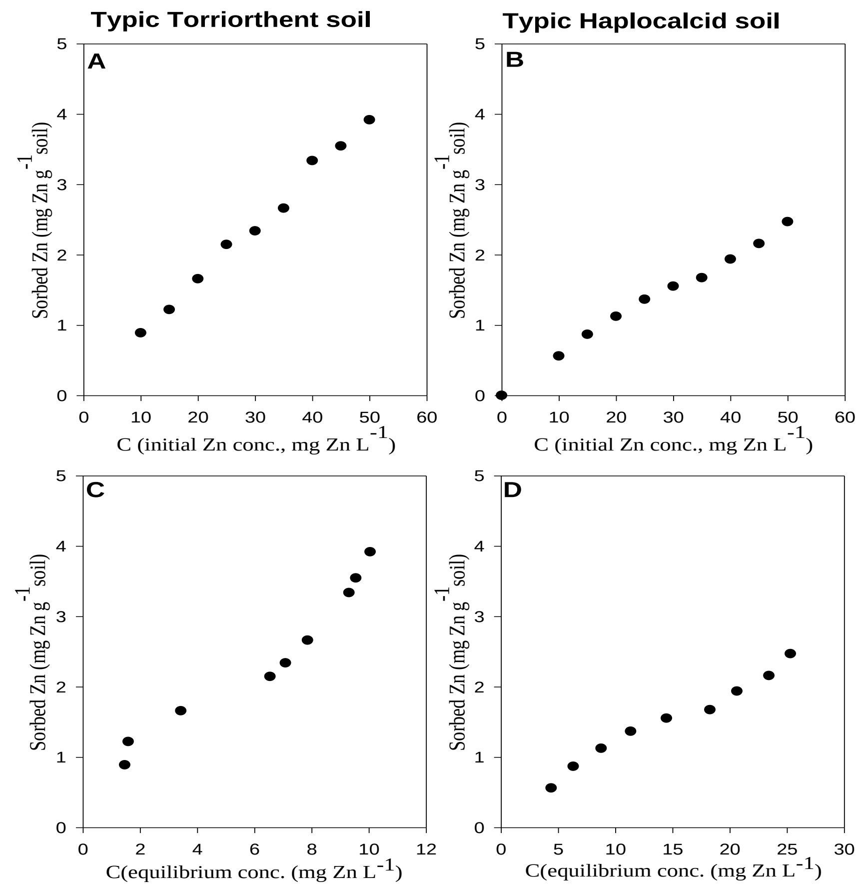

Fig 2. Zinc sorption on Typic Torriorthent and Typic Haplocalcid soils as affected by its initial and equilibrium concentrations.

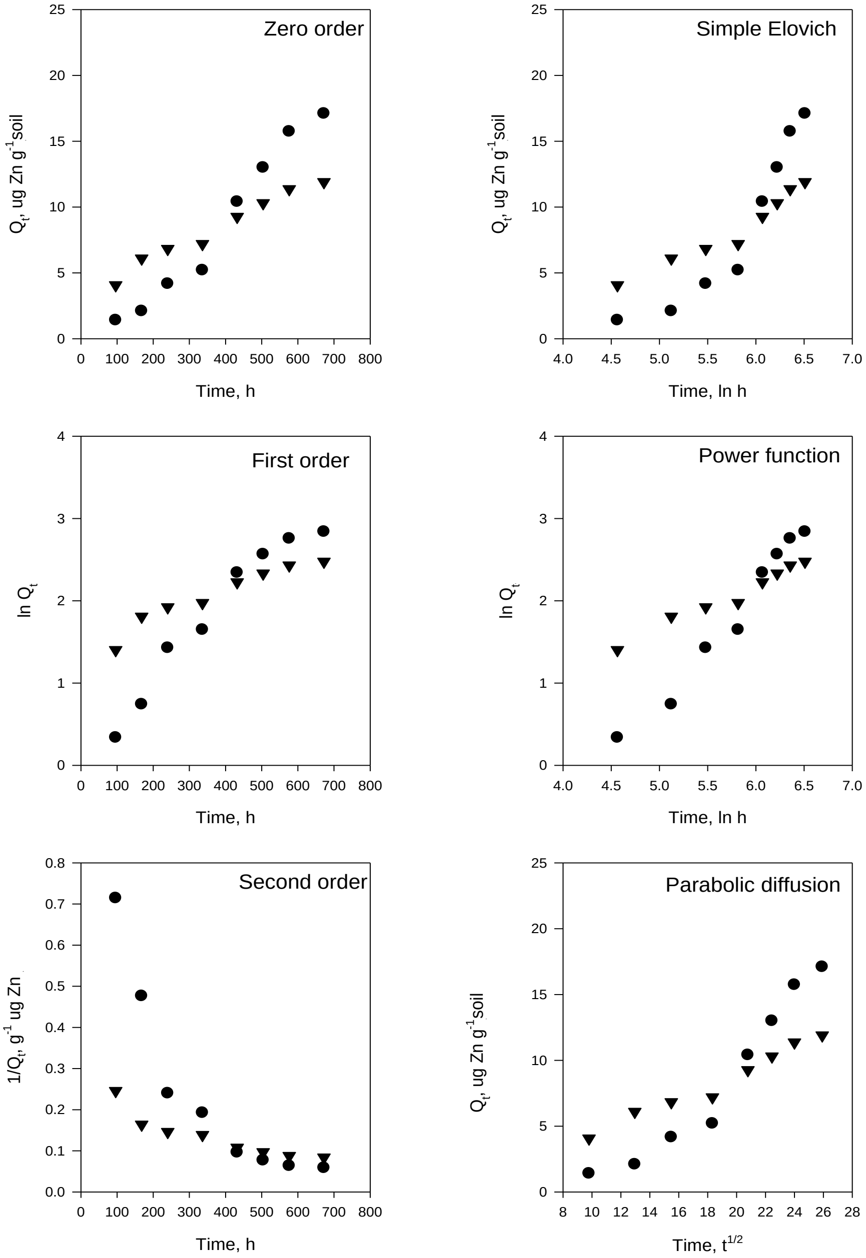

Fig. 3. Kinetics of Zn in Typic Torriorthent soil : Fe-Treatment (●),Fe + Zn Treatment (▼) .

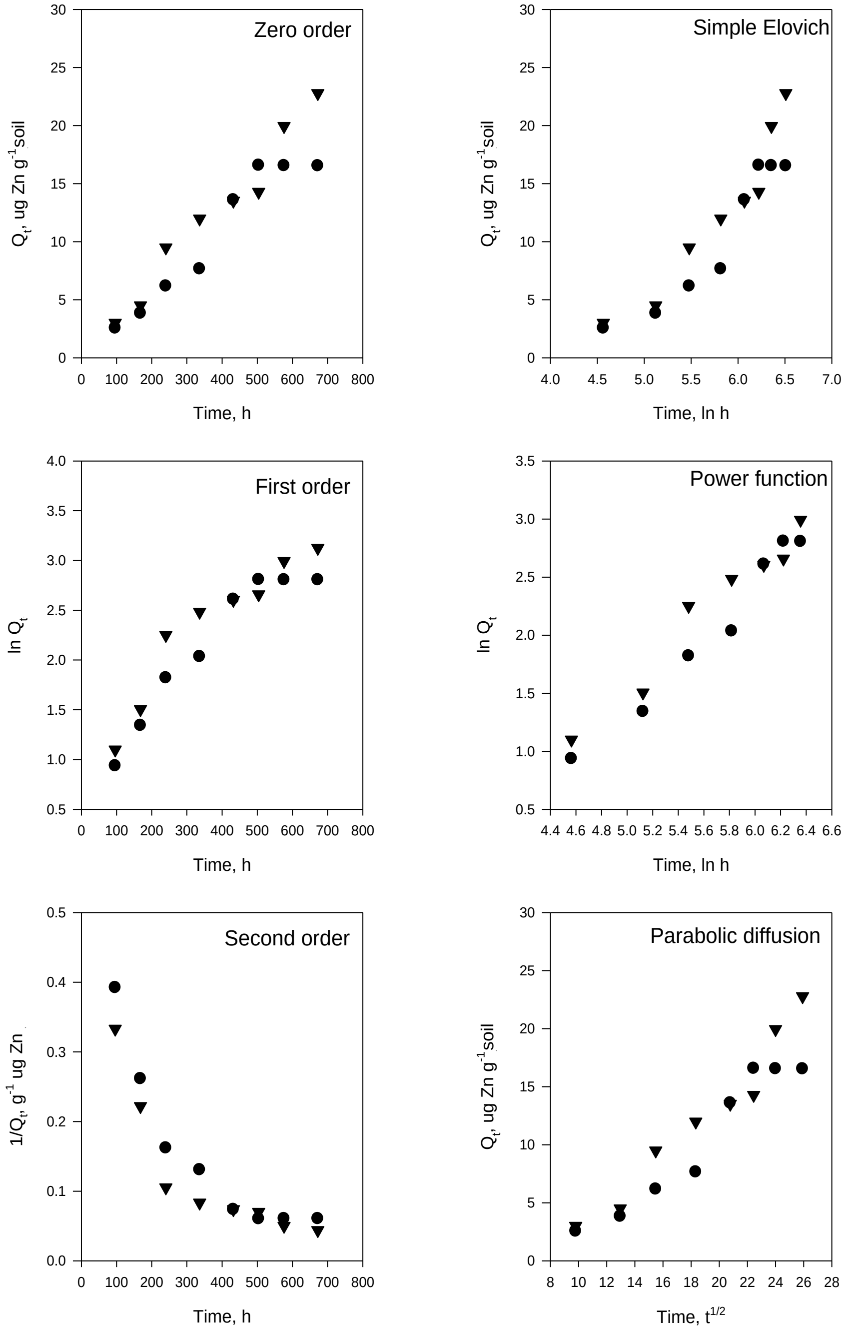

Fig 4. Kinetics of Zn in Typic Haplocalcid soil: Fe-Treatment (●), Fe + Zn Treatment (▼) .

Conclusion

The applications of Fe either singly or in combination with Zn increased concentration of AB-DTPA-extractable-Zn. Fe might replaced Zn on the sorption sites of the soil. Thus, it can be deduced that Fe-fertilization might improve Zn availability in soil. The kinetics of Zn aging in Typic Torriorthent soil reveal that Zn diffusion seemed to be the rate limiting step of Zn ageing in soil up to 336 hr (14 days), afterwards chemisorption became the rate limiting step. On the other hand, the first order model seemed to be the best fitting model for describing Zn ageing kinetics in Typic Haplocalcid soil.

The modeling of Zn retention data suggested specific and non-specific adsorption fittings on the heterogeneous sites in Typic Torriorthent soil; whereas, adsorption followed by precipitation fittings in Typic Haplocalcid soil.

Finally, the integrated sorption isotherms of Zn in soil, as in the studied Typic Torriorthent soil, could successfully be explained using the curve analysis models. On the other hand, further calculations should be helpful in explaining the consecutive sorption isotherms, as in the studied Typic Haplocalcid soil.

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References

Abbas, M.H.H. and Ismael, A.O.A. (2010) Mechanisms of cobalt (Co) retention by kaolinite, montmorillonite, calcium carbonate and humic acid. Res. *J. Agric. Biol. Sci.* **6:** 1103-1109.

Abbas, M.H.H. and Salem, H.M. (2011) Kinetics of iron retention by Typic Torriorthent and Typic Haplocalcid soils supplied with some micronutrients. *Annals of Agric. Sci. Moshtohor* **49:** 301-311.

Baeyens, B. and Bradbury, M.H. (1997) A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part I: Titration and sorption measurements. *J. Contam. Hydrol.* **27:** 199-222.

Cakmak, I. (2009) Enrichment of fertilizers with zinc: An excellent investment for humanity and crop production in India. *J. Trace Elem. Med. Biol.* **23:** 281-289.

Cakmak, I. (2010) Mineral improved crop production for healthy food and feed antalya. First annual meeting of the COST action FA 0905- Hurvestplus: global zinc fertilizer project, 1-5 November, Belek-Antalya, Turkey.

Dang, Y.P., Dalal, R.C., Edwards, D.G. and Tiller, K.G. (1994) Kinetics of zinc desorption from vertisols. *Soil Sci. Soc. Am. J.* **58:** 1392-1399.

Donner, E., McLaughlin, M., Hodson, M., Heemsbergen, D., Warne, M., Nortcliff, S. and K. Broos (2012) Ageing of zinc in highly-weathered iron-rich soils. *Plant Soil* **361:** 83-95.

Dudka, S. and Miller, W.P. (1999) Accumulation of potentially toxic elements in plants and their transfer to human food chain. *J. Environ. Sci. Health*, Part B **34:** 681-708.

Guilbert, J.J. (2002) The world health report 2002 - Reducing Risks, Promoting Healthy Life. Health World Organization Web.

Gupta, S.S. and Bhattacharyya, K.G. (2011) Kinetics of adsorption of metal ions on inorganic materials: A review. *Adv. Colloid Interfac.* **162:** 39-58.

Klute, A. (1986) "*Physical and Mineralogical Methods",* Part 1, ASA-SSSA-Agronomy, Madison, Wisconsin, USA.

Kumpiene, J., Lagerkvist, A. and Maurice, C. (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. *Waste Management* **28:** 215-225.

Lohan, M.C., Crawford, D.W., Purdie, D.A. and Statham, P.J. (2005) Iron and zinc enrichments in the northeastern subarctic Pacific: Ligand production and zinc availability in response to phytoplankton growth. *Limnol. Oceanogr*. **50:** 1427-1437.

Mesquita, M.E. and Vieira e Silva, J.M. (1996) Zinc adsorption by a calcareous soil. copper interaction. *Geoderma* **69:** 137-146.

Page, A.L., Miller, R.H. and Keeney, D.R. (1982) "*Methods of Soil Analysis*", ASA-SSSA. Agronomy, Madison, USA.

Prasad, A.S. (2012) Discovery of human zinc deficiency: 50 years later. *J. Trace Elem. Med. Biol.* **26:** 66-69.

Priadi, C., Le Pape, P., Morin, G., Ayrault, S., Maillot, F., Juillot, F., Hochreutener, R., Llorens, I., Testemale D., Proux, O. and Brown, G.E. (2012) X-ray absorption fine structure evidence for amorphous zinc sulfide as a major zinc species in suspended matter from the Seine river Downstream of Paris, Ile-de-France, France. *Environ. Sci. Technol.* **46:** 3712-3720.

Puls, R.W. and Bohn, H.L. (1988) Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. *Soil Sci. Soc. Am. J.* **52:**1289-1292.

Rashid, A. and Ryan, J. (2004) Micronutrient constraints to crop production in soils with Mediterranean-type characteristics: A review. *J. Plant Nutr.* **27:**959-975.

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

Singh, D., McLaren, R.G. and Cameron, K.C. (2006) Zinc sorption–desorption by soils: Effect of concentration and length of contact period. *Geoderma* **137:**117-125.

Soltanpour, P.N. (1985) Use of ammonium bicarbonate DTPA soil test to evaluate elemental availability and toxicity. *Commun Soil Sci. Plant Anal.* **16:** 323-338.

Sposito, G. (2008) *"The Chemistry of Soils"*, 2nd ed., Oxford University Press, Inc., New York.

Tiller, K.G., Gerth, J. and Brümmer, G. (1984) The sorption of Cd, Zn and Ni by soil clay fractions: Procedures for partition of bound forms and their interpretation. *Geoderma* **34:** 1-16.

Wang, J.J. and Harrell, D.L. (2005) Effect of ammonium, potassium, and sodium cations and phosphate, nitrate, and chloride anions on zinc sorption and lability in selected acid and calcareous Soils. *Soil Sci. Soc. Am. J.* **69:** 1036-1046.

Welch, R.M. (2002) The impact of mineral nutrients in food crops on global human health. *Plant Soil* **247:** 83-90.

Welch, R.M. and Graham, R.D. (2004) Breeding for micronutrients in staple food crops from a human nutrition perspective. *J. Exp. Bot.* **55:** 353-364.

Wolt, JD. (1994) *"Soil Solution Chemistry: Applications in Environmental Science and Agriculture"*, 1st ed., John Wiley & Sons, Inc., New York.

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حركيات الزنك في أراضي Typic Torriorthent و Typic Haplocalcid

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تهدف الدراسة الحالية إلي التحقق من حركيات الزنك كدالة للزمن في نوعين من أراضي المناطق الجافة بمصر كما تهدف أيضا إلي وصف حالة ادمصاص الزنك في تلك الأراضي وللوصول إلي تلك الأهداف فإنه تم تحضين عينتين من أراضي Typic Torriorthent و Typic Haplocalcid تحت ظروف المعمل لمدة 28 يوم في وجود أملاح الحديد و/أو الزنك ثم استخلص الزنك خلال فترات زمنية مختلفة بواسطة AB-DTPA وتم حساب قيم الاحتجاز التراكمي للزنك وتم اختبار مدي موائمة هذه القيم كدالة للزمن مع النماذج الحركية المختلفة، كذلك أجريت تجربة أخري عن طريق رج أوزان معلومة من الأراضي موضع الدراسة مع سلسلة متدرجة التركيز من المحاليل القياسية للزنك ثم الترشيح وقدر الزنك في الراشح ومن خلال النتائج تم حساب الزنك المحتجز ثم تم اختبار مدي موائمة بيانات الاحتجاز مع نماذج تحليل المنحنيات والنماذج الشائعة لوصف الادمصاص في الأراضي، وقد أظهرت النتائج أن إضافات الحديد (مع أو بدون إضافة الزنك) احدث زيادة معنوية في تركيزات الزنك المستخلصة بواسطة AB-DTPA وقد لوحظت هذه الزيادة خلال 24 ساعة عقب الاضافة تلاها نقص في تركيزات الزنك المستخلصة بواسطة AB-DTPA من الأراضي موضع الدراسة، كما دلت النتائج أن نموذج الانتشار هو الأكثر موائمة لحركة الزنك في أرض Typic Torriothent حتي 336 ساعة ثم اصبح نموذج الوفيش البسيط هو النموذج الاكثر موائمة بعد ذلك، أما بالنسبة لأرض Typic Haplocalcid فكان النموذج الأكثر موائمة هو نموذج تفاعلات الرتبة الأولي، وعلي الجانب الأخر فقد أوضحت نتائج تحليل المنحنيات ومدي موائمة منحنيات الادمصاص أن ادمصاص الزنك في أرض Typic Torriorthent ربما حدث من خلال نوعين من الادمصاص احدهما متخصص والاخر غير متخصص حيث تم الأخير علي مواقع ادمصاص غير متجانسة بينما كان احتجاز الزنك في أرض Typic Haplocalcid يرجع الي تفاعلات ادمصاص في التركيزات المنخفضة يعقبها ترسيب في التركيزات الأعلي، ومن هذه الدراسة يمكن ان نستنتج أن نماذج تحليل المنحنيات يمكن أن تستخدم بنجاح لوصف منحنيات الادمصاص المتلازمة (المتوازية) في الأراضي بينما نحتاج إلي حسابات أخري لوصف منحنيات الادمصاص المتعاقبة في الأراضي.