

Zinc sorption by some Torrifluvents soil of Sub-Saharan region South of Libya

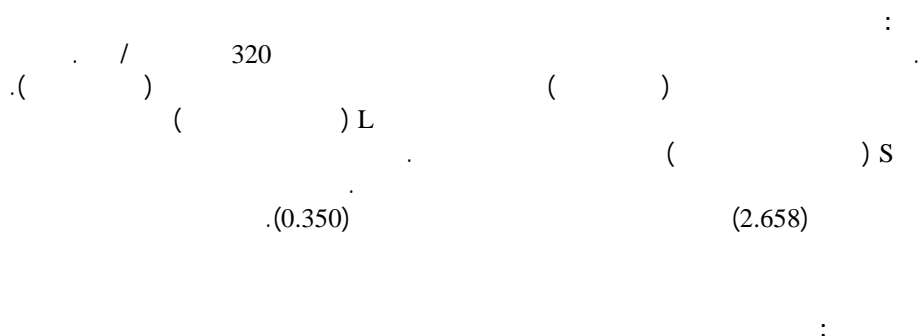
R. A. Al-Tamimi

Soil & Water Sci. Dept., College of Agric., Sebha Univ., P.O. Box 19332 , Libya

Abstract: Zinc sorption by four Torrifluvents soils from Sub-Saharan region, south of Libya was evaluated by equilibrating soil samples with concentrations of Zn covers a range of 0 to 320 ug/ml. Effect of zinc carrier were also examined by using two carriers i.e. sulphate and EDTA. Results obtained show that all soils have high affinity for Zn sorption. Sorption isotherm of L (high affinity) type was noticed with zinc sulphate whereas S (low affinity) type was noticed with EDTA. Curvilinear relation between sorbed zinc and zinc concentration in solution was proved by excellent fit of sorption to Freundlich equation. High mean values for sorption coefficient were noticed with sulphate (2.658) compared to EDTA carriers (0.350), While low mean value for regression coefficient (1/n) for mineral carrier (0.354) was found compared to organic carrier (1.376). Sorption coefficient were significantly correlated with clay, silt, carbonate and organic matter contents in case of sulphate carrier only. While negatively correlated with carbonate and organic matter contents when EDTA was used.

Keywords: Freundlich equation, Langmuire equation, sandy soils, sorption, Temkin equation, Zn-sulphate, and Zn-EDTA .

• •



Intoduction

Zinc is known as essential micro-nutrient for plant and haevy metal contaminant. Its sorption by soil is important in understanding its soil chemistry. Which is in turn important for agricultural and environmental purpose, by determining their availability to plant and their movment through soil. Zinc supplying power of soil, extraction by leaching and uptake by plant roots depending essentially on the amount of zinc present at sorption sites, (Sidhu et

al., 1977; Joshi et al., 1983). Jurinak and Bauer (1956) explained that there are two types of zinc sorption; non-specific sorption which occurred as a result of electrical attraction by active surface sites, and specific sorption which occurred as strong chemical bond at non-organic soil colloidal surfaces. In the later type of sorption, metal ion replace O^{-2} and OH^{-1} ions in inter crystal structure of oxides and hydroxides (Shuman, 1977; Kalbaski et al., 1978). Zinc may be irreversibly fixed by clay through

isomorphous substitutions or solid-state diffusion into the crystal structure of layer silicates (Adriano, 1986).

Zinc sorption by soils can be influenced by; soil reaction (Lindsay, 1979; Chatterjee and Mandal, 1985; Romkens and Salomons, 1998; Catlett et al., 2002; Dahiya, et al., 2005), clay content (Fahad, 1988; Razaq et al. 1993; Dahiya, et al., 2005), clay minerals type (Reddy and Perkins, 1974; Dahiya, et al., 2005), organic matter (Choudhari and Dhir, 1983; Falatah and Sheta, 1999; Catlett, et al., 2002; Dahiya, et al., 2005), total carbonate and active carbonate content (Sakal, et al. 1985; Fahad, 1988; Rahi, et al. 1990; Al-Kaysi, 2000), amount of zinc applied and zinc carrier (Norvell, 1977; Al-Ameri, 2001; Obrador et al., 2003). Zinc sorption may also be affected by chemical composition of soil solution (Wang and Dustin, 2005), ionic strength and complex formation with inorganic ligands in soil solution (Mattigod and Sposito, 1977). Al-Hadethi et al. (2001) mentioned that extractable Zn recovered from the added were negatively correlated with clay content, CEC, CaCO_3 , soluble calcium, and soluble magnesium. Zinc solubility also controlled by other reactions in soil such as mineral precipitation or adsorption onto Fe or Mn oxides (Catlett et al., 2002) and phosphate-Fe oxides interactions (Wang and Dustin, 2005). Continuous application of large amount of zinc to soil may be caused possible accumulation of this element and potential harm to the environment, as zinc can be transported downward in soil and possibly deteriorate ground water quality. Downward movement of zinc in soil may be occurred under conditions of excess rainfall or irrigation water especially in coarse-textured soils.

All soils in Sub-Saharan regions, south of Libya have been formed from alluvium material. Most of them classified as Torrifluvents and characterized by medium or coarse texture, neutral to

alkaline reaction and low content of organic matter. Our preliminary investigations show that zinc deficiency is widely dispersed in crops produced in these regions. Studies dealing with chemistry of zinc in soils of these regions are very scarce. So this study was carried out to explore zinc sorption in four Torrifluvents soils from these regions using two zinc carriers.

Materials and Methods

Four soil samples from surface layer (0-30 cm) of some cultivated fields of Maknussa agricultuer project, in Sub-Saharan region, south of Libya, were obtained. All studied soils classified as Torrifluvents. Before use, the soil samples were air dried and ground to pass through 2-mm sieve. Particle size analysis was carried out using pipet method. Organic matter by modified Walkley-Black method, electrical conductivity and pH, in soil paste extract, by conductometry and potentiometry respectively, total calcium carbonate equivalent by acid-neutralization method. All these analysis carried out as were described in Page et al. (1982). Available zinc was extracted by DTPA according to method proposed by Lindsay and Norvell (1978). Table 1 reported particle size distribution and some chemical characteristics of the studied soils. Sorption isotherm of Zn were determined by equilibrating 2 g soil in 70 ml plastic tube with 50 ml solution of Zn. Zinc equilibrating solution concentration were; 0, 10, 20, 40, 80, 160, and 320 $\mu\text{g ml}^{-1}$ as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or Zn-EDTA. All solutions were adjusted to pH 7 before used. Tubes were stoppered and placed in reciprocating shaker and shaken for 1 hr at a speeding rate enough to keep the soil particles in suspension. Samples then incubated for additional 23 hrs at 25 °C. After the equilibration time, the tubes were centrifuged and the supernatant then filtered. The filtrate was reserved for

determining Zn. Zinc was determined by using atomic absorption spectrophotometer. The amount of metal sorbed was calculated by subtracting the amount of metal remaining in the equilibrium solution from the initially added. Three physicochemical equations were used to characterize zinc sorption these are; Langmuir equation ($X/C = K_b - KX$), Freundlich equation ($\log X = \log K_f + 1/n \log C$) and Temkin equation ($X =$

$K_t + B \ln C$), where C = concentration of zinc ion in equilibrating solution, X= quantity of sorbed zinc ion ; K , K_f , K_t constant (k constant related to binding strength according to Langmuir equation) and b , B , n constant (b = maximum sorption according to Langmuir equation). Statistical parameters were used to choose most suitable equation characterize zinc sorption.

Table 1. Some physical and chemical characteristics of the soil used.

Field No.	EC dS m ⁻¹	pH	Zn-DTPA mg kg ⁻¹	g kg ⁻¹					Texture
				O.M	CaCO ₃	Clay	Silt	Sand	
7	1.19	8.58	0.40	17.0	57	80	81	839	Loamy sand
12	2.12	8.25	0.44	11.0	56	121	153	726	Sandy loam
31	0.76	8.34	0.36	5.6	17.5	49	48	903	Sand
60	0.68	8.34	0.33	3.3	19	40	41	919	Sand

Results and Discussion

All soils used showed a high sorption capacity at low concentration of zinc added (0-80 ppm) as ZnSO₄.7H₂O. A sharp increase in the amount sorped was found as the concentration of Zn initially added increased from 0 to 80 ppm. Continuous increase in the amount of sorped Zn with increasing concentration of the added was noticed by all soils, but with decreasing percent (Table 2). This clearly indicates the high ability of these soils to retain Zn. While, the amount and percent of sorbed zinc added as Zn-EDTA were low at low levels of addition and increased with increasing concentration of addition (Table 2). Sorption isotherms of Zn added as zinc sulfate for soils used are presented in Figure 1. The L type (high affinity type) of sorption isotherms for all soils

indicates the high affinity of these soils for Zn. Zinc sorption show curvilinear relation with its concentration in equilibrium solution within the range 5-30 ppm. This explained that rededy sorption sites were decreased. High increment in the sorped amount with incresing the concentration of the added Zn from 160 to 320 ppm indicate that this concentration was not large enough to saturation stage for all soils. Amount of Zn sorped by soils, as indicated by the position of sorption isotherms, was in the order: soil 12 > soil 7 > soil 31 > soil 60. This order of sorption was significantly correlated with clay, silt, calcium carbonate and organic matter contents (Table 3). This reslut was in agreement with the result of Choudhari and Dhir (1983); Razaq et al. (1993) and Falatah and Sheta (1999).

Table 2. Amount of sorped zinc in the studied soils.

Conc. Of added Zn ug ml ⁻¹	Sorped amount of Zn from the added (%)							
	Soil 7		Soil 12		Soil 31		Soil 60	
	ZnSO ₄	Zn- EDTA	ZnSO ₄	Zn- EDTA	ZnSO ₄	Zn- EDTA	ZnSO ₄	Zn- EDTA
10	99.2	12.9	99.8	17.5	99.0	20.3	98.8	6.7
20	98.9	16.1	99.7	21.0	95.9	20.3	97.2	17.9
40	95.2	17.4	98.9	19.5	86.1	20.7	87.2	12.5
80	81.7	23.6	85.7	25.6	71.6	24.6	68.5	20.7
160	63.3	33.6	80.2	34.1	57.5	33.8	53.4	33.9
320	55.2	29.8	65.4	35.3	55.0	30.7	50.1	26.0

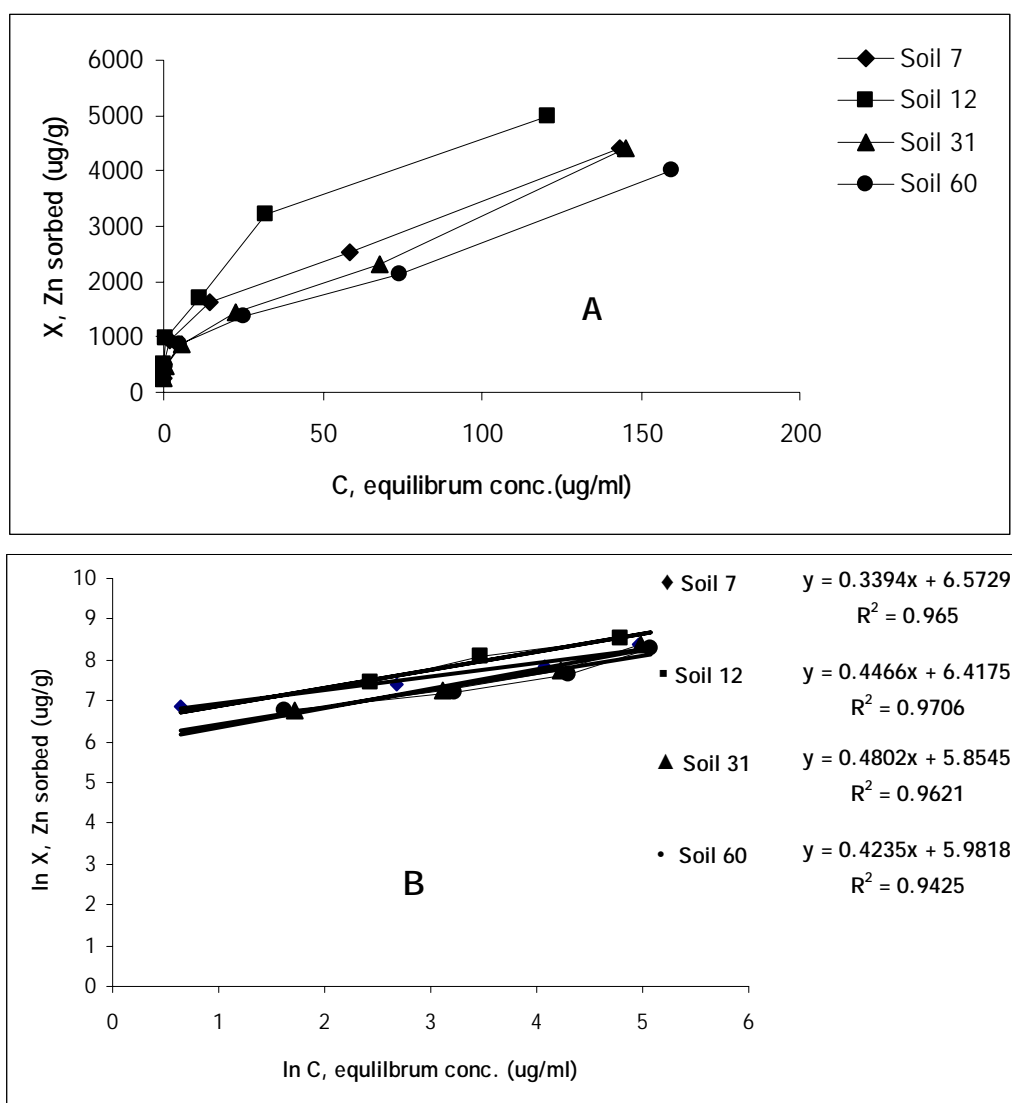
Figure 1. (A) Relationship between zinc sorped (X) and equilibrium concentration (C) when added as ZnSO₄.7H₂O, and (B) Sorption isotherm according to Freundlich equation.

Table 3. Linear regression analysis of quantity of zinc sorped as affected by clay, carbonate, and organic matter contents.

Soil parameter	Regression equation	Error df	Regression coefficient
ZnSO₄			
Clay	$Y = 1278 + 57.5 X$	3	0.986**
Silt	$Y = 1365 + 40.9 X$	3	0.981**
CaCO ₃	$Y = 1404 + 77.9 X$	3	0.805**
OM	$Y = 1510 + 200.6 X$	3	0.573**
Zn-EDTA			
Clay	$Y = 751.5 + 5.5 X$	3	0.509**
Silt	$Y = 752.4 + 4.8 X$	3	0.627**
CaCO ₃	$Y = 122.6 + 214.8 X$	3	0.09 ^{ns}
OM	$Y = 331.9 + 369.6 X$	3	- 0.325 ^{ns}

Where; Y is the mean of adsorped quantity ($\mu\text{g g}^{-1}$) and X is the percent of clay, CaCO₃ or OM ;
ns, not significant ,** significant at 0.01 level.

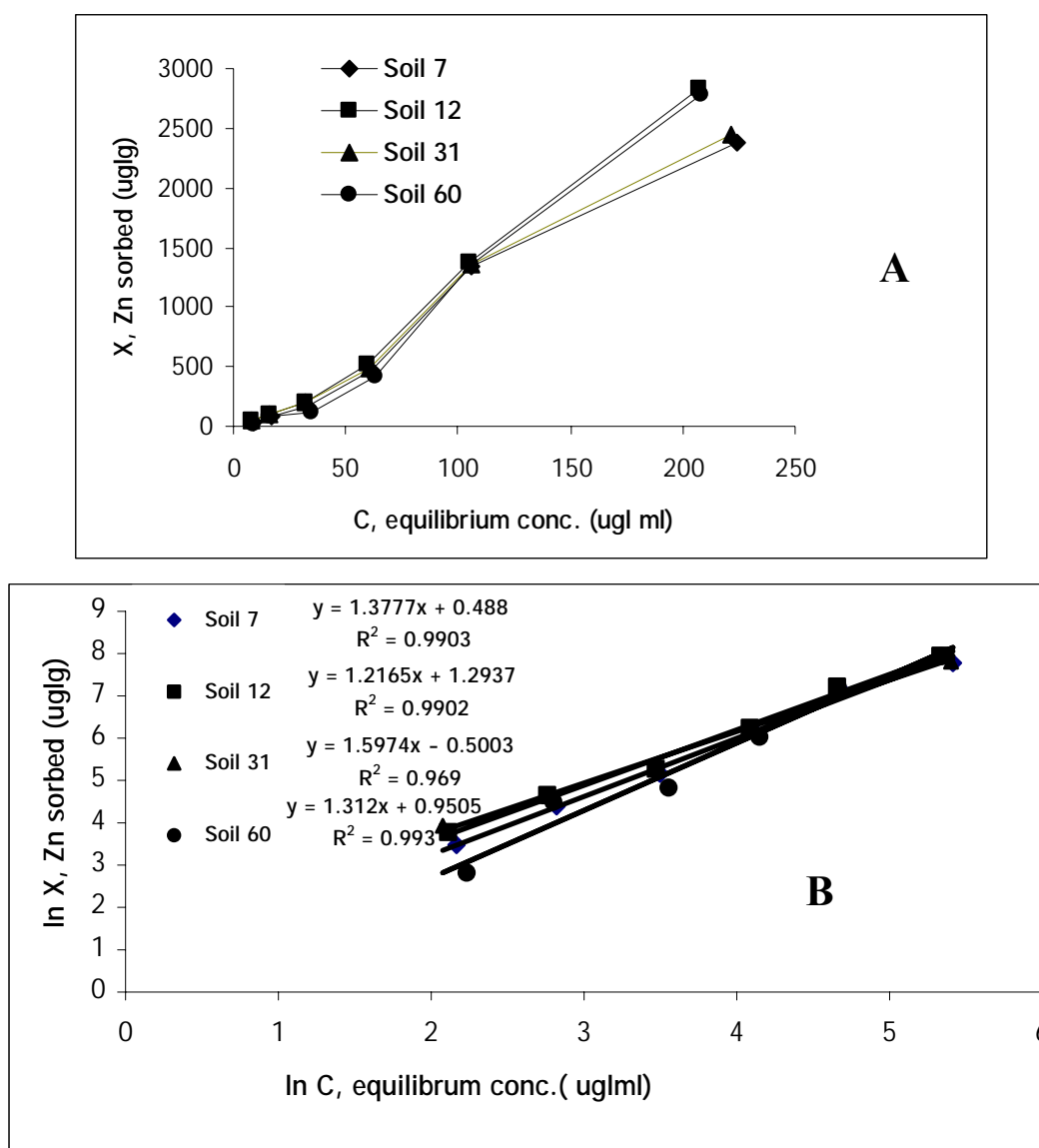


Figure 2. (A) Relationship between Zn sorbed (X) and equilibrium concentration (C) when added as Zn-EDTA, and (B) Sorption isotherm of Zn according to Freundlich equation.

Sorption isotherm of Zn added as Zn-EDTA presented in Figure 2. The S type of sorption isotherm for all soils with Zn-EDTA indicates low sorption affinity with low concentration. Continuous increase in the amount of Zn sorped also noticed with increasing added zinc. Sorption isotherm of Zn sorped from Zn-EDTA for the studied soils was in the order : soil 12 > soil 60 > soil 31 > soil 7. This indicate that reduction in the amount of sorped zinc as a result of using chelate carrier was different between soils used. This is may be attributed to differences in their chemical characteristics such as active carbonate, iron and manganese oxides and mineralogy. Sorption of zinc from Zn-EDTA was not correlated with carbonate and organic matter contents, but significantly correlated with clay and silt contents (Table 3). This result indicated that carbonate and organic matter effect on zinc sorption were sufficiency inhibited by EDTA carrier .

Statistical parameters (r^2 , t , SE_e) were used to find the best fit of Zn sorption to the three physicochemical equations used. Results obtained indicate that Frundlich equation was excellent to describe the relation between Zn concentration in equilibrium solution and its sorption by soils. Frundlich equation has highest value of r^2 and t in comparision to langmuir and temkin equations (Table 4). The excellent fit of Zn sorption to Frundlich equation was in agreement with Saeed and Fox (1979), El-Gundy et al. (1994), Falatah and Sheta (1999) and Al-Ameri (2001). The confirmation of Zn sorption to Frundlich equation suggest that sorption of this metal at high concentration in all soils used is curviline process (Shukla and Mittal, 1979, Elrashidi and O'Conner 1982) .

Frundlich equation's constant (Table 5) explain that soils vary in zinc sorption. Mean sorption coefficient ($\log k_f$) for soils used were in the order: soil 12 >

soil 7 > soil 60 > soil 31. This result are in good agrement with the clay, clay + silt and calcium carbonate contents. High values for $\log k_f$ was noticed with zinc sulphate in comparison with chelated zinc. Over all mean of $\log k_f$ with sulphate and EDTA carriers were 2.658 and 0.350 respectively. This clearly explain a reduction of 7.594 times in $\log k_f$ with Zn-EDTA compared to Zn-sulphate carrier. Differences in $\log k_f$ are related to differences in properties and behaviour of the two carriers used, such as stability in soil system and ability to form precipitated minerals and components in soil solution. McBride (1989) indicated that some metal complexing ligands formed with EDTA supprress metal adsorption. Thus sorped amount from each fertilizer and release constant of them will effectively affected (Lahav and Hochberg, 1975; Norvell, 1977).

Sgnificant correlation were found between sorption coefficient ($\log k_f$) and content of clay (0.663*), silt (0.655*), calcium carbonate equvilent (0.761*) and organic matter (0.516*) when mineral carrier was used. Using organic carrier show low correlation between $\log k_f$ and the content of clay (0.420) and silt (0.394) and negative correlation with calcium carbonate equivalent (- 0.692 *) and organic matter (- 0.797**) (Table 6). This clearly explain the differences in sorption reduction value occured between the studied soils and confirmed the previous finding that organic carrier inhibit sufficiently zinc sorption by carbonate and organic matter in the studied soils.

Mean regression coefficient ($1/n$) value for mineral and organic zinc carriers were 0.354 and 1.376 respectively, which indicate that this factor was increased 3.887 times with using organic carrier compared to sulfate carrier. This confirmed the previous results found with $\log k_f$.

Conclusion

In conclusions, zinc sorption in the studied soils highly correlated with clay, silt, calcium carbonate and organic matter

contents. Effect of calcium carbonate and organic matter were highly inhibited by using EDTA as a carrier. This must be considered when planning for fertilization program with zinc in these soils.

Table 4. Statistical parameters for zinc sorption according to physicochemical equations used in this study.

Field No.	Treatment	Freundlich Equation			Langmuir Equation			Temkin Equation		
		r^2	t	S.E _e	r^2	t	S.E _e	r^2	t	S.E _e
7	ZnSO ₄	0.983	15.13	0.067	0.897	5.10	551.97	0.830	4.36	719.8
	Zn-EDTA	0.990	20.18	0.079	0.625	2.58	2.433	0.815	4.19	451.8
12	ZnSO ₄	0.969	11.19	0.098	0.887	5.60	1790.4	0.828	4.39	886.4
	Zn-EDTA	0.992	22.92	0.066	0.563	2.27	2.667	0.770	3.66	582.8
31	ZnSO ₄	0.968	10.98	0.092	0.989	19.20	112.79	0.694	3.01	994.0
	Zn-EDTA	0.990	20.13	0.072	0.456	1.83	2.265	0.804	4.05	470.7
60	ZnSO ₄	0.966	10.72	0.088	0.963	10.25	180.15	0.713	3.15	823.8
	Zn-EDTA	0.984	11.12	0.162	0.591	2.40	3.443	0.751	3.47	610.6
mean		0.981	15.63	0.089	0.746	6.15	330.76	0.775	3.78	693.1

r^2 : determination factor.

S.E_e : Standard error estimated .

Table 5. Constant of Frundlich equation for zinc sorption in the studid soils.

Soil No.	Treatment	log K _f	1/n
7	ZnSO ₄	2.854	0.338
	Zn-EDTA	0.212	1.377
	Mean	1.533	0.857
12	ZnSO ₄	3.003	0.376
	Zn-EDTA	0.413	1.312
	Mean	1.708	0.844
31	ZnSO ₄	2.055	0.358
	Zn-EDTA	0.558	1.219
	Mean	1.306	0.788
60	ZnSO ₄	2.720	0.343
	Zn-EDTA	0.216	1.597
	Mean	1.468	0.970
Mean With ZnSO ₄		2.658	0.354
Mean with Zn-EDTA		0.350	1.376

Table 6. Correlation factor between sorption coefficient ($\log k_f$) and some soil parameters.

Soil parameter	Carrier	
	Sulphate	EDTA
Clay	0.663*	0.420
Silt	0.655*	0.394
Carbonate	0.761**	- 0.692*
Organic matter	0.516*	-0.797**

*, ** = significant at 0.05 and 0.01 level respectively.

References

- Adriano, D. C. 1986. Trace elements in the terrestrial environment. Springer-verlag, New York.
- Al-Ameri, B. H. 2001. Behavior and efficiency of some zinc fertilizers in calcareous soils. M.Sc. Thesis. Agric. College, Univ. of Baghdad, Iraq.(in Arabic).
- Al-Hadethi, A. A., J. K. Al-Uqaili and A. K. Abbas. 2001. Relationship between extractable Zn and plant Zn in calcareous soils. *Dirasat J. Agric.Sci.* 28(1): 24-32.
- Al-Kaysi, S. Ch. 2000. Effect of physical and chemical properties of carbonate minerals in some Iraqi soils in zinc fixation. 1: Properties of carbonate minerals. *Iraqi J. Agric. Sci.* 30 (2): 53-72. (in Arabic).
- Catlett, K. M., D. M. Heil; W. L. Lindsay and M. H. Ebinger. 2002. Soil chemical properties controlling Zn availability in eighteen colorado soil. *Soil Sci. Soc. Am. J.* 66: 1182-1189.
- Chatterjee, A. K. and L. N. Mandal. 1985. Adsorption and desorption of zinc in soils of different physicochemical characters. *J. Indian Soc. Soil Sci.* 33:669-671.
- Choudhari, J. S. and R. P. Dhir. 1983. Zinc adsorption by arid soil. *Clays Clay Res.* 2:52-56.
- Dahiya, S., A. V. Shanwal and H. A. G. Hedge. 2005. Studies on the sorption and desorption characteristics of Zn(II) on the surface soils of nuclear power plants sites in India using a radiotracer technique. *Chemosphere* 60 (9): 1253-1261.
- El-Gundy, M. M., H. H. Hassona, M. F. Abdel-Sabour and R. A. S. Zalalu. 1994. Zinc sorption and desorption of some Egyptian shales. *Egypt. J. Soil Sci.* 34:389-401.
- Elrashidi, M. M. and G. A. O'Connor. 1982. Influence of solution composition on sorption of zinc by soils. *Soil Sci. Soc. Am. J.* 46: 1153-1158.
- Fahad, A. A. 1988. Fate of zinc applied to calcareous soil using ^{65}Zn as tracer: 1. Fractionation with time. *Arid Soil Res. Rehabilitation.* 2: 217-225.
- Falatah, A. M. and A. S. Sheta. 1999. Influence of dissolved organic carbon and initial moisture on zinc sorption by two arid soils. *Arid Soil Res. & Rehabilitation.* 13(2):133-144.
- Joshi, D. C., B. K. Sharma and R. P. Dhir. 1983. Studies on the adsorption of Zn by fine textured alluvial soils of arid Rajasthan. *Clay Res.* 2: 39-45.
- Jurinak, J. J. and N. Bauer. 1956. Thermodynamics of zinc adsorption on calcite, dolomite and magnesite

- type minerals. Soil Sci. Soc. Am. Proc. 20:466-471.
- Kalbasi, M., G. J. Racz and L. A. Lowen-Rudgers. 1978. Mechanism of zinc adsorption by iron and aluminum. Soil Sci. Soc. Am. J. 39: 464-470.
- Lahav, N. and M. Hochberg. 1975. Kinetics of fixation of iron and zinc applied as Fe-EDTA, Fe-HDDHA and Zn-EDTA in the soil. Soil Sci. Soc. Am. Proc. 39:55-58.
- Lindsay, W. L. 1979. Zinc, In: Chemical Equilibria in Soils. pp. 211-220. John Wiley & Sons. Inc. New York.
- Lindsay, W. L. and W. A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42:421-428.
- Mattigod, S. V. and G. Sposito. 1977. Estimated association constants for some complex of trace metals with inorganic ligands. Soil Sci. Soc. Am. J. 41:1092-1097.
- McBride, M. B. 1989. Reactions controlling heavy metals solubility in soils. Adv. Soil Sci. 10:1-56.
- Norvell, W. A. 1977. Equilibria of Metal Chelates in Soil Solution. In: Mortvedt, J. J.; P. M. Giordano and W. L. Lindsay. (Eds). pp.115-138. Micronutrients In Agriculture. 3rd ed. Am. Soil Sci. Soc., Inc. Madison, Wisconsin, USA.
- Obrador, A., J. Novillo and M. Alvarez. 2003. Mobility and availability to plants of two zinc sources applied to calcareous soil. Soil Sci. Soc. Am. J. 67: 564-572.
- Page, A. L., R. H. Miller and D. R. Keeney. 1982. Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. Am Soc. Agron., Inc., Soil Sci. Soc. Am., Inc., Madison, Wisconsin, USA..
- Rahi, H. S., I. I. Khuder and J. I. Juzeli. 1990. Zinc sorption in some calcareous soils of Erbil valley. Iraqi J. Agric. Sci. 21:150-162. (In Arabic).
- Razaq, I. B., A. A. Fahad, A. A. Al-Hadethi, H. A. Tawfeek and J. S. Mahmmod. 1993. Adsorption and fractions distribution of Mn and Zn in response to salts, lime and clay content of soils of arid regions. Basrah J. Agric. Sci. 6(1):25-44.
- Reddy, M. R. and Perkins, H. F. 1974. Fixation of zinc by clay minerals. Soil Sci. Soc. Am. J. 38:229-230.
- Romkens, P. F. A. M. and W. Salomons. 1998. Cd, Cu, and Zn solubility in arable and forest soils: Consequences of land use changes for metal mobility and risk assessment. Soil Sci. 163:859-871.
- Saeed, M. and R. L. Fox. 1979. Relations between suspension pH and zinc solubility in acid and calcareous soils. Soil Sci. 124: 199-204.
- Sakal, R., A. P. Singh, B. P. Singh, R. B. Sinha, S. V. Jha and S. P. Singh. 1985. Distribution of available micronutrient cations in calcareous soils as related to certain soil properties. J. Indian Soil Sci. 33: 672-675.
- Shukla, U. C. and S. B. Mittal. 1979. Characterization of zinc adsorption in some soils of India. Soil Sci. Soc. Am. J. 43: 905-908.
- Shuman, L. M. 1977. Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH. Soil Sci. Soc. Am. J. 41:703-706.

Sidhu, A. S., N. S. Randhawa and M. K. Sinha. 1977 Adsorption and desorption of zinc in different soils. Soil Sci. 124:211-218.

Wang, Jim Jian and L. Dustin. 2005. Effect of ammonium, potassium and sodium cations and phosphate, nitrate and chloride anions on sorption and lability in selected acid and calcareous soils. Soil Sci. Soc. Am. J. 69:1036-1046.