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Artículos de investigación científica y tecnológica

# The effect of calcium carbonate content on the zinc quantity-intensity relationship in some soils of Mosul, Irak

Efecto del contenido de carbonato de calcio en la relación cantidad-intensidad de zinc en algunos suelos de Mosul, Irak

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**Abstract:** The quantity-intensity relationship (Q/I) was used to evaluate thermodynamic parameters of zinc in soils under different agricultural management. Ten soil samples were collected from Mosul city to study zinc distribution of calcium carbonate content in these soils. Generally, Q/I relationship of zinc may provide an index for the strength and quantity of effective zinc supply to plants in soils. The Q/I parameters of zinc were studied to quantify zinc release before and after removing carbonates in the studied soils. Results showed that the zinc activity ratio (AReZn) is related to changes with labile zinc ( $\pm\Delta Z_n$ ) at equilibrium and increased together with increasing zinc concentrations, intensity (I) ranged between 0.8584 and  $0.9972 \times 10^{-3}$  mol/L<sup>1/2</sup> before removing carbonates and between 0.0909 and  $2.7626 \times 10^{-3}$  mol/L<sup>1/2</sup> after removing carbonates. The ranges of labile Zinc (ZnL) values before and after removing carbonates were between 0.5755-0.7815 and 0.0009-0.0104 cmol/kg, respectively, while the Zinc (PBCZn) before and after removing carbonates fluctuated from 0.5839 to 0.9104 and 0.00112 to 0.00990 cmol/kg(mol/L)<sup>-1/2</sup>, respectively. That means calcium carbonate increases exchangeable zinc and zinc capacity at equilibrium conditions. The free energy ( $-\Delta F$ ) ranged between -1.001 and -0.979 kJ/mol before removing carbonates and between -1.319 and -0.841 kJ/mol after removing carbonates. Gapon Selectivity Coefficient (kG) ranged between 0.0193835 and 0.027453 and 0.000045 and 0.00450 (mol/L)<sup>1/2</sup> before and after removing carbonates, respectively. Therefore, these results may be used as a reference for zinc soil fertilization, whereas thermodynamic parameters values may be used to predict soil ability to supply available zinc.

**Keywords:** calcos, calcium carbonate, Q/I parameters, zinc buffering capacity, zinc thermodynamics

**Resumen:** La relación de cantidad-intensidad se utilizó para evaluar los parámetros termodinámicos del zinc en los suelos bajo diferentes tipos de manejo agrícola. Se recogieron diez muestras de suelo de la ciudad de Mosul, Irak, para estudiar la distribución de zinc de diferentes contenidos de carbonato de calcio en estos suelos. En general, la relación de cantidad-intensidad (Q/I) de zinc puede proporcionar un índice para la concentración y cantidad de suministro efectivo de zinc a las plantas en suelos. Los parámetros de (Q/I) de zinc se estudiaron para cuantificar la cantidad de zinc antes y después de eliminar carbonatos en los suelos estudiados. La relación de actividad de zinc (AReZn) se asoció a los cambios con el zinc lábil ( $\pm\Delta Z_n$ ) en equilibrio y aumentó junto con las concentraciones crecientes de zinc, a partir de 0,8584 y  $0,9972 \times 10^{-3}$  mol/l<sup>1/2</sup> antes de eliminar carbonatos y entre 0,0909 y  $2,7626 \times 10^{-3}$  mol/l<sup>1/2</sup> después de eliminar carbonatos. Los rangos de valores de zinc lábil (ZnL) antes y después de eliminar carbonatos oscilaron entre 0,5755-0,7815 cmol/kg y 0,0009-0,0104 cmol/kg, respectivamente, mientras que el zinc (PBCZn) antes y después de eliminar los carbonatos fluctuó entre 0,5839 cmol/kg y 0,9104 cmol/kg y entre 0,00112 cmol/kg y 0,00990 cmol/kg(mol/l)<sup>-1/2</sup>, respectivamente. Eso significa que el carbonato de calcio aumenta el zinc intercambiable y la capacidad del zinc en condiciones de equilibrio. La energía libre ( $-\Delta F$ ) osciló entre -1,001 kJ/mol y -0,979 kJ/mol antes de retirar carbonatos y entre -1,319 kJ/mol y -0,841 kJ/mol después de eliminar carbonatos. El coeficiente de selectividad de Gapon (kG) osciló entre 0,0193835 y 0,027453 y entre 0,000045 y 0,00450 (mol/l)<sup>1/2</sup> antes y después de eliminar carbonatos, respectivamente. Estos resultados pueden usarse como referencia para la fertilización del suelo con zinc, mientras que los valores de los parámetros termodinámicos se podrían usar en la predicción de la capacidad del suelo para suministrar el zinc disponible.

**Palabras clave:** calcos, capacidad amortiguadora del zinc, carbonato de calcio, parámetros Q/I, termodinámica del zinc



## Introducción

Zinc is an essential element for natural plant growth and development, but its content in the soil is low compared to other essential nutrients (Sidhu et al., 1977). Zinc deficiency is widespread in many soils, especially those with a basic reaction (high pH) (Mam-Rasul, 2019). Calcareous soils, which are estimated at 10-30 % of the total soils in the world, suffer from zinc deficiency (Akrawi et al., 2021) because adsorption, precipitation, and fixation mechanisms create many forms of zinc (Akrawi et al., 2021), including free ions in the soil solution and soil reaction (Pérez-Novo et al., 2011), complex and fixed in the mineral composition of carbonate minerals (Al-Kaysi, 2000), silicate clays (Dahiya et al., 2005), phosphate-Fe oxides interactions, or adsorbed on the solid surfaces of the soil particles (Dandanmozd & Hosseinpour, 2010).

Quantity/Intensity (Q/I) is the ratio of the element amount in the solid phase to its concentration in the soil solution. The change in the Q/I curve reflects the soil's capacity to resist change in the concentration of an element in the equilibrium solution (Beckett, 1964). Thermodynamic parameters are used to predict the final destination of an element in the soil system in the early stages of equilibrium; they are also considered when evaluating the change in the free energy related to the transport of an element from the soil solution to the sites near the double electrical layer. These are primary keys that help to understand the interactions or randomness associated with the equilibrium process (Adhikari & Singh, 2003).

We used Woodruff's (1955) equation to calculate free replacement energy based on the equilibrium constant values ( $ARZ_{ne}$ ) of the zinc ion's activity ratios when there is no gain or loss to it. The negative result of the amount of energy change means that the interaction of zinc with soil is a spontaneous reaction and it not need heat, while a positive signal means that the reaction is non-spontaneous and needs heat-free energy, which is an excellent parameter to predict the amount of change in energy.

Several processes control the behavior of Zn Q/I parameters in soils, including adsorption-desorption and precipitation-dissolution (Pasricha et al., 1987). Some physical and chemical properties of the soil affect the Zn adsorption process, such as the amount of clay, organic matter content, total active carbonate content (Osman et al., 1980), and increased soil pH. This research aims to study the behavior of zinc adsorption via Q/I parameters such as zinc potential buffering capacity, labile zinc, zinc activity ratio, Gapon Coefficient, and exchangeable zinc-free energy in order to evaluate zinc bioavailability in these soils using ten calcareous soils samples from Northern Iraq.

## Materials and methods

### Study area and sample collection

Ten samples of representative surface soil were collected from different locations in Mosul, Nineveh Governorate, Iraq (table 1; figure 1). Samples were dried, crushed, and passed through a 2 mm sieve for subsequent chemical and physical analyses. Soils belong to Haplocalcids, Vertic Haplocalcids, according to Natural Resources Conservation Service and Agriculture Department (2010). Chemical and physical characteristics were determined based on soil analysis methods

(Page et al., 1982). Organic matter was established by dichromate oxidation, and the cation exchange capacity was obtained by treating the soil with neutral 1N  $\text{NH}_4\text{OAc}$  and 1N  $\text{NH}_4\text{OANa}$ ; final Na removal was read using a flame photometer. Electrical conductivity (EC) and soil pH were measured using a 1:2.5 soil to water suspension, while texture was determined according to Bouyoucos (1962). A t-test paired was used to compare texture and CEC before and after carbonate removal under the probability level 0.05, as shown in table 2 (Johnson & Bhattacharyya, 2019).

**Table 1.** The coordinates of the soil sampling locations in the study areas using GPS

No.	Locations of soils in Mosul	E (Longitude)	N (Latitude)
1	Nineveh Forests	43.125403°	36.361244°
2	North	Alqiba	43.034137°
3		Shiraykhan	43.061455°
4		Alssadat and Biewayza	43.161998°
5	Northeast	Bieshiqa	43.231027°
6		Alshilalat	43.194889°
7		Aleabbasia	43.193657°
8	East	Alqasr	43.234571°
9	West	Hamidat	36.406012°
10		Alrihanian	36.375645°

Source: Elaborated by the authors



**Figure 1.** Soil sampling locations in Mosul, Iraq

Source: Taken from Google Maps

### ***Carbonate removal of soil samples***

Two hundred fifty grams of each soil sample was placed in a plastic container, and the removal process was carried out as follows:

- 1) Carbonate minerals were removed from the soil with 1N sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) at pH = 5 (Holford & Mattingly, 1975). This step was repeated three times until removing calcium carbonate.
- 2) The soil samples were washed three times with 0.5 N aqueous calcium chloride solution  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . This step was repeated three times with 0.05 N.
- 3) The soil samples were washed three times with 95 % ethyl alcohol to ensure all dissolved ions were removed, as confirmed by estimating the chloride ion concentration.

### ***Experimental method and procedure***

The quantity-intensity parameters of  $\text{Zn}^+$  were determined according to Salmon (1964) by adding 50 mL of 0.01M  $\text{CaCl}_2$  solution containing 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 5, 7, 10 mmol/L  $\text{ZnCl}_2$  to 2.5 gm of the soil sample before and after removing carbonates. The soil suspensions were shaken for 2 h and left overnight (24 h) for equilibration and then centrifuged. The suspensions of soil samples were filtered, and the supernatants were analyzed for Zn by atomic absorption photometer and  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  by titration with versinate (Pasricha et al., 1987). The Zn intensity (I) or activity ratio of Zn ( $\text{AR}^{\text{Zn}}$ ) relative to  $\text{Ca}^{++}$   $\text{Mg}^{++}$  species of each equilibrium solution was estimated. The change in the amount of Zn in solution gained or lost by the soil ( $\pm\Delta\text{Zn}$ ) was calculated by equation 1.

$$(\pm\Delta\text{Zn}) = (\text{ci}-\text{cf}) \times \text{V}/\text{W} \quad (1)$$

Where:

V = Volume of solution  $\text{cm}^3$

W = Weight of dry soil kg

ci = Concentration of added zinc

cf = Concentration of zinc after equilibrium (mg/L)

The Zn intensity factor in the liquid phase of soil is expressed as activity ratio AR Zn and computed from the measured Ca, Mg and Zn in the supernatant solution after equilibration. The activity ratio of Zinc ( $\text{AR}^{\text{Zn}}$ ) was calculated according to the ratio law (equation 2) (Salmon, 1964)

$$\text{AR}^{\text{zn}} = a_{\text{zn}} / \sqrt{a_{\text{Ca}} + a_{\text{Mg}}} \quad (2)$$

Where:

$a_i$  = Ionic activity species (Ca, Mg, and Zn)

The ionic activity was calculated according to the Lewis equation (equation 3).

$$a_i = C_i \times y_i \quad (3)$$

Where:

$a_i$  = Ionic activity

$C_i$  = The species concentration of ions in mol/L

The ionic activity coefficients were calculated using the empirical Davies equation (equation 4).

$$\text{Log } y_i = -0.509 Z_i^2 [\sqrt{I} / 1 + \sqrt{I} - 0.3 I] \quad (4)$$

Where:

$y_i$  = The mean activity coefficient of the electrolyte

$Z_i$  = Ion species valence

$I$  = Ionic strength in mol/L

$$I = 0.013 * EC \quad (5)$$

Where:

$I$  = Ionic strength in mol/L

$EC = dSm^{-1}$

From a plot of  $(\pm \Delta Zn)$  versus the activity ratio, the Q/I parameters were obtained. The intercept of the Q/I curves on the  $AR^{Zn}_{equ}$  axis, where  $Zn = 0$ , gave the soil Zn activity ratio at equilibrium ( $AR^{Zn}_0$ ), which means the soil solution Zn activity relative to the Ca + Mg at equilibrium. The  $(PBC^{Zn}_0)$  was calculated as the slope of the linear section of the Q/I curve. Labile zinc ( $\Delta Zn_0$ ) was obtained from the intercept of the extrapolated linear part of the Q/I isotherm on the quantity axis. The free energy of Zn replenishment ( $-\Delta G^{Zn}_{equ}$ ) was computed from equation 6, as reported by Salmon (1964).

$$-\Delta F^{Zn}_{equ} = 2.303RT \log AR^{Zn}_0 \quad (6)$$

Where  $R$  and  $T$  are gas constant and absolute temperature, respectively.

Gapon constant was calculated according to equation 7.

$$k_G = PBC^{Zn} / CEC \quad (7)$$

Where:

$k_G$  = Gapon constant

$PBC^{Zn}$  = Zinc potential of buffering capacity

$CEC$  = Cation Exchange Capacity

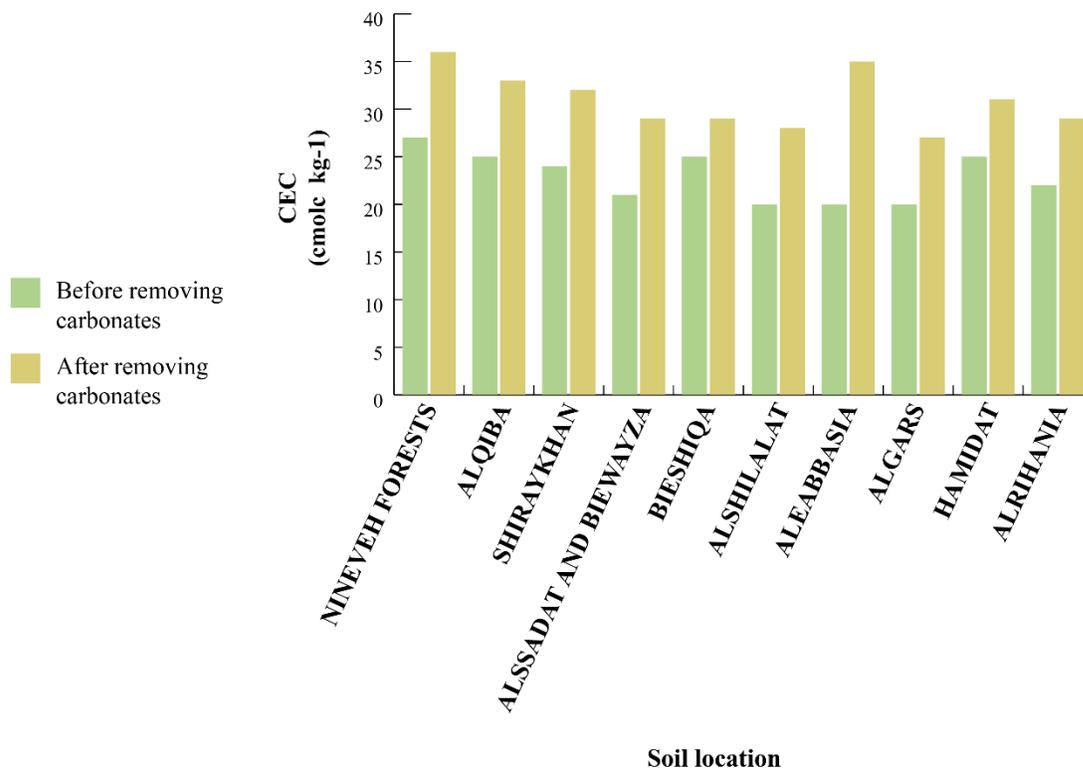
## Results and discussion

### Soil properties

The solubility of all Zn minerals decreases 100-fold for each unit increase in pH. Soil pH has been identified in many studies as one of the main factors affecting zinc mobility and sorption in soils (Girija et al., 2013). The pH values for the studied soil ranged between 7.4 -7.8 (table 3). Zinc becomes more soluble as pH decreases; therefore, zinc is more mobile and increasingly available, whereas at  $pH > 7.7$ , the dominant form is  $Zn(OH)_2$  (Giordano & Mortvedt, 1980). Higher pH values form low solubility complexes with carbonate and hydroxyl ions (McGowen et al., 2001). EC values of the studied soils ranged between 0.92-2.29 dS/m. These EC values indicated non-saline soils because they were affected by the relatively fewer amounts of rainfall, which reduced the concentration of saline ions and are related to the low solubility of calcium carbonate. Generally, calcareous soils are not saline, as suggested by Holford and Mattingly (1975). The EC values of the studied soil locations were low and non-saline according to Al-Kaysi (2000).

The presence of carbonate minerals in calcareous soils will lead to coating around clay particles

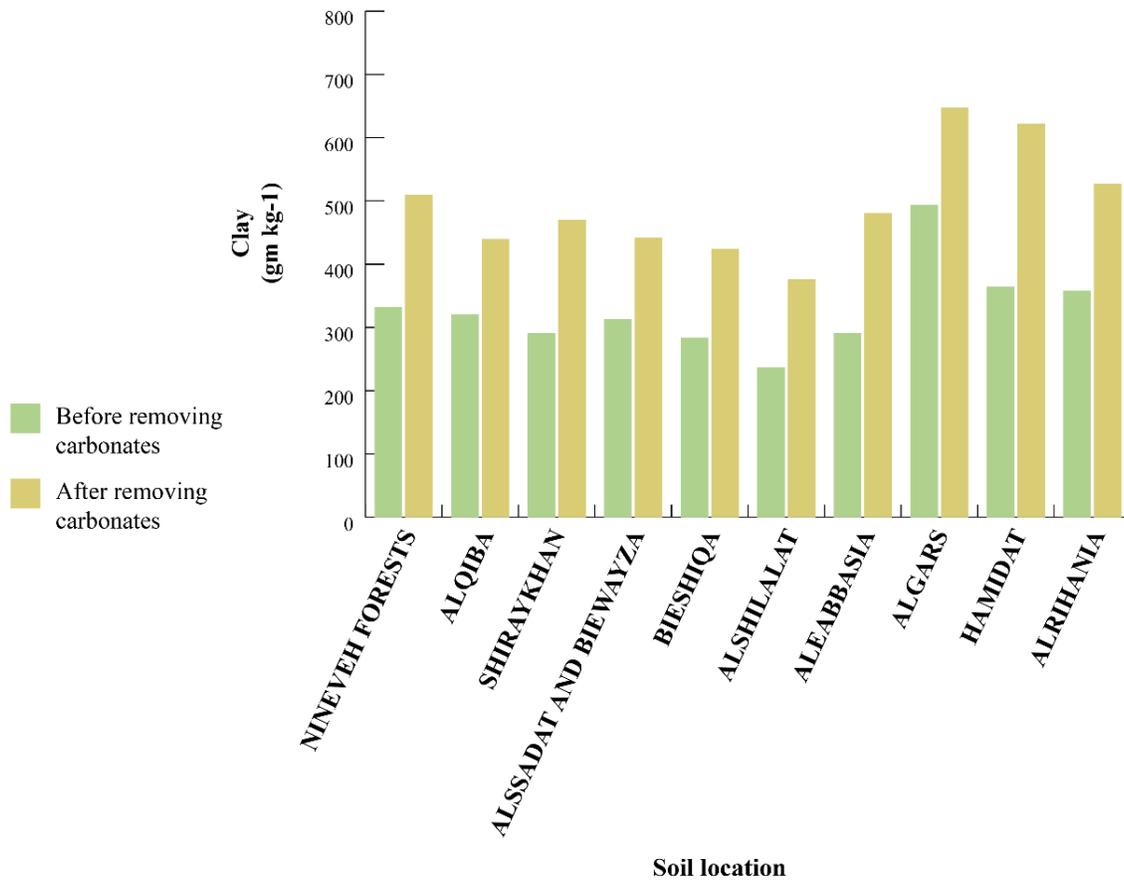
and organic matter, thus reducing the colloids' surface area responsible for ion exchange and adsorption. Also, Zn sorption by  $\text{CaCO}_3$  and precipitation as Zn hydroxide or Zn hydroxyl carbonates control Zn solubility in calcareous soils (Papadopoulos & Rowell, 1989). The removal process will result in the detection of the covered surfaces and the emergence of new surfaces for exchange, thus increasing the adsorption capacity of the ion, which is consistent with our findings, as it increased the cation exchange capacitance after removing carbonates (figure 2).



**Figure 2.** The cation exchange capacity values of the soils used in the study before and after removing carbonates.

Source: Elaborated by the authors

Carbonate minerals are one of the main components of the soil, especially in arid and semi-arid regions. The removal of these minerals from the soil can impact some of their characteristics. The results of the conducted experiment showed that removing carbonate minerals from the soil changed some of their physical and chemical properties (table 3) (Sheikh, 2019). After removing the carbonate minerals from the soil, an apparent change in the soil's texture appears before and after removing carbonate, as shown in Table 2. The percentage of clay also increased compared to the studied sites' soils, while the proportion of silt and sand decreased in these locations, which is due to the role of carbonate minerals in linking minute clay with silt and sand, or the presence of clay in clusters size of silt and sand coated with carbonate minerals, making it one of the largest (figure 3). This result was confirmed by Osman et al. (1980), who found a change in the texture after removing the carbonate minerals from all study soils.



**Figure 3.** Clay values in the soils under study before and after removing carbonate.  
Source: Elaborated by the authors

**Table 2.** Physical and chemical characteristics before and after removing carbonates from the calcareous soils

No.	Soil Locations in Mosul	Before removing carbonates								After removing carbonates						
		PSD g/kg				pH	EC <sub>e</sub> dSm <sup>-1</sup> at 25°C	CEC cmol <sub>c</sub> /kg	O.M. g/kg	CaCO <sub>3</sub> g/kg	PSD g/kg				CEC cmol <sub>c</sub> /kg	
		Sand	Silt	Clay	Texture						Sand	Silt	Clay	Texture		
1	North	Nineveh Forests	142	526	332	SCL	7.8	2.29	27	47	271	100 ns	390*	510*	C	36*
2		Alqiba	162	517	321	SCL	7.6	2.21	25	42.5	259	102.5*	457.5*	440*	SL	33*
3		Shiraykhan	238	471	291	CL	7.5	1.69	24	28	337	180*	350*	470*	C	32*
4	Northeast	Alssadat and Biewayza	233	454	313	CL	7.7	1.91	21	23.19	316	168.6*	389.6*	441.8*	C	29*
5		Bieshiqa	301	415	284	CL	7.5	1.47	25	33	342	244*	332 *	424*	C	29*
6		Alshilalat	253	510	237	SL	7.7	1.39	20	27.14	257	182.8*	440.8*	376.4*	SCL	28*
7	East	Aleabbasia	328	381	291	CL	7.5	1.66	20	34	335	288*	231*	481*	C	35*
8		Alqasr	209	297	494	C	7.4	1.42	20	21.61	290	135*	216.9*	648.1*	C	27*
9		Hamidat	215	421	364	SCL	7.5	1.63	25	22	311	131*	247 *	622*	C	31*
10	West	Alrihanian	244	398	358	CL	7.6	0.92	22	17.11	418	162*	311*	527*	C	29*

*Note.* \* means significant difference between before and after removing carbonates for Texture and CEC  
Ns means non-significant difference between before and after removing carbonates for Sand.

Source: Elaborated by the author

**Table 3.** Some quantity-intensity linear equations of zinc before and after removing carbonates

#	Soil Locations in Mosul	Before removing carbonates		After removing carbonates		
		Linear equation	(R <sup>2</sup> )	Linear equation	(R <sup>2</sup> )	
1	Nineveh Forests	$y = 0.9104x - 0.7815$	0.9725	$y = 0.00392x - 0.0104$	0.9711	
2	North	Alqiba	$y = 0.89115x - 0.7761$	0.9892	$y = 0.00257x - 0.0071$	0.9607
3		Shiraykhan	$y = 0.8785x - 0.7553$	0.9691	$y = 0.00231x - 0.0048$	0.9615
4		Alssadat and Biewayza	$y = 0.78208x - 0.7465$	0.9583	$y = 0.00211x - 0.0025$	0.9776
5	Northeast	Bieshiqa	$y = 0.73587x - 0.71685$	0.9674	$y = 0.00179x - 0.0022$	0.9705
6		Alshilalat	$y = 0.69552x - 0.69174$	0.9708	$y = 0.00158x - 0.0018$	0.9852
7		Aleabbasia	$y = 0.67841x - 0.6654$	0.9895	$y = 0.00151x - 0.0021$	0.9824
8	East	Alqasr	$y = 0.66588x - 0.66402$	0.9677	$y = 0.00145x - 0.0023$	0.9751
9		Hamidat	$y = 0.63291x - 0.62347$	0.9737	$y = 0.00112x - 0.0016$	0.9739
10	West	Alrihania	$y = 0.583892x - 0.575474$	0.9556	$y = 0.0099x - 0.0009$	0.9434

Note.  $y = \Delta Z_n =$  Adsorbed zinc (c.molc/kg)       $x = AR^{Z_n}_e$

Source: Elaborated by the authors

### *Characteristics of linear regression equations for the Q/I relationship of zinc for the study soils before and after carbonate removal*

The results shown in table 3 indicate the highly significant correlation of intensity and amplitude before and after removal, which is evident from the high R<sup>2</sup> values, which ranged between 0.9556 and 0.9895 before removal and between 0.9434 and 0.9852 after removal. The equations shown in table 3 revealed the difference in slope of the linear relationship before removal, whose value (0.9104-0.583892) decreased (0.00392-0.0099) after removal. As for the cut-off, which expresses the moving zinc values, it was higher before removal than after removal, as it ranged from 0.575474 to 0.7815 before removal, and decreased (0.0009-0.0104) after removal.

### *Zinc activity ratio (AR<sup>Zn</sup><sub>e</sub>) at equilibrium*

The AR<sup>Zn</sup><sub>e</sub> in soil solutions gave a reasonable estimate of zinc availability in soil. The differences in those soil parameters could be attributed to the difference in the Zn concentrations of equilibrating solutions, equilibration period, the Ca<sup>++</sup> or Mg<sup>++</sup> contents, and probably the differences in the soil minerals component. Q/I is defined as the ratio of the element amount in the solid phase to its concentration in the soil solution, while the change amount in Q/I reflects the soil's buffering capacity. The latter is the resistance that the soil exhibits towards change in the element concentration in the equilibrium solution.

The intensity and amplitude parameters of the studied soil and their adsorption state before and after removing calcium carbonate are shown in tables 4 and 5. There are differences in the slope coefficient and intercept values, which is related to the different textures, mineral composition, carbonate minerals content, organic matter, and zinc forms. The difference is that the straight-line equation shows that the values of the straight-line inclination increase with carbonates from the soil. According to Pasricha et al. (1987), the straight-line inclination represents the soil's buffering capacity.

The top of the linear curve allows estimating the zinc ion efficacy at equilibrium ( $AR^{Zn_e}$ ) and the ability of the soil to regulate zinc ion depletion, as shown in tables 4 and 5. The values of  $AR^{Zn_e}$  ranged between 0.8584 and  $0.9972 \times 10^{-3}$  (mol/L)<sup>1/2</sup> before removing carbonates and between 0.0909 and  $2.7626 \times 10^{-3}$  (mol/L)<sup>1/2</sup> after removing carbonates, decrease which may be due to the increase in the proportions of fine clay in the soil particles. Values after removing carbonates shows the zinc ion's preference for adsorption to the solid phase than for descending to the equilibrium solution, consistent with the results obtained for Gapon constant values.

As shown in tables 4 and 5, there is a reduction in Gapon values after removing carbonates. Also, there is a close relationship between the exchangeable soil capacity and the Gapon  $K_G$  constant by Equation 8:

$$K_G = PBC / CEC \quad (8)$$

**Table 4.** Thermodynamic parameters of Zinc in studied soil samples before removing carbonates

No.	Linear equation	(R <sup>2</sup> )	Before removing carbonates				
			$AR^{Zn_e} \cdot 10^{-3}$ (mol/L) <sup>1/2</sup>	$Zn_L$ cmol kg <sup>-1</sup>	$PBC^{Zn}$ cmol <sub>c</sub> kg <sup>-1</sup> (mol/L) <sup>-1/2</sup>	$-\Delta F$ kJ/mol	$k_G$ (L/mol) <sup>1/2</sup>
1	$y = 0.9104x - 0.7815$	0.9725	0.8584	0.7815	0.9104	-1.001	0.025289
2	$y = 0.89115x - 0.7761$	0.9892	0.8709	0.7761	0.8912	-0.999	0.027005
3	$y = 0.8785x - 0.7553$	0.9691	0.8598	0.7553	0.8785	-1.000	0.027453
4	$y = 0.78208x - 0.7465$	0.9583	0.9545	0.7465	0.7821	-0.986	0.026968
5	$y = 0.73587x - 0.71685$	0.9674	0.9742	0.7169	0.7359	-0.983	0.025375
6	$y = 0.69552x - 0.69174$	0.9708	0.9946	0.6917	0.6955	-0.980	0.024840
7	$y = 0.67841x - 0.6654$	0.9895	0.9808	0.6654	0.6784	-0.982	0.019383
8	$y = 0.66588x - 0.66402$	0.9677	0.9972	0.6640	0.6659	-0.979	0.024662
9	$y = 0.63291x - 0.62347$	0.9737	0.9851	0.6235	0.6329	-0.981	0.020416
10	$y = 0.583892x - 0.575474$	0.9556	0.9856	0.5755	0.5839	-0.981	0.020134

Note.  $AR^{Zn_e}$  = Zinc activity ratio;  $PBC^{Zn}$  = Potential buffering capacity;  $-\Delta F$  = Free energies;  $Zn_L$  = Labile zinc;  $k_G$  = Gapon Coefficient

Source: Elaborated by the authors

### **Potential buffering capacity ( $PBC^{Zn}$ )**

The potential buffering capacity of zinc ( $PBC^{Zn}$ ) is an indicator of the soil capacity to maintain

a given zinc activity at equilibrium conditions against zinc losses by plant uptake or leaching.  $PBC^{Zn}$  is calculated from the slope of the linear part of the Q/I plot, a measure of soil ability to supply zinc activity in soil solution. So, it denotes the ability of the soil to replenish the exchangeable zinc. Before removing carbonates, the highest  $PBC^{Zn}$  value was 0.9104 cmol/kg (mol/L)<sup>-1/2</sup> for soil site (1) and the lowest 0.5839 cmol/kg (mol/L)<sup>-1/2</sup> for soil site (10), while the value after removing carbonates ranged between 0.00112 and 0.00990 cmol/kg (mol/L)<sup>-1/2</sup> (table 4), which means an increase in the buffering capacity value. The buffering capacity of the soil under study increased due to the increase in carbonate content, which could be attributed to the carbonates factor's effect on the zinc behavior in the soil. Moreover, the influence of pH and the precipitation of zinc as Zn (OH)<sub>2</sub> reflects its release in soil and indicates an increase in the effort of the soil's buffering capacity, which shows the zinc ion's preference for adsorption to the solid phase than for descending into the equilibrium solution, similar to the results obtained by Pasricha et al. (1987) and Reyhanitabar (2012).

### ***The labile pool of Zinc (Zn<sub>L</sub>)***

It represents the amount of zinc capable of ion-exchange during equilibration between soil solids and soil solution. The labile zinc (Zn<sub>L</sub>) comprises two distinct components, namely non-specifically held or readily available zinc ( $\Delta Zn_0$ ) and specifically held or hardly available zinc (Zn<sub>x</sub>). The Q/I parameter values for studied soils before removing calcium carbonate are shown in table 4. The values of Zn<sub>L</sub> ranged between 0.5755 and 0.7815 cmol/kg, whereas the zinc values for studied soils ranged between 0.0009 and 0.0104 cmol/kg after removing calcium carbonate, which indicates that calcium carbonate plays a vital role in increasing zinc adsorption capacity via substitution and precipitation mechanisms. Thus, the increasing values of (Zn<sub>L</sub>) for natural soils are attributed to the high zinc affinity to the solid soil phase (table 4). Zinc behavior increases buffering capacity and Zn<sub>L</sub>. Besides high pH lets zinc be adsorbed as a monovalent cation such as Zn (OH)<sub>3</sub><sup>-</sup>, Zn HCO<sub>3</sub><sup>-</sup>, and Zn (OH)<sup>+</sup> (Girija et al., 2013). In the same way, they remove calcium carbonate, reducing the exchangeable surface reaction of zinc with the solid phase.

### ***Free exchange energies of Ca with Zinc (-ΔF)***

The standard free exchange energy (ΔF) expresses the potential of soil for zinc replenishment. It is an index of the amount of work needed to remove one mole of zinc from the exchange complex or fix it. It depends extensively on soil properties. This approach is used to characterize exchange equilibrium on clay and soil surface. The thermodynamic functions of soils have been used in recent years to describe zinc availability. Most of the thermodynamic studies on soils have involved calculating the free exchange energy from equilibrium. Also, thermodynamic parameters predict the final destination of elements in the soil system in the early stages of equilibrium. It is also considered to evaluate free energy change related to the transport of the element from the solution to the sites near the double electrical layer or clay equivalency layers. These primary keys help understand the interactions or randomness associated with the equilibrium process (Adhikari & Singh, 2003).

We used Woodruff (1955) to calculate the free replacement energy based on the equilibrium constant values.  $AR^{Zn}$  is the ionic activity ratios of the zinc ion when there is no gain or loss to it; the negative result of the amount of energy change means that the zinc's interaction with

the soil is a spontaneous reaction and does not need heat, while a positive signal means that the reaction is non-spontaneous and needs heat. Free energy is an excellent parameter to know the amount of change in energy. The  $-\Delta F$  values for studied soils before and after removing calcium carbonate are shown in tables 4 and 5. For natural soils,  $-\Delta F$  ranged between 1.001 and -0.979 kJ/mol, which is due to the negative turn of carbonates in covering clay minerals and prevents the occurrence of the specific adsorption process responsible for raising the free energy values of the adsorption process. Our results are consistent with Al-Othman et al. (2011) in that the low values of the substitution free energy indicate that the physical adsorption is the predominant mechanism in the adsorption process. After removing the calcium carbonate,  $-\Delta F$  was reduced and ranged between -1.319 and -0.841 kJ/mol because calcium carbonate removal exposed the specific exchangeable sites of clay mineral.

**Table 5.** Thermodynamic parameters of zinc in studied soil samples after removing carbonates

No.	Linear equation	$(R^2)$	After removing carbonates				
			$AR^{Zn_e} \cdot 10^{-3}$ (mol/L) <sup>1/2</sup>	$Zn_L$ Cmol/kg	$PBC^{Zn}$ cmol <sub>c</sub> /kg (mol/L) <sup>-1/2</sup>	$-\Delta F$ kJ/mol	$k_G$ (L/mol) <sup>1/2</sup>
1	$y = 0.00392x - 0.0104$	0.9711	2.6531	0.0104	0.00392	-0.841	0.000145
2	$y = 0.00257x - 0.0071$	0.9607	2.7626	0.0071	0.00257	-0.835	0.000103
3	$y = 0.00231x - 0.0048$	0.9615	2.0779	0.0048	0.00231	-0.875	0.000096
4	$y = 0.00211x - 0.0025$	0.9776	1.1848	0.0025	0.00211	-0.955	0.000100
5	$y = 0.00179x - 0.0022$	0.9705	1.2291	0.0022	0.00179	-0.950	0.000072
6	$y = 0.00158x - 0.0018$	0.9852	1.1392	0.0018	0.00158	-0.960	0.000079
7	$y = 0.00151x - 0.0021$	0.9824	1.3907	0.0021	0.00151	-0.932	0.000076
8	$y = 0.00145x - 0.0023$	0.9751	1.5862	0.0023	0.00145	-0.914	0.000073
9	$y = 0.00112x - 0.0016$	0.9739	1.4286	0.0016	0.00112	-0.928	0.000045
10	$y = 0.0099x - 0.0009$	0.9434	0.0909	0.0009	0.00990	-1.319	0.000450

Source: Elaborated by the author

### ***Gapon Selectivity Coefficient ( $k_G$ )***

The Gapon selectivity coefficient for Zn expresses the relative affinity soils may develop towards Zn in the presence of Ca and Mg both in the solid soil phase and soil solution under equilibrium conditions (Evangelou & Phillips, 1988).  $k_G$  values fluctuated within the range 0.0193835-0.027453 (mol/L)<sup>1/2</sup> before removing carbonates. Conversely, after the removal of carbonates, the values of the Gapon constant were 0.000045-0.00450 (mol/L)<sup>1/2</sup>. The changes in  $k_G$  values are attributable to the levels of exchangeable Ca and Mg. The effectiveness ratio

of clay surfaces is revealed after removing the carbonates and increases after washing, which resulted in a difference in the Gapon constant values (figures 2 and 3).

## Conclusions

Zinc is an essential trace element for humans and plants at low concentrations, but at high concentrations, it may be toxic to plant, animals and cause various disorders for living organisms. Accumulation of heavy metals and movement in soils depends on several soil characteristics: soil pH, CEC, type of clay minerals, organic matter, and calcium carbonate content. This research studies zinc behaviors in ten calcareous soils to evaluate zinc translocation between solid and liquid phases via Q/I parameters. In the presence of carbonate, zinc was retained more tightly to form complexes compounds with relatively low solubility and became unavailable to plant uptake. Removing calcium carbonate reduces the values of the parameters  $AR^{Zn}$ ,  $PBC^{Zn}$ ,  $-\Delta F$ ,  $Zn_I$ , and  $k_G$ , making zinc more bioavailable in the soil solution.

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## Disclaimer

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