

Adsorption and Desorption of Zn in Different Soils and Clay Minerals

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Abstract. Zinc adsorption was studied in three Ca-saturated soils that varied in their dominant clay minerals, organic matter and CaCO_3 contents and also in three Ca-saturated pure clay minerals, kaolinite, montmorillonite, and palygorskite that represented the dominant clays in the selected soils. The pH of all systems was maintained at 7 except Qarn calcareous soil where it was 7.5. The adsorbed Zn was sequentially extracted with 0.5 M CaCl_2 , 1 M MgCl_2 , 0.005 M DTPA and 0.1 M HCl. The linear fit of the adsorption data of all systems to Langmuir equation was excellent when the curve was resolved into two linear portions. The adsorption maxima of clay mineral systems were in the order montmorillonite > palygorskite >> kaolinite at low and high Zn concentrations. Kaolinite adsorbed less Zn with low bonding energy with most Zn adsorbed in the exchangeable form. Palygorskite adsorbed slightly less Zn than montmorillonite but with much higher affinity as indicated by the higher calculated bonding energy and the much higher percentage of Zn adsorbed in the difficulty available form (0.1 M HCl-extractable). The adsorption of Zn by soils was largely affected by the high organic matter (in Baha soil) and the high CaCO_3 content (Qarn soil) rather than by their dominant clay minerals, montmorillonite and palygorskite respectively. At low Zn concentrations, Zn adsorption maxima were in the order of their CEC; Baha > Qarn > Bakyria. At high Zn concentration the adsorption maxima were Qarn >> Baha >> Bakyria reflecting the role of CaCO_3 as an important adsorbent of Zn. Zinc adsorbed by Baha soil was mostly in the HCl-extractable fraction and such strong bonding was attributed to its high organic matter content. Zinc adsorbed by Qarn calcareous soil was largely in the DTPA extractable fraction and believed to be held on the CaCO_3 surface.

Introduction

The adsorption of Zn is one of the most important solid-liquid phase interactions determining the fixation and release of Zn in soil. Clay minerals play a major role in Zn retention in soil [1,2]. Other solid phase surfaces that can play an important role are carbonates [3,4], soil organic matter, [5] and hydrous oxide [6,7]. Sequential desorption of retained Zn by different extractants provides a measure of the different chemical pool of Zn of variable availability [8,9]. Zinc adsorption is known to be pH dependent [10, 11], and affected by exchangeable cations and ionic strength of the equilibrium solution [12, 13].

The aim of this work was to characterize Zn adsorption in some soils that represent the intensively cultivated areas in Saudi Arabia. These soils differ widely in their dominant clay minerals and CaCO_3 and organic matter content. This was carried out by comparing Zn adsorption using Langmuir equation and sequential desorption data of these soils with their respective pure clay minerals under constant conditions of pH, exchangeable cations and ionic strength.

Materials and Methods

Soils: Three surface soil samples (0-15 cm) varying in texture, organic matter and CaCO_3 contents as well as dominant clay mineral type (Table 1) were selected. These represent soils of the intensively cultivated areas in Saudi Arabia. The soil samples were air dried, ground, passed through 2 mm sieve and kept in plastic jars.

Clay minerals: The three clay minerals representing the dominant clay minerals in the selected soils were used; these were:

- Montmorillonite: (Wyoming bentonite) from Wards Nature Science Establishment Inc., Rochester, N. Y. (CEC = 67.3 cmole^+/kg).
- Kaolinite: from Ayerton Saunder & Co. LTD. Manufacturing Chemists, Dublin. (CEC = 6.2 cmole^+/kg).
- Palygorskite: from Gadsden County, Florida, USA. Supplied by Source Clay Minerals Respository, Dept. of Geology, Univ. of Missouri, Columbia, Missouri, USA (CEC = 21.7 cmole^+/kg).

Table 1. Chemical and physical characteristics of the investigated soils

| Soils | Bakyria | Qarn | Baha |
|---------------------------------|---------------|--------------|-------------------|
| Great soil group | Torrifluvents | | Haplustoll |
| pH (H_2O) 1:1 | 8.1 | 8.1 | 7.2 |
| EC, ms/cm | 3.2 | 1.9 | 2.3 |
| CaCO_3 , % | 3.3 | 22.6 | 3.8 |
| Humus % | 0.1 | 1.2 | 4.8 |
| CEC, cmol/kg | 4.3 | 9.6 | 25.6 |
| Dominant clay mineral | kaolinite | palygorskite | montmorillioinite |
| Sand, % | 81 | 54 | 27 |
| Silt, % | 5 | 21 | 49 |
| Clay, % | 14 | 24 | 24 |
| Soil texture | loamy sand | sandy loam | loam |

Samples of soils and clay minerals were repeatedly leached with neutral 0.5 M CaCl_2 to prepare Ca-saturated samples. The excess salts were removed by washing with dilute 0.005 M CaCl_2 solution followed by 90% ethanol.

Experimental procedure

Zn adsorption isotherm for Ca-saturated clays and soils at constant pH

Duplicate samples one gram of Ca-saturated soil and 0.5 g of Ca-saturated clay minerals were weighed in 25 ml polyethylene bottle, and 8-ml aliquot of 0.01 M CaCl_2 solution was added. The pH of the clay suspensions, Baha soil and Bakyrria soil were adjusted to 7.0, and that for Qarn calcareous soil was adjusted to 7.5 using a mixture of 0.1 M HCl- 0.005 M CaCl_2 or 0.05 M $\text{Ca}(\text{OH})_2$ -0.01 M CaCl_2 . The suspensions were equilibrated on a shaker for 2 hr, left to stand overnight and the pH of the suspensions was readjusted. The process was repeated until a constant pH reading was obtained. Five ml of 0.01 M CaCl_2 solution containing graded concentration of Zn (as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) was added to give final Zn concentrations ranging from 2 to 200 $\mu\text{g/ml}$ Zn, and the pH of the suspension was readjusted as above. The volume of the suspension was made up to 200 ml using 0.01 M CaCl_2 . The suspension was equilibrated for 24 hr, centrifuged and the content of Zn in solutions was determined by atomic absorption spectrophotometer. The amount of Zn adsorbed was calculated as the difference between the initial and final zinc concentrations in solution. The adsorption data were fitted to the Langmuir adsorption isotherm equation in the linear form:

$$C/x/m = 1/BK + C/B$$

where x/m is the amount of Zn adsorbed in mg per gram of soil or clay, C is the equilibrium Zn concentration in $\mu\text{g/ml}$, K is a constant related to the bonding energy of Zn to soil or clay, and B is the adsorption maximum. A plot of $C/x/m$ versus C gave a curvilinear relationship, and the sorption isotherm was resolved into two parts, each represented by a straight line of slope $1/b$ and intercept of $1/BK$. The slope and intercept were calculated separately by regression equations. The means of the two replicates were used to construct the straight line relationship of C Vs $C/x/m$ using regression analysis.

Sequential desorption of retained Zn

After equilibrating soil and clay samples with 50 μg Zn/ml in 1:20 soil-solution ratio at pH 7.0 for clay mineral and soil systems and pH 7.5 for Qarn calcareous soil, the samples were centrifuged and suspension was separated. The soil or clay residue was sequentially extracted with 20 ml of 0.5 M CaCl_2 , 1 M MgCl_2 , 0.005 M DTPA and 0.1 M HCl and Zn was determined in the extract according to Sidhu *et al.*, [8].

Results and Discussion

According to the Langmuir equation, a plot of C versus C/(x/m) in Ca-saturated soils and clay minerals showed a curvilinear relationship. The linear fit was excellent when the curve was resolved into two linear portions (Figs. 1 and 2). The differential affinity could be attributed to the surface heterogeneity of Ca-saturated soils and clays [9]. The two portions were considered separately as suggested by Shuman [10].

The linear relationship for the Langmuir isotherm (part 1) was valid up to Zn concentrations of 2–2.5 ug/ml in Baha, and Qarn soils, 4.0 ug/ml Zn in Bakyria soil and 4-5 ug/ml Zn in the clay mineral systems. The linear fit for soil and clay mineral systems was observed up to 11-14 ug/ml Zn. The adsorption maxima for part 1 (B_1) in

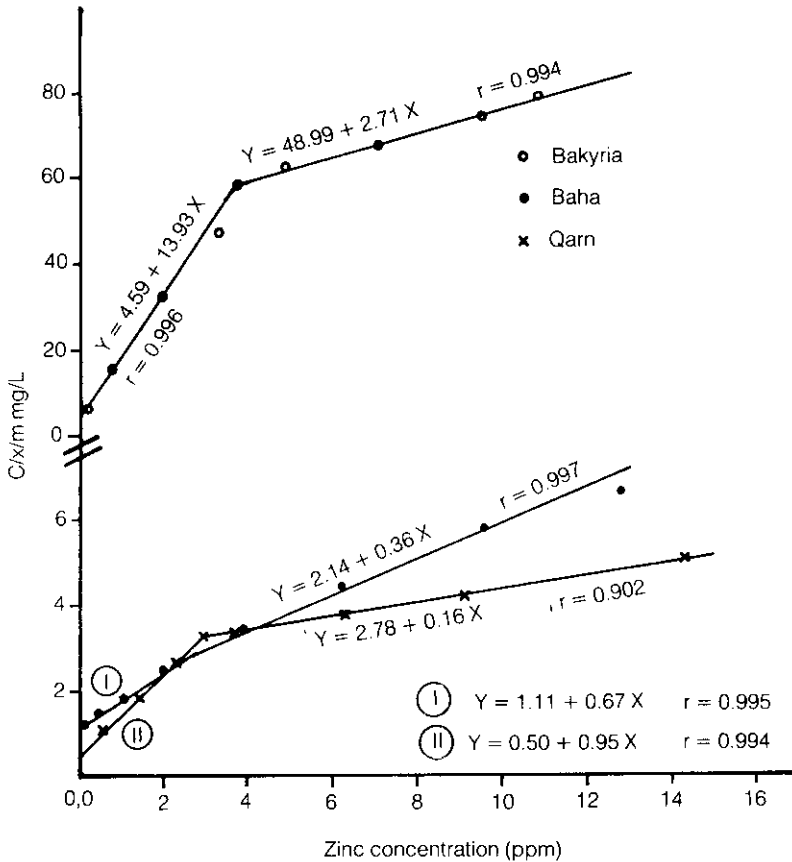


Fig. 1. Langmuir adsorption isotherm of Zinc in Ca-saturated soils.

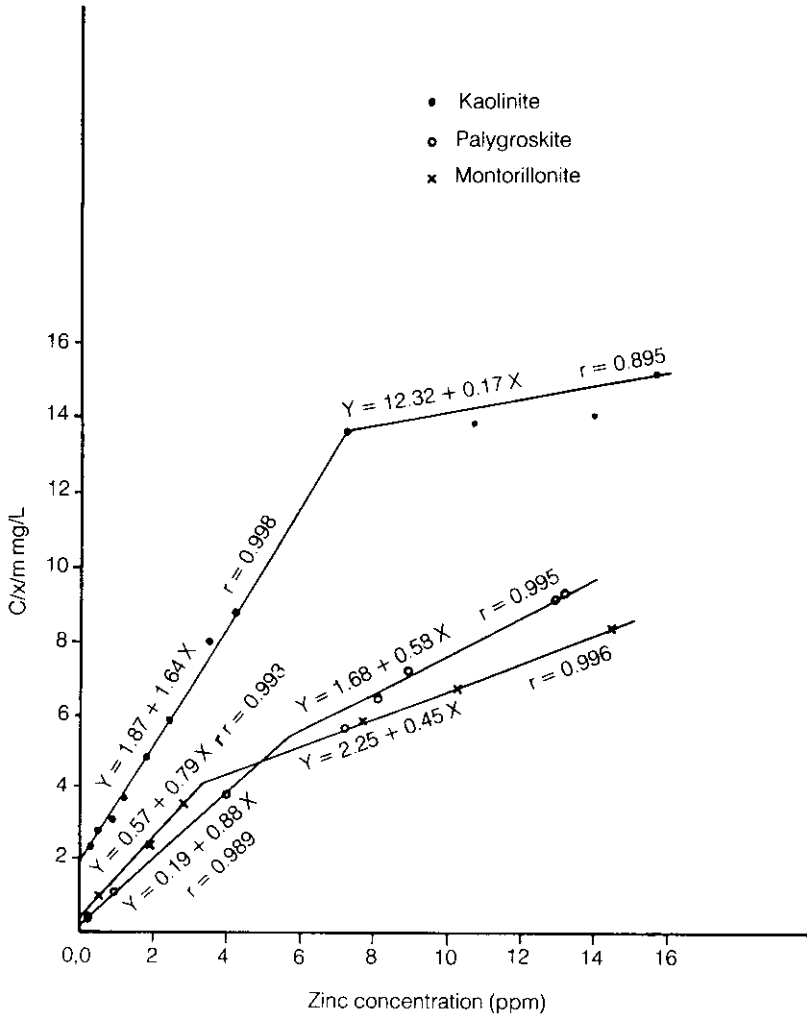


Fig. 2. Langmuir adsorption isotherm of Zinc in Ca-saturated clay minerals.

these Ca-systems were considerably lower than for part 2 and the inverse relationship between the adsorption maxima and the bonding energy was quite evident (Table 2). At low Zn concentrations (part 1), the adsorption maxima of Ca-saturated clay minerals were kaolinite < palygorskite < montmorillonite. Kaolinite, having the lowest CEC, adsorbed less Zn with much lower bonding energy. Palygorskite adsorbed approximately equal amount of Zn on the specific sites (B_1) as montmorillonite despite its much lower CEC. The adsorption maxima for part 1 (B_1) represented 5.9% of the CEC in montmorillonite and 16.2% of the CEC in palygorskite. This

Table 2. Langmuir coefficients for Zn adsorption on Ca-saturated soils and clay minerals

| Soil or clay minerals | pH in Suspension | Adsorption maximum (B) | | | | Bonding energy (K) | | Correlation coefficient (r*) | |
|-----------------------|------------------|------------------------|-------|---------------------|-------|--------------------|----------------|------------------------------|----------------|
| | | B ₁ mg/g | % CEC | B ₂ mg/g | % CEC | K ₁ | K ₂ | r ₁ | r ₂ |
| Kaolinite | 7.0 | 0.58 | 29 | 1.56 | 77 | 0.98 | 0.093 | 0.998 | 0.850 |
| Montmorillonite | 7.0 | 1.26 | 5.9 | 2.22 | 10.1 | 1.39 | 0.20 | 0.993 | 0.999 |
| Palygorskite | 7.0 | 1.14 | 16.2 | 1.64 | 23.2 | 4.63 | 0.45 | 0.999 | 0.997 |
| Bakyrria soil | 7.0 | 0.073 | 5.2 | 0.38 | 27.9 | 3.08 | 0.053 | 0.997 | 0.994 |
| Baha soil | 7.0 | 1.43 | 17.1 | 2.78 | 33.3 | 0.66 | 0.280 | 0.989 | 0.997 |
| Qarn soil | 7.5 | 1.01 | 32.0 | 5.88 | 26.2 | 2.15 | 0.063 | 0.998 | 0.998 |

* All values of the straight line regression were significant at 0.01 level.

indicated that the relative affinity of Zn to Ca-saturated palygorskite is higher than to montmorillonite at pH 7.0. The bonding energy of Zn on palygorskite (K_1) was considerably higher than on montmorillonite.

Zinc adsorption maxima for part 2 (B_2) were in the order of their respective CEC montmorillonite > palygorskite > kaolinite, but values of B_2 were not proportional to CEC (Table 2). Kaolinite adsorbed less Zn with considerably 7 lower bonding energy. The relatively high B_2 for kaolinite with respect to its CEC (77%) may be attributed to the relatively poor fit of linear relationship of part 2. The B_2 represented 10.1% of the CEC in Ca-saturated montmorillonite and 23.3% in Ca-saturated palygorskite. This again indicates the higher affinity of Zn to Ca-palygorskite. The higher bonding energy (K_2) of Zn in palygorskite, however, is probably attributed to inverse relationship between adsorption maxima (B) and bonding energy (K).

At low Zn concentrations (part 1), the adsorption maxima of Ca-saturated soils were Bakyrria < Qarn < Baha (Table 2). The low adsorption maximum of Bakyrria soil is attributed to its low CEC, clay content (dominantly kaolinite), CaCO_3 , and organic matter content. The amount of Zn adsorbed by Bakyrria soil on specific sites was very small and seemed to be relatively insignificant though held with much higher bonding energy. Specifically bonded Zn (B_1) was highest in Baha soil and was probably related to its high CEC and organic matter content [1,5].

Zinc adsorbed on more specific sites (B_1) represented only 5.2% of the CEC in Bakyrria though with high bonding energy. The respective value of Baha soil was

17.1% indicating its higher affinity for Zn due to higher clay and organic matter content. The amount of Zn retained with higher affinity in Qarn calcareous soil (B_1) represented a much higher percentage of CEC (32.0%). This may be attributed to its relatively higher pH (pH 7.5) and the higher CaCO_3 content of the soil.

It has been shown that Zn-precipitation, probably as $\text{Zn}(\text{OH})_2$, controlled Zn solubility at pH 7.5–9.0, whereas Zn adsorption was the controlling mechanism at pH 7.0 in Ca-saturated soil and clay mineral systems [14].

It was also demonstrated that Zn is strongly bonded on CaCO_3 surface [15]. The increase in the concentration of $\text{Zn}(\text{OH})^+$ with pH [16] and the higher affinity of Zn to palygorskite could also contribute to the higher affinity of Zn to Qarn calcareous soil.

Zinc adsorption maxima for part 2 (B_2) were in the order Bakyrria \ll Baha \ll Qarn (Table 2). The adsorption maxima of the noncalcareous soils were related to their respective CEC values. The adsorption maximum of the calcareous Qarn soil exceeded the determined CEC, suggesting the adsorption and/or the precipitation of Zn on CaCO_3 . Udo *et al.* [17], found that for calcareous soils, Zn adsorption maxima were related to soil carbonate and not to CEC. They reported that when Zn was added in excess of the adsorption maximum Zn was probably precipitation as ZnCO_3 rather than $\text{Zn}(\text{OH})_2$.

Sequential desorption of Zn

Zinc solubility in clay mineral and soil systems at pH 7.0 was shown to be controlled by Zn-adsorption mechanism [14]. The distribution of adsorbed Zn among different fractions of varying bonding energies was studied by sequential extraction with different extractants having varying power of extraction. Zinc extracted with 0.5 M CaCl_2 , 1 M MgCl_2 , 0.005 M DTPA, and 0.1 M HCl represents Zn associated electrostatically, specifically bonded, chelated with higher affinities, and associated with soil mineral pool, respectively [8, 18]. Data in Table 3 show that both kaolinite and Bakyrria soil adsorbed a small portion of the added Zn. A large portion of Zn adsorbed was in the readily exchangeable fraction (extracted by 0.5 M CaCl_2) and most of the Zn adsorbed was in the labile pool of Zn (extracted by 0.5 M CaCl_2 , 1 M MgCl_2 , and 0.005 M DTPA). Bakyrria loamy sand (kaolinitic soil) presented a similar pattern. Both systems exhibited low maximum adsorption capacity (B) and low Zn bonding energy at such high equilibrium Zn concentrations (Table 2).

The amounts of Zn desorbed from the montmorillonite clay system were more or less equally distributed among the four different Zn fractions with higher portion of adsorbed Zn held with higher affinities compared to the kaolinite system.

Table 3. Sequential desorption of Zinc added to Ca-saturated clays and soils at 1000 ug/g at pH 7.0 by different extractants

| Zn sorbed % of added | Zn desorbed % of added | | | | |
|-------------------------|----------------------------|--------------------------|----------------|--------------|------|
| | 0.5 M CaCl ₂ | 1 M MgCl ₂ | 0.005M DTPA | 0.1 M HCl | |
| Clay minerals | | | | | |
| Kaolinite | 12.6 | 5.8 | 2.8 | 2.6 | 1.5 |
| Montmorillonite | 39.1 | 8.2 | 9.5 | 9.4 | 12.2 |
| Palygorskite | 43.2 | 3.0 | 13.1 | 9.5 | 21.5 |
| Soils | | | | | |
| Bakyria | 15.7 | 3.6 | 2.9 | 1.7 | 2.4 |
| Baha | 84.4 | 15.0 | 4.4 | 10.1 | 46.8 |
| Qarn (pH 7.5) | 89.2 | 4.5 | 6.2 | 44.1 | 22.2 |
| Qarn (pH 7.0) | 66.2 | 6.1 | 6.3 | 30.7 | 17.0 |

Palygorskite adsorbed considerably lower Zn in the readily exchangeable form and much higher amounts of Zn in the difficulty available form (HCl extractant) compared to the montmorillonite system. This may indicate higher affinity of Zn to palygorskite and agree with the higher Zn bonding energy calculated from Langmuir isotherm (Table 2).

The distribution of the various fractions of adsorbed Zn in Baha loam and Qarn calcareous soils was different from their respective dominant clay minerals, montmorillonite and palygorskite, respectively. This indicates that soil constituents other than clay minerals largely affect Zn adsorption in these soils. Zinc adsorbed by Baha soil was mostly in the HCl extracted fraction. Such strong bonding of Zn is believed to be attributed to the high organic matter content of the soil. It has been shown that Zn moved less readily and the rates of Zn-diffusion and Zn-extractability by DTPA were lowest in soils high in organic matter despite their lower pH [5, 19, 20].

Zinc adsorbed by Qarn calcareous soil at pH 7.0 and pH 7.5 was mainly in the DTPA extractable fraction and to a less extent in HCl-extractable fraction. Very little Zn was adsorbed in the exchangeable form extracted by CaCl₂ and MgCl₂ (Table 3). Such distribution of adsorbed Zn among different fractions is quite different from that observed in palygorskite, the dominant clay mineral in Qarn soil. Qarn calcareous soil adsorbed Zn largely in excess of its CEC. These findings indicate that CaCO₃ surface plays a major role in Zn adsorption in calcareous soils [17, 21].

In conclusion, the adsorption of Zn on these soils was largely affected by the high organic matter content (Baha soil) and the high Ca CO₃ (Qarn soil) rather than by their dominant clay minerals, montmorillonite and palygorskite respectively. Zinc adsorbed by Baha soil (4.8% organic matter) was mostly in the difficultly available form (HCL extractable), whereas in Qarn calcareous soil it was largely in the chemically available form (DTPA extractable) and was believed to be held on CaCO₃ surface.

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ادمصاص وانطلاق الزنك في ثلاث ترب ومعادن طين مختلفة

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ملخص البحث . تمت دراسة ادمصاص وانطلاق الزنك في ثلاث ترب مشبعة بالكالسيوم وتختلف في محتوياتها المعدنية والعضوية ونسبة كربونات الكالسيوم . وشملت الدراسة كذلك ثلاثة معادن طينية هي الكاؤولنيت، الـمتموريللونيت وباليجورسكيت . وهي تمثل معادن الطين السائدة في الترب تحت الدراسة . وأوضحت النتائج أن ادمصاص الزنك على هذه الترب والمعادن تصفه معادلة لانجمير للادمصاص على سطح غير متجانس . وكان معامل الارتباط مرتفع جداً عندما حلل منحنى الادمصاص إلى خطين مستقيمين يصف كل منهما الادمصاص على مجموعة من مراكز الادمصاص تختلف في طاقة ارتباطها وسعة ادمصاصها عن الأخرى . وكانت قيم الادمصاص القصوى لمعادن الطين على النحو التالي :

الـمتموريللونيت أكبر من الباليجورسكيت وهذا أكبر من الكاؤولنيت . ادمصاص الزنك على الكاؤولنيت كان بكمية قليلة وبطاقة ارتباط منخفضة ، ومعظم الزنك المدمص كان في صورة قابلة للتبادل . وكان ادمصاص الزنك على الباليجورسكيت أقل من الـمتموريللونيت وبطاقة ارتباط أعلى وكان معظم الزنك المدمص في صورة صعبة الاستخلاص . تأثر ادمصاص الزنك في الترب بمحتوياتها من المادة العضوية وكربونات الكالسيوم أكثر من تأثرها بمعادن الطين السائد فيها . عند تراكيز الزنك المنخفضة كانت قيم الادمصاص القصوى مرتبطة بالسعة التبادلية الكاثيونية لهذه الترب وعند التركيزات العالية للزنك كانت قيم الادمصاص القصوى على النحو التالي :

تربة القرن الكلسية أعلى من تربة الباحة والأخيرة أعلى من تربة البكيرية مما يدل على الدور المهم لكربونات الكالسيوم في ادمصاص الزنك . ويعتقد أن معظم الزنك المدمص في تربة الباحة مرتبط بالمادة العضوية لهذه التربة في حين أن معظم الزنك المدمص في تربة القرن الكلسية كان على أسطح كربونات الكالسيوم .

