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RELATIONSHIP BETWEEN ZN AND CD IN SOIL AND PLANT

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ABSTRACT. The relationship between Zn and Cd uptake by plants is somewhat controversial according to the lack of information about this subject. The objective of this study was to increase our scientific understanding of soil about plant factors controlling Zn and Cd bioavailability and uptake. This experiment was carried out in the winter season of 2019. It aimed to solve the mystery of the Zn and Cd relationship in soil and plant uptake. Five plant species were under observation (carrot – *Daucus carota*, radish – *Raphanus sativus*, wheat – *Triticum aestivum* L., lettuce – *Lactuca sativa* and bean – *Vicia faba*). Plants were planted in plastic pots containing 2 kg sandy loam soil with duplicate and exposure to six Zn:Cd ratios (1:0.5, 1:1, 2:1, 3:1, 4:1 and 5:1) with increasing elements molar ratio of Zn to Cd in soil. After 45 days, plants were harvested. Zn and Cd were determined in roots and shoots. Results showed, that at low molar ratios of Zn:Cd in soil, the relationship between these metals in soil is almost synergistic and both elements are accumulated easily in plant tissues, but at high molar ratios, the relationship between these metals is almost antagonistic where Cd be more competitive to Zn uptake by plants. It was concluded that the 2:1 Zn:Cd ratio in the soil is the border between synergistic and antagonistic relationships.

Introduction

Heavy metals are naturally accruing in soil, but their excessive accumulation of them in the environment creates serious ecological problems (Badora, 2002). Because this enhances plant uptake causing accumulation of those metals in plant tissues and leading to high phytotoxicity and change in the plant community (Zayed *et al.*, 1998). The mobility of any heavy metals in the soil-plant system depends on their availability, which is influenced by soil heavy metal content, soil pH, type of clay minerals, cation exchange capacity, organic matter content, $CaCO_3$ content and plant species (Narwal, Singh, 1998; McLaughlin, Singh, 1999; Aljumaily *et al.*, 2022). Both heavy metals zinc (Zn) and cadmium (Cd) belong to group twelve in the periodic table. Cd is a toxic element but Zn is an essential nutrient for living organisms and is relatively active in biochemical processes at low levels, which can be toxic at high levels (Meharg, 2011). Cakmak and Marshner (1993) and Wu *et al.* (1995) reported that interaction between different elements creates a different toxic effect on an ecosystem compared to that of a single pollutant. However, most researchers have focused on the uptake of Cd and Zn in the plant rather than the availability of those metals in the soil. Some of them reported that cadmium treatment increased Zn concentration in plant shoots (Narwal, Singh, 1998). Other researchers reported that Zn application reduced the concentration of cadmium in plants (Abdel-Sabour *et al.*, 1998). However, results by Haghiri (1974) showed that the addition of Zn significantly increased cadmium concentration in plant shoots. Moreover, the availability of each Zn and Cd can be also affected by phosphorus fertilizer application (Lee, Doolittle, 2004). According to the lack of information about the relationship between Zn and Cd, it seems to be somewhat controversial because there are reports of both antagonism and synergism phenomena between these elements in the uptake and transport processes, (Kabata-

Pendias, Szteke, 2015). Zn and Cd have very similar chemical properties; they are taken up and translocated by similar pathways and transporter proteins (Waters, Sankaran, 2011). During transport, metals are either bound to ligands, chelated with amino acids or incorporated into protein. In high concentrations, Zn and Cd are phytotoxic to most plants. Sensitive plants at low levels of heavy metals show some visible toxicity symptoms include, including reddish colouration, chlorosis, necrotic lesions, and growth reduction (Milner, Kochian, 2008). To avoid heavy metal uptake, some plants may restrict metal transport across the root endodermis, sequester metal at the root cell wall and in vacuoles or complex those metals with organic acids and specific metal-binding proteins to reduce toxic effects in the plant tissue (Manceau *et al.*, 2008). Non-accumulating plants typically contain 30–100 mg kg^{-1} dry weight Zn and 0.1–10 mg kg^{-1} dry weight Cd (Waters, Sankaran, 2011). Threshold values for hyperaccumulation in plants vary based on the metal properties. In comparison to non-accumulating plants, hyperaccumulation for Zn is defined as >1% dry weight, and a threshold value for Cd is 0.01% dry weight (Assunção *et al.*, 2003). Because of the enhanced metal uptake, the root systems of hyperaccumulate can substantially alter the chemical composition within the rhizosphere surrounding their roots (Ru *et al.*, 2006). Each soil minerals, organic material and soil organisms co-exist in the rhizosphere and create a highly complex environment by influencing and altering one another. It has been hypothesized that Zn controls Cd uptake by the plant – Cd molar ratio rather than exchangeable Cd or total soil Cd (Chaney *et al.*, 2009). However, recent studies showed a relationship between total soil Cd and exchangeable soil Cd with plant Cd uptake in some plant ecotypes (Rosenfeld, 2013).

Therefore, the objective of this study was to investigate the effect of some soil chemistry concepts on the uptake and availability of these two metals using five plants belonging to different families.

Materials and Methods

This study was carried out in a greenhouse in the experimental farm Tikrit University, Iraq (2018–2019) located at 34° 36'N latitude and 43° 41'E longitude at an altitude of 250 m above mean sea level. The climate of the study area is semi-arid and sub-tropical with an average annual rainfall of 150 mm. The rainfall occurs from October to April (rainy season), which has uneven distribution. Averages of annual temperature, relative humidity, wind speed, sunshine duration per day, and potential evapotranspiration were 17.4 °C, 52.9%, 2.8 m s^{-1}, 11.2 h, and 1986 mm, respectively. This study was carried out to investigate the effect of interaction between Zn and Cd in the soil on an accumulation of these metals in plant tissues using different Zn:Cd ratios and five crops, including wheat, lettuce, carrot, bean, radish, belonging to five plant families on sandy loam soil. The soil sample was air-dried, crushed, and passed through a 2 mm sieve for laboratory tests to determine soil characteristics. Soil pH was measured in the soil:water suspension 1:1 with a pH meter and electrical conductivity (EC) was measured by using the Rhoades method (Page *et al.*, 1982). Cation exchange capacity was measured according to (Hendershot *et al.*, 1993). Particle size distribution was determined by the pipette method (Day, 1965). Calcium carbonate was determined by using acid-base back titration and organic carbon was determined by dichromate oxidation (Page *et al.*, 1982). Some physicochemical properties of the studied soil are given in Table 1. The soil was neutral to slightly alkaline and low in EC, calcium carbonate, organic matter, and clay content. The cation exchange capacity was 15 $cmole_c$ kg^{-1}.

Table 1. Physicochemical properties of the studied soil

PSD g kg^{-1}	Clay	120
	Silt	200
	Sand	680
	Texture	sandy loam
pH		7.31
EC_e	dS m^{-1} at 25ºC	0.68
CEC	$cmol_c$ kg^{-1}	15.0
O.M.	g kg^{-1}	12.5
$CaCO_3$		30.41
Available Zn	mg kg^{-1}	0.538
Available Cd		0.0820

EC – electrical conductivity; CEC – cation-exchange capacity; O.M. – organic matter

Experimental method and procedure

Two grams of soil samples were placed in polyethene tubes and treated with a 40 ml solution of different Zn:Cd ratios in duplicate for each ratio (0.5:1, 1:1, 2:1, 3:1, 4:1 and 5:1). The solutions were prepared by using sulfate salts ($ZnSO_4$, $CdSO_4$) of both metals in a background of 0.01 M of $CaCl_2$. Samples were shaken for two hours and left to equilibrate overnight. Tubes were centrifuged at 2 500 rpm and the supernatants were filtered. The filtrates were analyzed to obtain Zn and Cd concentrations in each filtrate. The sorbed metal by soil was calculated with the following equation (Dandanmozd, Hosseinpur, 2010):

$$M = \left(\frac{C_i - C_f}{W}\right) \times V \quad (1)$$

where:

M – the concentration of adsorbed metal, mg kg^{-1};

C_i – the initial concentration of metal in an equilibrated solution, mg L^{-1};

C_f – the final concentration of metal in equilibrium solution after filtration, mg L^{-1};

V – the solution volume, ml;

W – the weight of the soil, g.

Isothermal adsorption models

Freundlich and Langmuir equations (Giles *et al.*, 1974) were applied to fit the data from isotherm studies (Eq. 2).

$$qe = K_f \, Ce^b$$
$$\text{(linear form) Log qe} = \log K_f + 1/n \log Ce \quad (2)$$

$$qe = \frac{K_L\, q_m\, Ce}{1 + K_L Ce} \qquad (3)$$

where:

qe – the amount of adsorbed metal concentration at equilibrium, mg kg^{-1};

Ce – the concentration of the metal in solution at equilibrium, mg L^{-1};

q_m – the maximum adsorption of metal on soil, mg kg^{-1};

K_L (L kg^{-1}), K_f (L kg^{-1}) and b are constants.

Distribution coefficient K_d (Sposito, 1989):

$$K_d = \frac{S}{C} \qquad (4)$$

where:

S – adsorb metal on solid phase, mg kg^{-1};

C – metal concentration in equilibrium solution, mg L^{-1}.

Agricultural pots experiment

About 50 plastic pots were filled with 2 kg of soil and fertilized with nutrient solution containing N, P and K (40, 30 and 40 ppm, respectively). After a week pots were planted with five types of plants and after two weeks of growing these plants were treated with solutions of contained six Zn:Cd ratios (1:0.5, 1:1, 2:1, 3:1, 4:1 and 5:1, which is equal to 1:0.5. 5:5, 20:10, 45:15, 80:20 and 125:25 ppm) in duplicate for each ratio, besides control treatment (0:0).

Plant harvest and analysis

Plants were harvested after eight weeks of growth and cut about 1 cm above pot soil. The green part (shoots) and the roots were washed with deionized water and 0.01 M HCl solution. Shoots and roots were separated, cut off and kept in separate paper bags for drying in an oven at 60 °C. Dry weight for each plant (shoot and roots) were homogenized by grinding in a plastic mixer and passed through a 1 mm sieve. A 0.5 g of dried sample was digested in 5 mL of tri-acid mixture HNO_3, H_2SO_4, HCl (2:1:1), and 1 ml of $HClO_4$ dropwise during digestion at 150 °C till the clear solution was obtained. The final solution was diluted to 50 ml with distilled water and filtered through Whatman No. 42 filter paper (Tandon, 2005). The concentration of Zn and Cd were determined in plant parts using the atomic absorption Unicam 969 AA spectrophotometer (Unicam Sistemas Analíticos Lda, Lisbon, Portugal).

Statistical analysis

Student t-test in SPSS V24 software was used to compare K_d for each method in Cd and Zn at a 5% significance level. In addition, pairwise comparison for Zn and Cd and shoots and roots for all plants in our study was done by using Duncan Multiple Range Test (D.M.R.T).

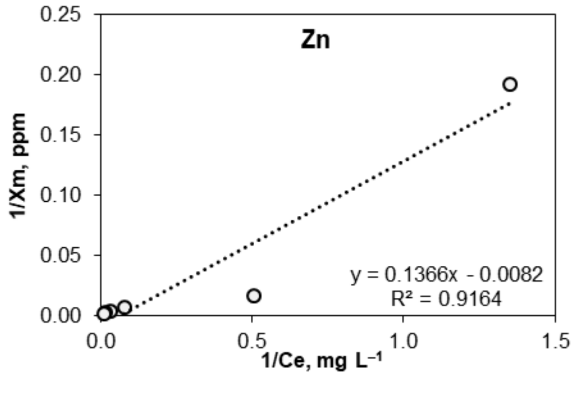
Results and Discussion

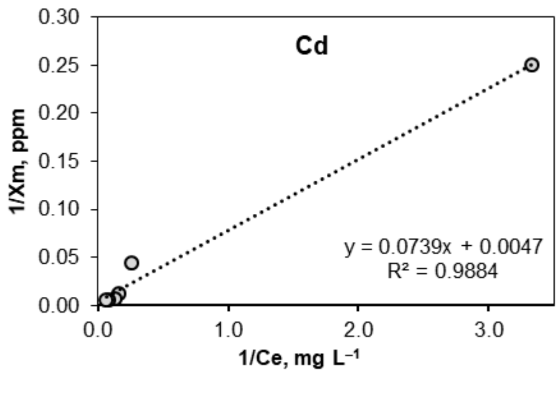
Sorption isotherms

Sorption isotherms batch experiments are very important in soil science because analysis of it is a useful technique to study the retention, availability of metals in soil and other important adsorption parameters (Dandanmozd, Hosseinpur, 2010). Many researchers have pointed out that Langmuir and Freundlich's isotherms are suitable for Zn and Cd adsorption studies (Shuman, 1975; Hooda, Alloway, 1994; Hanafi, Sjiaola, 1998; Maftoun *et al.*, 2004; Arias *et al.*, 2006). In this study, we try to investigate the effect of a different relationship between Zn and Cd in the soil on plant uptake for these two elements.

Figure 1 shows Zn and Cd adsorption on studied soil according to Langmuir and Freundlich equations when both elements exist together in soil solution with different ratios for each of them. The determination coefficient (R^2) for the Langmuir equation for both elements (Zn, Cd) ranged between (0.92–0.99) and for Freundlich equation R^2 ranged between (0.91–0.93). That means both equations succeeded in the mathematical description of Zn and Cd adsorption on solid phase (soil practical).

Langmuir equation





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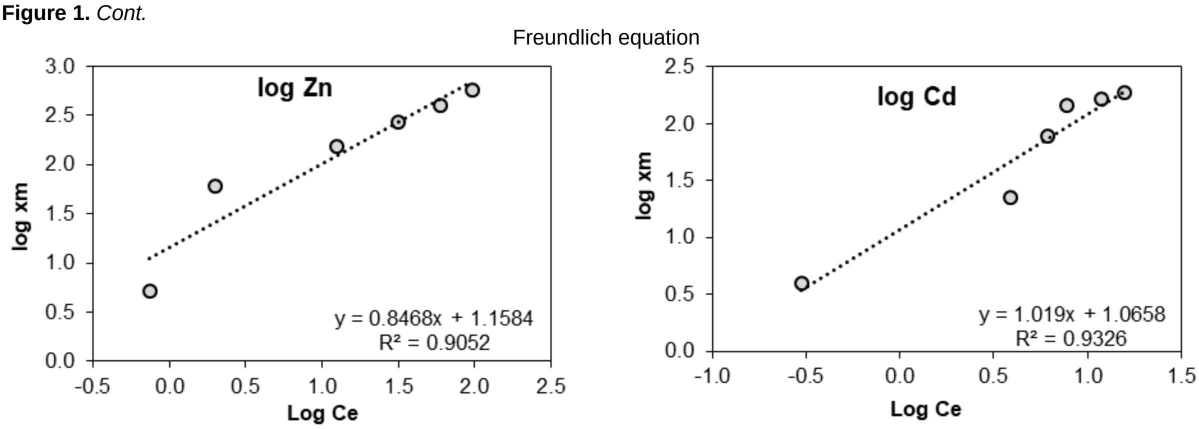


Figure 1. Langmuir and Freundlich equations for Zn and Cd in soil

Adsorption parameters for Langmuir and Freundlich equations are shown in Table 2. The amount of Zn adsorbed (Q_{max}) is 121.95 mg kg^{-1}, but (Q_{max}) for adsorbed Cd is 212.76 mg kg^{-1} on the same soil in this study. The difference in adsorbed elements may be attributed to their different adsorption affinities, and other factors related to ion characterization for example ionic size, electronegativity, charge:radius ratio, hydrate radius and so on. Many other types of research have reported the preferential adsorption of metals; they also found that the co-existence of metals reduces their tendency to be sorbed in the soil solid phase (Echeverria *et al.*, 1998).

Table 2. Langmuir and Freundlich equation parameters values

	Langmuir		Freundlich	
Cd	Q_{max}, mg kg^{-1}	212.76	1/n	0.98
	K_L, L g^{1}	0.063	K_f	11.63*
	K_L b, L kg^{-1}	13.40		
Zn	Q_{max}, mg kg^{-1}	121.95	1/n	1.18
	K_L, L g^{-1}	0.060	K_f	14.40*
	K_L b, L kg^{-1}	7.31		

* – means differ significantly at 5% according to the Students t-test between K_d for each equation in Cd and Zn

Bonding energy (K_L) for the Langmuir equation is similar for Zn and Cd (0.06 L g^{-1}) on the same soil, but Q_{max} values are different for Zn (121.95 mg kg^{-1}) and Cd (212.76 mg kg^{-1}). The difference in adsorbed metal quantities may be attributed to the soil pH because sorption of Cd is higher at high pH due to lower recombination with H_3O^+ ions compared to soils having low pH (Reed *et al.*, 2002). At a very low equilibrium concentration, the value of X/C represents the amount of adsorbed metal by the unit weight of the solid phase relative to that remained in the volume of the solution phase. This concept rearranged the Langmuir equation to the form X/C = K_Lb, which is termed the distribution coefficient (K_d) and designated by Iyengar and Raja (1983). Thus, K_d represents the sorption affinity of metal cations in a solution for the solid phase and this term can also be called (maximum buffering capacity). Although K_L values of the Langmuir equation are the same for Zn and Cd (0.06) L g^{-1}, the maximum buffering capacity is different widely from 7.31–13.40 L kg^{-1} for Zn and Cd respectively. This contradiction between K_L and K_Lb values resulted in Langmuir parameters is in disagreement with the results of many researchers. Higher bonding energy coefficient values have been related to specifically sorbed metal at high energy surfaces with low dissociation constant (Serrano *et al.*, 2005) and lower bonding coefficient values appear to be related to sorption on low energy surfaces with high dissolution constant (Ma, Rao, 1997; Adhikari, Singh, 2003). So, the relationship between bonding energy (1/n) and distribution coefficient (K_f) in Freundlich equation is more close to the previous scientific facts. Low 1/n value has high bonding energy with low dissociation constant (K_f) (Wong *et al.*, 2007). For Cd, 1/n value 0.99 and K_f value 11.63 L kg^{-1} and for Zn element, high 1/n value 1.18 has lower bonding energy with high dissolution constant value (K_f) 14.40. This fact may mean that the Freundlich equation is more suitable to describe Cd and Zn adsorption in the binary system than the Langmuir equation. Besides, the mean values of K_d at different equilibrium concentrations in this study for Zn and Cd are 11.82 and 12.66, respectively, also more close to Freundlich K_f than Langmuir K_Lb (Table 3).

Table3. K_d-values at different equilibrium concentrations for different ratios of Zn and Cd

Zn:Cd ratio, ppm	K_d-value	
	Cd	Zn
1:0.5	13.33	7.02
5:5	5.77	30.50
20:10	12.52	12.12
45:15	18.86	8.70
80:20	13.75	6.61
125:25	11.77	5.97
Mean	12.66	11.82

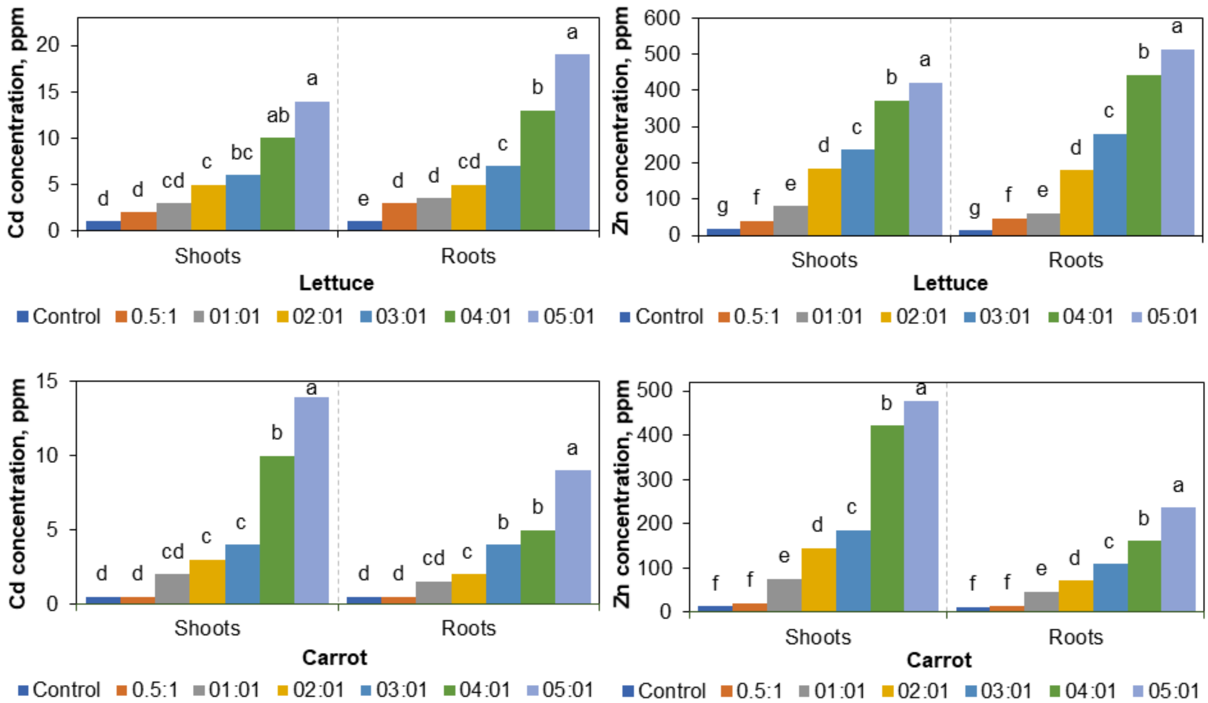
The results of Wen-Bo *et al.* (2009) indicated that K_d value for Zn was about 10 for competitive adsorption of Zn and Cd. Antoniadis and Tsadilas (2007) reported that the sorption of Cd into the soil can be well described by a Freundlich linear isotherm, whereas the closeness of Langmuir isotherm to the experimental results is low. Hanafi and Singh (1998) pointed out that the adsorption of Cd and Zn by Malaysian soils was best described by the Freundlich equation. The relatively high value of K_d indicates that the metal has been retained by the solid phase through sorption reactions, while relatively low values of K_d indicate that a large fraction of the metal remains in solution (Anderson, Christensen, 1988). Table 3 showed at very low concentrations of Zn and Cd 1:0.5 ppm, Cd adsorption is higher than Zn, whereas some equilibrium competitive has been achieved at 2:1 ratio but with higher concentrations 10:5 ppm, 12.52 K_d for Cd and 12.12 for Zn. In general, Zn concentration in the liquid phase increased with increasing Cd application and the solubility of Zn in soil solution was more complicated than the solubility of Cd as affected by interactions between them. Lee and Doolittle (2004) indicated that sorption and/or desorption of Zn and Cd affected pH in the soil solution system. The pH values increased with increasing Cd applications and values of pH decreased with increasing the concentration of Zn in soil solution.

Relationship between Zn and Cd in plant

Both elements Zn and Cd are taken up by the plant from the soil solution through the root hair epidermis, which is driven by passive transport through mass flow or diffusion mechanism (Waters, Sankaran, 2011). Pectins in the cell walls contain the carboxylic groups of polgalacturonic acid, which have a negative charge and act as cations exchangers in the cell wall. This negative charge cause accumulation of positively charged ions in the Donnan free space. Both elements, Zn and Cd, have a positive charge and therefore accumulation in the Donnan free space and in the plant, parts pass at first through roots and shoots (White, 2012).

Element bioavailability in soil solution is identified; interaction of soil properties with each other, but plant uptake of any element is a result of element bioavailability interaction with plant species and ecosystem. This study is carried out to investigate the optimum Zn: Cd ratio for plant uptake using five plant species – lettuce, carrot, bean, wheat, and radish, which belong to different plant families. Many previous studies showed both antagonistic and synergistic relationships between Zn and Cd by plant uptake of these two metals (Lagerwerff, Biersdorf, 1972; Oliver *et al.*, 1994; Nan *et al.*, 2002; Papoyan *et al.*, 2007). In our study, we used six Zn:Cd ratios (1:0.5–5:1) with increasing ionic strength for both metals to investigate the effect of the Zn: Cd ratio and ionic strength on plant uptake for these two metals.

Figure 2 shows that both elements were accumulated in all studied plants (roots and shoots) and increased as Zn and Cd increased in soil. According to our results, it may be stated that the ratio of Zn:Cd in soil solution controls the occurrence of synergism and antagonism between these metals. In addition, Shute and Macfie (2006) reported that interaction between Zn and Cd can be synergistic and antagonistic or they can have no effect on each other depending on growth conditions – Zn and Cd status of the soil, and plant species. Chaoui *et al.*, (1997) also mentioned that the increase of Cd and Zn in plant tissue might be related to the interaction between these metals and their combination in soil and soil characteristics.



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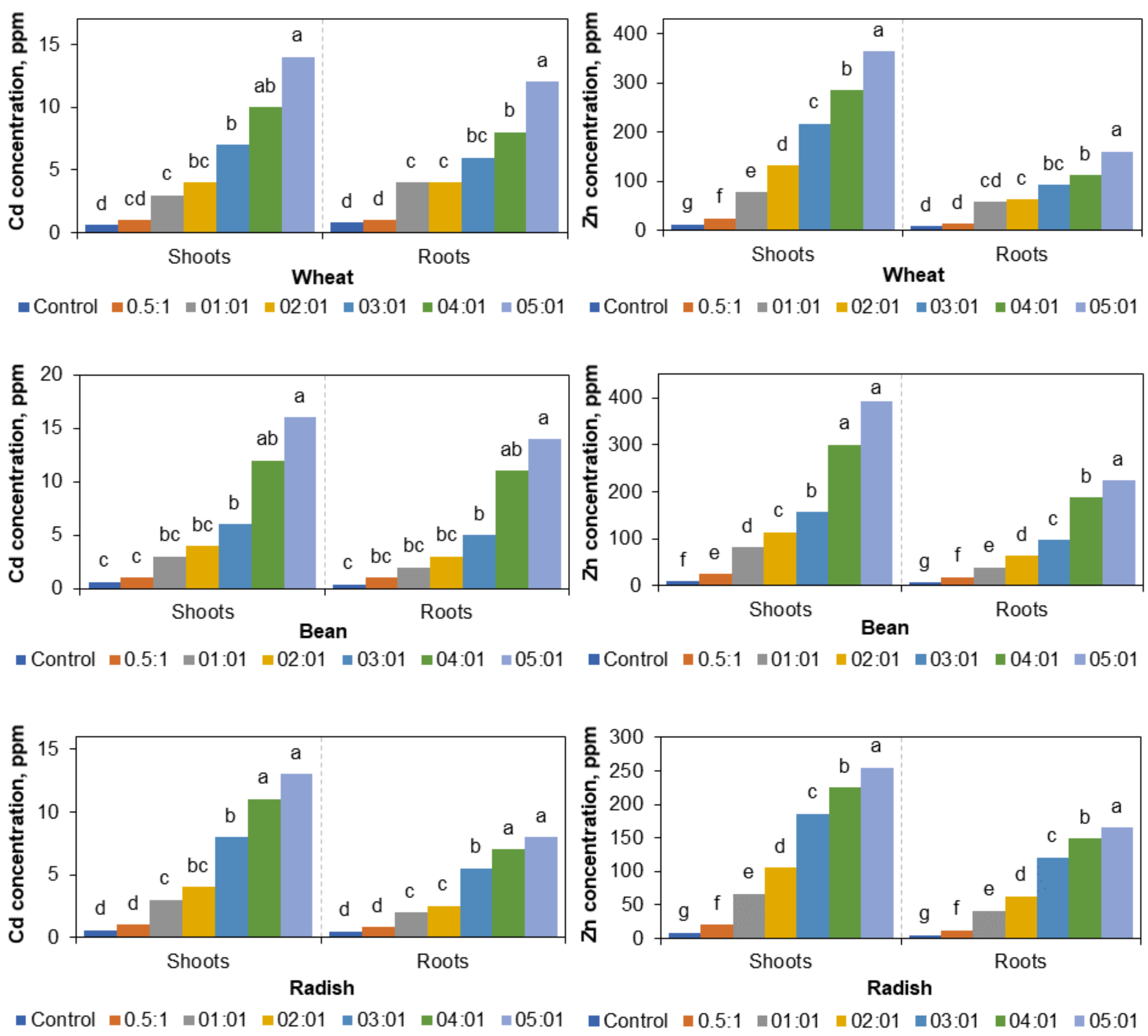


Figure 2. Zn and Cd concentration (ppm) in the studied plants (roots and shoots) (the different lowercase letters indicate a significant difference (P <0.05) by Duncan Multiple Range Test between different ratios)

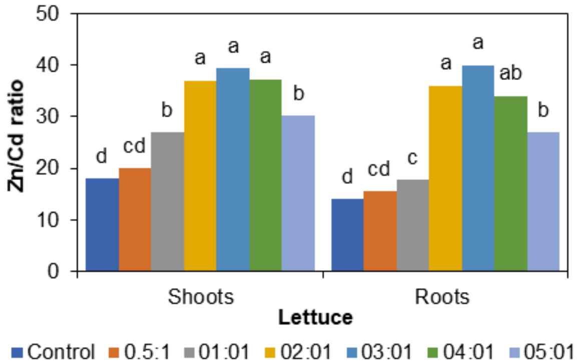
Zn and Cd combination in soil and soil characteristics

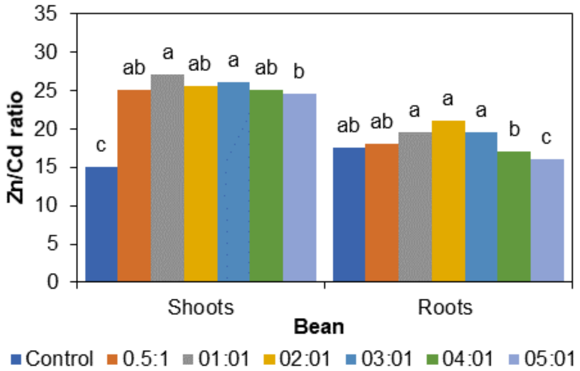
As we mentioned before, studied soil thermodynamic parameters showed that both elements Zn and Cd are available in soil solution at different ratios, but Cd at low concentration (1:0.5) seems to be more adsorbed than Zn. At equal Zn:Cd ratio (1:1), distribution coefficient (K_d) remarked opposite direction, high adsorbed Zn and high available Cd. The noteworthy relationship between Zn and Cd is at (2:1) ratio where K_d values for Zn and Cd are close (12.12 and 12.52, respectively).

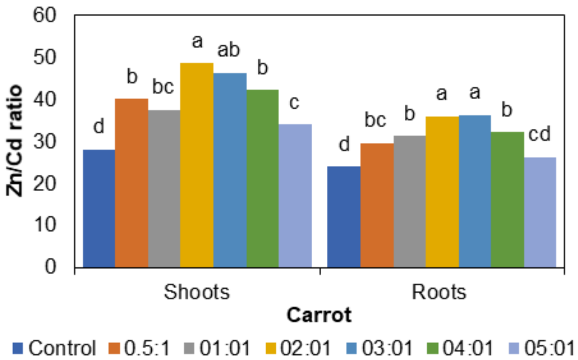
Over 2:1 Zn:Cd ratio, the relationship between these metals was more complicated because the opposite effect of these metals on soil pH and K_d value followed more availability and more retention for Zn and Cd.

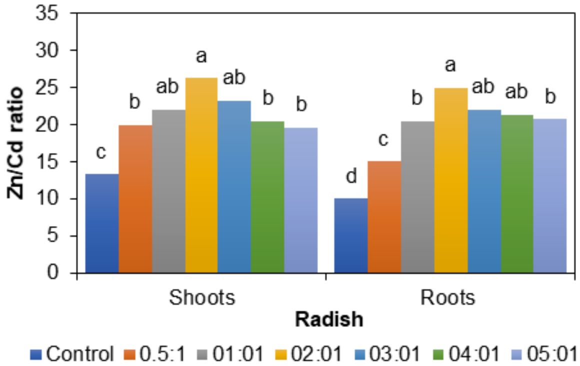
For all ratios of Zn and Cd, studied plants showed no Cd or Zn toxicity symptoms. At low ratios of Zn and Cd in soil, plant Cd content (green parts and roots) showed semi-close except wheat roots remarked more Cd content (4 ppm) compared to green parts. This result is in agreement with (Mahmood *et al.*, 2009) that the roots of wheat accumulated higher levels of Cd than shoots at low doses. Therefore, we like to demonstrate two reasons: 1) Cd tends to be more desorption in soil compared to other toxic elements (Lokeshwari, Chandrappa, 2006); 2) binding sites of clay particles, organic matter and calcium carbonate have a higher affinity to Zn than Cd. Therefore, according to these competition effects, increasing Zn concentration in soil solution results in more Cd desorption, Also, Shute and Macfie (2006) confirmed this fact.

A more important result in our study is illustrated in Figure 3, where is Zn and Cd ratio in green parts and roots of studied plants. At a low concentration of Zn:Cd ratio in soil, both elements increased and reached a maximum value at 2:1 ratio for all studied plants except lettuce and decreased over 2:1 Zn:Cd ratio in the soil. For the lettuce plant, the maximum value of Zn and Cd was at 3:1 Zn:Cd ratio in the soil. Lettuce contravention to this base may be attributed to the individual characteristics of plant species. It may be stated that at low concentrations of Zn:Cd ratio, the interaction relationship between Zn and Cd could be synergistic where Zn enhanced Cd desorption to be more available in soil solution. At 2:1 Zn:Cd ratio in soil, the distribution coefficient (K_d) was equal for each of these metals. At 2:1 Zn:Cd ratio in the soil the K_d values were equal for each of these metals(table3), but over 2:1 Zn to Cd ratio in soil Zn availability was found to be more than Cd according to studied soil thermodynamic parameters. The decrease of Zn:Cd ratio values in plant parts over 2:1 in soil showed a high competition relationship between these ions in combination which indicates some kind of antagonistic relationship. These findings are in agreement (Abou Auda, Ali, 2010). They stated that the effect of these two ions in combination was different when Zn to Cd ratio was (75/40 ppm). In our study, four of five plant species responded to the change in the relationship between Zn and Cd in soil solution – wheat, radish, carrot and bean except for lettuce. That can be attributed to plant species. Generally, soil thermodynamic parameters are good indicators to explain Zn and Cd bioavailability in soil solution and plant uptake. At low concentration ratios, Zn enhanced Cd desorption where both elements are accumulated easily in plant tissues via synergistic interaction relationship, At high molar ratios for both elements, Zn tends to decrease soil solution pH and enhanced Cd to be more available in soil solution and create highly competitive on plant roots via antagonistic interaction relationship.









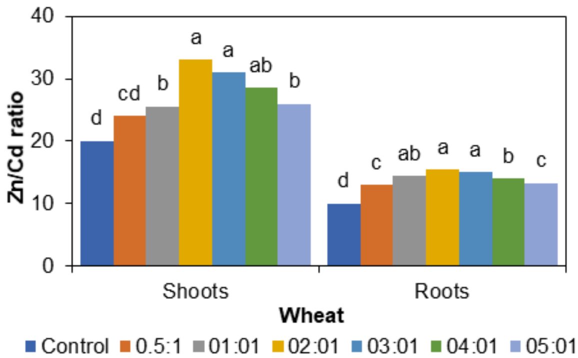


Figure 3. Zn and Cd ratio for studied plants (roots and shoots) (the different lowercase letters indicate a significant difference ($P < 0.05$) by Duncan Multiple Range Test between different ratios)

Conclusion

The result showed that a relationship between Zn and Cd in soil solution is reflected in the uptake of these two elements by the plant. At low Zn:Cd ratios, Zn adsorption enhanced Cd desorption into soil solution and both elements are accumulated easily in plant tissues. This synergistic relationship reaches a maximum value at 2:1 Zn:Cd ratio. At 3:1 Zn:Cd ratio and over, an antagonistic relationship starts and the accumulation level of these two elements depend on plant species.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

MMA – writing a manuscript, analysis, and interpretation of data;
MJF – acquisition of data, author of the idea, guided the research;
HAK– analysis and interpretation of data and is the corresponding author, guided the research;
HMA-H – critical revision and approval of the final manuscript, guided the research.

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