연구보문

Investigation of Cadmium and Zinc Interactions in Soils using Desorption Isotherms

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ABSTRACT: Investigation of Cd and Zn availability in four different soils as affected by the interactions of these two heavy metals was conducted using the metal desorption quantity-intensity (Q/I) isotherms. The soils were artificially contaminated with proper concentrations of Cd and Zn as $CdSO_4$ and $ZnSO_4$ solutions. DTPA (diethylene triamine pentaacetic acid) - extractable and water-extractable Cd or Zn from the soils were used as Q_{Cd} or Q_{Zn} and I_{Cd} or I_{Zn} factors, respectively. The coefficient of determination for Cd and Zn desorption Q/I linear regression in the soils ranged from 0.947 to 0.999, which indicated that Q and I factors were closely correlated. The buffering capacity of Cd, BC_{Cd}, in the soils decreased with increasing Zn treatments, and the BC_{Cd} values were ranged between 205.8 and 2255.6. The decreases of BC_{Cd} values were mainly dependent upon the increases of I_{Cd} factors. However, Zn buffering capacity, BC_{Zn}, decreased with increasing Cd treatments in acidic soils, and increased in neutral and calcareous alkaline soils. The BC_{Zn} values were ranged from 143.2 to 6158.0. The values of BC_{Zn} as influenced by the treatments of Cd were also controlled by the solubility of water-extractable Zn, I_{Zn} factor. The solubility of water-extractable Cd and Zn was significantly dependent upon the changes of soil pH that were impacted by the treatments of Zn and Cd, respectively. Also, the availability of Cd was higher than Zn availability in the acidic and neutral soils, but Zn was higher than Cd in the calcareous alkaline soil.

Key Words: Cadmium, zinc, quantity, intensity, buffering capacity

INTRODUCTION

Many researchers have studied cadmium (Cd)-zinc (Zn) interactions in soil-plant systems because of the chemical similarity between Cd and Zn^{1-7}. Although bivalent transition metal cations, such as Cd and Zn, exhibit a similar pH-dependent adsorption behavior, the adsorption extent at given pH is varied between the metals. Several workers investigated adsorption sequences by different adsorbents for metal cations including Cd and Zn. The adsorption sequences reported were Cu > Pb > Zn > Cd by hydrous aluminum oxide[8], Pb > Cu > Zn > Cd[8] and Zn > Cd

> Ca^{9} by hydrous ferric oxide, Cu > Pb > Zn > Co > Cd^{10}, Zn > Ni > Cd^{11} and Ni > Zn > Cd^{12} by goethite, and Pb > Cu > Cd > Zn by organic matter[13]. These may lead to the conclusion that Cd is relatively more bioavailable than Zn in soils with some exceptions. However, the validity of the selectivity series for the majority of soils may be due to the types and amounts of clays, oxides, organic matter found in soils. Each soil constituent has its own adsorption properties for the metal cations.

Also, most researchers have focused on uptake or absorption of Cd and Zn in plants rather than availability of those metals in soils. Turner[1] studied the effect of cadmium application on Cd and Zn uptake by plants. He reported that Cd treatment increased the concentration and total uptake of Zn in plant tops. Other researchers found that Zn application

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reduced the concentration of Cd in plants[4,5,14]. Sinkora and Wolt[15] reported an increase in Zn levels of sludge increased the solubility of Cd in sludge and soil even though the Zn addition decreased concentration of Cd in plant root. However, Haghiri[16] reported that the addition of Zn (5-50 mg kg^{-1} range) significantly increased the Cd concentration of plant shoots, and also Nan et al.[6] showed that the effects of Cd-Zn interaction can be synergistic to increasing the accumulations of Cd and Zn in wheat and corn plants with increasing Zn and Cd contents in soils. Kuo et al.[17] reported that soil organic matter had little relation to Cd and Zn availability. However, Abdel-Sabour[4] reported Zn uptake by plants was best related to the soil organic fraction. White and Chaney[2] also showed that the higher organic matter soil was more effective than others in reducing Zn uptake. They reported that soil type also can strongly influence Cd and Zn uptake, and the Zn levels differed with soil pH. The availability of Cd and Zn in soils can be also affected by phosphorus fertilizer application[18,19]. Therefore, we are concerned about the availability of soil Cd and Zn as affected by the presence of Zn and Cd, respectively, because there is a lack of information about the relationships between Cd and Zn in different soils.

The objective of this study was to investigate the interactions of Cd and Zn as affected by additional treatments of Zn and Cd in soils using the desorption isotherms.

MATERIALS AND METHODS

Soils

The surface 15 cm of four different soils were collected and studied: Egan (fine-silty, mixed, mesic Udic Haplustolls), Egeland (coarse-loamy, mixed, frigid Calcic Hapludolls), Glenham (fine-loamy, mixed, mesic Typic Argiustolls), and Maddock (sandy, mixed, frigid Entic Hapludolls).

The soil samples were air dried, crushed to pass through a 2-mm sieve, and analyzed for selected physical and chemical properties (Table 1).

Preparation of Soil Samples

Two sets of 20 g soil samples were prepared. One set of soils was treated with the application of 0-, 20-, 40-, and 80 mg Cd kg^{-1} using CdSO$_4$ solution, and the other set of soils was applied with 0-, 20-, 40-, and 80 mg Zn kg^{-1} using ZnSO$_4$ solution in 125 mL

Table 1. Selected physical and chemical properties of soils

Property	Soil			
	Egan	Egeland	Glenham	Maddock
Classification	Udic Haplustolls	Calcic Hapludolls	Typic Argiustolls	Entic Hapludolls
Particle size distribution (%)				
Sand	10.4	57.0	39.2	42.6
Silt	60.6	29.0	37.1	37.5
Clay	29.0	14.0	23.7	19.9
pH (soil : water = 1:1)	5.76	5.55	7.88	6.66
Available P (mg kg^{-1})	3.4	22.9	21.6	4.1
DTPA extractable metals (mg kg^{-1})				
Cd	0.21	0.14	0.11	0.10
Zn	2.83	1.18	1.22	0.53
Organic Matter (mg kg^{-1})	32.4	23.0	24.2	23.5
Cation exchange capacity(cmolc kg^{-1})	20.3	11.3	22.9	14.8
Iron (mg kg^{-1})				
Free Fe	527	374	214	322
Exchangeable Fe	3.35	1.62	2.83	2.18
Lime[a]	-	-	++	-

[a] Strong (++) and no effervescence (-) with 10 % acid solution.

polystyrene vials in duplicates. The soils in the polystyrene vials was brought to field capacity moisture with ultra-high quality deionized water and thoroughly mixed. The soil samples containing Cd or Zn in the polystyrene vials were incubated for 1 week at 24℃. After incubation, those samples were air-dried. Then the Cd treated soils were enriched with 0-, 5-, 10-, 20-, 40-, 60-, 80-, and 120 mg Zn kg^{-1} applied as ZnSO$_4$ solution, and the Zn treated soils were enriched with 0-, 5-, 10-, 20-, 40-, 60-, 80-, and 120 mg Cd kg^{-1} applied as CdSO$_4$ solution. The metal enriched samples were thoroughly mixed, incubated at field capacity and 24℃ for 2 weeks. After incubation, the samples were allowed to air-dry and finely ground.

Determination of Cd and Zn desorption

The determination procedures of metal desorption quantity-intensity relationships were partly introduced in one of our earlier studies[19].

Ten grams of soils from the two replicates were weighed in 125 mL polystyrene vials and analyzed for diethylenetriaminepentaacetic acid (DTPA)-extractable Cd or Zn on an atomic absorption spectrophotometer[20].

Also, 5 g of soils from the replicates were weighed in 125 ml polystyrene vials and brought to 25 mL with high-quality deionized water. The vial equilibrated for 48 h on an orbital shaker set at a speed of 160 rpm. After equilibration, the soil suspension was centrifuged (45,000 x g) for 10 min and filtered (1.0- and 0.22 μm pore size) to obtain soil solution. The Cd or Zn analysis of the soil solution was determined by use of the graphite furnace method for an atomic absorption spectrophotometer with a deuterium lamp as the background correction source.

The metal buffering capacity of the soils was defined in terms of the total amount of diffusible metal ion per unit volume of soil solution metal ion. Thus, Cd or Zn buffering capacity can be measured from the relationships between the changes in quantity of Cd or Zn desorbed (Q) and the change in intensity (I) of soil solution Cd or Zn concentration, which would be:

$$BC = \Delta Q / \Delta I = \theta_v + \rho K_d \qquad (1)$$

where BC is the Cd or Zn buffering capacity, θ_v is the measured volumetric moisture content (m^3 m^{-3}), r is the bulk density (kg L^{-1}), and K$_d$ is the distribution

coefficient (L kg^{-1}). The K$_d$ is calculated from the following linear desorption (or adsorption) isotherm:

$$Q = K_d I + b \qquad (2)$$

where Q is the DTPA-extractable Cd or Zn (mg kg^{-1}), I is the equilibrium total Cd or Zn concentration in soil solution (mg L^{-1}), and b is a constant[21-23].

Measurement of pH for Cd and Zn Enriched Soil-Water Systems

The pH value of extracts was measured after obtaining extract solutions from Cd-Zn or Zn-Cd enriched soil-water (1:5) systems equilibrated for 48 h on an orbital shaker set at a speed of 160 rpm.

RESULTS AND DISCUSSION

Effects of Zn treatments on Cd availability

Cadmium desorption quantity (Q)-intensity (I) linear relationships and the Cd buffering capacity (BC$_{Cd}$) as affected by Zn treatments in soils are shown in Figure 1 and Table 2, respectively. The coefficient of determination (R^2) for Cd desorption Q/I linear regression in the given soils ranged from 0.947 to 0.999, which indicated that the quantity and intensity

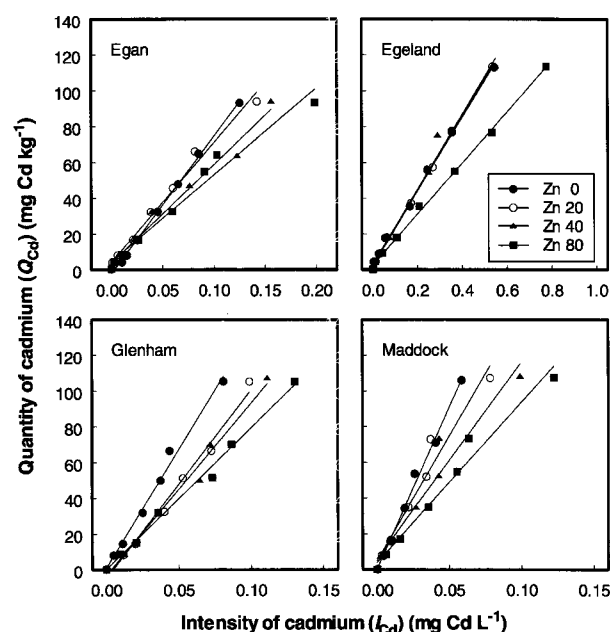

Fig. 1. Cadmium desorption quantity-intensity linear fittings as affected by zinc treatments in soils. Zn 0 to Zn 80 represents no Zn to 80 mg Zn kg^{-1} applied, respectively, in soils.

Table 2. Cadmium distribution coefficient (K_d) and Cd buffering capacity (BC_{Cd}) affected by Zn treatments

Soil	Zn treatment (mg kg^{-1})	K_d (L kg^{-1})	BC_{Cd}	R^2 [a]
Egan	0	769.6	819.6	0.998
	20	669.8	713.3	0.986
	40	551.4	587.2	0.982
	80	486.0	517.6	0.973
Egeland	0	204.0	294.8	0.997
	20	208.9	301.9	0.999
	40	209.4	302.6	0.986
	80	142.4	205.8	0.998
Glenham	0	1325.0	1690.7	0.991
	20	1055.0	1346.2	0.986
	40	964.4	1230.6	0.986
	80	793.0	1011.9	0.993
Maddock	0	1803.0	2255.6	0.995
	20	1393.0	1742.6	0.962
	40	1103.0	1379.9	0.947
	80	898.3	1123.8	0.977

[a] Coefficients of determination for Cd desorption Q/I curves fitted by $Q = K_d I + b$.
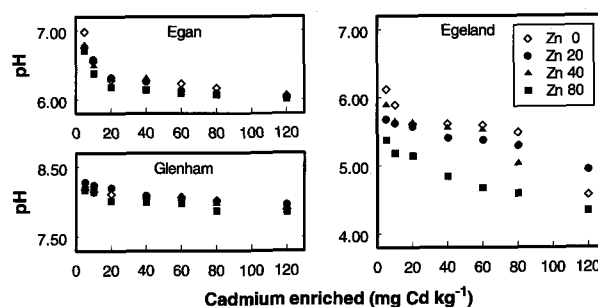

Fig. 2. Effect of zinc treatments on soil pH (1:5) in cadmium enriched soils. Zn 0 to Zn 80 represents no Zn to 80 mg Zn kg^{-1} applied, respectively, in soils.

factors in the soils were closely correlated. BC_{Cd} values were the lowest in acidic Egeland sandy loam soil and the highest in neutral Maddock loam soil, and these values ranged between 206 and 2256 in the soils with all ranges of Zn treatments.

The BC_{Cd} values decreased with increasing the concentrations of Zn applied in the soils. When the soils were treated with various Zn concentrations, the quantity of Cd, DTPA-extractable Cd (Q_{Cd}), was almost not changed in all of Zn application ranges, whereas the intensity of Cd, water-extractable Cd (soil solution Cd; I_{Cd}), usually increased with increasing Zn treatments in most soils, except in the Egeland soil. In this case, the I_{Cd} values impacted the decease of BC_{Cd} values. Sinkora and Wolt[15] reported similar results that increasing Zn levels with sludge application increased the solubility of Cd in the sludge and soil. In the acidic Egeland sandy loam soil, however, the concentration of water-extractable Cd (intensity of Cd) almost did not change (increase or decrease) until 40 mg Zn kg^{-1} applications, but it markedly increased at 80 mg Zn kg^{-1} of the Zn treatment level.

Also, the values of BC_{Cd} were considerably dependent

upon soil properties. The BC_{Cd} values were clearly differentiated among the soils studied, which was the highest with neutral Maddock loam as followed by calcareous Glenham loam > acidic Egan silty clay loam > acidic Egeland sandy loam soils. White and Chaney[2] reported that soil type can strongly influence Cd and Zn uptake by plants, and Zn levels differed with soil pH. Their research results indicated that the solubility of the metals is markedly dependent upon the soil properties, and the applications of additional Zn can change soil pH that is one of the most important factors for the solubility of metals in soil-solution systems.

The pH changes in the soil-solution systems related to the enrichment of Cd source with Zn applications is shown in Figure 2. The values of soil pH decreased with increasing the concentrations of Cd source enriched in all systems. In particular, the pH values in the acidic Egeland sandy loam soil system were much impacted by the enrichments of Cd contamination source as comparing with the pH changes in other soil systems. Also, the pre-applications of Zn impacted decrease of pH in the soil-solution systems. Thus, the decreases of soil system pH allowed to increase desorption of Cd ions from soil surfaces, organic matter, and/or Fe oxides to soil solution, and then the concentrations of soil solution Cd increased.

Effects of Cd treatments on Zn availability

Zinc desorption Q/I linear relationships and the Zn buffering capacity (BC_{Zn}) affected by four selected Cd treatments for soils are shown in Figure 3 and Table 3, respectively. The values of R^2 for the linear regression in the four soils ranged from 0.988 to 0.999. The BC_{Zn} values were lowest in the Egeland

Table 3. Zinc distribution coefficient (K_d) and Zn buffering capacity (BC_{Zn}) affected by Cd treatments

Soil	Cd treatment (mg kg^{-1})	K_d (L kg^{-1})	BC_{Zn}	R^2 [a]
Egan	0	556.1	592.3	0.995
	20	422.3	449.7	0.988
	40	380.0	404.7	0.997
	80	367.3	391.2	0.999
Egeland	0	140.1	202.4	0.993
	20	100.4	145.1	0.999
	40	99.1	143.2	0.999
	80	100.7	145.5	0.998
Glenham	0	3511.0	4480.3	0.998
	20	4091.0	5220.1	0.996
	40	4826.0	6158.0	0.999
	80	4694.0	5989.5	0.999
Maddock	0	1088.0	1361.4	0.996
	20	1101.0	1377.4	0.992
	40	1192.0	1491.2	0.998
	80	1429.0	787.7	0.999

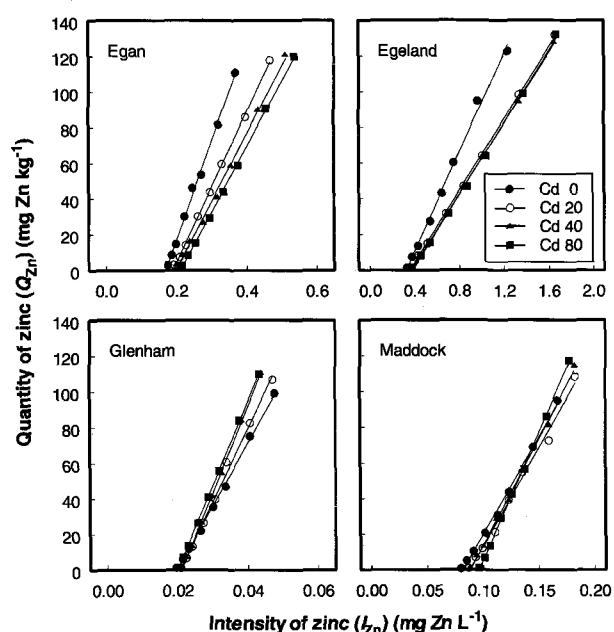[a] Coefficients of determination for Zn desorption Q/I curves fitted by $Q = K_d I + b$.

Fig. 3. Zinc desorption quantity-intensity linear fittings as affected by cadmium treatments in soils. Cd 0 to Cd 80 represents no Cd to 80 mg Cd kg^{-1} applied, respectively, in soils.

soil with the lowest values of soil pH, CEC, organic matter, exchangeable Fe, and were highest in the calcareous Glenham soil. The BC_{Zn} values varied from 143 to 6158 with all ranges of Cd treatments for the soils. The values of BC_{Zn} decreased with increasing Cd treatments in acidic Egan and Egeland soils, whereas the values were increased with increasing Cd applications in calcareous Glenham and neutral Maddock soils.

The solubility of Zn in the given soils was more complicated than the solubility of Cd as affected by interactions between them. The concentrations of DTPA-extractable Zn (Q_{Zn}) and water-extractable Zn (soil solution Zn; I_{Zn}) gradually increased with increasing the concentrations of Cd treated in the Egan soil. In the Egeland soil, both Q_{Zn} and IZn values increased with Cd applications, but with higher than 20 mg Cd kg^{-1} of Cd applications, the increases of Q_{Zn} and I_{Zn} values were almost not changed. It is very different trend as comparing with the result of Q_{Cd} and ICd values as affected by Zn treatments in the same soil. In the calcareous Glenham soil, the Q_{Zn} values were

increased with Cd treatments even though there were almost no different Q_{Zn} increments among 20 and 80 mg Cd kg^{-1} treatments, whereas the I_{Zn} values decreased with increasing the concentrations of Cd treated. In the neutral Maddock soil, the Q_{Zn} values increased with increasing Cd treatments, but the I_{Zn} values increased with Cd treatments in lower Zn enriched (contaminated) soil samples only, but then they decreased in higher Zn contaminated soil samples.

These results might be caused by pH changes with the enrichments of Zn source with Cd treatments (Figure 4). The values of pH decreased with increasing the concentrations of Zn enriched in all soil-solution systems studied. Also, the pH values usually decreased with increasing Cd treatments in most of soil systems. However, in the calcareous Glenham soil, the pH values increased with increasing Cd applications. Therefore, the Cd treatments impacted the changes of soil pH, and the soil pH changes affected the solubility or desorption of Zn ions from the soils. Also, difference between the solubility of DTPA-extractable Zn and water-extractable Zn may have induced the changes of BC_{Zn} values in the soil-solution systems.

When comparing between the values of BC_{Cd} and BC_{Zn} affected by Zn and Cd treatments, respectively,
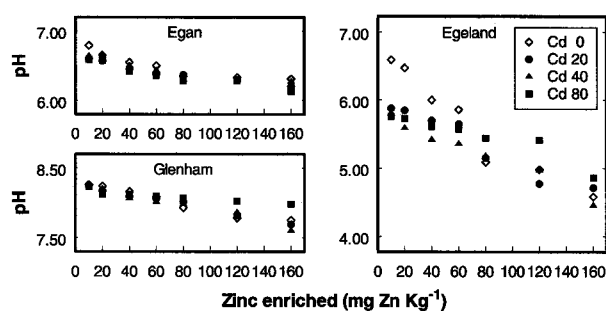
Fig. 4. Effect of cadmium treatments on soil pH (1:5) in zinc enriched soils. Cd 0 to Cd 80 represents no Cd to 80 mg Cd kg^{-1} applied, respectively, in soils.

in the soils, the BC_{Cd} values were lower than the BC_{Zn} values for the calcareous Glenham soil, but for other soils the BC_{Cd} values were higher than the BC_{Zn} values. These results indicated that the relative ratios of Q/I changes for Cd with Zn applications were lower than those of Q/I changes for Zn with Cd treatments in Glenham soils, but they were higher than those of Q/I changes for Zn with Cd applications in other soils. Thus, in the calcareous Glenham soil, Zn is relatively more available than Cd, whereas the opposite results were obtained in other soils. Several workers have studied adsorption sequence by soils using different adsorbents for equal initial solution levels of Cd and Zn. They have reported that the adsorption sequence as comparing between Cd and Zn was mostly Zn > Cd[8,12,13]. In the other hand, Tiller et al.[11] found that when Cd and Zn were associated with organic surface, Cd was somewhat preferred over Zn, with the opposite relationships at high pH values. Therefore, the availability of Cd and Zn as affected by the interactions between those metals was clearly dependent on soil properties, especially soil pH and texture. Also, according to the results of BC of Cd and Zn, the availability of Cd was higher than Zn availability in the acidic and neutral soils but it was lower than that of Zn in the calcareous alkaline soil.

CONCLUSION

This study focused on the solubility of Cd and Zn in four selected soils affected by interactions of those metals. For determining the solubility/availability of target metals in soils, the desorption quantity-intensity (Q/I) linear relationships and the buffering capacity

(BC) of target metals were measured using DTPA-extractable and water-extractable metals as quantity and intensity factors, respectively. The quantity and intensity factors were closely correlated as showing with the Cd and Zn desorption Q/I linear curves. The buffering capacity of Cd (BC_{Cd}) in the given soils decreased with increasing Zn treatments. The decreases of BC_{Cd} values were controlled by Cd intensity factor (I_{Cd}), the solubility of water-extractable Cd, rather than Cd quantity factor (Q_{Cd}), the solubility of DTPA-extractable Cd. Also, the availability of Cd was clearly dependent upon soil pH because the pH values decreased with increasing the enrichment of Cd source and the treatment of Zn in all soils studied. The availability of Zn in the soils was much complicated than that of Cd as impacted by the interactions between Cd and Zn. The values of Zn buffering capacity (BC_{Zn}) decreased with increasing Cd treatments in acidic Egan and Egeland soils, and increased in calcareous Glenham and neutral Maddock soils. The values of BC_{Cd} and BC_{Zn} as influenced by the interactions between Cd and Zn were mostly controlled by the solubility of water-extractable metals, intensity factor, and significantly dependent on soil pH and texture. According to the results of BC of Cd and Zn, the availability of those metals was Cd > Zn in the acidic and neutral soils but Zn > Cd in the calcareous alkaline soil.

ACKNOWLEDGMENTS

REFERENCES

1. Turner, M. A. (1973) Effect of cadmium treatment on cadmium and zinc uptake by selected vegetable species. *J. Environ. Qual.* 2(1), 118-119.

2. White, M. C., Chaney, R. L. (1980) Zinc, Cadmium and Manganese uptake by soybean from two zinc- and cadmium-amended coastal plain soils. *Soil Sci. Soc. Am. J.* 44, 308-313.

3. Pepper, I. L., Bezdicek, D. F., Baker, A. S., Sims, J. M. (1983) Silage corn uptake of sludge-applied zinc and cadmium as affected by soil pH. *J. Environ. Qual.* 12(2), 270-275.

4. Abdel-Sabour, M. F., Mortvedt, J. J. and Kelsoe, J.

J. (1988) Cadmium-zinc interactions in plants and extractable cadmium and zinc fractions in soils. *Soil Science* 145(6), 424-431.

5. Oliver, D. P., Hannam, R., Tiller, K. G., Wilhelm, N. S., Merry, R. H., Cozens, G. D. (1994) The effects of zinc fertilization on cadmium concentration in wheat grain. *J. Environ. Qual.* 23, 705-711.

6. Nan, Z., Li, J., Zhang, J., Cheng, G. (2002) Cadmium and zinc interactions and their transfer in soil-crop system under actual field conditions. *Sci. Total Environ.* 285, 187-195.

7. Zhu, Y. G., Zhao, Z. Q., Li, H. Y., Smith, S. E., Smith, F. A. (2003) Effect of zinc-cadmium interactions on the uptake of zinc and cadmium by winter wheat (*Triticum aestivum*) grown in pot culture. *Bull. Environ. Contam. Toxicol.* 71, 1289-1296.

8. Kinniburgh, D. G., Jackson, M. L., Syers, J. K. (1976) Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gel of iron and aluminum. *Soil Sci. Soc. Am. J.* 40, 796-799.

9. Kuo, S. (1986) Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. *Soil Sci. Soc. Am. J.* 50, 1412-1419.

10. Forbes, E. A., Posner, A. M., Quirk, J. P. (1976) The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. *J. Soil Science* 27, 154-166.

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

12. Bruemmer, G. W., Gerth, J., Tiller, K. G. (1988) Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. *J. Soil Sci.* 39, 37-52.

13. Elliott, H. A., Liberati, M. R., Huang, C. P. (1986) Competitive adsorption of heavy metals by soils.

J. Environ. Qual. 15(3), 214-219.

14. Choudhary, M., Bailey, L. D., Grant, C. A. (1994) Effect of zinc on cadmium concentration in the tissue of durum wheat. *Can. J. Plant Sci.* 74, 549-552.

15. Sinkora, F. J., Wolt, J. (1986) Effect of cadmium- and zinc-treated sludge on yield and cadmium-zinc uptake of corn. *J. Environ. Qual.* 15(4), 341-345.

16. Haghiri, F. (1974) Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. *J. Environ. Qual.* 3(2), 180-183.

17. Kuo, S., Jellum, E. J., Baker, A. S. (1985) Effects of soil type, liming, and sludge application on zinc and cadmium availability to Swiss chard. *Soil Sci.* 139(2), 122-130.

18. Lee, J. H., Doolittle, J. J. (2002) Phosphate Application Impacts on Cadmium Sorption in Acidic and Calcareous Soils. *Soil Sci.* 167(6), 390-400.

19. Lee, J. H., Doolittle, J. J. (2004) Determination of Soil Phosphorus and Zinc Interactions using Desorption Quantity-Intensity Relationships. *Korean J. Soil Sci. Fert.* 37(2), 59-65.

20. Lindsay, W. L., Norvell, W. A. (1978) Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42, 421-428.

21. Anderson, P. R., Christensen, T. H. (1988) Distribution coefficients of Cd, Co, Ni, and Zn in soils. *J. Soil Sci.* 39, 15-22.

22. van Rees, K. C. J., Comerford, N. B., Rao, P. S. C. (1990) Defining soil buffer power: Implications for ion diffusion and nutrient uptake modeling. *Soil Sci. Soc. Am. J.* 54, 1505-1507.

23. Dang, Y. P., Dalal, R. C., Edwards, D. G., Tiller, K. G. (1994) Zinc buffer capacity of vertisols. *Aust. J. Soil Res.* 32, 1231-1242.