

Lixiviation and Extraction of Zinc in a Calcareous Soil Treated with Zinc-Chelated Fertilizers

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When Zn is added to calcareous soils to avoid Zn deficiencies, it can be fixed, if the source is a soluble inorganic salt, and leached, if it is a stable complex. Relative mobilities of Zn-EDTA and Zn-lignosulfonate (LS) chelates added to calcareous soil columns as coated and uncoated fertilizers were determined. Zn-EDTA migrated and distributed throughout the columns. About 51% of the Zn was leached with uncoated fertilizers but only about 10% when coated fertilizers were used. Zn-LS migrated very little, especially with coated fertilizers; the Zn remained mostly in the upper zone of the column and was not leached. The distribution of the added Zn between different fractions of soil was determined by a sequential extraction procedure. When Zn-EDTA was added, the percentage of the most labile fractions increased slightly with respect to the control soil throughout the entire profile of the column. Zn-LS displayed higher increases in the most labile fractions but only in the top layer of the column. Correlations between the extracted fractions ($P < 0.001\%$) showed that in general a dynamic equilibrium existed between them. DTPA-extractable Zn correlated ($P < 0.001\%$) with the two most labile fractions and to a lesser extent with the nonbioavailable forms. Comparisons between coated and uncoated fertilizers show that the presence of coatings benefits Zn-EDTA fertilizers, decreasing the leaching and increasing the amount of bioavailable Zn, but had no beneficial effect for Zn-LS fertilizers.

Keywords: Zn chelates; controlled-release; calcareous soil columns; speciation; leaching

INTRODUCTION

Zinc is present in soils in different chemical forms, the relative distributions of which vary with the type of soil and its physicochemical properties (Viets, 1962). The availability of Zn to plants is governed by a dynamic equilibrium between the different forms rather than by the total content of the cation in the soils (Elsokkary and Lag, 1978). Among the factors which decisively influence the mobility and extractability of Zn are pH and concentration of CaCO_3 (Adriano, 1986). For this reason, an alkaline soil with a large content of free calcium carbonate was chosen for study.

Controlled-availability micronutrient fertilizers containing chelates, to avoid losses when correcting Zn deficiencies, have been used very little until now (Mortvedt, 1994; Holden and Brown, 1965). Nevertheless, they have been studied lately due to the good results obtained with other micronutrients (Natt, 1992). These products provide a series of advantages, including reduced contamination risk to the various environmental compartments (Joyce et al., 1988).

When Zn is added to calcareous soils in the form of soluble inorganic salts, it is fixed to a large extent (Arce et al., 1992). If stable chelates, such as Zn-EDTA, are used on alkaline soils, they migrate through the substrate due to irrigation and are leached (Modaihsh, 1990), but less stable complexes such as Zn-lignosulfonate (LS) can be fixed in the upper zone of the substrate. The differences between these two sources of Zn have been pointed out by Mikkelsen and Kuo (1977) and Mikkelsen and Brandon (1975), when adding both to flooded soils in which rice was cultivated.

For the present study, fertilizers that contained the micronutrient in the form of Zn-EDTA and Zn-LS coated with rosin were used (Rico et al., 1996). Controlled-release technology was employed with the aim

of avoiding leaching of the applied Zn and reducing, as much as possible, losses induced by the precipitation and fixation of the microelement by components in the soil.

The mobility of heavy metals in soils can be studied by the use of packed soil columns (Emmerich et al., 1982). Using this method, the migration and distribution of Zn through the soil, as well as the evolution of the amounts of micronutrient that are accessible to plants, have been studied. Speciation was used to determine the chemical form of the cation (Adriano, 1986), and the DTPA-extractable Zn was used to determine the quantity of micronutrient available to plants (Liang and Karamanos, 1993).

MATERIALS AND METHODS

Soil Characterization. The soil used came from Alcalá de Henares in the province of Madrid, Spain. Surface material was taken from horizon A, an ochric type (depth 0–25 cm); samples were air-dried at room temperature and sieved, and the fraction < 2 mm was used. Some properties of the soil are texture (USDA), clay loam; clay, 32.0%; permeability, $140 \text{ cm}\cdot\text{h}^{-1}$; pH 8.5; phosphorus, 7.1 ppm; organic matter, 1.2%; carbon/nitrogen ratio, 9.2; free CaCO_3 , 12.9%; cation exchange capacity, $190 \text{ mmol (+)}\cdot\text{kg}^{-1}$; and base saturation, 100%. The analytical procedures used here are described in the *Metodos Oficiales de Análisis*, Ministerio de Agricultura, Pesca y Alimentación, Spain (1994).

Extraction Procedures. Fractionation of Zn in the soil was performed by the technique proposed by Murthy (1982) and Mandal and Mandal (1986) with slight modifications. The procedure consists of successively extracting 5 g of soil (< 2 mm) in a glass centrifuge tube (100 mL) for different Zn fractions: (F1) water soluble plus exchangeable through neutral 1 M NH_4OAc , (F2) organic complexed with 0.05 M $\text{Cu}(\text{OAc})_2$, (F3) amorphous sesquioxide bound released by 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, pH 3.0, (F4) crystalline sesquioxide bound solubilized by citrate-dithionite buffered with NaHCO_3 , and

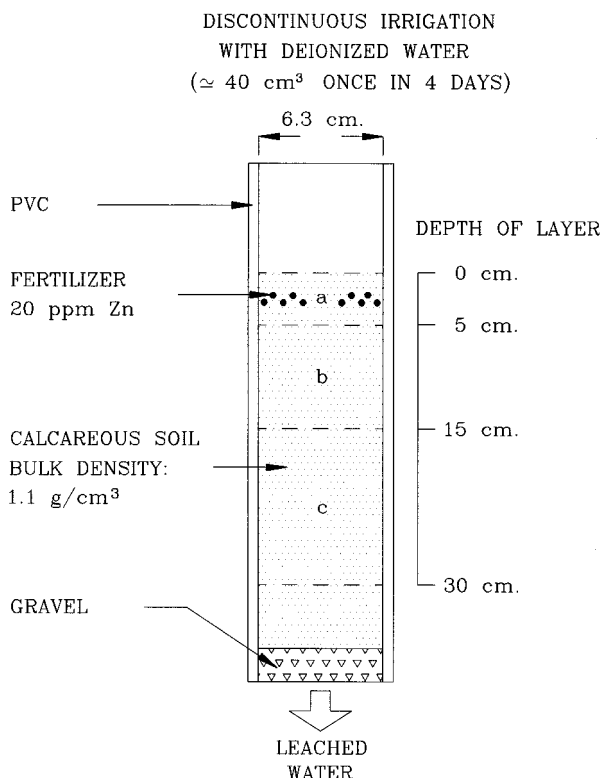


Figure 1. Experimental scheme of the soil columns used.

(F5) residual Zn estimated by digesting the soil residue with $\text{HNO}_3 + \text{HClO}_4$ (2:1). Total Zn was calculated as the sum of the five fractions extracted. The results obtained for the original soil were (ppm) F1 = 0.08 (0.18%), F2 = 0.77 (1.76%), F3 = 0.47 (1.08%), F4 = 1.28 (2.93%), and F5 = 41.08 (94.05%); total Zn was expressed as the sum of fractions = 43.68 ppm. The plant-available portion of Zn was assessed following the method of Lindsay and Norvell (1978). The DTPA-extractable Zn of the soil was 0.40 ppm, which represented only 0.91% of the total Zn. This level of available Zn can lead to a deficiency of the microelement in certain plants as the sufficiency level is more than 1.8 ppm for soils with pH 8 (Loué, 1988). The concentration of Zn was determined with an atomic absorption spectrometer (Perkin-Elmer, Model 3300).

Fertilizers Applied. The compositions of the fertilizers used in this work are Zn-EDTA-0 (uncoated), 1.40% Zn; Zn-EDTA-2, 1.07% Zn and 19.2% coating; Zn-EDTA-3, 0.96% Zn and 36.1% coating; Zn-LS-0 (uncoated), 1.27% Zn; Zn-LS-2, 1.08% Zn and 21.9% coating; and Zn-LS-3, 0.89% Zn and 32.8% coating. These fertilizers were prepared following the procedure described by Rico et al. (1996) and were selected for their physicochemical properties and percentage of coating.

Column Study. The experiment was carried out in triplicate (Figure 1) for each of the fertilizers described. Soil columns without Zn fertilizers were used as controls. The PVC pipes were cut and joined with silicone cement in order to aid sample removal from soil columns after the appropriate time had elapsed. The two halves were separated along the longitudinal axis with a nylon thread and divided transversally into the various portions.

Statistical Procedures. Regression analysis, variance analysis, and multifactor analysis of variance (Duncan's multiple range test) were obtained using a statistical program, Statgraphics version 7.0.

RESULTS AND DISCUSSION

Leachability of Zn. Lixiviation of Zn from the original soil was not observed in the columns without fertilizer. When the Zn-chelated fertilizers were applied to the soil columns, the mobility, and thus leachability, of Zn depended on the kind of chelate and on the

Table 1. Percentages of Zn Leached when Applied as Zn-EDTA as a Function of Time

treatment	months			total Zn leached
	1	2	3	
Zn-EDTA-0	16.8	33.6	0.29	50.7
Zn-EDTA-2	10.1	28.1	4.28	42.5
Zn-EDTA-3	2.04	7.47	2.35	11.9

Table 2. Concentrations of Total Zn (Sum of F1-F5) in Column Soil with Fertilizers (ppm)

treatment	depth	months		
		1	2	3
Zn-EDTA-0	a	56.4	48.7	48.4
	b	59.4	50.4	50.4
	c	59.7	52.7	53.5
Zn-EDTA-2	a	61.4	57.4	51.7
	b	63.8	53.3	51.8
	c	58.9	56.1	53.7
Zn-EDTA-3	a	78.3	63.9	57.3
	b	64.0	56.6	52.1
	c	63.5	58.2	53.3
Zn-LS-0	a	158	155	134
	b	51.7	58.7	57.2
	c	45.5	51.4	50.3
Zn-LS-2	a	172	164	157
	b	47.9	51.6	54.3
	c	43.9	47.4	47.3
Zn-LS-3	a	189	172	169
	b	46.6	47.5	51.7
	c	44.1	46.1	47.3

presence and thickness of coating. Fixation of Zn in the soil occurred with the Zn-LS complex; therefore, Zn was not lixiviated from the Zn-LS fertilizers. In contrast, the stability of the Zn-EDTA chelate, which is rather stable in an alkali medium, reduced the possibilities of Zn fixation in the soil. For the uncoated product, Zn-EDTA-0, the major losses of Zn by leaching occurred in the first 2 months; the amount lixiviated is almost stabilized at the end of this period (Table 1). The effect of the coatings was clearly beneficial for the Zn-EDTA products, both reducing and making more gradual the lixiviation. The Zn leached by the irrigation waters was 40% less than that of the uncoated product for the highest percentage coating.

Distribution of Zn in Soil Columns after Treatment. From the results obtained with the leachates, it may be deduced that the total Zn content in the columns where Zn was applied as Zn-EDTA was appreciably less than in those where Zn was added as Zn-LS. When all three zones of the column are analyzed, it can be seen (Table 2) that whereas Zn-EDTA is distributed in all three zones, Zn-LS remains in the upper zone. The high concentration of Zn in zone a when Zn-LS was added justifies the mentioned differences of Zn contents in the columns. Migration of Zn-EDTA continues with time. The Zn-LS complex migrates only slightly, but it is notable at the end of the experiment. The coatings were beneficial in the fertilizers with Zn-EDTA because they reduced the mobility of the cation through the soil and increased the concentrations of the microelement in all zones as the coatings increased. In the case of Zn-LS, the increase in the coating produced a large concentration of the microelement in zone a, but reduced still further the migration to other zones with respect to the uncoated fertilizer.

Partitioning of Zn between the distinct fractions of soil after treatment also depended on the source of Zn used (Figure 2). The percentage distributions of Zn in the fractions showed analogous trends for the three Zn-

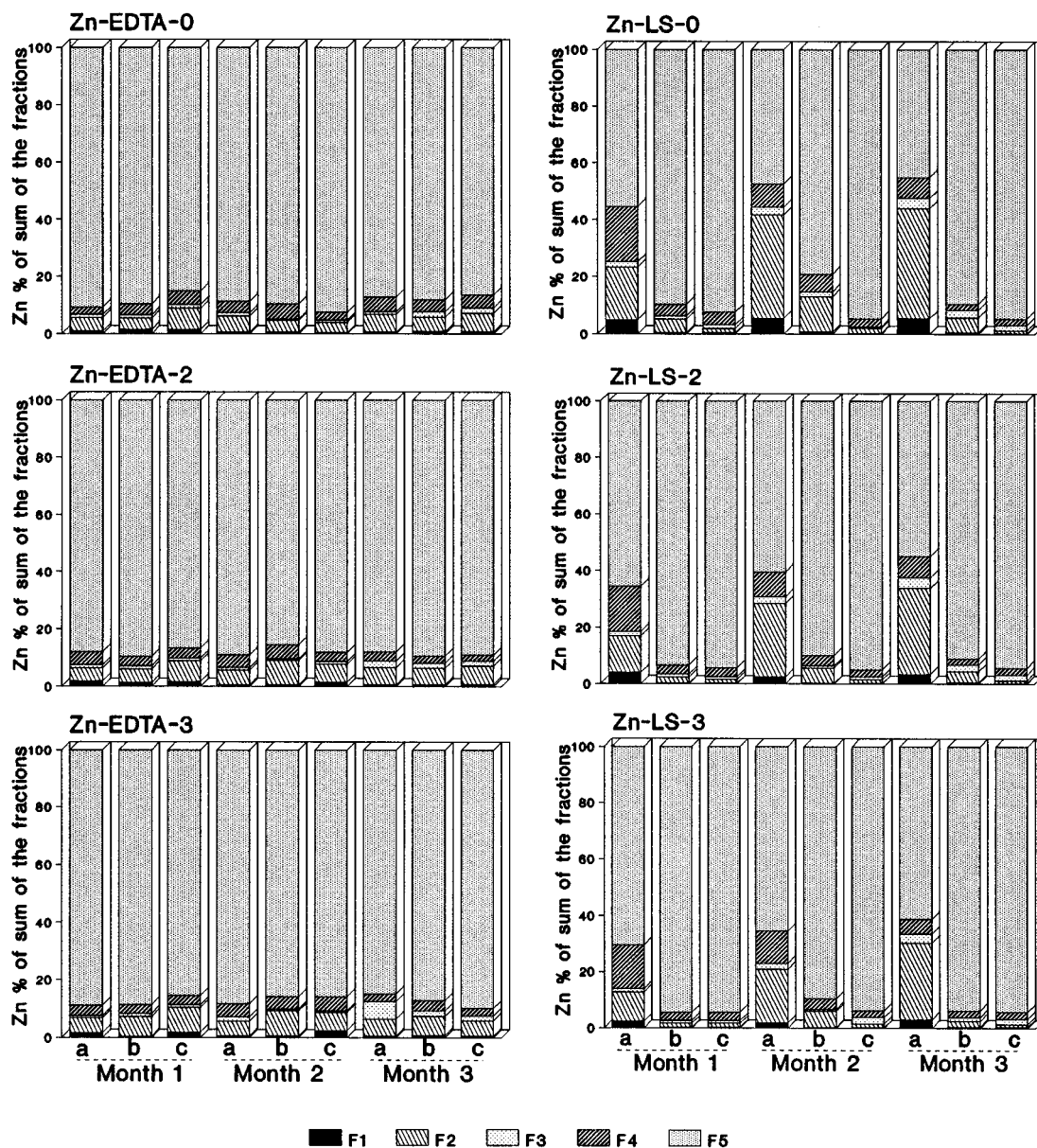


Figure 2. Percentage distribution of Zn in fractions versus the fertilizers, months, and depths in the soil columns.

EDTA fertilizers and a greater bioavailability of Zn, compared with that in the control soil at all depths. The bioavailability of Zn was maintained, and the percentage of the more fractions even slightly increased with the coated products. In zone a, fertilizers which incorporated Zn-LS showed the largest differences in the distribution in fractions compared with both the original soil and Zn-EDTA fertilizers. The percentage of the residual fraction was much less than in untreated soil and increased considerably in F1, F2, and F4 with the treatments. For example, at the end of the second month, F1, F2, and F4 were 0.18%, 2.08%, and 2.73%, respectively, in the control soil and 5.46%, 36.2%, and 8.26% in the soil treated with Zn-LS-0. When the fertilizer applied was Zn-EDTA-0, F1, F2, and F4 were 0.60%, 5.65%, and 3.94%, respectively. The principal cause for the increase in the percentage in zone a was that the cation remained largely in the zone where the pellets were applied and the coating impeded Zn-LS chelate migration. In zones b and c availability or extractability of Zn was less for the Zn-LS chelate than for Zn-EDTA and more similar to the control soil. In all cases the presence of coating increased the residual fraction and diminished amounts of the more available

fractions when Zn-LS was applied. The distribution of Zn in fractions is affected by the Zn leached from the column that mostly comes from the more mobile fractions.

Increases of concentrations of Zn in the residual fraction (F5), observed in all cases (for example, at the end of the first month 51.2 ppm for Zn-EDTA-0 and 133 ppm for Zn-LS-0), were due mainly to the displacement of Zn by Ca in the complexes added to the soil. As Ca is abundant in this soil, it competes with the microelement, displacing it from the Zn-EDTA chelate (Abouloos, 1981) and more easily from the Zn-LS because this complex is less stable (Loué, 1988). The Zn insolubilization process is accentuated by the physicochemical characteristics of the soil employed. The alkaline pH and rather large clay content (in this soil smectites, montmorillonite type, predominant) cause immobilization of Zn through formation of hydroxides and carbonates and by Zn adsorption on the clays (Adriano, 1986).

Available Zn in Soil Columns after Treatment. In zone a, where the pellets were deposited, the Zn-LS fertilizers provide a larger percentage of available Zn, with respect to the total Zn than did the Zn-EDTA

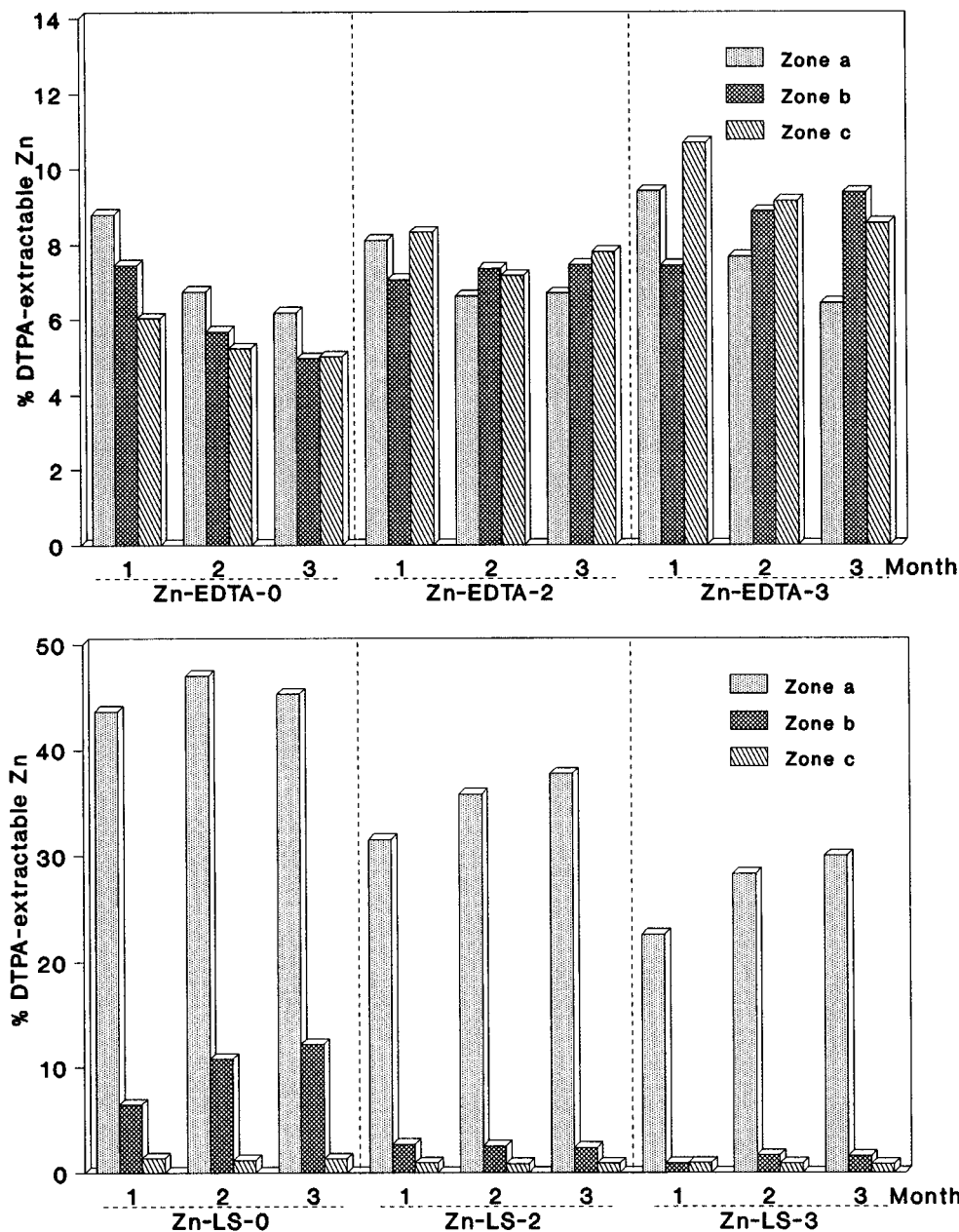


Figure 3. Percentages of DTPA-extracted Zn with respect to the total in soil columns treated with Zn-EDTA and Zn-LS.

(Figure 3). However, in the rest of the column profile, due to the leaching of the Zn-EDTA complex, this order is reversed. Thus, the DTPA-extractable Zn was distributed throughout the whole column when Zn-EDTA was added, while when Zn-LS was used, the amount was minimal in the deepest zone. The amounts and fractions extracted increased with amount of coating for the Zn-EDTA series, but the opposite occurred for the Zn-LS series.

A variance analysis was carried out between the DTPA-extractable Zn and the variables: fertilizer, time, and depth (Table 3). Differences were obtained between the fertilizers and the depths, showing a positive interaction between both ($P < 0.01\%$). However, time had no measurable effect on DTPA-extractable Zn, with no significant differences found.

Correlation Study between the Distinct Extraction Systems. To establish how different forms of Zn in soil contribute to its availability to plants, a simple linear regression analysis between the different fractions of Zn and between them and the Zn extracted with

Table 3. Variance Analysis of the DTPA-Extractable Zn with Factors of Fertilizer, Time, and Depth

source of variation	df	mean square	F-ratio ^a
fertilizer treatment	5	748.58	167.12**
time (month)	2	2.05	0.46NS
depth (zone)	2	4727.78	1055.46**
fertilizer·time	10	4.88	1.09NS
fertilizer·depth	10	967.20	215.92**
time·depth	4	2.51	0.56NS
residual	20	4.48	
total (corrected)	53		

^a**Significant at 0.01% level. NS = not significantly different.

DTPA was carried out (Table 4). Large correlation coefficients were obtained which indicated the existence of a dynamic equilibrium between the fractions throughout the length of the column. The greater correlation coefficients corresponded to DTPA-extractable Zn and fractions F1 and F2.

In order to check for an effect of the residual coating, a separate analysis was carried out for zone a, where the fertilizer granules were deposited, between the

Table 4. Linear Correlation Coefficients (*r*) between Forms of Zn Extractable by Sequential Fractionation Procedure and Zn Extracted with DTPA^a

Zn forms	F2	F3	F4	F5	DTPA-Zn
F1	0.91***	0.81***	0.83***	0.75***	0.97***
F2		0.92***	0.66***	0.70***	0.95***
F3			0.59***	0.68***	0.87***
F4				0.88***	0.84***
F5					0.80***

^a ***Significant at 0.001 % level.

amounts extracted with DTPA and each of the fractions from the speciation procedure. Positive correlation existed between the DTPA-extractable Zn and the F1 $r = 0.96$ and F2 $r = 0.92$ ($P < 0.001\%$) and with F3 $r = 0.80$ ($P < 0.01\%$). The same occurred with the rest of the soil column analyzed, where the best correlations were also found with these fractions.

Conclusions. The migration and distribution of Zn in soil columns depended on the stability of the chelates used. The Zn added as Zn-EDTA moved throughout the soil columns, and that added as Zn-LS remained in the zone where it was applied.

The use of coatings decreased the mobility of Zn but did not impede its availability to the plant. Due to this, the performance of the Zn-EDTA fertilizers, calculated as the percentage which remained available in each column with respect to that applied, doubled on going from the treatment with Zn-EDTA-0 to that with Zn-EDTA-3. The lixiviation of Zn when using Zn-EDTA as a source diminished notably with the use of controlled-released fertilizers. The DTPA-extractable Zn increased with the use of coatings in Zn-EDTA fertilizers, while it diminished in those with Zn-LS. Thus, use of rosin coatings were beneficial when Zn-EDTA was employed but not when Zn-LS was used.

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