Mobility and Leachability of Zinc in Two Soils Treated with Six Organic Zinc Complexes

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A study of soil columns was conducted to evaluate Zn movement potential in two reconstructed soil profiles. Zn-phenolate, Zn-EDDHA, Zn-EDTA, Zn-lignosulfonate, Zn-polyflavonoid, and Zn-heptagluconate were applied in the upper zone of the column. The different physicochemical properties of the two soils and the micronutrient source may influence Zn leaching, the distribution of Zn among soil fractions, and the Zn available to the plant in the depth of the layers. In Aquic Haploxeralf soil, the application of six fertilizers produced little migration and very small leaching of Zn in the soil profiles. In Calcic Haploxeralf soil, Zn-EDTA migrated and was distributed throughout the soil columns. This Zn chelate produces a loss of Zn by leaching, which was 36% of the added Zn. In the latter soil, Zn leached very little with the other five fertilizer treatments. The same as for these organic Zn complexes, the retention of added Zn indicated the potential of metal accumulation in the A_p horizons of the two soil profiles. A large portion of applied Zn was available to plants [diethylenetriaminepentaacetic acid (DTPA) and Mehlich-3 extractable Zn] in the depths reached by the different commercial formulations. The relationship between the two methods was highly significant (Mehlich-3-Zn = 1.25 + 1.13 DTPA-Zn, R^2 = 99.19%). When Zn was added as Zn-EDTA, the amounts of the most labile fractions (water-soluble plus exchangeable and organically complexed Zn) increased throughout the entire profile column in comparison with the control columns, although in the B_t horizon of the Aquic Haploxeralf soil they increased only slightly.

Keywords: *Zn chelates; soil columns; mobility; leaching; speciation; plant available Zn*

INTRODUCTION

Organic Zn complexes are applied to agricultural soils because they are good sources of plant nutrients (*1, 2*). Some complexing agents can be effective ligands to form soluble organic Zn complexes (*3, 4*). Differently chelated forms of Zn have different labilities, bioavailabilities, and susceptibilities to leaching (*5*) and, therefore, deteriorate groundwater quality. The effectiveness of the chelating compounds as metal carriers in soils depends on their keeping the metal in soluble forms. Two separate processes were reported as reasons of ineffectiveness (*6*). One of them was the fixation of the entire metal chelate molecule on clay colloids. The second process of inactivation of the chelated metal was metal displacement in the metal–chelate molecule by other cations (e.g., Ca^{2+}) from the soil with subsequent metal precipitation. The extent to which this reaction takes place depends on the soil pH, the stability constants of the metal chelates, and the solubility products of the inorganic metal compounds (*7*). The transformations of Zn added to soil depend on chemical soil reactions. Studies on Zn have revealed that the extent and nature of its transformation are mainly governed by the reaction time in soil, the amount of Zn added, the type of clay mineral, and the extent of organic matter content in soil (*8, 9*). The movement of Zn to different depths in an agricultural soil was reported when Zn was applied to soils. The mobilities of different products are usually studied by means of packed soil columns (*10–12*). Under these conditions, there are factors able to influence the movement of Zn through the soil profile; for example, a drop of pH may increase

the solubility of metal and contribute to the movement. The transformations of Zn retained by soils may be mainly related to the groovy structure on the surfaces of Fe oxides (*13*) and/or the microporosity of soil components (*14*). Also, the movement of water through the soil and, therefore, the nutrients dissolved in the water are closely related to the structure of the soil profile, in the first place, and, second, to its granulometric distribution (*15*).

Viets (*16*) suggested the concept of various pools of micronutrients existing in soil and defined five pools as water soluble, exchangeable, adsorbed, chelated or complexed secondary clay minerals, and insoluble oxides and primary minerals. Subsequently, attempts were made to suggest procedures for selective sequential extraction of metal in soil fractions (*17, 18*). The water-soluble and exchangeable forms characterize the most mobile and immediately bioavailable fractions. They are the most labile Zn fractions in the soil environment and have a greater leaching potential than the other fractions (*19, 20*). However, the approach of sequential extraction depends on the heterogeneous composition of the soils. Partial selectivity of the reagents used to attack a specific component of the soil is mostly responsible for the operational character of this method. Despite its severe restrictions, the value of sequential extractions is generally recognized (*21, 22*). Diethylenetriaminepentaacetic acid (DTPA) and Mehlich-3 extractions are methods usually employed for diagnosing Zn deficiency, and adjustments were found to be essential for soil tests predicting the micronutrient available to the plant in soil (*23*). There is not much literature on

Table 1. Some Characteristics of Zn-Complexed Fertilizers

complexing agent	fertilizers[a]	richness (% Zn) w/w	richness (% Zn) w/v
Zn-phenolate	CE-Zn	7.0	8.9
Zn-EDDHA	FL-Zn	7.0	9.1
Zn-EDTA	LU−Zn	8.8	10.5
Zn-lignosulfonate	MA-Zn	7.5	9.6
Zn-polyflavonoid	QU−Zn	5.0	NI[b]
Zn-heptagluconate	WE-Zn	6.0	8.1

[a] Corresponding to abbreviated names of commercial formulation (24). CE-Zn, Cekustran Zinc; FL-Zn, Flowal Cinc; LU-Zn, LuqsaZinc-8; MA-Zn, Manvert Zinc; QU-Zn, Quelapron Zn; and WE-Zn = Welgro Zinc. Mass density of fertilizers ranging from 1.21 to 1.36 g cm^{-3}. [b] NI, not indicated.

the research of the correlation between DTPA and Mehlich-3 extractions for the soil micronutrients.

This study is above all a discussion of reported Zn movement and redistribution downward through two layers of soil amended with six (natural and synthetic) organic Zn complexes. In addition, it was designed to determine the influence of the chelate and soil type on the migration of Zn under controlled conditions.

MATERIALS AND METHODS

Zinc Chelates. The six fertilizers used in this study were Zn-phenolate (CE-Zn), Zn-EDDHA (FL-Zn), Zn-EDTA (LU-Zn), Zn-lignosulfonate (MA-Zn), Zn-polyflavonoid (QU-Zn), and Zn-heptagluconate (WE-Zn), with various Zn contents (Table 1). Liñan (24) described the properties of these liquid commercial formulations.

Characteristics of the Experimental Soils. The two soils used were collected from two different rural areas in the region of Madrid (Spain). These soils are representative, and their properties are listed in Table 2. The A$_p$ horizons of the soil profiles for soils 1 and 2 were 6.28 and 7.02 pH, respectively. The B horizon of these soils was argilic (B$_t$). In all horizons, the permeability was slow to moderate except in the B$_t$ horizon of soil 1, which was very slow. Soil 1 has aquic conditions for some time in most years. Samples were air-dried at room temperature (18−23 °C) and sieved, and the fraction used was smaller than 2 mm. Grain size analysis was carried out by a hydrometric method, and the soil pH was measured in water at a 1:2.5 (w/v) soil/water ratio. Organic matter (OM) was measured using the Walkley−Black procedure, whereas total nitrogen (N) was determined according to the Kjeldhal digestion. The cation exchange capacity (CEC) was assessed using both sodium acetate (NaOAc) and ammonium acetate (NH$_4$-OAc) extraction procedures. The analytical procedures used are described in the *Official Methods* manual (26). The predominant clay type in the B$_t$ horizon of soil 1 and the in the A$_p$ horizon of soil 2 was montmorillonite; illite was also found in the other two horizons. This determination was carried out using the EUF technique (27).

Experiments in Soil Columns. Plexiglas columns were employed to study the mobility of Zn in soils (Figure 1). Triplicate columns were packed for each of the different combinations of soil, fertilizer treatment, and experimental time (30 and 60 days). The soils were packed at a height of 57 cm in columns that were 75 cm long and had an inside diameter of 7.2 cm. The columns were saturated using deion-
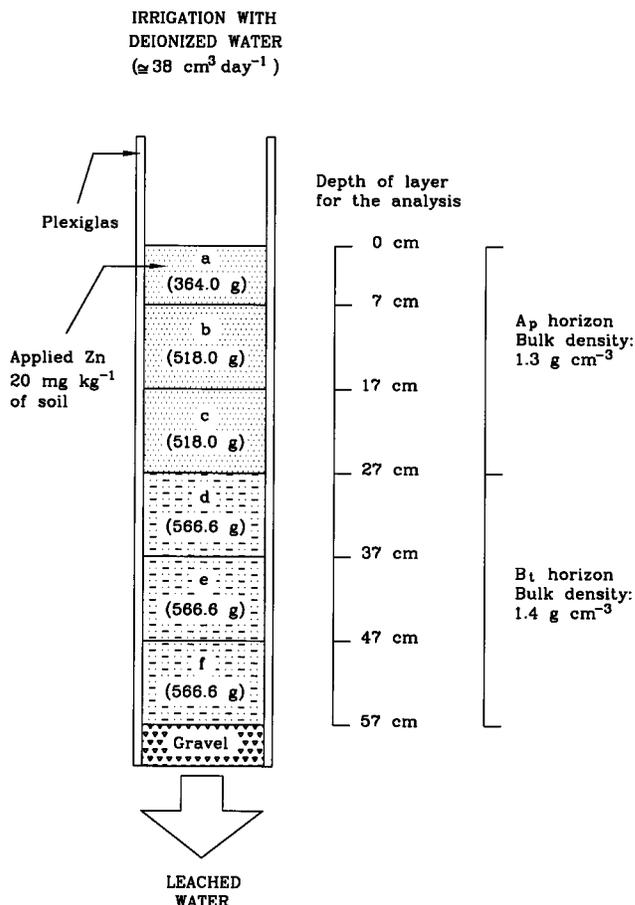
Figure 1. Experimental scheme of the soil columns used.

ized water. Excess water was allowed to drain overnight. The top soils at a depth of 1.5 cm in each column were mixed with the respective amendments. An unamended soil column was also included in the experiment as a control treatment. The columns were irrigated with deionized water, and the leachate was collected in 150 mL fractions (0.13 pore volume) for a total volume of 1200 mL (1.04 pore volume). After leaching, the soils in the columns were air-dried and ground to pass a 2 mm sieve. The samples from different depths of the layers were collected according to the methodology proposed by Alvarez (5).

The "plant-available" portion of Zn was determined by DTPA (28) and Mehlich-3 (29) methods. Zinc was fractionated in the soils as described by several authors (30−32) with slight modifications (Table 3). The concentrations of Zn in the filtrates were measured by flame atomic absorption spectrophotometry. Total Zn was calculated as the sum of the six fractions (F1−F6) extracted. The concentrations of Zn obtained from the original soils are given in Table 4. The amounts of Zn extracted with DTPA and Mehlich-3 in the A$_p$ horizon of soil 1 were 0.38 (0.95%) and 1.16 mg kg^{-1} (2.91%), respectively. In the A$_p$ horizon of soil 2, they were 0.39 (1.03%) and 1.28 mg kg^{-1} (3.38%), respectively. These levels of available Zn can lead to deficiency in plants (33, 34).

Data Analysis. Analysis of variance and correlation (simple regression analysis) techniques were applied using Statgraphics plus for Windows (version 4.0). In the statistical analyses,

Table 2. Properties and Classification of Soils Used in This Study

soil	classification[a]	horizon	sand (%)	silt (%)	clay (%)	OM (%)	N (%)	CEC (cmol$^+$·kg^{-1})	pH$_w$ (1:2.5)	BS[b] (%)
1	Aquic	A$_p$	54	22	24	1.10	0.11	10.4	6.28	56
	Haploxeralf	B$_t$	39	19	42	0.40	0.08	24.3	6.10	61
2	Calcic	A$_p$	39	32	29	0.59	0.08	21.7	7.02	71
	Haploxeralf	B$_t$	36	20	44	0.40	0.06	24.0	7.13	76

[a] Soil Survey Staff (25). [b] Base saturation (%) = exchangeable base·CEC^{-1}·100.

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Table 3. Sequential, DTPA, and Mehlich-3 Extraction Methods for Zn

procedure (form/association)	solution	soil (g)	solution (mL)	conditions
DTPA extraction				
"plant available"	0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M TEA (pH 7.3)[a]	10	20	horizontal shaker, 2 h
Mehlich-3 extraction				
"plant available"	0.2 M HOAc + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA[b]	3	30	rotative shaker, 5 min
sequential extraction				
water soluble plus exchangeable (F1)	1 M $Mg(NO_3)_2$ (pH 7.0)[c]	5	50[e]	shake for 30 min
organically complexed (F2)	0.7 M NaOCl (pH 8.5)[c]	5	50	boiling water bath, 30 min; stir occasionally (repeat extraction twice)
Mn oxides bound (F3)	0.1 M $NH_2OH \cdot HCl$ (pH 2.0)[d]	5	50	shake for 30 min
amorphous Fe oxides bound (F4)	0.2 M $(NH_4)_2C_2O_4$ + 0.2 M $H_2C_2O_4$ (pH 3.0)[c]	5	50	shake for 4 h in dark
crystalline Fe oxides bound (F5)	solution as for preceding step + 0.1 M ascorbic acid[c]	5	50	boiling water bath, 30 min; stir occasionally (repeat extraction twice)
residual (F6)	HCl, HNO_3, and HF in mixture	2	12[f]	digestion in microwave oven in four steps, maximum pressure of 120 psi

[a] Reference *28.* [b] Reference *29.* [c] Reference *30.* [d] Reference *31.* [e] Reference *32.* [f] 2 HCl, 5 HNO_3, and 5 HF.

Table 4. Zinc Fractions, DTPA, and Mehlich-3 Extractable Zn in Original Soils (Milligrams per Kilogram)[a]

soil	horizon	F1	F2	F3	F4	F5	F6	SUM[b]	DTPA	M-3[c]
1	A_p	0.23 (0.58)[d]	0.72 (1.80)	0.25 (0.63)	0.67 (1.68)	2.40 (6.01)	35.62 (89.30)	39.89	0.38 (0.95)	1.16 (2.91)
	B_t	0.17 (0.30)	0.45 (0.80)	0.09 (0.16)	0.82 (1.46)	3.63 (6.47)	50.96 (90.81)	56.12	0.28 (0.50)	0.79 (1.23)
2	A_p	0.23 (0.61)	0.87 (2.30)	0.16 (0.42)	1.20 (3.17)	3.47 (9.15)	31.98 (84.35)	37.91	0.39 (1.03)	1.28 (3.38)
	B_t	0.10 (0.18)	0.68 (1.23)	0.07 (0.13)	1.85 (3.34)	3.94 (7.13)	48.65 (87.99)	55.29	0.31 (0.56)	1.00 (1.81)

[a] Average of three replications. Coefficients of variation of all forms ranged from 0.53 to 3.52%. [b] SUM, sum of the fractions. [c] Mehlich-3 extractable Zn. [d] Values in parentheses represent the percentage of total Zn (sum of the fractions).

a probability level of $P = 0.05$ was chosen to establish statistical significance.

RESULTS AND DISCUSSION

Zinc Leaching in the Soil Columns. In this study, the lixiviation of Zn is different in accordance with the soil used. The amounts of Zn leached in soil 1 were very small for all cases. In the untreated soil columns, total leaching of Zn in the leachate (1200 mL, at 60 days) was 0.30 mg, which was <1% of the total Zn content in the soil. Similar results were obtained when the fertilizer treatments CE-Zn (0.35 mg of Zn), MA-Zn (0.34 mg of Zn), QU-Zn (0.34 mg of Zn), and WE-Zn (0.34 mg of Zn) were applied. For the soil columns treated with FL-Zn and LU-Zn, the amounts of Zn obtained in leachate were 0.49 mg (1.75% of Zn applied) and 0.72 mg (2.57% of Zn applied), respectively. Although, the concentration of Zn in the leachate increased with time when LU-Zn (Zn-EDTA) was added, the amount of Zn recovered was not important considering the volume collected. The pH of soil 1 (A_p horizon, 6.28; B_t horizon, 6.10) may have contributed to the lixiviation of the micronutrient. However, the soil components retained the major part of Zn (e.g., montmorillonite and illite clay types content). It was found in the B_t horizon (very slow permeability), which causes a similar lixiviation of Zn complexed with both synthetic and natural complexing agents. This suggests that under natural soil conditions, Zn may be resistant to leaching with fertilizer treatments similar to these.

The application of organic Zn complexes to soil 2 produced different effects depending on the Zn source used. In the soil columns untreated with Zn, the amount of Zn recovered was 0.11 mg when the volume collected was 1200 mL. However, in the columns treated with CE-
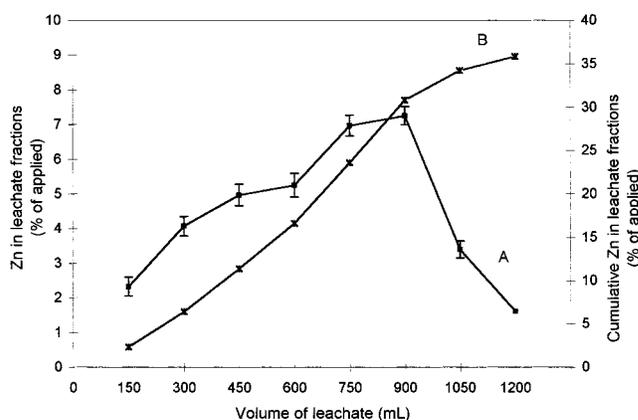
Figure 2. Measurement of Zn in leachates as a function of leachate collected in soil 2 treated with LU-Zn (Zn-EDTA): percentages (A); cumulative percentages (B).

Zn, MA-Zn, QU-Zn, and WE-Zn, 0.49, 0.39, 0.36, and 0.40 mg of Zn were recovered, corresponding to 1.75, 1.39, 1.29, and 1.43% of applied Zn, respectively. The amounts of Zn leached were slightly higher in soil columns with FL-Zn (0.74 mg of Zn, 2.64% of applied Zn) than with the fertilizers mentioned earlier. However, in the columns amended with LU-Zn the concentrations of Zn in the leachate fractions increased notably compared with those of the control columns. Figure 2 shows the variation of Zn percentages and cumulative percentages found in the column leachates (percent of applied Zn) with the water volume leached when this fertilizer was applied. The percentage of Zn in the leachate reached its peak in the sixth leachate fraction (7.25% of applied Zn), followed by a sharp decline in the subsequent leachate fractions. After 60 days, the total

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Table 5. Variance Analysis of the Total Zn, DTPA, and Mehlich-3 Extractable Zn with Factors of Soil Type, Fertilizer Treatment, Depth, and Time

source of variation	df	F ratio[a] total Zn	DTPA	Mehlich-3
main effects				
soil	1	3.29 NS	1.36 NS	2.27 NS
fertilizer treatment	6	30.45***	34.30***	30.74***
depth (zone)	5	374.61***	560.62***	497.14***
time (day)	1	0.80 NS	4.00 NS	3.43 NS
positive interactions				
soil × depth	5	3.53*	13.73***	13.37***
fertilizer treatment × depth	30	26.18***	33.01***	28.59***
depth × time	5	5.99**	13.01***	7.64**
soil × fertilizer treatment × depth	30	4.82***	4.12**	3.66**
residual	30			
total (corrected)	167			

[a] ***, **, and *, significant at 0.01, 0.1, and 1% levels. NS = not significant differences.

Table 6. Total Zn in Soil Columns Treated with Fertilizer Treatments after 60 Days (Milligrams per Kilogram)[a]

horizon	zone	control	CE-Zn	FL-Zn	LU-Zn	MA-Zn	QU-Zn	WE-Zn
				Soil 1				
A_p	a	38.93	92.76	97.07	66.93	69.90	67.68	80.57
	b	37.99	48.98	44.95	51.58	51.03	55.37	58.58
	c	37.82	43.49	43.08	51.66	49.68	48.37	39.63
B_t	d	54.84	54.59	55.82	57.43	59.88	55.65	54.38
	e	54.33	54.32	54.33	56.75	55.57	57.81	53.77
	f	55.30	54.34	54.29	55.13	55.09	54.04	53.67
				Soil 2				
A_p	a	38.99	103.52	91.44	47.24	102.90	101.58	78.84
	b	38.50	43.03	42.47	41.33	40.03	42.63	54.99
	c	38.62	40.51	41.09	43.43	39.91	39.89	40.73
B_t	d	54.26	53.05	56.34	61.24	53.83	55.25	53.87
	e	53.94	52.53	55.16	60.39	54.41	53.76	55.49
	f	52.94	53.76	55.05	58.24	54.98	52.50	53.46

[a] Average of three replications. Standard error of total Zn ranged from 0.87 to 2.13.

recovery of Zn in the leachates from soil amended with this fertilizer was 10.03 mg (35.82% of applied Zn). In accordance with Li and Shuman (*35*), the results of leaching with soil columns may represent a long period of time under natural field conditions.

Migration and Availability of Applied Zn. The migration was studied by determining the total Zn and the bioavailability by means of DTPA and Mehlich-3 extractable Zn. All Zn concentration values in these variables were examined using a multifactor variance analysis to determine the main effects of soil type, fertilizer treatment, depth, and experimental time (Table 5). Significant differences for the three variables were found between the fertilizer treatments ($P <$ 0.01%) and between the depths ($P <$ 0.01%), showing significant interaction between both ($P <$ 0.01%). For total Zn, significant interaction was obtained between the type of soil, fertilizer treatment, and depth ($P <$ 0.01%). Thus, for DTPA and Mehlich-3 extractable Zn, significant interaction was also obtained between the type of soil and depth ($P <$ 0.01%). On the other hand, experimental time had no measurable effect on DTPA and Mehlich-3 extractable Zn.

Multiple-range analysis for DTPA and Mehlich-3 extractable Zn (for the fertilizer treatments and for the depth of layer), employing Duncan's separation of means methods, indicates that there were no significant differences between the following fertilizer treatments: CE-Zn, FL-Zn, MA-Zn, QU-Zn, and WE-Zn; however, the existence of significant differences between those treatments and LU-Zn, which had the least mean concentration of the treatments, was established. For the factor depth of layer, the test established in general

three homogeneous groups: zone a; zone b; and zones c, d, e, and f.

The total concentrations of Zn for each zone of the columns in soils after 60 experimental days are presented in Table 6. These results show that the amounts of Zn remaining in the zones of the two soils depended on the organic Zn complexes used. In soil 1, Zn was strongly retained in soil columns and Zn complexes remained in the upper zones. The fertilizers LU-Zn, MA-Zn, and QU-Zn were the most mobile of all in A_p horizon. In general, the migration of Zn was largely restricted to the B_t horizon (zones d−f) because Zn increased only slightly compared with that in the control column. In this horizon, most Zn concentrations were obtained in the columns with LU-Zn and MA-Zn fertilizers, especially in zone d. In soil 2, the total concentration of Zn in zone a showed that there was a great difference in the behaviors of the fertilizers studied. When CE-Zn, FL-Zn, MA-Zn, QU-Zn, and WE-Zn fertilizers were applied, Zn migration through the column was very low. It was observed that most of the added Zn remained in the A_p horizon, and it remained especially where the fertilizers were placed (zone a). When Zn was applied as LU-Zn fertilizer, Zn was distributed throughout the whole profile of the column as it was observed by means of the increases in concentration of Zn in the B_t horizon compared to that of the control column.

The different behavior of the LU-Zn (Zn-EDTA) product is probably due to the greater stability of this chelate (log $K = 17.5$) compared with the other products. This protects the microelement from fixation by the soil. If so, then there should be an inverse correlation between Zn complex stability and retention in soils.

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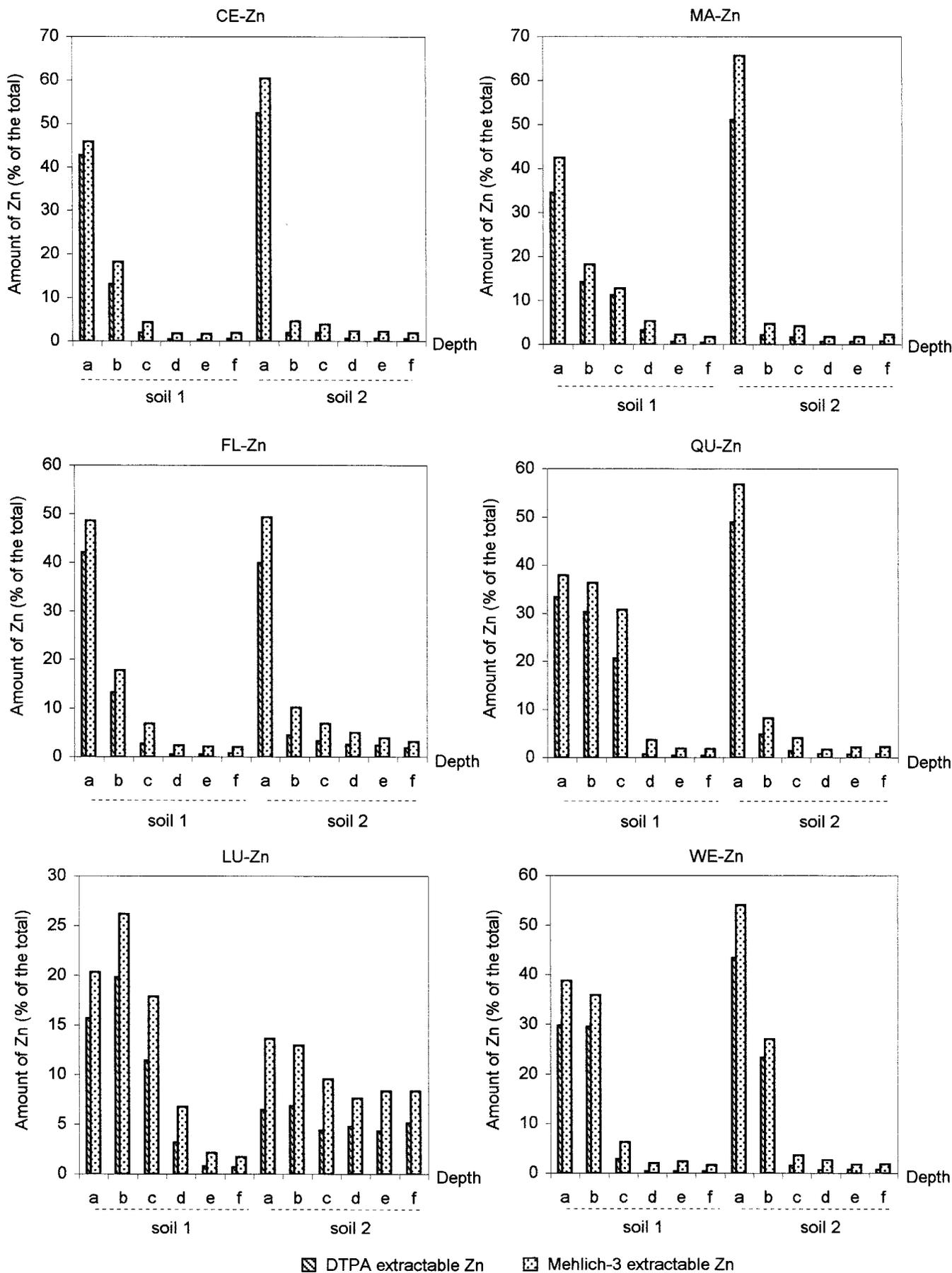
Figure 3. Percentages of DTPA and Mehlich-3 extractable Zn with respect to the total Zn in soil columns treated with organic Zn complexes.
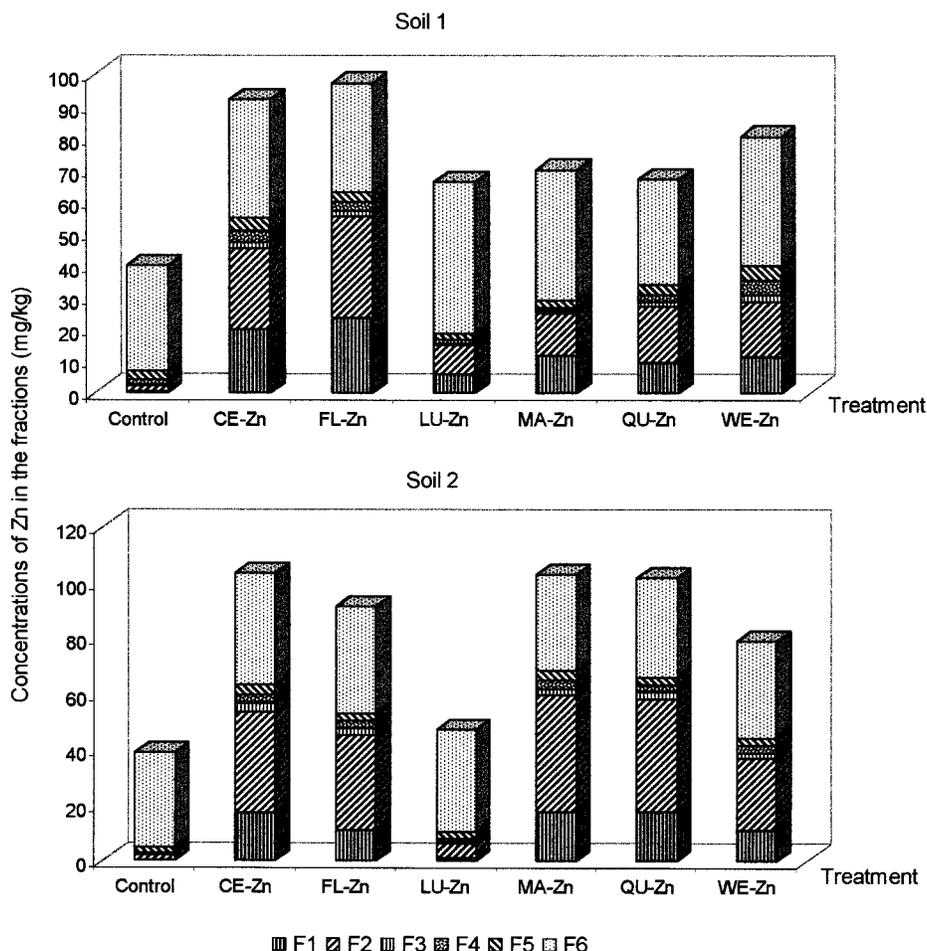
Figure 4. Distribution of Zn in fractions versus the fertilizers in zone a.

Therefore, this chelate should transport Zn for a longer period of time than other less stable organic Zn complexes. Although some metal-complexing ligands such as EDTA suppress metal adsorption, others enhance adsorption by forming stable surface metal–ligand complexes (*36*).

In view of these results, the Zn retention process could be emphasized by some physicochemical characteristics of the soils used (soil 1, very slow permeability; soil 2, pH nearly neutral and a content of montmorillonite and illite clay types in the two soils).

The analysis of the soil columns and the Zn leached is an adequate method to study the mobility of a metal in a soil as it allows a follow-up, which is close enough. The percentages of Zn recovered were nearly 100%. Thus, for example, at 60 days of experimental time when Zn was added as LU-Zn to soil 1, 96% was recovered (recovered Zn is calculated as Zn in the depth of column layers with respect to initial and added Zn). In soil 2, 98% of total Zn was recovered (recovered Zn is calculated as Zn in depth of layers plus leached Zn of the columns with respect to initial and added Zn).

The concentrations of DTPA and Mehlich-3 extractable Zn in depth of layers showed trends analogous with the results obtained for total Zn. The values expressed as percentages of total Zn after 60 experimental days are presented in Figure 3. The use of CE-Zn, FL-Zn, MA-Zn, QU-Zn, and WE-Zn as sources of Zn provided higher plant availability due to the low mobility of these sources, and the micronutrient remained almost entirely in the A_p horizon. When Zn was added as LU-Zn to soil

2 columns, the total percentage of available Zn was less than found for the other five fertilizer treatments, although the amount of leached Zn (35.82%) must be taken into account. This fertilizer diffused progressively further with time as indicated by decreases of the DTPA and Mehlich-3 extractable Zn in zones a–c and its increases in zones d–f with respect to control columns after 60 days of experiment.

Finally, a simple linear regression analysis was calculated for the two methods of extraction. The relationship between DTPA and Mehlich-3 extractable Zn concentrations was highly significant ($N = 168$). The following regression equation was obtained:

$$\text{Mehlich-3-Zn} = 1.25 + 1.13 \text{ DTPA-Zn},$$
$$R^2 = 99.19\% \quad (1)$$

The two extractants may therefore be useful in predicting the plant available Zn in soils under conditions similar to those in this study.

Zinc Speciation at the End of the Experiment. A better understanding of the situation of the remaining Zn in the soil columns is obtained by studying its distribution in fractions resulting from a sequential extraction procedure. Most of the Zn in control columns was found as residual forms (F6, soil 1, 86.6%, and soil 2, 87.8%) (abbreviations are defined in Table 3). This fraction is considered to consist mainly of Zn present in primary and secondary silicate minerals or associated with refractory organic materials, and it is therefore extremely inert and completely unavailable for plant

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uptake (*37*). The concentrations of water-soluble plus exchangeable Zn (F1) were low in control columns (soil 1, 1.13%; soil 2, 0.38%). Adriano (*38*) demonstrated that the distribution of metals in fractions depends on soil properties, and, for most mineral soils, the largest amounts of Zn were present in the residual fraction. The distribution in fractions of the soil column layers where the fertilizers were placed (zone a) is given in Figure 4. In soil columns with fertilizer treatments, the amounts of Zn decreased in the various soil fractions in the following order:

$$\text{soil 1: } F6 > F2 > F1 > F5 > F4 > F3$$

$$\text{soil 2: } F6 \overset{<}{>} F2 > F1 > F5 > F4 > F3$$

In soil 2, this order changed with the LU-Zn fertilizer and was as follows:

$$F6 > F2 > F5 > F4 > F1 > F3$$

The percentage increases of F1 and F2 compared with the control columns led to similar decreases in F6. In general, every treatment gave high percentages of Zn in F1 and F2 fractions in both soils. These fractions are very important for plant nutrition as they potentially represent the main labile Zn (F1, water-soluble and clay surface sorbed Zn; and F2, Zn–organic complexes). Dang et al. (*39*) indicated that the complexed Zn in soil solution of Vertisols ranged from 23 to 69% of the total soluble Zn. The higher levels of metal complexation observed in soil solutions and determined by speciation techniques indicate that strongly acidic organic acids are good chelating ligands (*36*, *40*).

The leaching process affected the chemical forms present in the layers at the end of the experiment, and this was corroborated in soil columns treated with LU-Zn. Thus, Zn concentrations in the F1 and F2 fractions decreased in comparison with the other five fertilizer treatments (see Figure 4). As was seen earlier in soil 2, most of the soluble and exchangeable Zn may have been leached by water over a long period of time.

In the other depths of the layers, the distribution of Zn changed only slightly in some cases and it was not altered in others. In general, the fertilizer treatments that produced a higher mobility of Zn in time increased the amounts of Zn in the F1 and F2 fractions opposed to what happened in zone a.

A simple linear regression analysis was calculated between the different fractions of Zn obtained by the sequential fractionation procedure. Statistically significant (*P* ranged from <0.1% to <0.01%) coefficients were found (*r* ranged from 0.85 to 0.89), suggesting the existence of a dynamic equilibrium between the fractions (F1–F2, F2–F3, F3–F4, and F4–F5). To establish how these Zn fractions could contribute to DTPA and Mehlich-3 extractable Zn, a simple linear regression analysis was also calculated. Correlation coefficients (*r*) between DTPA extractable Zn and F1, F2, and F3 (*P* < 0.01%) were 0.91, 0.97, and 0.89, respectively. Correlation coefficients between Mehlich-3 extractable Zn and F1, F2, and F3 (*P* < 0.01%) were 0.88, 0.98, and 0.90, respectively. These results indicate the important contribution of these fractions to available Zn that was evaluated by DTPA and Mehlich-3 extractions. The sequential extraction used in this study is useful to indirectly assess the potential mobility and bioavailability of Zn in the soils.

Conclusions. The mobility, distribution, and leachability of Zn in soil columns depend on the soil type and the stability of the chelates used. High concentrations of total Zn and available Zn were detected in the upper zones of the soils when Zn-phenolate, Zn-EDDHA, Zn-lignosulfonate, Zn-polyflavonoid, and Zn-heptagluconate were added, and these concentrations were lower in the deep layers. When Zn-EDTA was used as a source, the migration of Zn increased notably in the soil profiles and Zn was leached in the Calcic Haploxeralf soil (slow to moderate permeability, pH nearly neutral, and montmorillonite and illite clay predominant). The leaching of Zn caused changes in the most labile forms of Zn due to the migration of the micronutrient through the soil profiles. The sources of Zn with little mobility and moderate stability could behave like a stock of micronutrients as the water soluble plus exchangeable and organically complexed fractions increased in the upper zones of the soil profiles.

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