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RESEARCH ARTICLE

ZINC MIGRATION IN THE SANDY SOIL AND ITS IMPACT ON THE BIOAVAILABILITY OF SOME NUTRIENT IN THE ROOT ENVIRONMENT

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ABSTRACT

This study investigated the effect of different leaching amounts on the downward movement of zinc applied, as fertilizer, on the surface of a sandy soil. The experiment was conducted in polyethylene bags filled to 30 cm depth with sandy soil. A zinc supply of 15.3 10^{-3} $cmol_c$ kg^{-1} was applied to the soil surface as a solution of zinc sulfate. Three leaching amounts were tested: 31 mm, 208 mm and 497 mm. Results showed the absence of zinc in the leachate for all leaching amounts. Within the soil profile, the highest content on exchangeable zinc (15.3 10^{-3} $cmol_c$ kg^{-1}) was recorded in the top soil layer (0-10cm) for all leaching amounts. In the middle (10-20 cm) and in the lower (20-30 cm) layers, the exchangeable zinc content remained similar to that recorded before leaching (0.76 10^{-3} $cmol_c$ kg^{-1}). The percentage of the cation exchange capacity occupied by zinc in the top soil layer increased after leaching. It averaged 0.35% for all leaching amounts while it remained similar to that recorded before leaching (0.03%) for the middle and the lower layers. This increase was linked to the adsorption saturations sites particularly released by manganese, potassium, calcium and ammonium after their downward movement.

Keywords: cation exchange capacity, exchangeable cations, mobility, sandy soil, zinc.

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INTRODUCTION

Zinc (Zn) deficiency is a nutritional constraint for crop production in many countries (Cakmak, 2008; Gupta *et al.*, 2008). It commonly occurs in calcareous soils, waterlogged soils and sandy soils (Singh *et al.,* 2005). Generally, an adequate inorganic or organic soil Zn supply corrects this deficiency (Murphy and Walsh, 1972; Drissi *et al.*, 2015). The adequate supply on this micronutrient is based on the knowledge of several parameters, namely its mobility through the soil profile.

In the context of the sandy soils of Loukkos area (Northwestern Morocco), naturally poor in Zn, the leaching of mineral Zn brought as fertilizer is a subject of query. Indeed, the low cation exchange capacity of this soil (3.7 $cmol_c$ kg^{-1}) and the common high rainfall (750 mm annual average) resulted in a high risk of nutrient losses through leaching. On the other hand, Zn may contaminate either ground water through leaching (Jung, 2001) or soil through its accumulation (Jalali and Khanboluki, 2007) which may pose a serious threat to the environment. Several studies have reported the low mobility of Zn in different soil types. Brennan (1988) showed

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that Zn is a little movable element in the sandy soil. He reported that 95% of a total Zn supply (22.5 kg ha^{-1}) remained in the upper 5 cm of the soil after a high rainfall (1100 mm). Also, Singh (1974a) showed that the radioisotope Zn (Zn65) remained in the upper 3 cm of sandy and silty soils after a rainfall of 300 mm. He also reported that even after a rainfall of 1200 mm, Zn was weakly mobilized beyond the first 3 cm of the silty soil relatively rich in Zn. On the other hand, Jalali and Khanboluki (2007) reported the low migration of exchangeable Zn in a sandy soil leached with distilled water than that leached with a solution of 0.01M of EDTA used as an organic ligand. According to the literature, the mobility of Zn depends on several factors such as soil pH, cation exchange capacity of the soil, water regime, Zn soil content and mobility of other chemicals in the soil (Singh, 1974a; Zhang and Xia, 2005). These multiple factors make the evaluation in situ of Zn mobility essential for an appropriate reasoning of its supply. Thus, the present study aims to evaluate whether the downward movement of this micronutrient, supplied as sulfated form ($ZnSO_4.7H_2O$), is high or low under different leaching amounts in the context of the sandy soil of Loukkos area.

MATERIAL AND METHODS

Physicochemical characteristics of soil

Soil samples from 0-30 cm of the plough layer were collected from the sandy area of Loukkos (34.96° N, 6.21° W, 60 m above the sea level, Northwestern Morocco). Then, they were air dried and homogenized. The soil is sandy (88.8% of sand, 7.5% of clay and 5.3% of silt) with a low cation exchange capacity (CEC) of 3.7 $cmol_c\ kg^{-1}$. It is deficient in DTPA extractable Zn (0.76 10^{-3} $cmol_c\ kg^{-1}$), not calcareous (0.1% of carbonate), with a pH of 6.4. The other basic soil chemical properties are presented in Table 1.

Table 1. Basic properties of the experimental soil

Soil property	
$pH^{a)}$	6.40
Cation exchange capacity ($cmol_c\ kg^{-1}$)$^{b)}$	3.70
Electrical conductivity ($dS\ m^{-1}$)$^{a)}$	0.06
Organic matter (%)$^{c)}$	0.91
Exchangeable cations content ($cmol_c\ kg^{-1}$ soil)	
$NH_4^{+a)}$	0.04
$K^{d)}$	0.15
$Mg^{d)}$	0.36
$Ca^{d)}$	2.92
$Na^{d)}$	0.07
$Mn^{e)}$	0.15
$Fe^{e)}$	52 10^{-3}
$Cu^{e)}$	0.59 10^{-3}
$Zn^{e)}$	0.76 10^{-3}

Remarks :

a) Determined in a soil: water ratio of 1\5.
b) Determined by the method of Cobaltihexamine Chloride.
c) Determined by the method of Walkley and Black.
d) Extracted by the Ammonium acetate.
e) Determined by the DTPA extraction.

Leaching experiment

Polyethylene bags used as mini-lysimeters (0.35 m depth, 0.13 m length and 0.13 m width) were filled with 20 kg of the soil to have profiles depth of 30 cm. The soil bulk density in the bag was 1.36 g cm^{-3}, which was the approximate bulk density in the field. A drainage system was placed in the bottom of each bag. It is compounded of 5 cm gravel layer and of a valve to assure drainage out flow. In order to assure the stability of soil inside the bags, these latter were placed in iron stands. A Zn supply of 15.3 10^{-3} $cmol_c\ kg^{-1}$ (5 mg kg^{-1} soil) was applied uniformly to the soil surface of each bag as solution of Zn sulfate ($ZnSO_4.7H_2O$, 22.5% of Zn). To note, this rate of Zn is the optimal supply to correct Zn deficiency on corn -as a high Zn sensitive crop- grown on sandy soil of Loukkos (Drissi *et al.*, 2015). Three annual leaching amounts were tested: 31 mm, 208 mm and 497 mm. These amounts were determined from a 40-years frequency analysis of annual leaching

Table 2. Properties of water used for leaching

Water property	
pH	7.6
Electrical conductivity (dS m^{-1})	0.6
Cations content ($mmol_c$ L^{-1})	
K	0.23
Na	1.23
NH_4^+	0.003
Mg	0.44
Ca	3.41
Mn	0.01
Fe	<0.001
Zn	<0.001
Cu	<0.001
Anions content ($mmol_c$ L^{-1})	
SO_4^{2-}	0.70
Cl	1.84
NO_3^-	0.68
$H_2PO_4^-$	<0.001
HCO_3^-	3.16

beyond a sandy soil profile of 0.3 m in Loukkos area (from 1971 to 2010). Based on this analysis, the leaching of 31 mm is registered at most one year every decade (less common in the area). The leaching of 208 mm is recorded at most five years every decade (moderately common). Finally, the leaching of 497 mm is recorded at most nine years every decade (common in the area) (DATA not shown). Each treatment of the study was replicated four times in a fully randomized block design. The water used for leaching did not contain Zn and had both a low electrical conductivity (0.6 dS m^{-1}) and a pH 7.6. The other chemical properties of the water are shown in Table 2. The soil was wetted to saturation. Then, the leaching amounts were applied to the soil surface using a can watering approximating a water flow of 8 L h^{-1} and maintaining 2-3 cm leaching water above the soil. This rate varied slightly according to the leachate flow. The experiment was conducted at ambient temperature varied from 24 °C to 28 °C.

Measurements

When drainage stopped, the leachate of each drainage amount was well mixed, and a sample of 500 ml was taken to determine its content on Zn and on other cations and anions. The leachate content on Zn, iron (Fe), copper (Cu), manganese (Mn) and potassium (K) was determined by an atomic absorption spectrophotometer (Varian 240 AA Fast Sequential, air + acetylene). The content on ammonium (NH_4^+), nitrate (NO_3^-), chloride (Cl), sulfate (SO_4^{2-}), phosphorus ($H_2PO_4^-$), calcium (Ca) and magnesium (Mg) was determined colorimetrically on a Skalar San ++ autoanalyzer according to Skalar standard methods. Soil cations and anions losses through leaching were deduced from the difference between amounts of cations and anions in the leachate and those supplied by water for leaching. In addition, the soil profile of each bag was divided into three superposed layers: top layer (0-10 cm), middle layer (10-20 cm) and lower layer (20-30 cm). Then, a sample of each soil layer was taken and dried at 40 °C in order to determine its content on exchangeable cations and its CEC. Soil exchangeable Zn, Fe, Cu and Mn were extracted in the presence of DTPA, and the extract was analyzed by the atomic absorption spectrophotometer. Soil exchangeable K, Mg, Ca and Na were extracted with ammonium acetate (1 mole L^{-1}), and the extract was analyzed by the atomic absorption spectrophotometer. The soil content on NH_4^+, extracted in water (1/5), was determined colorimetrically using the Autoanalyzer. The CEC was determined according to the method of chloride cobaltihexamine (Aran *et al.*, 2008).

Statistical analysis

Analysis of variance was used to test the effect of leaching amounts on the soil losses of cations and anions as well as on the distribution of cations along the soil profile. If significant treatment effects are revealed (at P ≤0.05), the multiple comparisons of means are performed using the Student-Newman-Keuls test. All statistical analyses are performed using the SPSS software (Version17.0).

RESULT AND DISCUSSIONS

The leachate analysis showed the absence of Zn for all leaching amounts. The result suggests that Zn did not move more than 30 cm down the soil profile (Table 3). This is consistent with the earlier finding of Brennan (1988), who reported the negligible movement of Zn on a sandy soil even after a high rainfall (1225 mm). On the other hand, the soil losses on other cations were recorded. The highest cation loss was noticed for Ca even if it is considered the less mobile cation after H^+ in the soil (Gaucher, 1968). The Ca soil loss averaged almost 43.7 $cmol_c$ kg^{-1} for different leaching amounts. This result can be explained by the high exchangeable Ca soil content compared to other cations (Table 1). Also, the soil losses of Na and K were respectively 8.2 $cmol_c$ kg^{-1} and 0.64 $cmol_c$ kg^{-1} for different leaching amounts. Besides, soil losses of NH_4^+, Mg, Fe and Mn are small and increased significantly with increasing leaching rate. However, Cu has behaved similarly to Zn through its absence on the leachate for all leaching amounts. Taking into account the electrical neutrality of the leachate, an equivalent amount of anions to the cations are carried out of the soil profile (Lehmann and Schrott, 2003). From Table 3, the soil anions losses are recorded for NO_3^- , SO_4^{2-}, Cl^- and $H_2PO_4^-$.

The high soil DTPA exchangeable Zn content (15.3 10^{-3} $cmol_c$ kg^{-1} soil) was recorded on the top layer (0-10 cm) for different leaching amounts compared to the middle and the lower layers (Table 4). These latter had a low exchangeable Zn content, which was similar to that recorded before leaching (0.76 10^{-3} $cmol_c$ kg^{-1}). This result can be attributed to the low mobility of Zn as reported by several authors (Brennan, 1988; Singh, 1974a; Jurinak and Thorne, 1955). This

Table 3. Soil profile (0-30cm) losses of cations and anions through different leaching amounts

	Leaching amount (mm)		
	31	208	497
	Soil cations losses (10^{-3} $cmol_c$ kg^{-1})		
Zn	<0.0001a	<0.0001a	<0.0001a
Ca	41.88 ± 0.98a)ab)	68.77 ± 16.82a	44.74 ± 11.32a
Mg	19.87 ± 2.12c	33.21 ± 3.22b	64.41 ± 4.92 a
NH_4^+	7.17 ± 1.90c	26.41 ± 9.46b	43.74 ± 7.70 a
Na	6.15 ± 1.46b	10.06 ± 4.06ab	13.25 ± 3.68a
K	1.41 ± 0.36a	0.98 ± 0.52a	4.86 ± 3.46a
Fe	0.008 ± 0.00a	0.029 ± 0.01a	0.116 ± 0.08a
Mn	0.12 ± 0.02c	0.90 ± 0.52b	2.15 ± 0.67a
Cu	<0.0001a	<0.0001a	<0.0001a
	Soil anions losses (10^{-3} $cmol_c$ kg^{-1})		
NO_3^-	46.61 ± 19.92b	112.95 ± 12.77a	94.61 ± 19.97a
SO_4^{2-}	6.09 ± 1.61c	24.74 ±1.36b	35.40 ±7.22 a
Cl	8.10 ± 0.44b	18.62 ± 3.26a	26.82 ±7.64 a
$H_2PO_4^-$	0.04 ± 0.01c	0.40 ± 0.11b	0.82 ± 0.23 a

Remarks :

a) Data are the means ± standard deviation (n=4).

b) For a given element, means without common letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test.

Table 4. Distribution of exchangeable zinc (Zn) in the soil depth varying from 0 to 30 cm under different leaching amounts

Soil depth (cm)	Leaching amount (mm)		
	31	208	497
	Exchangeable Zn (10^{-3} $cmol_c$ kg^{-1} sol)		
0-10	13.39 ± 1.29a) Ab)abc)	13.67 ± 1.75 Aa	10.99 ± 2.14 Ab
10-20	0.76 ± 0.19 Ba	0.87 ± 0.12 Ba	1.07 ± 0.33 Ba
20-30	0.81 ± 0.13 Ba	0.96 ± 0.22 Ba	1.03 ± 0.16 Ba

Remarks :

a) Means ± standard deviation (n=4).

b) For each leaching rate, means without common capital letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test.

c) For the same soil layer, means without common lowercase letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test.

result also suggests that Zn loss, applied as sulfated form, through leaching from the rooting zone of most plants grown on sandy soil of Loukkos is null. Many researchers have reported that the low mobility of Zn in not calcareous soils, like in Loukkos sandy soil, is linked to the retention that plays iron oxide (Fe_2O_3) and aluminum oxide (Al_2O_3) as well as the CEC (Kalbasi *et al.*, 1978; Ghiri *et al.*, 2011).

Furthermore, the percentage of the CEC occupied by Zn was significantly increased on the top layer (0-10 cm) compared to the underlying ones. This percentage reached almost 0.35% on the top soil layer for different leaching amounts. However, the middle and the bottom layers showed a similar percentage of occupation to that recorded before leaching (0.03%) (Figure 1). Such Zn immobility will induce its accumulation in the top soil layer which may pose a threat to the environment (Jalali and Khanboluki, 2007). So, the reasoning of Zn supply must take into account its residual effect. In contrast, the risk to contaminate shallow groundwater by Zn seems unlikely to occur.

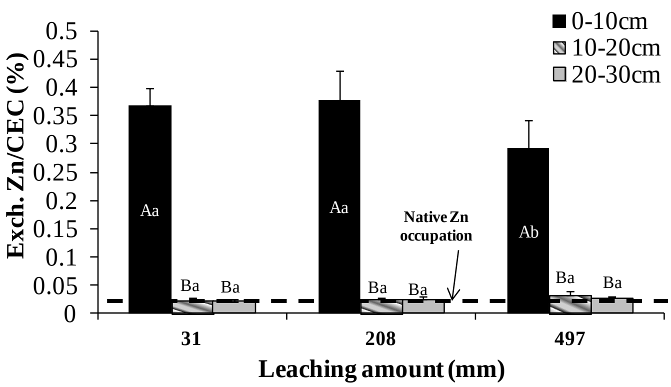

Figure 1. Percentage of the cation exchange capacity (CEC) occupied by zinc (Zn) in three soil layers after leaching. For each leaching rate, percentages without common capital letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test. For the same soil layer, percentages without common lowercase letter are significantly different according to the same test. The horizontal broken line indicates the native CEC occupation before leaching and Zn supply. Vertical bars denote standard deviation (n=4).

Table 5. Distribution of exchangeable manganese (Mn), potassium (K), calcium (Ca), ammonium (NH_4^+), copper (Cu), iron (Fe), magnesium (Mg) and sodium (Na) in the soil depth varying from 0 to 30 cm under different leaching amounts.

	Leaching amount (mm)		
Soil depth (cm)	31	208	497
	Exchangeable K (cmol$_c$ kg^{-1} soil)		
0-10	0.10 ± 0.00a) Bb)ac)	0.09 ± 0.01 Bab	0.08 ± 0.00 Bb
10-20	0.11 ± 0.00 Aa	0.10 ± 0.02 Aa	0.11 ± 0.02 Aa
20-30	0.12 ± 0.01 Aa	0.11 ± 0.01 Aa	0.11 ± 0.01 Aa
	Exchangeable Ca (cmol$_c$ kg^{-1} soil)		
0-10	2.77 ± 0.12 Aa	2.82 ± 0.34 Aa	3.04 ± 0.14 Aa
10-20	2.53 ± 0.07 Aa	2.44 ± 0.14 Aa	2.45 ± 0.17 Ba
20-30	2.36 ± 0.43 Aa	2.55 ± 0.14 Aa	2.39 ± 0.43 Ba
	Exchangeable NH4+ (cmol$_c$ kg^{-1} soil)		
0-10	0.03 ± 0.00 Ba	0.04 ± 0.00 Aa	0.03 ± 0.00 Aa
10-20	0.03 ± 0.00 ABa	0.04 ± 0.00 Aa	0.03 ± 0.00 Aa
20-30	0.04 ± 0.00 Aa	0.04 ± 0.00 Aa	0.04 ± 0.00 Aa
	Exchangeable Mg (cmol$_c$ kg^{-1} soil)		
0-10	0.46 ± 0.02 Aa	0.42 ± 0.02 Bb	0.36 ± 0.01 Bc
10-20	0.49 ± 0.03 Aa	0.48 ± 0.04 Aa	0.48 ± 0.04 Aa
20-30	0.50 ± 0.02 Aa	0.49 ± 0.01 Aa	0.48 ± 0.02 Aa
	Exchangeable Na (cmol$_c$ kg^{-1} soil)		
0-10	0.13 ± 0.01 ABa	0.14 ± 0.02 Aa	0.12 ± 0.00 Aa
10-20	0.11 ± 0.01 Ba	0.14 ± 0.01 Aa	0.13 ± 0.03 Aa
20-30	0.14 ± 0.00 Aa	0.15 ± 0.01 Aa	0.11 ± 0.01 Aa
	Exchangeable Mn (10^{-3} cmol$_c$ kg^{-1} soil)		
0-10	50.98 ± 8.02 Ba	43.12 ± 5.35 Bab	34.64 ± 2.90 Bb
10-20	87.46 ± 11.71 Ba	70.89 ± 18.46 Ba	90.55 ± 24.92 Ba
20-30	496.56 ± 176.68 Aa	346.21 ± 137.19 Aa	508.06 ± 275.71 Aa
	Exchangeable Fe (10^{-3} cmol$_c$ kg^{-1} soil)		
0-10	58.96 ± 7.42 Ba	53.48 ± 4.53 Aa	50.03 ± 7.20 Ca
10-20	81.79 ± 15.78 Ba	71.61 ± 16.62 Aa	83.90 ± 15.08 Ba
20-30	90.73 ± 20.65 Aa	81.71 ± 29.98 Aa	114.03 ± 24.47 Aa
	Exchangeable Cu (10^{-3} cmol$_c$ kg^{-1} soil)		
0-10	0.51 ± 0.01 Ba	0.59 ± 0.06 Ba	0.57 ± 0.12 Ba
10-20	0.65 ± 0.03 ABa	0.51 ± 0.11 Ba	0.51 ± 0.06 Ba
20-30	0.74 ± 0.14 Aa	0.66 ± 0.15 Aa	0.83 ± 0.18 Aa

Remarks :

a) Means ± standard deviation (n=4).

b) For each cation and for a given leaching rate, means without common capital letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test.

c) For each cation and in the same soil layer, means without common lowercase letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test.

The increase on the percentage of the CEC occupied by Zn may be attributed to the release of adsorption saturations sites by other cations moved into depth after leaching (Table 5). In this regard, an increase in the exchangeable soil Mn content with depth for all leaching amounts was noticed. Its native soil content was reduced by almost 14.2% on the top layer (0-10 cm) for different leaching amounts (Table 5).

Such decline resulted in the highest CEC saturation release of 3% (Figure 2A). The high mobility of Mn was reported by Singh (1974b), who demonstrated, on the other hand, the absence of competition between Mn and Zn for absorption sites (Singh, 1974a; Singh, 1974b). The exchangeable K content also increased with depth. Its native content was significantly reduced on the top layer (0-10 cm) by 35.28% and by 45.84%, respectively, for low (31 mm) and high (497 mm) leaching amounts (Table 5). This K content decline

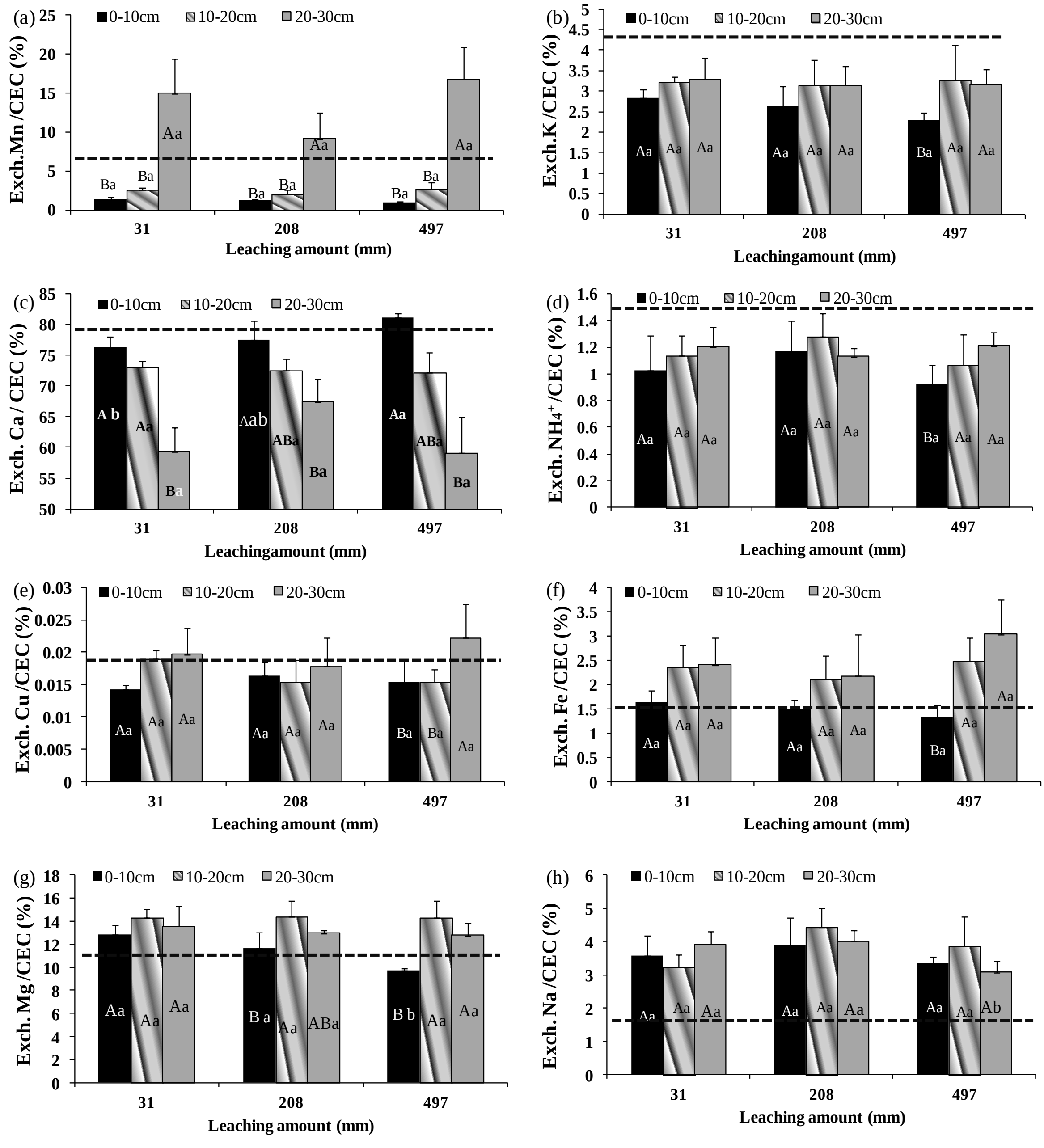

Figure 2. Percentages of the cation exchange capacity (CEC) occupied by manganese (Mn) (a), potassium (K) (b), calcium (Ca) (c), ammonium (NH_4^+) (d), copper (Cu) (e), iron (Fe) (f), magnesium (Mg) (g) and sodium (Na) (h) in three soil layers after leaching. For a given cation and for each leaching amount, percentages without common capital letter are significantly different (at P ≤0.05), according to Student-Newman-Keuls test. For a given cation and for the same soil layer, percentages without common lowercase letter are significantly different according to the same test. For a given cation, the horizontal broken line indicates its CEC occupation before leaching. Vertical bars denote standard deviation (n=4).

released a CEC saturation of almost 1.67% for all leaching amounts (Figure 2B). The CEC saturation ceded by the Ca on the top soil layer was almost only 0.67% for all leaching amounts (Figure 2C) despite the high content on this element in the leachate. The low mobility of Ca compared to K was reported by Gauchet (1968). However, the soil Ca enrichment from water used for leaching, that contains a considerable amount of Ca, cannot be excluded. Besides, the lowest CEC saturation (0.25%) was released by NH_4^+ (Figure 2D); its content became low along the the Cu, Fe and Mg contents increased with depth (Table 5) without ceding any CEC saturation sites in the top layer (Figure 2E, 2F, 2G). This result may be explained by the release of these cations from the non exchangeable fraction after leaching. Also, the exchangeable Na did not release any part of its CEC saturation (Figure 2H); its content increased along the soil profile (Table 5) which can be attributed to the enrichment made by water used for leaching through its content on Na. The distribution of these cations along the soil profile suggested that the increase on the percentage of the CEC occupied by Zn on the top soil layer was linked particularly to the release of adsorption saturations sites by Mn, K, Ca and NH_4^+.

CONCLUSIONS

Results of this study have shown the absence of Zn loss through leaching in the sandy soil of Loukkos which received Zn sulfate ($ZnSO_4.7H_2O$) on surface. Also, it has showed that even after a high leaching amount (497 mm), frequently recorded in this area, Zn was retained on the top 10 cm of soil. Also, the increase on the percentage of the CEC occupied by Zn in the top soil layer was at the expense of other exchangeable cations, particularly Mn, K, and NH_4^+ mobilized in depth after leaching. Hence, the reasoning of Zn supply in this soil may neglect its losses through leaching and take into account its residual effect.

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