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Speciation of Zn in Arid Soils With Saline Accumulations. Case Study of the Biskra Region, Algeria
Especiación del Zn en Suelos Áridos con Acumulaciones Salinas. Estudio de Caso de la Región de Biskra, Argelia

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SUMMARY

Zinc (Zn) deficiency in plants is closely related to its bioavailability in soil. However, the behaviour of Zn in soils, especially in saline areas, remains complex. This research aims to clarify the distribution and dominant forms of Zn in arid soils with salt accumulations from the Biskra region by studying soil samples from ten representative profiles. Soil samples were collected from different horizons of each profile to a depth of 120 cm and subjected to speciation analysis using sequential extraction. The results indicate a deficiency of Zn in all soil samples, resulting in reduced concentrations of different forms of Zn. The dominant forms were residual Zn (R-Zn) and oxide-bound Zn (O-Zn), which accounted for over 90% of total Zn. The study revealed a negative correlation between soil salinity and all Zn forms, except for R-Zn, which showed a positive correlation. Additionally, Zn concentrations showed a negative correlation with gypsum, except for exchangeable Zn (E-Zn). It is important to note that the presence of gypsum in soils was significantly and negatively correlated with O-Zn. Although the sequential extraction method used may have limitations in accurately quantifying all forms of Zn, this study fills a gap in the literature on Zn assessment and speciation in arid soils. The study emphasizes the significance of soil characteristics, particularly salinity and gypsum content, in shaping Zn distribution. Overall, these results contribute to a better understanding of Zn availability and mobility in arid and saline environments, providing valuable insights for improved soil management practices in such regions.

Index words: *dry lands, gypsum-rich land, micronutrient deficiency, micronutrient distribution, saline environment.*

RESUMEN

La deficiencia de Zinc (Zn) en las plantas está estrechamente relacionada con su biodisponibilidad en el suelo. Sin embargo, el comportamiento del Zn en los suelos, especialmente en zonas salinas, sigue siendo complejo. Esta investigación tiene como objetivo esclarecer la distribución y las formas predominantes de Zn en suelos áridos con acumulación de sal de la región de Biskra, mediante el estudio de muestras de suelo de diez perfiles representativos. Se recopilaron muestras de suelo de diferentes horizontes de cada perfil hasta una profundidad de 120 cm y se sometieron a análisis de especiación mediante extracción secuencial. Los resultados indican una deficiencia de Zn en todas las muestras de suelo, resultando en concentraciones reducidas de diferentes formas de Zn. Las formas dominantes fueron el Zn residual (R-Zn) y el Zn unido a óxidos (O-Zn), que representaron más

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del 90% del Zn total. Se encontró una correlación negativa entre la salinidad del suelo y las diferentes formas de Zn, excepto para el R-Zn, que mostró una correlación positiva. Además, las concentraciones de Zn mostraron una correlación negativa con el yeso, excepto para el Zn intercambiable (E-Zn). Cabe destacar que la presencia de yeso en los suelos se correlacionó significativa y negativamente con el O-Zn. Aunque el método de extracción secuencial utilizado puede tener limitaciones para cuantificar con precisión todas las formas de Zn, este estudio llena un vacío en la literatura sobre la evaluación y especiación del Zn en suelos áridos. Destaca la importancia de las características del suelo, en particular la salinidad y el contenido de yeso, en la conformación de la distribución del Zn. En resumen, estos resultados contribuyen a una mejor comprensión de la disponibilidad y movilidad del Zn en ambientes áridos y salinos, proporcionando información valiosa para mejorar las prácticas de gestión del suelo en estas regiones.

Palabras clave: *tierras secas, tierras ricas en yeso, carencia de micronutrientes, distribución de micronutrientes, entorno salino*.

INTRODUCTION

Zn is essential for growth, development, and immune function maintenance (Read, Obeid, Ahlenstiel, and Ahlenstiel, 2019). Its deficiency can disrupt crucial biophysicochemical processes involved in normal plant function and detoxification under stress conditions (Sousa, Lopes, Fernandes, and Ramos, 2009; Hafeez, Khanif, and Saleem, 2013; Noman *et al*., 2019)

Zn deficiency afflicts around a quarter of the global population, specifically in Latin America, Africa, and South Asia, due to the impoverished fertility of soils in these regions (Bortolon and Gianello, 2009; Mossa *et al*., 2021). Understanding the complex behavior of Zn in soils, dictated by natural and human-influenced factors, poses challenges in grasping its retention, bioavailability, and mobilization (Alexakis, 2010).

Soil properties, like pH, texture, organic carbon (OC) content, calcium carbonate ($CaCO_3$), total Zn (T-Zn) concentration, and the presence of competing cations, impact the distribution of Zn among various forms: E-Zn, carbonate-bound (Zn-CO_3), organic matter-bound (OM-Zn), O-Zn, and R-Zn forms (Liu *et al*., 2020). The proportions of these forms are influenced by factors such as salinity level (EC), soluble salt type, ionic strength, and kinetic effects (Kabata-Pendias, 2001; Moreno-Lora and Delgado, 2020; Salinitro, Van Der Ent, Tognacchini, and Tassoni, 2020; Mohiuddin *et al*., 2022).

Bioavailable Zn includes soluble Zn (Zn^{2+}) and E-Zn. Its concentration is generally low, ranging from 0.1 to 2 mg kg^{-1} in soil, representing a small percentage of T-Zn (Natasha *et al*., 2022). Zn deficiency in plants is mainly attributed to its low solubility and high retention in the solid phase of the soil, where a significant portion (30 to 60% of T-Zn) exists in an unattainable form, especially attached to mineral colloids (Alonso, Arias, Fernandez, Fernandez, and Serrano, 2006; Natasha *et al*., 2022). Factors contributing to Zn deficiency include excessive phosphorus, high pH, and concentrations of Na^+, HCO_3^-, and CO_3^{2-} in the soil solution (Mousavi, Galavi, and Rezaei, 2012; Natasha *et al*., 2022).

Soils in arid regions, classified as Aridisols and Entisols, pose unique challenges, with alkaline pH, meager organic matter (OM) content, and accumulation of $CaCO_3$, gypsum, and soluble salts. T-Zn concentrations in arid soils typically span between 41 to 130 mg kg^{-1}, with E-Zn varying from 0.24 to 1.28 mg kg^{-1} (Praveen-Kumar, Tarafdar, Soni, and Mahesh, 2009). Zn speciation, influenced by factors like pH, displays variations like $ZnCO_3$, $ZnSO_4$, $ZnPO_4$, and $ZnCl^+$ at different pH ranges (Sadiq, 1991).

Extensive research has explored the field of Zn speciation in different soils and climates, encompassing calcareous soils (Sadiq, 1991), Vertisols (Dang, Tilled, Dalal, and Edwards, 1996), Regosols (Korchagin, Moterle, Escosteguy, and Bortoluzzi, 2020), Fluvisols (Ruzicic and Rako, 2017), paddy soils (Weiss *et al*., 2021), Chernozems (Bauer *et al*., 2019), Alfisols (Chakraborty, Chidanandappa, Dhananjaya, and Padhan, 2016), hydromorphic soils (Azouzi, Charef, and Hamzaoui, 2015), and saline soils (Mohiuddin *et al*., 2022). Nonetheless, the comprehension of Zn conduct in soils characterized by the simultaneous existence of gypsum, calcium carbonate, and soluble salts remains limited.

The research aims to investigate Zn speciation in soils from the Biskra region, located close to the Algerian desert and known for its advanced agriculture, particularly, date palm cultivation (Benmehaia, 2019). Focusing mainly on soils characterized by the accumulation of gypsum, $CaCO_3$, and soluble salts, this study aims to explore the impact of these specific soil characteristics on Zn dynamics and bioavailability. The research involves an in-depth assessment of Zn distribution across various fractions, including exchangeable, carbonate-bound, organic matter-bound, oxide-bound, and residual forms. This analysis will provide valuable information on the factors governing the mobility, retention, and bioavailability of Zn to plants in arid soils. The results of this study will contribute significantly to the development of effective strategies to improve Zn availability to plants in arid regions, in order to effectively combat Zn deficiency in agricultural systems.

MATERIALS AND METHODS

Main Characteristics of the Study Area

Biskra is classified as a hyperarid climate with a mild winter in the bioclimatic stage (NATP, 2003[1]; GFOA, 2019[2]). Summer temperatures in this locale are scorching, averaging around 40 °C, while winter temperatures generally remain at approximately 28 °C. Precipitation in Biskra is notably scarce, measuring a mere 139.8 mm per year, and its infrequent occurrence is irregular (Faci, 2021[3]).

In terms of pedoclimate, this region exhibits an arid humidity regime coupled with a hyperthermal temperature regime. The soils of Biskra manifest a diverse composition, predominantly comprising accumulations of $CaCO_3$, gypsum, and saline deposits. Interestingly, in certain instances, two or three of these salts accumulate concurrently in the soil profile (Khechai, 2001[4]; Bensaid, 1999).

Soil Sampling

Ten profiles representative of the region (Figure 1) were selected based on various criteria, including the type and form of saline accumulations ($CaCO_3$, gypsum, soluble salts), land use, natural vegetation, and the presence of eolian sand deposits on the surface. A total of 28 soil samples were taken from each horizon of the different profiles to a depth of 120 cm. Sampling took place in June 2021, with the aim of describing the main aspects of each profile.

Soil Analysis

The soil samples were analyzed after being air-dried, crushed, and sieved to 2 milimeter.

We measured the pH of the soil solution with pH meter using a diluted 1: 2.5 extract, and the EC was determined by conductometry using a diluted 1: 5 extract. The total $CaCO_3$ content was determined using the Bernard calcimeter method, and the gypsum content was determined gravimetrically (Mathieu and Pieltain, 2003; Bashour and Sayegh, 2007).

The Anne method was used to measure the quantity of OC; OM content was determined using the OC rate (Mathieu and Pieltain, 2003).

After pretreating the samples to eliminate gypsum, we quantified the different particle size fractions using the universal Robinson pipette method (Mathieu and Pieltain, 2003). Sequential extraction was used to determine the different forms of Zn (Table 1), (Tessier, Campbell, and Bisson, 1979).

The extraction process of different forms of Zn is conducted on the same aliquot in the order listed in Table 1. It is important to note that no pretreatment is performed on the soil samples prior to the extraction process, thereby ensuring the extraction of Zn quantities in the presence of all types of salts.

[1] NATP (National Agency for Territorial Planning). (2003). *Master Plan for Water Resources in the Biskra Province*. Summary Report. Biskra, Algeria: ANAT.

[2] GFOA (Government Finance Officers Association). (2019). *Monograph of Biskra Province 2018*. Biskra. Algeria: DPSB.

[3] Faci, M. (2021). *Impacts du changement climatique sur le cycle phénologique du palmier dattier* (Cas de Deglet Nour aux Ziban). Thèse de doctorat. Université de Biskra. Algérie. Available in http://thesis.univ-biskra.dz/5564/1/FACI_Thèse_2021.pdf

[4] Khechai, S. (2001). *Contribution à l'étude du comportement hydrophysique des sols du périmètre irrigué de l'ITDAS dans la plaine d'Outaya (Biskra)*. Thèse de Magister. Université de Batna. Algérie.

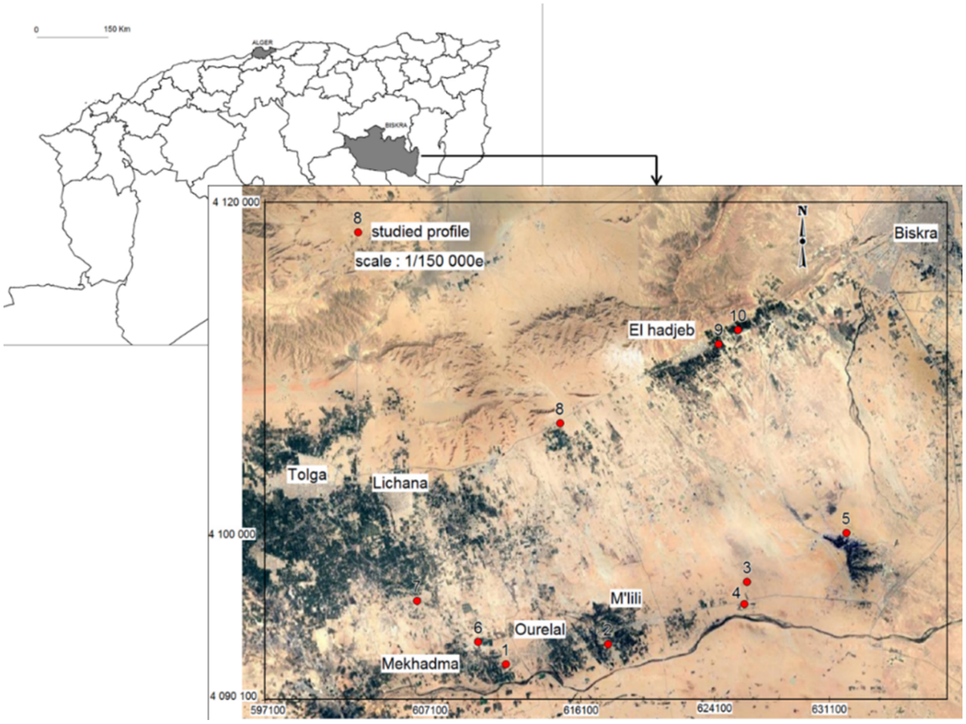

Figure 1. Location of the sampling profiles in the Biskra region.

Table 1. Sequential extraction of Zn (Tessier, Campbell, and Bisson, 1979).

Fractions extracted	Reagent(s)	Volume of extraction solution	Quantity of soil	Agitation time and temperature
E-Zn	MgCl2 (1 M), pH=7	8 mL	1 g	1 hour at room temperature
Zn-CO3	CH3COONa (1M)/ CH3COOH, pH=5	8 mL	Aliquot of the exchangeable fraction	5 hours at room temperature
O-Zn	NH2OH•HCl (0.04 M) in 25% CH3COOH, pH = 2	20 mL	Aliquot of the carbonate-bound fraction	Occasional agitation for 6 hours at 96°C
OM-Zn	HNO3 (0,02M)/ H2O2 (30%) at pH =2 (3.2 M) NH4OAc dans 20% HNO3	3 mL HNO3, 8 mL H2O2, 5 mL NH4 COOH 20 mL dilution	Aliquot of the oxide-bound fraction	Occasional agitation for 5 hours at 85°C, followed by cooling and continuous agitation for 30 minutes at room temperature
R-Zn	HClO4-HF/ HCl	4 mL-20 mL 25 mL dilution	Aliquot of the organic matter-bound fraction	Alternatively, drying in an oven at 30 ± 2°C for 48 hours

Statistical Analysis

Data were presented as mean, standard deviation, and coefficient of variation (CV). Correlation coefficient and Student's t-test were used to determine the effect of soluble salts and gypsum on the distribution of Zn.

RESULTS AND DISCUSSION

Characteristics of the Studied Samples

Table 2 shows the statistical characteristics of the studied samples, including alkaline pH values and high salinity, indicating their characteristic conditions. The samples exhibit moderate calcareousness with varying levels of gypsum content, low OC content, and predominantly sandy texture with some silt. The analyzed parameters display significant variability, reflecting local variations that can influence Zn speciation. The selected profiles accurately represent the soils in the study area, making them suitable for conducting this research.

Zn Content in Different Forms

The studied soils show a notable Zn deficiency compared with Loué (1993) standards, with low T-Zn contents (0.41 mg kg^{-1} < T-Zn < 4.90 mg kg^{-1}), which translates into low quantities of the other forms of Zn. Soil E-Zn content is extremely low (0.01 < E-Zn mg kg^{-1} < 0.11), around one-tenth of Loué's (1993) standards. Similarly, concentrations of the other forms of Zn are very low, at around 0.03 mg kg^{-1} for Zn-CO_3, 0.11 mg kg^{-1} for OM-Zn, 0.79 mg kg^{-1} for O-Zn, and 1.21 mg kg^{-1} for R-Zn. Despite their derisory quantities, the different forms of Zn show significant variations between samples (46% < CV < 230%), probably due to the variability of the soil parameters that govern Zn speciation. These results align with the findings of Sandstead (2015), Noulas, Tziouvalekas, and Karyotis (2018), Rahman, Hangs, Peak, and Schoenau (2021), and Tolay (2021), who showed that Zn deficiency is common in soils with high pH, alkalinity, abundant $CaCO_3$ content, coarse texture, and low OM content.

The data in table 3 highlight the glaring inequality of Zn distribution in the studied soils. R-Zn (54.81%) and O-Zn (35.9%) predominate, accounting for over 90% of T-Zn. The remaining forms are extremely weak, with only 5.26% for OM-Zn, 2.55% for E-Zn, and only 1.45% for $ZnCO_3$. Consequently, the hierarchy of Zn form distribution in these soils is R-Zn > O-Zn > OM-Zn > E-Zn > $ZnCO_3$. These results agree with those of Milivojević, Nikezic, Krstic, Jelic, and Dalovic (2010) in Vertisols, Mohiuddin *et al*. (2022) in saline soils, and Kabala and Singh (2001) in calcareous soils. Notably, Chlopecka, Bacon, Wilson, and Kay (1996) also highlighted the dominance of R-Zn and O-Zn in the soils they studied, while Hashemi and Baghernejad (2009) attribute the abundance of R-Zn in gypsum soils to its strong adsorption by palygorskite (Girija, Rattan, and Datta, 2013).

The presence and limited proportions of OM-Zn can be attributed to extremely low OC contents, particularly in subsurface and deep horizons.

Effect of Depth on Zn Variation

The one-way ANOVA analysis used to assess the depth factor's impact on variations in the concentrations of various forms of Zn showed non-significant results, indicating that these concentrations vary independently along the horizon (depth).

Table 2. statistical characteristics of the studied samples.

Parameter	Minimum	Maximum	Mean	Standard Deviation	CV*
					%
pH	7.48	8.56	7.80	0.31	4
EC dS m-1	1.54	30	7.05	7.11	101
CaCO3 %	Traces	24.4	9.5	5.7	60
CaSO4.2H2O %	1.5	87.5	36.6	23	63
Organic Carbon %	0.06	1.17	0.52	0.34	70
Clay %	Traces	28	10	11.6	117
Silt %	0.5	37	16	8.8	55
Sand %	25.4	77.5	54.5	17.8	33

Table 3. Statistical characteristics of Zn forms content in soils.

Forms of Zn	Minimum	Maximum	Mean	Standard Deviation	Content form/ T-Zn content	CV
	- - - - - - - - - - - - - - - - - - - -	- - - mg kg^{-1} - - -	- - - - - - - - - - - - - - - - - - - -		- - - - - - - - - - - %	- - - - - - - - - - -
E-Zn	0.01	0.11	0.06	0.03	2.55	47
ZnCO3	0.00	0.27	0.03	0.05	1.45	171
OM-Zn	0.00	0.83	0.12	0.27	5.26	230
O-Zn	0.05	3.24	0.79	0.74	35.9	94
R-Zn	0.24	2.82	1.21	0.63	54.81	52
T-Zn	0.41	4.90	2.21	1.03	100	47

Relationship Between EC, Gypsum, and Different Forms of Zn

The soil samples that were studied were characterized by extreme variations in salinity (EC) (CV = 101%) and gypsum content (CV = 63%). This prompted research into the relationship between these two factors and the different forms of Zn. As a first step, simple regressions were used, the entire data set was analyzed and then the means of Zn forms were compared between homogeneous classes of CE and gypsum. The results of the simple regressions, examining the relationship between Zn forms with EC and gypsum rates, are reported in Table 4.

Table 4 shows that the correlations between EC on the one hand and E-Zn, $ZnCO_3$, OM-Zn, and O-Zn on the other are weak, negative, and statistically insignificant ($P > 0.05$). However, these results show that although this correlation is not statistically significant, it does suggest that increasing EC is associated with a slight decrease in the levels of these Zn species. This result agrees with those of Keshavarz, Malakouti, Karimian, and Fotovat, (2006), who asserted that EC negatively influences the diversity and distribution of Zn in calcareous soils. Similarly, Khoshgoftar *et al*. (2004) demonstrated that T-Zn and E-Zn concentrations decrease with increasing EC. In contrast, table 4 reveals that the correlation between EC and R-Zn is strong, positive, and statistically highly significant (r = 0.682; $P < 0.01$), indicating that R-Zn contents increase with EC. This result may be linked to the retention of Zn in mineral silicate networks and its low solubility due to soil alkalinity (Pierangeli, Guilherme, Oliveira, Curi, and Silva, 2003; Girija *et al*., 2013) and salinity. These results are exactly in line with those of Mohiduddin *et al*. (2022), who showed that the R-Zn is the dominant form of Zn under saline conditions.

Table 4 also reveals weak, statistically insignificant correlations between gypsum and E-Zn, $ZnCO_3$, OM-Zn, and R-Zn ($r < 0.3$; $P > 0.05$). Except for the E-Zn form, which is positively correlated with gypsum (r = 0.179), all Zn forms decrease with increasing gypsum values. Lombnæs, Chang, and Singh (2008) reported that the increase in ionic strength caused by the abundance of exchangeable Ca from gypsum could be responsible for the decrease in Zn sorption, which explains the relationship between E-Zn and gypsum. Shukla and Mukhi (1980) have also shown that gypsum enriches the soil solution in Ca^{2+} ions, increasing the Ca:Na ratio and thus promoting Zn availability. On the other hand, Table 4 reveals that the correlation between gypsum and O-Zn is statistically highly significant and negative (r = -0.542; $P < 0.01$), describing the inverse relationship between gypsum abundance and O-Zn content. Ma *et al*. (2020) showed that Zn hydroxides and Zn sulfates represent a significant proportion of Zn-containing species in high pH gypsum soil samples, which is the case of the soils studied in this research.

Comparison of the Means of Zn Forms According to EC and Gypsum Classes

To achieve this, a one-way analysis of variance was performed. The results of this analysis reveal three homogeneous classes for CE (dS m^{-1}) and three homogeneous classes for gypsum (%), as shown in Table 5.

Table 4. Correlation coefficients (r) between EC, gypsum, and Zn forms.

	E-Zn	$ZnCO_3$	OM-Zn	O-Zn	R-Zn
EC dS m-1	-0.254	-0.160	-0.363	-0.290	**0.682****
Gypsum%	0.179	-0.367	-0.130	**-0.542****	-0.190

** significance threshold $\alpha < 0.01$

Table 5. EC and gypsum classes.

Parameter	Classes	Intervals	Number
	1	EC dS m-1 < 6	19
EC (dS m^{-1})	2	6 ≤ EC dS m^{-1} < 15	5
	3	EC dS m^{-1} ≥ 15	4
	1	Gypsum % < 25	9
Gypsum (%)	2	25 ≤ Gypsum % < 60	16
	3	Gypsum % ≥ 60	3

It is noteworthy that group sizes exhibit significant variability for both CE and gypsum levels. Given this observation, a t-test was performed to compare the means of each Zn form within the three CE classes initially and subsequently between the three gypsum rate classes.

Comparison of Mean Values of Zn Forms According to CE Classes

According to the analysis presented in Table 6, there were no significant differences ($P > 0.05$) in the means of the E-Zn, $ZnCO_3$, and OM-Zn forms between the three EC classes. This suggests that variation in EC levels has no significant influence on these forms of Zn in the studied samples. The low pH of the extraction solution used for extracting OM-Zn and the high ionic strength resulting from high Ca^{2+} concentrations could explain this result, by reducing carbonate solubility and subsequently decreasing $ZnCO_3$ contents, as noted by Keshavarz *et al*. (2006).

As far as the O-Zn and R-Zn forms are concerned, there are significant differences ($P < 0.05$) only between classes 1 and 2. However, the differences in means between classes 2 and 3, as well as between classes 1 and 3 are not statistically significant ($P > 0.05$).

Overall, variations in EC classes have little impact on the levels of the various forms of Zn in the studied samples. However, it should be noted that EC class 2, corresponding to a salinity range of 6 dS m^{-1} to 15 dS m^{-1}, appears to represent a critical threshold for variation in mean O-Zn and R-Zn contents. This finding is in line with the observations of Keshavarz *et al*. (2006), who stated that high salinity levels, around 15 dS m^{-1}, affect O-Zn and R-Zn concentrations.

Comparison of Means of Zn Forms According to Gypsum Classes

According to Table 7, there are no statistically significant differences ($P > 0.05$) in the means of $ZnCO_3$, OM-Zn, and R-Zn forms among the different classes of gypsum content. These findings suggest that the variation in gypsum content within the studied samples does not have a significant impact on the variation of these forms of Zn. However, elevated quantities of gypsum do exert a notable influence on both E-Zn and O-Zn. The difference in means of E-Zn between gypsum class 1 (gypsum < 25%) and class 2 (25 ≤ gypsum% < 60) is not statistically significant ($P > 0.05$). However, the differences in means of E-Zn between class 3 (gypsum > 60%) and classes 1 and 2 are significant ($p < 0.05$). Similarly, the difference in means of O-Zn between class 3 (gypsum > 60%) and class 1 is also significant ($P < 0.05$).

These results suggest that the variation in gypsum content does not significantly impact the different forms of Zn in the studied samples, except for E-Zn and O-Zn when gypsum levels are excessive (gypsum > 60%). Elrashidi *et al*. (2010) observed that low concentrations of gypsum negatively affect the bioavailability of Zn in the soil. They found that gypsum quantities between 1% and 30% had no effect on Zn bioavailability, while quantities between 30% and 50% significantly increased the concentration of E-Zn. The authors attributed this result to the dissolution of Zn-containing minerals due to the high presence of sulfate and the acidity of the extraction solution. This observation aligns with the findings of Lindsay (1979) and previous studies.

Table 6. Comparison of means (p-values) of Zn forms according to CE classes.

EC classes	E-Zn	$ZnCO_3$	OM-Zn	O-Zn	R-Zn
1 × 2	0.344	0.536	0.934	****0.004**	****0.001**
2 × 3	1	0.948	0.590	0.604	0.240
1 × 3	0.392	0.817	0.298	0.103	0.183

Table 7. Comparison of means (p-values) of Zn forms according to gypsum classes.

Gypsum Classes	E-Zn	Zn-CO_3	OM-Zn	O-Zn	R-Zn
1 × 2	0.996	0.908	0.493	0.495	0.899
2 × 3	**< 0.01****	0.909	0.566	0.091	0.145
1 × 3	**< 0.01****	0.990	0.966	**0.027***	0.107

CONCLUSIONS

Soil analysis conducted in the arid environment of the Biskra region reveals a conspicuous deficiency in T-Zn. The manifestation of Zn deficiency is evident in the low levels observed for the five studied forms. The distribution of Zn forms in the studied soils is predominantly governed by R-Zn and O-Zn, while the diminished levels of OM-Zn stem from the low proportions of OC in the subsurface and deep horizons. The hierarchical order of Zn form distribution in these soils is as follows: R-Zn (55%) > O-Zn (36%) > OM-Zn (5%) > E-Zn (3%) > $ZnCO_3$ (1%).

The results indicate that EC and gypsum levels have no significant influence on the variation of Zn concentrations in the samples studied, except for R-Zn, which is influenced by EC (r = 0.682; $P < 0.01$), and O-Zn, which is influenced by gypsum levels (r = -0.542; $P < 0.01$). Overall, the comparison of the means of the different Zn forms between the three EC classes and the three gypsum content classes corresponds well with the previous results, confirming that, in general, the differences in means for Zn forms between EC and gypsum classes are statistically insignificant ($P > 0.05$), except O-Zn and R-Zn between EC classes 1 and 2, Zn-E between gypsum classes 1 and 3, and 2 and 3, and O-Zn between gypsum classes 1 and 3.

This study highlights that EC and gypsum rates have different impact on Zn forms in arid soils. Although the comparison of means for different Zn forms between EC and gypsum classes has revealed some minor differences, it overall confirms these findings. These results expand our knowledge of Zn speciation and availability in arid soils. Nevertheless, they emphasize the need for further research in order to acquire a deeper comprehension of this phenomenon and focus on its effect on Zn biogeochemical processes in such soils.

ETHICS STATEMENT

Not applicable.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF SUPPORTING DATA

All data generated or analyzed during this study are included in this published article.

COMPETING INTEREST

The authors declare no conflict of interest.

FINANCING

Not applicable.

AUTHORS' CONTRIBUTION

Conceptualization and methodology: N.D., K.D., Y.D., and S.B. Investigation: N.D. and S.B. Data Curation and formal analysis: N.D and Y.D. Writing original draft: N.D. Writing-reviewing and editing: N.D., K.D., Y.D., and S.B.

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REFERENCES

Alexakis, D. (2010). Diagnosis of stream sediment quality and assessment of toxic element contamination sources in East Attica, Greece. *Environmental Earth Sciences, 63*(6), 1369-1383. https://doi.org/10.1007/s12665-010-0807-9

Alonso, F. P., Arias, J. S., Fernandez, R. O., Fernandez, P. G., & Serrano, R. E. (2006). Agronomic implications of the supply of lime and gypsum by-products to palexerults from western Spain. *Soil Science, 171*(1), 65-81. https://doi.org/10.1097/01.ss.0000200557.253069.50

Azouzi, R., Charef, A., & Hamzaoui, A. H. (2015). Assessment of effect of pH, temperature and organic matter on zinc mobility in a hydromorphic soil. *Environmental Earth Sciences, 74*(4), 2967-2980. https://doi.org/10.1007/s12665-015-4328-4

Bashour, I., & Sayegh, A. (2007). *Methods of Analysis for Soils of Arid and Semi-Arid Regions*. Rome, Italy: FAO. ISBN: 978-92-5-105661-5

Bauer, T. V., Pinskii, D. L., Minkina, T. M., Zamulina, I. V., Sushkova, S. N., Zamulina, I. V., & Barakhov, A. V. (2019). Copper and zinc adsorption by Chernozems of different textures. *IOP Conference Series*. *Earth and Environmental Science*, *368*, 012007. https://doi.org/10.1088/1755-1315/368/1/012007

Benmehaia, M. A. (2019). Farmers' Income Risks and marketing channel choices: Case of date palm processing in Biskra. *Algeria. New Medit, 18*(3), 47-58. https://doi.org/10.30682/nm1903d

Bensaid, R. (1999). Gypso-calcareous soil accumulations in the Aain-Benoui region (BISKRA). *Algerian Annals of Agronomy, 20*(1), 1-8.

Bortolon, L., & Gianello, C. (2009). Disponibilidade de cobre e zinco em solos do sul do Brasil. *Revista Brasileira de Ciência do Solo, 33*, 647-658. https://doi.org/10.1590/s0100-06832009000300017

Chakraborty, M., Chidanandappa, H. M., Dhananjaya, B. C., & Padhan, D. (2016). Zinc dynamics in an Alfisol as influenced by levels of farm yard manure. *Journal of Applied and Natural Science, 8*(1), 329-332. https://doi.org/10.31018/jans.v8i1.795

Chlopecka, A., Bacon, J. R., Wilson, M. J., & Kay, J. (1996). Heavy metals in the environment. *Journal of Environmental Quality*, *25*(1), 69-79. https://doi.org/10.2134/jeq1996.00472425002500010009x

Dang, Y. P., Tilled, K. G., Dalal, R. C., & Edwards, D. G. (1996). Zinc speciation in soil solutions of Vertisols. *Soil Research, 34*(3), 369-383. https://doi.org/10.1071/SR9960369

Elrashidi, M. A., West, L. T., Seybold, C. A., Benham, E. C., Schoeneberger, P. J., & Ferguson, R. (2010). Effects of Gypsum Addition on Solubility of Nutrients in Soil Amended with Peat. *Soil Science, 175*(4), 162-172. https://doi.org/10.1097/SS.0b013e3181dd51d0

Girija, V. V., Rattan, R. K., & Datta, S. P. (2013). Adsorption study: A systematic approach to determine zinc availability in soils of divergent characteristics. *International Journal of Agricultural Sciences, 4*(2), 102-105.

Hafeez, B., Khanif, Y. M., & Saleem, M. (2013). Role of zinc in plant nutrition- A Review. *American Journal of Experimental Agriculture, 3*(2), 374-391. https://doi.org/10.9734/AJEA/2013/2746

Hashemi, S. S., & Baghernejad, M. (2009). Zinc Sorption by Acid, Calcareous and gypsiferous soils as related to soil mineralogy. *Iran Agricultural Research, 28*(1), 1-16. https://doi.org/10.22099/IAR.2010.142

Kabala, C., & Singh, B. R. (2001). Fractionation and mobility of copper, Lead, and Zn in soil profiles in the vicinity of a copper smelter. *Journal of Environment Quality, 30*(2), 485-492. https://doi.org/10.2134/jeq2001.302485x

Kabata-pendias, A. (2001). Trace Element in Soils and Plants. Boca Raton, FL, USA: CRC Press.

Keshavarz, P., Malakouti, M. J., Karimian, N., & Fotovat, A. (2006). The effects of salinity on extractability and chemical fractions of zinc in selected calcareous soils of Iran. *Journal of Agricultural Science and Technology*, *8*, 181-190.

Khoshgoftar, A. H., Shariatmadari, H., Karimian, N., Kalbasi, M., Van Der Zee, S. E. A. T. M., & Parker, D. R. (2004). Salinity and zinc application affects on phytoavailability of cadmium and zinc. *Soil Science Society of America Journal, 68*(6), 1885-1889. https://doi.org/10.2136/sssaj2004.1885

Korchagin, J., Moterle, D. F., Escosteguy, P. A. V., & Bortoluzzi, E. C. (2020). Distribution of copper and zinc fractions in a regosol profile under centenary vineyard. *Environmental Earth Sciences, 79*(19), 439. https://doi.org/10.1007/s12665-020-09209-7

Lindsay, W. L. (1979). *Chemical Equilibrium in Soils*. New York: John Wiley & Sons.

Liu, Y. M., Liu, D. Y., Zhao, Q. Y., Zhang, W., Chen, X. X., Xu, S. J., & Zou, C.Q. (2020). Zinc fractions in soils and uptake in winter wheat as affected by repeated applications of zinc fertilizer. *Soil and Tillage Research*, *200*, 104612. https://doi.org/10.1016/j.still.2020.104612

Lombnæs, P., Chang, A. C., & Singh, B. R. (2008). organic ligand, competing cation, and pH effects on dissolution of Zinc in soils. *Pedosphere, 18*(1), 92-101. https://doi.org/10.1016/S1002-0160(07)60107-6

Loue, A. (1993). *Les oligo-éléments en agriculture*. France: SCPA-NATHAN.

Ma, X., Gomez, M. A., Yuan, Z., Bi, R., Zhang, J., Wang, S., ... & Jia, Y. (2020). Incorporation of trace metals Cu, Zn, and Cd into gypsum: Implication on their mobility and fate in natural and anthropogenic environments. *Chemical Geology, 541*, 119574. https://doi.org/10.1016/j.chemgeo.2020.119574

Mathieu, C., & Pieltain, F. (2003). *Analyse chimique des sols : Méthodes choisies*. France : Tec & Doc/Lavoisier. ISBN 978-2-7430-0620-4.

Milivojević, J., Nikezic, D., Krstic, D., Jelic, M., & Dalovic, I. (2010). Influence of Physical-chemical characteristics of soil on zinc distribution and availability for plants in vertisols of Serbia. *Polish Journal of Environmental Studies* 20(4), 993-1000.

Mohiuddin, M., Irshad, M., Sher, S., Hayat, F., Ashraf, A., Masood, S., ... & Waseem, M. (2022). Relationship of selected soil properties with the micronutrients in salt-affected soils. *Land, 11*(6), 845. https://doi.org/10.3390/land11060845

Moreno-Lora, A., & Delgado, A. (2020). Factors determining Zn availability and uptake by plants in soils developed under Mediterranean climate. *Geoderma*, *376*, 114509. https://doi.org/10.1016/j.geoderma.2020.114509

Mossa, A. W., Gashu, D., Broadley, M. R., Dunham, S. J., McGrath, S. P., Bailey, E. H., & Young, S. D. (2021). The effect of soil properties on zinc lability and solubility in soils of Ethiopia–an isotopic dilution study. *Soil, 7*, 255-268. https://doi.org/10.5194/soil-7-255-2021

Mousavi, S. R., Galavi, M., & Rezaei, M. (2012). The interaction of zinc with other elements in plants: a review. *International Journal of Agriculture and Crop Sciences, 4*(24), 1881-1884.

Natasha, N., Shahid, M., Bibi, I., Iqbal, J., Khalid, S., Murtaza, B., ... & Arshad, M. (2022). Zinc in soil-plant-human system: A data-analysis review. *Science of the Total Environment, 808*, 152024. https://doi.org/10.1016/j.scitotenv.2021.152024

Noman, A., Aqeel, M., Khalid, N., Islam, W., Sanaullah, T., Anwar, M., & Lou, Y. (2019). Zinc finger protein transcription factors: Integrated line of action for plant antimicrobial activity. *Microbial Pathogenesis, 132*, 141-149. https://doi.org/10.1016/j.micpath.2019.04.042

Noulas, C., Tziouvalekas, M., & Karyotis, T. (2018). Zinc in soils, water and food crops. *Journal of trace elements in medicine and biology, 49*, 252-260. https://doi.org/10.1016/j.jtemb.2018.02.009

Pierangeli, M. A. P., Guilherme, L. R. G., Oliveira, L. R., Curi, N., & Silva, M. L. N. (2003). Efeito da força iônica da solução de equilíbrio na adsorção de cádmio em latossolos brasileiros. *Pesquisa Agropecuária Brasileira, 38*(6), 737-745.

Praveen-Kumar., Tarafdar, J.C., Soni, M.L., & Mahesh-Kumar. (2009). Variability in arid soil characteristics. In Amal Kar, B. K. Garg, M. P. Singh, & S. Kathju (Eds.). *Trends in arid zone research in India* (pp. 78-112.). Jodhpur, India: Central Arid Zone Research Institute.

Rahman, N., Hangs, R., Peak, D., & Schoenau, J. (2021). Chemical and molecular scale speciation of copper, zinc, and boron in agricultural soils of the Canadian prairies. *Canadian Journal of Soil Science, 101*(4), 581-595. https://doi.org/10.1139/cjss-2020-0162

Read, S. A., Obeid, S., Ahlenstiel, C., & Ahlenstiel, G (2019). The role of zinc in antiviral immunity. *Advances in Nutrition, 10*(4), 696-710. https://doi.org/10.1093/advances/nmz013

Ruzicic, S., & Rako, T. J. (2017). Multielement sorption of cadmium, zinc, copper, and lead onto a fluvisol profile at the Stara Loza site, Croatia. *International Journal of Environment and Pollution, 62*(1), 63-73. https://doi.org/10.1504/IJEP.2017.10009317

Sadiq, M. (1991). Solubility and speciation of zinc in calcareous soils. *Water, Air, and Soil Pollution, 57*, 411-421. https://doi.org/10.1007/BF00282904

Salinitro, M., Van Der Ent, A., Tognacchini, A., & Tassoni, A. (2020). Stress responses and nickel and zinc accumulation in different accessions of Stellaria media (L.) Vill. in response to solution pH variation in hydroponic culture. *Plant Physiology and Biochemistry, 148*, 133-141. https://doi.org/10.1016/j.plaphy.2020.01.012

Sandstead, H. H. (2015). Zinc. In G. F. Nordberg, B. A. Fowler, & M. Nordberg (Eds.). *Handbook on the Toxicology of Metals* (p.p 1369-1385). Cambridge, MA, USA: Academic Press. https://doi.org/10.1016/b978-0-444-59453-2.00061-5

Shukla, U. C., & Mukhi, A. K. (1980). Ameliorative role of Zn, K and gypsum on maize: growth under alkali soil conditions. *Agronomy Journal*, *72*, 85-88. https://doi.org/10.2134/agronj1980.00021962007200010017x

Sousa, S. F., Lopes, A. B., Fernandes, P. A., & Ramos, M. J. (2009). The zinc proteome: a tale of stability and functionality. *Dalton Transactions, 38*, 7946-7956. https://doi.org/10.1039/B904404C

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*(7), 844-851. https://doi.org/10.1021/ac50043a017

Tolay, I. (2021). The impact of different Zinc (Zn) levels on growth and nutrient uptake of Basil (*Ocimum basilicum* L.) grown under salinity stress. *PLoS One, 16*(2), e0246493. https://doi.org/10.1371/journal.pone.0246493

Weiss, D., Northover, G., Hanif, M., García-España, E., Vilar, R., Arnold, T., ... & Delgado, E. (2021). Isotope fractionation of zinc in the paddy rice soil-water environment and the role of 2'deoxymugineic acid (DMA) as zincophore under Zn limiting conditions. *Chemical Geology, 577*, 120271. https://doi.org/10.1016/j.chemgeo.2021.120271