

The Effects of Salinity on Extractability and Chemical Fractions of Zinc in Selected Calcareous Soils of Iran

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ABSTRACT

Use of saline water for irrigation has shown considerable promise. However, its effect on the solubility and bioavailability of native soil nutrients is not well understood. This study was conducted to evaluate the effects of salinity on the behavior of zinc (Zn) in calcareous soils. The soil samples with different physiochemical properties were collected from four locations in Khorasan province (Iran). The factorial experiment was carried out as a completely randomized design on soils with four levels of water salinity (0, 37.5, 75 and 150 mole m⁻³ prepared with the same equivalents of NaCl and CaCl₂) and four reaction times (0, 10, 20, and 30 days) with three replications. DTPA-extractable Zn was measured in the incubated soil samples after the given reaction times. Different chemical forms of Zn were characterized after 30 days using the sequential extraction procedure. DTPA-extractable Zn increased by 1 to 6.3% with the increasing levels of salinity, and decreased from 8.7 to 3.9% by increasing the reaction time significantly ($P < 0.05$). The determination of Zn compounds by the sequential extraction procedure revealed significantly different forms of Zn with the average amounts in the following order: (KNO₃+H₂O)-Zn(soluble+exchangeable forms) < NaOH-Zn(organic form) < EDTA-Zn(carbonate form) << HNO₃-Zn(residual). Salinity affected various forms of Zn i.e. soluble + exchangeable, organic and residual. Increasing soil salinity level increased the KNO₃+H₂O extractable Zn by 20 to 80% and the NaOH extractable form by 8.6 to 43%. DTPA-Zn was significantly correlated with the NaOH extractable form ($r = 0.98$ $P < 0.05$) and with the (KNO₃+H₂O)-Zn, ($r = 0.94$ $P < 0.05$). It was concluded that increasing salinity redistributed HNO₃-extracted Zn (residual) to the KNO₃+H₂O extractable (soluble + exchangeable) and NaOH extractable (organic) forms of Zn.

Keywords: Chemical forms, DTPA, Salinity, Sequential extraction, Zn.

INTRODUCTION

Irrigation with saline waters for agricultural purposes has produced favorable results (Rhoades, 1987). Nevertheless, the final outcome of such a practice on crop nutrition of mineral elements and on soil fertility is not well recognized. Soil salinity affects the yields of agricultural crops in various ways

including a reduced level of plant available water, increased amounts of toxicity levels for certain toxic ions, reduced activity levels for the essential nutrients, high ratios of Na⁺/Ca⁺⁺, Na⁺/K⁺, Mg⁺⁺/Ca⁺⁺, and Cl⁻/NO₃⁻ in plant tissues, nutritional problems, and a reduction in crop yields and qualities as the most pronounced effects (Feigin, 1985; Grattan and Grieve, 1992). Under saline conditions, the concentrations of Na⁺ and Cl⁻

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usually exceed those of macro and microelement causing unbalanced nutrition in crops (Abrol *et al.*, 1988). Hassan *et al.* (1970) reported a positive correlation between salinity levels on Zn and manganese (Mn) concentrations in barley plants and a negative correlation with iron (Fe) and copper (Cu) in that plants tissues. Most of the studies on the interaction between salinity levels and nutrient concentrations have been conducted in hydroponic systems or sand cultures, which are less complicated than saline soil systems. Therefore, the results do not necessarily apply to the agricultural systems.

Research results show that the most severe nutritional problem for plants growing under saline conditions is either low rates of availability which result from the changes in maintenance, fixation and chemical reactions of soil nutrients, or interference with the absorption and translocation of the nutrients by the roots with the resulting low rates of growth. Also, the disturbances in the plants metabolic processes of the adsorbed nutrients mainly related to the lowered rates of water absorption (Homaei, 2002). The concentration as well as the composition of the salts involved, affects nutrient availability.

Furthermore, salinity affects nutrient availability differently depending on the pH, the ionic strength of the solutions, and on the activity coefficient of a particular nutrient. For example, the compounds that get hydrolyzed and cause a change in the solution pH can have more drastic effects on plant nutrition under salinity. The ionic activities of such compounds can also affect the solubilities of soil carbonates and gypsum materials. This process can determine the chemical forms as well as the extent of availability of soil nutrients (Fujiyama, 1996). As a result, the interpretation of soil analysis data would be different for saline and nonsaline soils (Hosseini and Karimian, 1999). So, it is necessary to distinguish between the two groups of soil (Malakouti and Nafisi, 1995).

Reports on the effects of salinity on the availability of soil Zn are limited to only a few in numbers. Ravikovich *et al.* (1986) showed that the extent of availability of soil Zn increased with salinity (NaCl content) because of the replacement of exchangeable Zn with Na. On the other hand, Page *et al.* (1996) and Qadir *et al.* (1997) reported that the availability and solubility of microelements (Mn, Cu, Fe, Zn) are extremely low in saline and sodic soils showing as deficient in crops. Therefore, under saline conditions the rates of uptake of these nutrients are reduced because of less root volume as well as the antagonistic effects between the nutrient elements and the toxic ions (Yahya, 1998).

Based on these facts, the objectives of this experiment were to investigate: i) The extractability of DTPA-Zn as affected by reaction time (incubation) and salinity levels [NaCl-CaCl₂]; ii) the distribution of various forms of soil Zn as affected by salinity, using the sequential extraction; and finally, iii) determine the salinity effect on the relationship between available Zn and soil fractions of Zn.

MATERIALS AND METHODS

Soils

Samples were collected from the 0-30 cm top surface of soil from four regions in Khorasan. Some physicochemical characteristics of the samples are given in Table 1. The soils were selected on the basis of the differences in their extractable Zn.

The 250 g of each air-dried soil sample (<2mm) was placed in 8 cm x 8 cm plastic containers. The factorial experiment was carried out as a completely randomized design with three replications. The soil samples were brought to field capacity with four levels of water salinity 0 (as distilled water), 37.5, 75 and 150 mole m⁻³ (prepared with the same equivalents of NaCl and CaCl₂) only once. The samples were covered with aluminum foil punctured with holes in

Table 1. Physical and chemical properties of soils.

Soil No.	Location	ECe ^a	Clay	TNV ^b	OC ^c	CEC ^d	pH	DTPA-Zn
		dS m ⁻¹		g kg ⁻¹		cmol _c kg ⁻¹		mg kg ⁻¹
1	Kashmar	1.10	200	228	1.1	13.5	8.3	0.36
2	Torbat Haydarieh	0.77	170	173	2.5	17.8	8.2	0.80
3	Mashad	0.94	220	157	5.5	20.4	7.9	1.72
4	Fariman	0.65	180	197	7.6	14.2	8.1	3.20

^a electrical conductivity, ^b total neutralizing value, ^c organic carbon, ^d cation-exchange capacity

order to allow air exchange, and incubated at 25°C (room temperature) and 60% relative humidity. DTPA (Diethyl Triamine Penta Acetic Acid) extractable Zn (Lindsay and Norvell, 1978), ECe and the pH values were determined for the incubated samples after 0, 10, 20 and 30 days.

Chemical Forms of Soil Zn

The different chemical forms of Zn were determined after 30 days using the sequential extraction procedure proposed by Sposito *et al.*, (1982). The nature of chemical extractants and the times of extraction were as follows: 0.5 M KNO₃ with 16 hours of shaking time; twice distilled water and shaken for 2 hours (extracting three times and combining extractants); 0.05 M Na₂EDTA and 6 hours of shaking; and, finally, 4 M HNO₃ and maintaining the mixture at 80°C for 16 hours. Since the amount of water extractable Zn was quite low, it was combined with the KNO₃ extractable Zn as the KNO₃+H₂O extractable Zn form.

The chemical forms of extracted Zn include soluble+exchangeable organic, carbonated, and residual obtained with KNO₃+H₂O, NaOH, EDTA, and HNO₃, respectively. Since the extraction of Zn by the successive processes is a result of chemical reactions of soil Zn with the extracting agents rather than the form of Zn, the controlling solid phase of the soil, the chemical forms described above are

designated as such (Takashi Kunito *et al.*, 2001). The concentrations of Zn in every stage were determined by the Perkin Elmer-2380 atomic absorption spectrophotometer. The statistical analysis of the experimental data was performed using MSTAT-C and STATG-6 software's.

Correlation coefficients were calculated between DTPA extracted Zn and other chemical forms of Zn.

RESULTS AND DISCUSSION

Salinity Vs DTPA-Zn

The amounts of DTPA-Zn increased significantly ($P < 0.05$) with increasing salinity levels so that, at the highest level of 150 mole m⁻³, the DTPA-Zn increased by 6.3% as compared with blank (distilled water). Similarly, soil salinity levels (ECe) increased in every case with the increases in the solution's salinity levels, so that on the average the initial soil ECe of about 0.8 dS m⁻¹ increased to a value of 20.7 dS m⁻¹ with the irrigation water that had the highest level of salinity. The increases in the amounts of extracted Zn might also be obtained due to the replacement of exchangeable Zn with Na⁺ and Ca⁺⁺, as well as to the lower pH values resulting from high saline waters. Khattak and Jarrell (1988) have shown that, under saline conditions, low pH values and cation exchange processes result in increased rates of Mn extraction with DTPA.

Various researchers have also shown that,



among the different factors that affect the solubility of soil Zn, pH plays an important part so that every unit decrease in soil pH causes a 100-fold increase in the solubility of soil Zn. A negative correlation has been reported between soil pH and Zn extractability (Lindsay, 1978). Soil pH (saturated paste) decreased significantly ($P < 0.05$) with increasing levels of irrigation water salinity so that, for example, adding the solution with the highest salinity of 150 mole m^{-3} caused the initial soil pH 8.01 to

Soils 1 and 2 (Table 3). This can be explained in terms of lower contents of organic carbon in those soils (Table 1). In fact some reports pointed to a direct correlation between the amounts of extractable Zn and the levels of soil organic matter (Kunito *et al.*, 2001), as evidenced by Soils 3 and 4. McBride *et al.* (1997), however, reported that due to pH variations as well as to the differences in the chemical structure of soil organic compounds, it would be difficult to relate the levels of soil

Table 2. The effects of water salinity levels on soil DTPA-Zn, electrical conductivity, and pH.

Salinity ^a mole m^{-3}	Zn mg kg^{-1}	ECe dS m^{-1}	pH
0	1.43	0.79	8.01
37.5	1.45	5.52	7.75
75	1.48	10.80	7.62
150	1.53	20.77	7.49
LSD (0.05)	0.053	0.13	0.02

^a [NaCl+CaCl₂]

Table 3. The effects of water salinity levels on DTPA-Zn of different soils.

Salinity ^a mol m^{-3}	Soil No.			
	1	2	3	4
	Zn (mg kg^{-1})			
0	0.272	1.06	1.61	2.80
37.5	0.294	0.99	1.66	2.85
75	0.264	0.97	1.76	2.91
150	0.275	0.95	1.89	3.02
LSD (0.05)= 0.11				

^a [NaCl+CaCl₂]

decrease by 0.51 units. As can be seen in Table 2, the pH of saturated pastes showed a generally decreasing trend in relation to the increased levels of water salinity. This can be possibly explained by the substitution of exchangeable H^+ with Na^+ and Ca^{++} (Doner *et al.*, 1982; Khattak and Jarrell, 1989).

However, despite the general trend of increasing Zn extractability with increasing salinity levels, the trend was only significantly measurable in Soils 3 and 4 while a slightly reversed trend was seen in

organic matter to the extent of Zn availability.

Incubation Vs DTPA-Zn

Incubation duration had a significantly ($P < 0.05$) negative effect on the amount of Zn extracted with DTPA so that, after 30 days, a decrease of 8.7% in extracted Zn was observed as compared with the control (no incubation, Table 4). This finding agrees

with those of other investigators (Armour *et al.*, 1989; Ma and Uren, 1997). Sieviera and Sommers (1997) reported that, by increasing the duration of soil incubation, the more soluble forms at soil Zn were converted to the less soluble types (oxides and residual materials). Sposito *et al.* (1983) state that by increasing the duration of soil incubation, soil organic matter is gradually converted to carbonates making Zn less soluble and less available to the plants' roots. Nevertheless, the factors that cause a decrease in the extractability of soil Zn with time are not well explained. Ma and Uren (1997) believe that the decreases in Zn extractions that are caused by lengthy incubations can be explained in terms of $\text{Zn}(\text{OH}^+)$ diffusion into soils minute pores.

Likewise, significant ($P < 0.05$) effects of

incubation duration on soil pH were observed. For example, the average initial pH value of 7.74 decreased to 7.67 after an incubation period of 30 days. This decrease was possibly caused by exchange reactions involving release of H^+ ions into the soil solution with soils that have high buffering capacities and medium to heavy textures. Khattak and Jarrell (1988) reported that, in clay soils, pH decreased with incubation time because of a higher buffer capacity which requires a longer time to reach equilibration as compared with light-textured soils. It was also noted that the incubation period had no significant effect on soil ECE (Table 5). A decreasing trend in DTPA-extractable Zn was observed between the salinity level of 150 mole m^{-3} and the control as a result of the duration of

Table 4. The effect of water salinity levels and incubation times on soil DTPA-Zn.

Salinity ^a mol m^{-3}	Incubation Time (days)			
	0	10	20	30
	Zn (mg kg^{-1})			
0	1.52	1.42	1.43	1.37
37.5	1.62	1.43	1.39	1.37
75	1.49	1.49	1.47	1.45
150	1.56	1.60	1.51	1.46
LSD (0.05)= 0.11				

^a [NaCl+CaCl₂]

Table 5. The effect of water salinity level and incubation times on soil electrical conductivity and pH.

Salinity ^a mol m^{-3}	Incubation Time (days)			
	0	10	20	30
	ECe (dS m^{-1})			
0	0.76	0.77	0.81	0.83
37.5	5.50	5.56	5.49	5.54
75	10.72	10.95	10.76	10.76
150	20.90	20.59	20.66	20.94
LSD (0.05)=0.26				
	pH			
0	8.00	8.03	7.99	7.99
37.5	7.75	7.76	7.75	7.72
75	7.65	7.66	7.61	7.54
150	7.55	7.53	7.49	7.42
LSD (0.05)=0.04				

^a [NaCl+CaCl₂]



incubation.

Chemical Forms of Soil Zn

The determination of the chemical forms of soil Zn by sequential extraction (Table 6) showed that there were significant differences among the various forms and that their average amounts followed an increasing order as follows: (KNO₃+H₂O)-Zn (soluble and exchangeable) < NaOH-Zn (organic) < EDTA-Zn (carbonate) << HNO₃-Zn (residual). The total amounts of extracted Zn varied between 70 and 99 mg kg⁻¹. About 75% of the total extracted Zn were extracted with HNO₃ (residual) and the remaining 25% extracted by EDTA, NaOH,

Based on this finding, Soil 4 (Fariman location) contained the highest concentration of Zn (30.87 mg kg⁻¹) and the greatest percentage (31.16 %) of available Zn obtained with the three named extractants. More DTPA extractable Zn (available), was also found in Soil 4. The same trend was also observed with the other soils. The distribution of different forms of Zn was significantly ($P<0.05$) affected by salinity levels (Table 7). However, the differences with respect to the carbonate form (Zn-EDTA) were not significant. Nevertheless, the increases in salinity levels caused more soluble and exchangeable Zn to be extracted. When the salinity level increased from 0 (distilled water) to 150 mole m⁻³, the amounts of Zn extracted by H₂O+KNO₃

Table 6. The concentrations and the relative amounts of Zn soil fractions in the experimental soils.

Soil No.	Extractable Zn Fractions (mg kg ⁻¹)								
	KNO ₃ +H ₂ O		NaOH		EDTA		HNO ₃		Total
1	0.48	(0.68) ^a	0.62	(0.88)	12.14	(17.30)	56.66	(81.04)	69.9
2	0.54	(0.72)	0.95	(1.21)	14.27	(19.07)	59.06	(79.00)	74.8
3	0.89	(1.15)	0.85	(1.10)	17.76	(23.11)	57.32	(74.64)	76.8
4	0.76	(0.76)	3.88	(3.91)	26.23	(26.47)	68.18	(68.82)	99.0

^a Relative amounts in percentage

and KNO₃+H₂O. Leclaire *et al.* (1984) reported that the chemical forms of Zn extracted with KNO₃, NaOH and EDTA were available for crops.

increased 5-fold. It seems that, the replacement of exchangeable Zn by sodium and calcium increased at high salinity levels, yielding more extractable Zn. The NaOH

Table 7. The effect of water salinity on the concentrations and relative amounts of Zn soil fractions.

Salinity ^a mol m ⁻³	Extractable Zn Fractions (mg kg ⁻¹)							
	KNO ₃ +H ₂ O		NaOH		EDTA		HNO ₃	
0	0.23	(0.29) ^b	1.09	(1.37)	14.71	(18.5)	63.4	(79.8)
37.5	0.47	(0.58)	1.26	(1.57)	18.21	(22.7)	60.0	(75.2)
75	0.83	(1.00)	2.0	(2.42)	19.44	(23.5)	60.2	(73.0)
150	1.15	(1.46)	1.92	(2.44)	18.04	(22.9)	57.4	(73.2)
LSD (0.05)	0.19		0.44		NS		3.9	

^a [NaCl+CaCl₂], NS indicate not significant at $P<0.05$.

^b Relative amounts in percentage.

extractable Zn (the organic form) also significantly improved with increasing salinity levels. As the salinity level increased from 0 to 75 mole m^{-3} , the amount of Zn-NaOH increased by 75%. Further increases up to 150 mole m^{-3} however, caused slight decreases in the amount of extracted Zn. It is likely that the increases in the salinity levels along with the decreases in soil pH might cause less NaOH extractable Zn (the organic form) to be extracted at the salinity level of 150 mole m^{-3} . The EDTA extractable Zn (the carbonate form) did not significantly increase with salinity levels, possibly due to the increased ionic strength and higher levels of soluble calcium and lowered solubility of calcium carbonate. HNO_3 -extracted Zn (residual) significantly

acidification, Zn was redistributed from the residual to the exchangeable and organic fractions which would increase Zn plant availability. These results indicated that the $\text{KNO}_3+\text{H}_2\text{O}$ extractable (soluble + exchangeable) and NaOH extractable (organic) forms of Zn increased at the expense of decreased residual Zn as the salinity level increased. Furthermore, DTPA extractable Zn had no significant correlation with EDTA extractable Zn (the carbonate form) at different salinity levels. Thus, the EDTA-Zn fraction does not play the dominant role in increasing the DTPA-Zn under saline conditions.

CONCLUSION

Table 8. The correlation coefficients between DTPA-Zn soil and chemical forms of Zn.

Soil No.	Extractable Zn Fractions							
	$\text{KNO}_3+\text{H}_2\text{O}$		NaOH		EDTA		HNO_3	
1	0.788	ns	0.947	*	0.789	ns	-0.985	**
2	0.947	*	0.965	*	0.540	ns	-0.900	ns
3	0.994	**	0.870	ns	0.547	ns	-0.860	ns
4	0.952	*	0.978	*	0.643	ns	-0.950	*
Mean	0.947	*	0.980	*	0.647	ns	-0.739	ns

* $P<0.05$, ** $P<0.01$, ns: indicate not significant at $P<0.05$.

($P<0.05$) decreased with increasing salinity levels, possibly due to salt-induced pH drop. Nyamangara (1998) found that lowering pH will increase the availability of metals of bound to oxides.

Regression analysis between DTPA extractable Zn and the other chemical forms of Zn for each soil in different salinity levels (Table 8) showed that the DTPA extractable Zn had a significant positive correlation only with NaOH extractable and $\text{KNO}_3+\text{H}_2\text{O}$ extractable forms of Zn. However, for HNO_3 -extracted Zn (residual) there was a negative correlation. This finding shows that, by increasing the salinity levels in these soils, DTPA-Zn (available) is mostly in organic or (soluble + exchangeable) forms. Nielsen *et al.* (1986) reported that, with

Increasing salinity significantly increased DTPA extractable Zn, but it might depend on soil characteristics such as the organic carbon (OC) level. By increasing the duration of soil incubation, the more soluble forms at soil Zn were converted to the less soluble types. The different forms of Zn distribution were significantly affected by salinity levels. The salinity has influenced soil Zn in two ways: salt cations (Na, Ca,...) and salt induced pH level drop. DTPA extractable Zn had a significant positive correlation only with NaOH extractable and $\text{KNO}_3+\text{H}_2\text{O}$ extractable forms of Zn, but for HNO_3 -extracted Zn (residual) it had a negative correlation as the salinity level increased. Salinity redistributed Zn from the residual fraction to the exchangeable and



organic fractions. DTPA extractable Zn had no significant correlation with EDTA extractable Zn (the carbonate form) at different salinity levels. These results indicated that the chemical behavior of Zn in the saline calcareous soils might differ from one to another. It seems, then, that native soil Zn becomes more plant available with salinity.

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اثر شوری بر استخراج پذیری و شکل های شیمیایی روی دربرخی خاکهای آهکی ایران

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چکیده

بهره برداری از آبهای شور برای آبیاری نوید مهمی است، ولی اثر آن بر حلالیت و قابلیت استفاده عناصر غذایی بومی خاک بخوبی روشن نمی باشد. این مطالعه به منظور ارزیابی اثر شوری بر رفتار روی در خاکهای آهکی انجام شده است. بر این اساس تعداد چهار نمونه خاک از مناطق مختلف استان خراسان با خصوصیات فیزیکوشیمیایی متفاوت انتخاب گردید. سپس آزمایشی بصورت فاکتوریل بر روی این نمونه ها با چهار سطح شوری آب (۰، ۳۷/۵، ۷۵ و ۱۵۰ مول بر مترمکعب تهیه شده از محلول $\text{NaCl} + \text{CaCl}_2$ با نسبت اکی والان یکسان) و چهار سطح زمان خواباندن (۰، ۱۰، ۲۰ و ۳۰ روز) در قالب طرح کاملاً تصادفی و در سه تکرار انجام شد. در زمانهای مورد نظر روی قابل استخراج با DTPA و علاوه بر آن پس از ۳۰ روز شکلهای مختلف روی خاک با استفاده از روش عصاره گیری دنباله ای تعیین گردید. نتایج نشان داد که روی قابل استخراج با DTPA با بالا رفتن میزان شوری خاک بطور معنی داری ($P < 0.05$) افزایش (۱ تا ۶/۳٪)، و با زیاد شدن زمان خواباندن، استخراج روی با DTPA در میانگین سطوح شوری بطور معنی داری ($P < 0.05$) کاهش می یابد (۳/۹ تا ۸/۷٪). تعیین شکلهای مختلف روی در خاک نیز نشان داد که با یکدیگر اختلاف بسیار معنی داری داشته و میانگین آنها از این ترتیب برخوردار است. $\text{KNO}_3 + \text{H}_2\text{O}-\text{Zn}$ (محلول و تبادل) $> \text{NaOH}-\text{Zn}$ (آلی) $> \text{EDTA}-\text{Zn}$ (کربناته) $>> \text{HNO}_3-\text{Zn}$ (تتمه). علاوه بر این اثر شوری بر استخراج شکلهای محلول + تبادل، آلی و تتمه روی خاک معنی دار گردید ($P < 0.05$)، ولی بر شکل کربناته روی اثر معنی داری نداشت. با افزایش شوری خاک به میزان روی استخراج شده از بخش $\text{KNO}_3 + \text{H}_2\text{O}$ ۲۰ تا ۸۰٪ و به بخش NaOH



۸/۶ تا ۴۳٪ افزوده شد. علاوه بر این مشاهده گردید که روی قابل استخراج با DTPA با روی استخراج شده از بخش NaOH ($r=0.98$ $P<0.05$) و بخش $KNO_3 + H_2O$ ($r=0.94$ $P<0.05$) همبستگی مثبت و معنی داری دارد، ولی با بخش HNO_3 (تتمه) این همبستگی منفی است. این موضوع نشان می دهد که شوری موجب توزیع مجدد روی از بخش HNO_3 (تتمه) به شکل های $KNO_3 + H_2O$ (محلول + تبادل) و NaOH (آلی) شده است.