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Availability of Manganese in Calcareous Soil of Saudi Arabia

Wagih A. Al-Mustafa
Soil Science Department, College of Agriculture, King Saud University,
Riyadh, Saudi Arabia

Abstract. A total of 96 surface soil samples were collected from four major agricultural areas in Saudi Arabia to determine Mn availability in soils and Mn content of crops grown on these soils. Visual Mn deficiency symptoms were not observed in any of the crop samples and Mn concentrations in crops were adequate by accepted criteria. About 15 and 35% of the soils extracted with DTPA and NH_4OAc, respectively, were considered deficient while less than 1% were deficient according to criteria for the NH_4HCO_3–DTPA extract. The level of Mn extracted by different extractants increased with increases in organic matter, silt and clay content but decreased with increases in $CaCO_3$ content, soil pH, Ca+Mg/K and Fe/Mn ratios.

Extractable Mn was the lowest in Qassim and Riyadh areas as these soils were low in organic matter and high in $CaCO_3$ content. Correlation between extractable Mn and Mn concentration in various crops decreased in the following order: DTPA > NH_4HCO_3–DTPA > NH_4OAc. Inclusion of pH, Ca+Mg/K and $CaCO_3$ content in prediciton equations for each soil test improved the correlation between extractable Mn and concentration in plants.

Introduction

Manganese is one of the essential nutrients needed for plant growth. Manganese occurs in several oxidation states and in different phases; i.e. water soluble, exchangeable or available, insoluble oxides and primary minerals [1]. The chemistry of soil Mn could lead to the conclusion that most Mn deficiencies would occur in well alkaline and calcareous soils, soils frequently found in semiarid and arid areas [2]. However, not many observations of Mn deficiency are reported from these areas. Surveying soils of major agricultural areas of Lebanon and Saudi Arabia did not reveal Mn deficiencies [3, 4].

Soil test methods are needed to assess both activity and potentially plant- available forms of Mn in alkaline and calcareous soils to optimize both fertilizer and land use. Several methods have been compared by various investigators as to their capabilities to assess plant available-Mn. Salcedo *et al.* [1] using six extractants on 12 calcareous soils of Michigan and Indiana, found the best correlation with plant- Mn to be with Mn extracted by H_3PO_4 and NH_4OAc. A recent development has been the use of chelates which theoretically obviate some of disadvantages of other extractants. Mashhady and Metwally [5] reported that extraction with DTPA was the best method for determining available Mn in soils, while other researchers [6] have utilized EDTA and H_3PO_4 extractants in determining available Mn. Ayed and Choudary [7] reported that NH_4HCO_3–DTPA could be a very useful multielement extractant for Saudi Arabia. Correlation of DTPA extractable Mn with Mn concentration in wheat and soybean was shown to depend on soil pH [8].

Within the last few years, soil chemical and physical properties, such as pH, organic matter, $CaCO_3$ content and texture have been included with the Mn soil test to improve the prediction of plant availability [1, 6, 9]. The inclusion of soil pH and $CaCO_3$ content in the regression equation significantly improved the prediction of plant available Mn in calcareous soils of Lebanon [3].

Since agricultural soils in Saudi Arabia are being intensively used for major field crops, correct appraisal for Mn status and other nutrients is very important. Except for the reports of Duheash *et al.* [5, 10, 11] practically no information is available on the Mn status of soils and crops in Saudi Arabia. Therefore, a study was initiated to assess the status of Mn in soils and crops from major agricultural regions of Saudi Arabia. different soil extractants such DTPA, NH_4HCO_3–DTPA and NH_4OAc were used, and the effect of different soil properties on the correlation between crop content and extractable soil Mn was evaluated.

Materials and Methods

Soil analysis

Ninety-six surface soil samples (0-20 cm) were taken from four different agricultural areas of Saudi Arabia (Riyadh, Qassim and along the Eastern and Western coasts). The sampling in each area was from sites which had not recently received any micronutrient fertilizer. The soils used in this study were light textured soils typical of arid regions with low organic matter, high $CaCO_3$ and alkaline pH (Table 1).

The 96 bulk samples (about 8 kg soil each) were taken from 15 to 20 cores from surface horizons and mixed well for homogenization. Three sub-samples, about 1 kg each, were then taken from each bulk sample. These were stored in clean bottles and later used for the various laboratory determinations.

Table 1. Ranges and means of soil properties, extractable soil Mn and Mn concentrations in four plant species

		Wheat (36)*		Alfaifa (18)		Tomato (18)		Corn (24)	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
					Soil properties				
Clay	%	3.5–21.2	11.2	7.2–20.0	11.6	8.5–16.2	12.8	11.5–33.0	19.8
Silt	%	4.2–22.3	12.5	1.2–39.0	20.6	7.1–21.8	14.8	13.2–42.1	25.6
pH	(1:1)	7.2– 8.5	7.7	7.2– 9.0	7.9	7.4– 8.4	7.6	7.1– 8.2	7.6
O.M.	%	0.1– 1.1	0.5	0.7– 2.8	1.1	0.9– 2.2	1.6	0.8– 2.6	1.9
$CaCO_3$	%	10.6–50.2	30.3	6.3–53.3	23.2	4.2–30.2	14.2	4.9–30.1	10.2
Ca+Mg/K		1.8–20.2	12.8	4.5–23.4	12.9	3.5–47.0	12.5	3.7–19.3	9.3
Fe	pmm	1.9– 6.8	4.1	0.9– 8.2	3.1	1.9– 7.6	4.1	1.6–13.2	5.1
Fe/Mn ratio		1.0– 4.0	1.6	0.3– 2.6	1.1	0.2– 2.4	1.1	0.5– 3.6	0.9
					Extractable Mn (ppm)				
AB-DTPA#		1.6– 4.0	2.5	2.0– 4.5	2.8	1.9– 5.2	3.5	2.1–12.4	6.2
DTPA		0.6– 3.6	2.3	0.7– 3.9	2.6	1.3– 4.6	3.3	1.6–13.2	5.6
NH_4OAc		4.6–29.8	12.2	6.2–32.8	18.8	9.4–38.8	19.3	8.1–48.2	23.1
					Plant Mn (ppm)				
Concentration		22.0–50.8	34.8	28.0–51.3	37.2	53.6–88.5	73.2	31.8–92.5	61.2

* Number of crop samples.

NH_4HCO_3–DTPA.

Determination of extractable (available) Mn in the sub-samples was done with DTPA [12] NH_4HCO_3–DTPA [13] and NH_4OAc [5]. Particle size distribution of soils was determined on organic matter free soils following the method of Day [14]. Organic mater in the soils was determined according to Walkley and Black's method as described by Jackson [15]. Soil pH was also determined by a pH meter at a soil: water of 1:1 and $CaCO_3$ content was measured by the standard HC1 neutralization test [15]. Available Fe was extracted by using NH_4HCO_3–DTPA according to the procedure of Soltanpour and Schwab [13]. Manganese and iron were determined by atomic absorption using Perkin Elmer Model 2380 spectrophotometer.

Plant analysis

Crops growing on the selected sites were also sampled. Each species was sampled at approximately the same age. The leaves were collected from the upper half of the plant. For plants less than 25 cm in height, the whole plant above ground was taken. Samples of at least 15 plants were collected at each crop sampling. Plant samples were washed twice with distilled water before drying at 65°C. Samples were digested using an HNO_3–$HC1O_4$ acid mixture [4] and Mn concentration was determined by atomic absorption.

The statistical analyses were conducted using SAS on the main computer at King Saud University. Soil Mn as measured by the three extractants was correlated with Mn concentrations in each crop species and with soil physical and chemical properties. These soil properties were included with extractable Mn in multiple regression analysis for Mn concentrations in crops of wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), tomato (*Lycopersicon esculentum* L.) and alfalfa (*Medicago sativa* L.).

Results and Discussion

Table 1 presents a summary of physical and chemical properties of soils, extractable Mn using NH_4HCO_3–DTPA, DTPA and NH_4OAc, and the concentrations of Mn in plant samples of four major crops growing in these soils. Soils used in this study were alkaline in reaction with pH ranging from 7.2 to 9.0 and $CaCO_3$ content from 4.2 to 53.3%. Visual Mn deficiency symptoms were not apparent in any of the crop samples. Adequacy of plant Mn was supported by Mn content in crop tissue, although some samples could be considered low to deficient using the criteria of Khan and Ryan [3] and Mengel and Kirkby [16]. However, because of various factors affecting Mn uptake of plants [1], critical levels are difficult to establish with broad ranges most frequently given.

Extractable Mn levels for each extractant obtained for 96 soils are summarised in Table 2. Mn extracted with NH_4OAc varied from 4.6 to 48.2 ppm with an average 18.4 ppm. NH_4HCO_3–DTPA extractable Mn ranged from 1.6 to 12.4 ppm with a mean value of 3.8 ppm. Values for DTPA extractable Mn were very close to those for NH_4HCO_3–DTPA extractable Mn, ranging between 0.7 to 13.2 ppm with an average 3.5 ppm. It was observed that out of 96 soil samples collected, 14 samples were deficient according to the critical level (DTPA test) given by Lindsay and Norvell [12]. Data show that soils of western coast contain the highest level of extractable– Mn (Table 2) while soils from Riyadh and Qassim areas contain the lowest content. soils associated with the latter two areas were also low in organic matter and silt fraction while high in $CaCO_3$ content (Table 2). The relatively higher extractable Mn in the western area could be due to the fact that the soils were derived from metamorphic parent material or to accelerated weathering associated with higher rainfall.

The mean values of Mn extracted by NH_4OAc (Table 1) were all higher than the critical value of 10 ppm postulated by Salcedo *et al.* [1], i.e. 12.2, 18.8, 19.3 and 23.1 ppm for soils collected from wheat, alfalfa, tomato and corn fields, respectively.

The NH_4HCO_3–DTPA extractant, which is more reliable for calcareous soils [7], indicated that only 8 samples were below the critical level of 1.8 ppm as reported by Soltanpour and Schwab [13]. The results indicate that all three extractants were equally effective in measuring some proportion of available– Mn. However, the NH_4HCO_3–DTPA soil test was more accurate regarding critical levels which are the ultimate determinations of availability.

The NH_4HCO_3–DTPA soil test is being used successfully for Saudi Arabia soils to evaluate plant– available P [17] available– ZN [18] and extractable – Fe [19].

The influence of soil properties on available Mn is shown from correlation data in Table 3. Simple correlation coefficeints (r) between soil characteristics and Mn extracted by AB-DTPA and DTPA methods were generally higher than for NH_4 OAc. Variability of extracted Mn from the 96 calcareous soils was quantitatively described using stepwise regression procedure with soil pH, $CaCO_3$ and organic matter contents, texture fractions, Ca+Mg/K and Fe/Mn ratios as independent variables. The multiple linear regression equations for predicting extractable Mn by the three soil tests and the respective coefficients of determination (R) are shown in Table 4. The results showed that soil properties that affect extractable Mn the most vary with the method of extraction. Soil Mn extracted by NH_4OAc was strongly influenced by organic matter (33.2% of variation) while DTPA extractable Mn was strongly influenced by clay content (56% of variation). On the other hand,

Table 2. Ranges and means of soil properties extractable Mn in soils from four major agricultural areas

Area	Samples No.	Clay (%)	Silt (%)	O.M. (%)	$CaCO_3$ (%)	pH (1:1)	Ca+Mg/K ratio	Fe/Mn ratio	Extractable Mn ppm: NH_4HCO_3 DTPA	Extractable Mn ppm: DTPA	Extractable Mn ppm: NH_4OAc
Around Riyadh	16	3.5–21.2 (10.2)*	4.2–16.2 (10.4)	0.13–1.12 (0.50)	11.8–50.2 (31.9)	7.4–8.5 (7.9)	1.8–20.2 (11.4)	1.0–4.0 (1.5)	1.6– 3.8 (2.4)	0.9– 3.2 (2.1)	4.6–21.8 (11.9)
Around Qassim	20	7.2–20.1 (12.2)	8.2–22.3 14.6)	0.31–0.98 (0.52)	10.6–50.2 (28.7)	7.2–8.4 (7.8)	8.3–20.0 (13.1)	1.0–3.6 (1.7)	1.8– 4.0 (2.6)	0.6– 3.6 (2.5)	4.8–29.8 (12.5)
Eastern area	36	6.0–20.0 (11.7)	1.2–39.0 (17.7)	0.71–2.81 (1.29)	4.2–53.3 (19.7)	7.2–9.0 (7.8)	3.5–47.0 (12.7)	0.2–2.6 (1.1)	1.9-5.2 (3.2)	0.7– 4.6 (3.0)	6.2–38.8 (19.1)
Western area	24	11.5-33.0 (19.8)	13.2–12.0 (25.6)	0.81–2.63 (1.92)	4.9–30.1 (10.2)	7.1–8.2 (7.6)	3.7–19.3 (9.3)	0.5–3.6 (0.9)	2.1–12.4 (6.2)	1.6–13.2 (5.6)	8.1–48.2 (23.1)

*Mean values of the samples.

Table 3. Linear correlation coefficients of soil and plant Mn with soil properties

Dependent variables	% Clay	% Silt	% O.M	% $CaCO_3$	pH	Ratios Ca+Mg/K	Ratios Fe/Mn	NH_4HCO_3–DTPA	DTPA	NH_4OAc
					Extractable Mn					
NH_4HCO_3–DTPA	0.589***	0.499**	0.265*	–0.368*	–0.406**	–0.262 n.s	–0.331*	–	0.804***	0.467**
DTPA	0.747***	0.530***	0.271*	–0.460**	–0.427	407**	–0.296*	0.804***	–	0.545**
NH_4OAc	0.466**	0.572***	0.576***	–0.408**	–0.334*	–0.225 n.s	–0.331*	0.467**	0.545**	–
					Plant Mn.					
Wheat (36)	0.332*	0.129 n.s	–0.110 n.s	–0.306*	–0.534**	–0.581**	–0.580**	0.806***	0.806***	0.560**
Alfalfa (18)	0.328*	0.216 n.s	0.445*	–0.220 n.s	–0.558*	–0.193 n.s	–0.246 n.s	0.809***	0.841***	0.513*
Tomato (18)	0.412*	0.506**	0.438*	–0.367*	–0.749**	–0.290 n.s	–0.263 n.s	0.810***	0.865***	0.572*
Corn (24)	0.890***	0.790***	0.764***	–0.660*	–0.810***	–0.632*	–0.456*	0.891***	0.901***	0.620**

n.s = not significant.
* = significant at 0.05 level
** = significant at 0.01 level
*** = significant at 0.001 level

the NH_4HCO_3–DTPA test was largely affected by soil texture (clay and silt) with 39.6% of variation and least by pH and $CaCO_3$ content (Table 4).

Table 4. Regression equations for the three extractants describing extractable Mn as a function of other soil properties as independent variables.

Step No.	Independent variables		Coefficeint b	Multiple $R^2 \times 100$	F Value
			NH_4HCO_3–DTPA		
1	Clay	(%)	+0.345	34.7	28.04***
2	Silt	(%)	+0.143	39.6	7.18**
3	pH	(1:1)	–2.304	48.2	7.23**
4	$CaCO_3$	(%)	(Constant = 20.37)		
			DTPA		
1	Clay	(%)	+0.146	55.8	90.94***
2	$CaCO_3$	(%)	–0.033	58.5	4.50*
3	Silt	(%)	+0.575	63.8	7.24**
4	pH	(1:1)	–0.857	66.7	5.39**
5	Ca+Mg/K		–0.043	69.2	4.01*
			(Constant = 8.30)		
			NH_4OAc	*OAc*	
1	Organic matter (%)		+0.676	33.2	60.69***
2	$CaCO_3$	(%)	–0.408	45.7	20.34***
3	Silt	(%)	+0.572	57.8	9.95**
4	pH	(1:1)	–0.212	64.3	6.13**
5	Ca+Mg/K		–0.22	68.1	4.31*
			(Constant = 7.55)		

* = significant at 0.05 level.
** = significant at 0.01 level.
*** = significant at 0.1001 level.

Nutrient uptake, rather than nutrient concentration, is usually considered a more reliable criterion for assessing nutrient availability. Studies performed in this laboratory (unpublished) showed that Mn fertilizer application had no effect on Mn uptake by corn and alfalfa crops. Therefore, Mn content of plants is more appropriate than total Mn uptake correlation in this case. Simple correlation coefficeints (r) between soil Mn extracted by different extractants and Mn concentration in various crops are presented in Table 3. All three extractants showed a significant positive relationship with Mn concentration in all four crops ($p < 0.01$). Simple correlation coefficients (r) with plant Mn concentration were: DTPA > NH_4HCO_3–DTPA>NH_4OAc.

Evaluation of soil test results and soil factors in predicting Mn in plants was accomplished by using multiple regresion analyses. The relative contribution of each significant independent variable in the regression equation for soil Mn extracted the three extractants and soil properties (Table 2) can be estimated from the size of the standard partial regression coefficients "b" and the multiple correlaiton coefficients R^2 (Table 5). The results showed that the partial regression coefficients "b" for soil reaction (pH) was significant (P<0.05) for alfalfa and corn with the NH_4HCO_3–DTPA test, for tomato and corn with DTPA extractant, and for wheat, alfalfa and corn with the NH_4OAc (Table 5). Exclusion of pH from the regression analysis with these extractants reduced the multiple correlation coefficient values R^2 to varying degrees. Soil pH is known to relate negatively with soluble Mn [12], and inclusion of this variable in prediction equations has proven successful for use of NH_4OAc [6], and DTPA [1].

Table 5. Regression equations describing Mn concentration in various crops as a function available Mn and soil properties as independent variables.

Crops	Regression equations	Multiple R^2
	NH_4HCO_3–DTPA	
Wheat	Y= 10.26 + 11.25 Mn – 0.41 Ca+Mg/K – 0.31 silt	0.769
Alfalfa	Y= 13.56 + 11.35 Mn – 3.82 pH – 0.45 silt	0.788
Tomato	Y= 24.98 + 10.86 Mn + 0.84 $CaCO_3$ – 0.43 Ca+Mg/K	0.783
Corn	Y= 62.80 + 5.09 Mn –27.93 pH – 26.83 O.M.	0.968
	DTPA	
Wheat	Y= 12.86 + 11.45 Mn – 0.53 Ca+Mg/K – 0.48 silt	0.819
Alfalfa	Y= 14.44 + 6.63 Mn – 0.54 Ca+Mg/K – 0.21 Clay	0.865
Tomato	Y= 42.17 + 10.14 Mn – 5.23 pH – 0.81 Ca+Mg/K	0.878
Corn	Y= 193.80 + 4.96 Mn – 17.72 pH – 27.37 O.M. – 0.62 $CaCO_3$	0.958
	NH_4OAc	
Wheat	Y= 138.40 – 0.60 Ca+Mg/K – 12.05 pH – 21.41 O.M. + 1.23 Mn	0.698
Alfalfa	Y= 93.55 – 7.80 pH + 1.12 Mn – 0.21 Ca+Mg/K – 0.21 silt	0.598
Tomato	Y= 284.74 – 23.30 pH + 1.13 O.M. – 0.65 $CaCO_3$	0.698
Corn	Y= 23.94 + 1.01 clay + 1.42 Mn – 0.96 $CaCO_3$	0.731

In chemical behaviour, Mn shows properties of both the alkali earth cations such Ca^{2+}, Mg^{2+} and K^+ [1]. The results in Table 5 show that bases ratio (Ca+Mg/K) was more important than $CaCO_3$ in explaining variation of the data in prediction equations for three extractants. The "b" value for Ca+Mg/K ratio was significant for wheat and tomato with NH_4HCO_3–DTPA; wheat, alfalfa and tomato with DTPA and wheat, alfalfa and corn with NH_4OAc (Table 5). The size of "b" for bases ratio was small but exclusion of this independent variable from the regression analysis with these extractions reduced the multiple correlation coefficient R^2 value to varying degrees. On the other hand, the "b" for $CaCO_3$ was significant for tomato with NH_4HCO_3–DTPA; corn with DTPA and wheat with NH_4OAc (Table 5). also excluding this property from regression equation with these soil tests reduced the R^2 value. The inclusion of soil factors improved the R^2 value in all cases particularly in cases where simple correlation r value was low as shown with NH_4OAc extractant (Table 3). the significance of soil pH; $CaCO_3$ and organic matter contents and Ca+Mg/K ratio in relation to available Mn would have been more clearly demonstrated if the Mn uptake data were considered rather than Mn content in plants which is influenced by factors in addition to soil properties.

Conclusion

The results in this study have shown that despite high $CaCO_3$ content; soil pH and Ca+Mg/K ratio most soils of Saudi Arabia contain adequate levels of available Mn as measured by NH_4HCO_3–DTPA; DTPA and NH_4OAc procedures. The higher Mn values were associated with soils high in organic matter and tended to increase plant Mn concentration. The absence of deficiency was attributed to high levels of soil Mn. By simple correlation, levels of soil in Mn extracted by three methods showed a significant positive relationship to crop Mn content. However, the relationship could be improved by considering soil pH, $CaCO_3$ content, and Ca+Mg/K ratio, which appear more important than organic matter and Fe/Mn ratio regarding Mn availability in these soils.

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تيسير عنصر المنجنيز في الترب الجيرية بالمملكة العربية السعودية

وجيه علي المصطفى

قسم علوم التربة، كلية الزراعة، جامعة الملك سعود، الرياض،

المملكة العربية السعودية

ملخص البحث. أجريت الدراسة على ست وتسعين عينة تربة في أربع مناطق زراعية في المملكة وذلك لمعرفة مدى تيسر عنصر المنجنيز في التربة ومحتواه في النباتات النامية فيها. ولم تشاهد أعراض نقص عنصر المنجنيز على النباتات تحت الدراسة، مما يدل على أن محتوى تلك النباتات لهذا العنصر كانت في الحدود المناسبة. إلا أنه تبين من الدراسة أن حوالي ١٥، ٣٥٪ من الترب المدروسة تعتبر في حدود النقص عند استخلاصها بواسطة DTPA، NH_4OAc على التوالي، وأقل من ١٪ عند استخلاص الترب بواسطة محلول NH_4HCO_3-DTPA. وقد زاد تركيز عنصر المنجنيز المستخلص بالمستخلصات المختلفة بزيادة محتوى الترب من المادة العضوية والسلت + الطين، بينما قل التركيز بزيادة محتوى الترب في كربونات الكالسيوم وتفاعل التربة وأيضًا النسبة بين مجموع الكالسيوم + المغنسيوم/ البوتاسيوم ونسبة الحديد إلى المنجنيز.

وتبين من الدراسة أيضًا أن كمية عنصر المنجنيز الميسر كانت أقل ما يمكن في ترب منطقة القصيم والرياض والتي تحتوي على نسبة قليلة من المادة العضوية وزيادة في محتواها من كربونات الكالسيوم. وأن العلاقة الإحصائية بين كمية المنجنيز المستخلص من التربة كانت على النحو التالي: NH_4HCO_3 < DTPA < NH_4OAc وعند إضافة كل من تفاعل التربة pH والنسبة لكل من الكالسيوم + المغنيسوم/ البوتاسيوم وأيضًا محتوى التربة من كربونات الكالسيوم للعلاقة الإحصائية لكل مستخلص فإنها تؤدي إلى زيادة هذه النسبة مع النباتات المختلفة.