EFFECT OF CHELATING AGENTS ON THE AVAILABILITY OF EASILY REDUCIBLE Mn^{54} AND MANGANESE IN THREE DIFFERENT SOILS*

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ABSTRACT

Carrier-free Mn^{54} was uniformly mixed into individual pots of three different soils. The soils were Yolo loam (slightly acid), Hacienda loam (calcareous), Dinuba fine sandy loam (neutral). *Phaseolus vulgaris* var. 'Improved Tendergreen ' (bush bean) and *Zea mays* var. 'Golden Cross' bantum(corn) were grown in the soils with the presence and absence of various chelating agents. Yields and total Mn and Mn^{54} were determined in the leaves and specific activities were calculated. After cropping, the control soils were assayed for water soluble, exchangeable, easily reducible, and 10^{-3} *M* EDDHA, EDTA, DTPA, and NTA soluble Mn^{54} and Mn. Bush bean leaves contained more Mn^{54} and Mn per plant than did corn and the content of each decreased with increasing pH of the three soils used. The specific activities of the Mn in bush bean leaves were similar to

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those for the easily reducible Mn for the three different soils but the specific activities in the corn, in contrast, were more nearly like those in the exchangeable Mn in the soils. DTPA tended to increase the amounts of both Mn^{54} and Mn in plants with the Yolo and Dinuba soils with concommitant decreasing specific activity of Mn. With corn DTPA apparently added easily reducible Mn to the pool of available Mn.

INTRODUCTION

This study was undertaken primarily to determine interactions of carrier-free Mn^{54} with various forms of Mn in different soils and the availability of the Mn^{54} to different plant species as influenced by chelating agents. Lindsay et al. (4) have shown that chelating agents can predict availability to plants of some micronutrients. One reason for this type of study is that Mn^{54} is an important by-product of some nuclear reactions.

MATERIALS AND METHODS

The three soils used in the study were obtained in California. Yolo loam is a slightly acid soil and the sample used had a pH in paste of 5.7. Hacienda loam is calcareous and the sample used had about 10% $CaCO_3$ and a pH in paste of 7.8. Dinuba fine sandy loam has a pH in paste of 7.5. None of the soils had either a history of or characteristics of manganese deficiency (1).

Sufficient carrier-free Mn^{54} was added in solution to give about 1 μc Mn^{54} to each of thirty 500 g lots of each of the soils and the soils were dried and mixed thoroughly to give uniform distribution.

Three bush bean (*Phaseolus vulgaris* var. Improved Tendergreen) seedlings previously germinated in sand were transplanted into each of 15 pots of each kind of soil. Three corn (*Zea mays* var. Golden Cross bantum) were also transplanted into each of 15 pots of each kind of soil. One crop of plants was grown for preliminary analyses without further treatment. Plants were watered daily and moisture was kept near field capacity. Nitrogen at the rate of 200 lbs per acre was added to the soils. No other macronutrients were added. Another crop of plants was transplanted and sodium salts of the chelating agents EDTA (ethylenediamine tetraacetic acid), EDDHA [di o-(hydroxyphenylacetic acid)] NTA (nitrilotriacetic acid), and DTPA (diethylenetriaminepentaacetic acid), were each applied in solution to three different pots for each soil at a rate equivalent to 50 lbs Mn an acre (25 ppm in soil) but without manganese and assuming a 1:1 chelate. After this crop was removed a third was planted. Each crop was grown for 16 days. Plastic dishes to prevent loss of Mn^{54} and to facilitate irrigation were placed under the pots which had single drain holes.

After the third crop was removed, soil from the pots receiving no chelating agent for each soil was assayed at room temperature for water soluble Mn^{54} and Mn, for 1N NH_4 acetate (pH 7) soluble Mn^{54} and Mn (2), for 0.1N hydroquinone in NH_4 acetate (pH 7) soluble Mn^{54} and Mn (2), and then for 10^{-3}*M*, Na_2EDDHA, 10^{-3}*M* Na_2EDTA, and 10^{-3}*M* Na_2DTPA, and 10^{-3}*M* Na_2NTA soluble Mn^{54} and Mn. The soils were air dried before weighing but had been kept near field capacity.

Plants, soils, and soil extracts were counted for Mn^{54} with a scintillation-well counter and total Mn assays were made with a permanganate procedure of nitric-perchloric digested materials where necessary (5). Specific activities of the Mn in various soil fractions and in plants were calculated.

RESULTS AND DISCUSSION

The data for extraction of Mn^{54} and Mn from the three soils (control pots) following removal of the third crop of plants are in table 1. The easily reducible Mn of all three soils were above the critical level reported in the literature (1, 2). The chelating agents EDTA and DTPA extracted sizeable quantities for the noncalcareous soils of Mn. In the calcareous soils the EDTA resulted in a high specific activity of the hydroquinone reducible manganese but in a low quantity extracted. As will be shown later, DTPA extraction may be a good quick test procedure for available Mn in soil since it does extract much of the easily reducible Mn.

Results for the third crop of plants only are reported because they adequately describe the observations. In table 2 are main effects for soils. Bush beans extracted more Mn^{54} and total Mn from the soils than did corn. The specific activities of the bush bean leaves were very nearly like that of the easily reducible Mn. The correlation coefficient between the specific activity of Mn in bush beans and that of the easily reducible Mn was high. The correlation coefficient was also high between the specific activity of Mn in 10^{-3}*M* DTPA extractable Mn and that in bush bean leaves.

In contrast to bush beans the specific activity of the Mn in corn was much more comparable with that in the exchangeable Mn than with that in the easily reducible Mn. The correlation coefficient between specific activity in the corn and the exchangeable Mn was greater than that for the specific activity in corn and the easily reducible Mn. There was sufficient Mn in the exchangeable fraction to supply all that taken up by either corn and bush beans (the range of the percentage of the total exchangeable Mn that was present in leaves for a given pot varied from less than 1 to 13%) but nevertheless the bush beans tended to absorb considerable Mn from the easily reducible fraction.

In table 3 are the effects for chelating agents. EDTA tended to increase the Mn^{54} and the Mn in the plants. This was paralleled by a yield decrease so that total uptake was not increased even though the specific activity was. This latter indicates that EDTA did not efficiently make easily reducible Mn available to the plants. This was very apparent for the calcareous Hacienda soil (see table 1). Failure of EDTA to efficiently extract easily reducible Mn may make the soluble and exchangeable Mn more available with Hacienda and Dinuba soils when EDTA is added to them, thus giving higher specific activities in plants for these two soils (table 4).

DTPA had less effect on yields than did EDTA. It tended to increase both Mn^{54} and Mn in plants and it decreased the specific activity in corn (tables 3 and 4). This would indicate that DTPA was making at least some of the easily reducible Mn available to corn. The specific activity of Mn in the $10^{-3}\underline{M}$ DTPA soluble Mn was essentially that of the easily reducible Mn (table 1) indicating that DTPA extraction could be used to monitor that portion of the soil Mn. In this study the specific activities of both easily reducible Mn and that extracted by DTPA corresponded with those in bush bean plants. Lindsay and Norvell (3, 4) have found that DTPA could be used to predict availability of Fe and Zn.

NTA, like DTPA, tended to decrease specific activity of Mn in corn (table 3). Soil extraction, however, did not parallel this (table 1). EDDHA efficiently extracted easily reducible Mn from the Hacienda and Dinuba soils but not from the Yolo (table 1). The pH factor was probably involved. Lindsay et al. (4) have found that the relationships between chelating agents and the equilibrium among micronutrients in soil solution is very complex and for this the suggestions made in this report may be too simple.

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TABLE CAPTIONS

Table 1. Extractable Mn^{54} and Mn from control soils following removal of the third crop of plants.

Table 2. Main effects for soils of the third crop of plants grown in the Mn^{54}-contaminated soils (dry wt basis).

Table 3. Effects for chelating agents as averages for the three soils of the third crop of plants grown in the Mn^{54}-contaminated soils.

Table 4. Some specific effects of chelating agents.

Table 1. Extractable Mn^{54} and Mn from control soils following removal of the third crop of plants

	Yolo	Hacienda	Dinuba
	Extractable Mn^{54}, cpm/g soil		
Total	1254	1260	1070
Water soluble	38	51	44
Exchangeable	338	54	101
Easily reducible	767	403	547
10^{-3} M Na_2EDDHA soluble	39	142	237
10^{-3} M Na_2EDTA soluble	525	59	320
10^{-3} M Na_2DTPA soluble	259	74	286
10^{-3} M Na_2NTA soluble	18	10	56
	Extractable Mn, ppm soil		
Water soluble	0.19	0.05	0.08
Exchangeable	10.3	1.5	2.2
Easily reducible	67.5	18.5	17.6
10^{-3} M Na_2EDDHA soluble	1.3	6.2	8.2
10^{-3} M Na_2EDTA soluble	56.5	1.4	11.1
10^{-3} M Na_2DTPA soluble	27.2	2.9	8.7
10^{-3} M Na_2NTA soluble	0.8	0.3	1.2
	Specific activity of extractable Mn, cpm Mn^{54}/µg Mn		
Water soluble	200	1020	550
Exchangeable	32.8	36.0	65.0
Easily reducible	11.4	21.8	31.1
10^{-3} M Na_2EDDHA soluble	30.0	22.9	28.9
10^{-3} M Na_2EDTA soluble	9.3	42.1	28.8
10^{-3} M Na_2DTPA soluble	9.5	25.5	32.9
10^{-3} M Na_2NTA soluble	22.5	33.3	46.7

Table 2. Main effects for soils of the third crop of plants grown in the Mn^{54}-contaminated soils (dry wt basis).

	Leaf yield	Mn in leaf	Mn in leaf	Mn^{54} in leaf	Mn^{54} in leaf	Specific Activity
	mg	ppm	µg	cpm/g	cpm	cpm/µg Mn
			Corn (means of 15)			
Yolo	138	278	38	6902	952	25.2
Hacienda	83	195	16	4811	399	25.1
Dinuba	123	87	11	4900	603	64.1
LSD (.05)	21**	25**	5**	1060**	152**	10.0**
			Bush bean (means of 15)			
Yolo	420	1566	657	17650	7413	11.3
Hacienda	193	167	32	4680	903	29.4
Dinuba	401	150	60	5358	2150	35.8
LSD (.05)	57**	119**	43**	2040**	810**	4.6**

**Significant at the .01 level

Table 3. Effects for chelating agents as averages for the three soils of the third crop of plants grown in the Mn^{54}-contaminated soils.

	Leaf yield	Mn in leaf	Mn in leaf	Mn^{54} in leaf	Mn^{54} in leaf	Specific Activity
	g	ppm	µg	cpm/g	cpm	cpm/µg Mn
			Corn (means of 9)			
Control	116	143	17	4787	555	46.7
EDTA	99	184	18	6491	689	50.4
EDDHA	115	183	21	5713	658	35.1
NTA	117	216	25	5145	617	28.6
DTPA	125	208	26	5529	691	29.8
LSD (.05)	N.S.	31**	6**	N.S.	N.S.	12.9**
			Bush bean (means of 9)			
Control	434	461	200	7134	3096	23.1
EDTA	274	777	213	11340	3107	34.1
EDDHA	284	632	179	8913	2531	22.5
NTA	378	537	203	7787	2943	25.5
DTPA	320	732	234	10974	3511	22.5
LSD (.05)	75**	154**	N.S.	2646*	N.S.	9.4**

*Significant at the .05 level

**Significant at the .01 level

Table 4. Some specific effects of chelating agents.

Treatment	Leaf yield	Mn in leaf	Mn in leaf	Mn^{54} in leaf	Mn^{54} in leaf	Specific Activity
	mg	ppm	µg/plant	cpm/g	cpm/plant	cpm/µg Mn
			CORN			
			Yolo			
Control	143	212	30	5472	782	25.8
EDTA	120	311	37	8585	1030	27.6
EDDHA	123	239	29	7446	940	31.9
NTA	134	322	43	6915	927	21.4
DTPA	170	308	52	5891	1000	19.1
			Hacienda			
Control	92	167	15	1524	416	27.0
EDTA	52	185	10	5804	302	31.3
EDDHA	89	226	20	5389	479	20.1
NTA	86	234	20	4271	467	18.2
DTPA	94	161	15	4065	382	25.2
			Dinuba			
Control	114	50	6	4365	498	87.3
EDTA	125	55	7	5085	635	92.4
EDDHA	133	84	11	4173	555	49.6
NTA	131	92	12	4248	556	46.1
DTPA	123	156	19	6631	814	42.5
LSD (.05)	29*	54**	10*	2330**	341**	22.3*
F value of soil X chelate interaction	0.83	3.84**	2.78*	1.44	0.80	3.71**

(Table continued on page 13)

Table 4. Some specific effects of chelating agents. (Continued from page 12)

Treatment	Leaf yield	Mn in leaf	Mn in leaf	Mn^{54} in leaf	Mn^{54} in leaf	Specific Activity
	mg	ppm	µg/plant	cpm/g	cpm/plant	cpm/µg Mn
			BUSH BEAN			
			Yolo			
Control	505	1116	563	13830	6986	12.4
EDTA	340	2059	700	21545	7325	10.5
EDDHA	329	1614	531	18700	6156	11.6
NTA	507	1337	678	14300	7254	10.7
DTPA	417	1702	710	19870	8287	11.7
			Hacienda			
Control	299	131	39	3223	964	24.6
EDTA	140	142	20	6819	954	48.0
EDDHA	206	128	27	2949	616	23.0
NTA	203	137	27	4204	849	30.7
DTPA	115	298	34	6209	714	20.8
			Dinuba			
Control	498	134	67	4345	2164	32.4
EDTA	342	129	44	5097	1934	43.9
EDDHA	513	155	80	5097	2630	32.9
NTA	425	138	59	4848	2060	35.1
DTPA	428	196	84	6842	2928	34.9
LSD (.05)	128**	266**	96**	4586**	1810**	10.4**
F value of soil X chelate interaction	1.5[illegible]	[illegible]	[illegible]	0.91	0.51	1.75

*Significant a[illegible] [illegible]ant at the .01 level

Synopsis

Bush beans (*Phaseolus vulgaris* var. Improved Tendergreen) and corn (*Zea mays* var. Golden Cross bantum) differed in their ability to extract easily reducible manganese from three different soils. Bush beans extracted more manganese than did corn and more of it appeared to come from the easily reducible fraction. The chelating agent DTPA tended to add easily reducible manganese to the pool of that available to plants.