

MANGANESE AVAILABILITY AS MEASURED BY CROP UPTAKE, SOIL EXTRACTION AND ISOTOPIC DILUTION

Dissoriation for the Degree of Ph. D. Michigan State University Ignacio Hernan Salcedo 1976





This is to certify that the

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ABSTRACT

MANGANESE AVAILABILITY AS MEASURED BY CROP UPTAKE, SOIL EXTRACTION AND ISOTOPIC DILUTION

By

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This investigation was divided in three main parts. First, the effect of 12 shaking time -- solution:soil ratio combinations on Mn extracted by 0.1N HC1, $0.1N H_3PO_4$, DTPA and 1N NH₄OAc (pH 7) from 12 soils was studied. Results were analyzed to determine which treatment combination gave the greatest quantities of extractable Mn; how extractable Mn correlated with Mn uptake by soybeans and sudangrass at each time-ratio combination; and which soil characteristics were important in determining the quantities of Mn extracted.

Secondly, a greenhouse study with these 12 soils was conducted. Soybeans were grown in the soils, that had received 0, 10 and 20 ppm of Mn (as $MnSO_4$). After harvest, soil samples were removed and analyzed for extractable Mn by six procedures, namely, the four mentioned above plus extraction with 1.5M $NH_4H_2PO_4$ and steam/ NH_4OAc . The 0.1N H_3PO_4 was the one giving the highest correlation with plant uptake. Soil acidity and bases ratio (Ca+Mg/K) were included in the prediction equations of these soil tests.

Thirdly, the residual effect of the Mn applied in the prior experiment was evaluated. The check pots and those that had received 20 ppm of Mn were tagged with ⁵⁴Mn and sown to sudangrass. The determination of the Mn labile pool was done by obtaining the L and E-values for each soil. These results plus those of the six chemical extractions done before were correlated with Mn uptake by the three sudangrass harvests.

MANGANESE AVAILABILITY AS MEASURED BY CROP UPTAKE, SOIL EXTRACTION AND ISOTOPIC DILUTION

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Ignacio Hernan Salcedo

A DISSERTATION

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INTRODUCTION

There have been numerous studies related to micronutrients in recent years, among which, zinc is probably the one that has been more thoroughly studied. For soil testing purposes, some researchers have extrapolated extraction procedures well suited for this element, proposing them as tests for Mn, Cu and Fe as well. Although such a procedure would be highly desirable for any soil testing laboratory, differences in the behavior and properties of these elements in soils raise some doubts as to the possibility of developing such a technique.

Several extracting methods to estimate available Mn for plants have been studied with varying degrees of success depending on the soils and crops used by each researcher. The increasing use of chelating agents as aids for maintaining sufficient levels of soluble micronutrients in soils for plant uptake, have prompted the use of these substances as extractants for soil testing purposes. Published information in the use of some of these chelating agents for determining soil available Mn is still scarce. In spite of all the methods available for testing soil Mn, little work has been done concerning the effect of extraction conditions upon their ability to predict Mn deficienty situations. In the case of procedures which extract sufficient soil Mn to be measured without analytical difficulties, the selection of solution:soil ratios and lengths of extraction should be based on that combination giving the highest correlation with plant uptake or yields.

The objectives of this investigation were, therefore, to study the

effect of different experimental conditions upon several extractants, relating them to: a) the quantities of Mn extracted from the soil, b) the sources of the extracted Mn and c) the correlation of extracted Mn with plant uptake. Also, six extracting solutions including a chelating agent were compared in the effectiveness to predict Mn uptake by plants. Furthermore, radioactive Mn was used to assess the residual effect of Mn fertilizer, and to determine the labile Mn of the soils used (E and L values) correlating these results with plant Mn uptake. PART I

STUDIES IN SOIL MANGANESE

1. FACTORS AFFECTING MANGANESE EXTRACTABILITY

Introduction

Several extracting procedures to evaluate available Mn in soils have been developed. Reviews in this subject have been published by Cox and Kamprath (7) and by Viets and Lindsay (13).

The selection of a certain solution: soil ratio and time of shaking arises in most cases from practical considerations. Few detailed studies have been reported establishing the relationship between these two variables, extractable Mn and plant uptake. Boken (2) studied the influence of these parameters on the quantitiy of Mn extracted by 1M Mg(NO₃)₂ and Ca(NO₃)₂ as a percentage of total Mn. Sorensen, et al., (12) used 0.1N HCl at various solution: soil ratios and shaking periods to characterize the release of Mn from several Nebraska soils, but did not correlate this information with plant uptake. Using this same extractants, Dolar and Keeney (9) correlated the Mn, Zn and Cu extracted from several soils with uptake by oats, using one solution:soil ratio and two extraction periods. Hoff and Mederski (11) used 0.1N H_3PO_4 as an extractant for soil Mn. Using a fixed solution: soil ratio they studied the influence of acid concentration and time of shaking on the quantities of this nutrient extracted from soils of different textures and with varying degrees of Mn insufficiency. Although Mn extracted by 1N NH_4OAc (3) and DTPA extractable Mn (13) have been considered to correctly predict deficiency situations in soils, no studies on the effect of the time and ratio variables have been published for these extractants either.

The purpose of this study was to characterize the release of Mn from soils from Michigan and Indiana by four extractants, as affected by several solution:soil ratios and shaking time combinations and,

furthermore, to see how these variables affect the relationship between extractable Mn and plant uptake by soybeans and sorghum. An attempt to characterize the main Mn fractions and soil properties that closely related to the quantities of extracted Mn was also done.

Materials and Methods

Soils

Surface soil samples from 12 different soil types were collected from various locations in Michigan and Indiana. The soils were selected to give varying levels of available Mn for plant growth. The following subgroups were included: Typic Haplaquolls (Maumee and Granby series), Typic Argiaquolls (Brookston series), Mollic Haplaquets (Toledo and Parkhill series), Arenic Hapludalfs (Metea series), Aquic Arenic Hapludalfs (Selfridge series), Aeric Ochraqualfs (Fulton series), Udollic Ochraqualfs (Conover series), Typic Hapludalfs (Miami series), Typic Medisaprists (Houghton series) and Typic Udipsamments (Plainfield series). The main characteristics of these soils are given in Table 1.

Methods of Analysis

All soil samples were air dried and then ground to pass a 10 mesh sieve. Small subsamples for total nutrient determination were finely ground with mortar and pestle.

Total C: 0.1 g of the finely ground soil was analyzed by the dry combustion method (Ovejera Belo, 1970)¹ with a Leco carbon analyzer. Inorganic C: 3.0 g of the finely ground soil was analyzed following the procedure described by Bundy and Bremner (4).

¹ Determination of total C by dry combustion and its relation to forms of soil N as measured in the laboratory and in the greenhouse. Ph. D. Thesis, Michigan State University, East Lansing.

				,		and the second sec							and the second se		
So1 No.	1 Soil Type	Sand	Silt	Clay	Soil PH	Organic Carbon	cac0 ₃	Ca.	Mg	Х	Na	CEC	Total Mn	Mn Oxides	Chelated Mn
			- 2 -			и	и		ă	eq/100				mdd -	
-1	Plainfield sand	89.0	6.3	4.7	7.4	1.45	1.02	10.1	1.5	0.47	0.07	6.1	201	50.8	5.5
7	Maumee sand	94.3	2.9	2.9	6.6	3.57	0.06	9.4	1.8	0.72	01.0	10.1	126	34.6	4.4
e	Fulton silty clay	15.8	42.6	41.6	6.1	2.58	!	19.2	3.7	0.57	0.16	28.5	330	70.9	14.8
4	Toledo silty clay	17.7	41.3	41.0	7.4	3.16	0.28	29.9	5.3	.0.77	0.14	32.2	353	79.9	12.2
Ś	Selfridge sand	91.4	5.2	3.4	7.5	1.05	0.10	5.6	1.7	0.22	0.05	7.6	136	17.8	1.8
9	Brookston loam	47.7	32.5	19.8	6.3	4.78	ł	25.6	4.3	0.22	0.22	29.6	151	15.3	5.2
2	Metea loamy sand	75.6	19.9	4.5	6.6	1.06	1	3.4	0.93	0.45	11.0	5.9	413	207	21.4
80	Conover sandy loam	55.0	28.3	16.6	6.4	2.10	:	14.2	2.5	0.35	0.13	17.8	655	279	56.8
9	Miami loam	49.3	16.7	14.0	6.0	1.35	ł	8.1	1.8	0.43	0.16	12.4	558	218	50.5
10	Parkhill sandy loam	56.4	30.2	13.4	6.1	1.94	ł	11.3	1.9	0.38	0.13	16.8	413	145	22.2
H	Houghton muck	ł	ſ	ł	6.3	69.4	0.27	97.4	20.2	0.82	0.57	163	310	98.4	21.7
12	Granby sand	89.5	7.0	3.5	6.1	2.74	ł	8.9	2.2	0.10	0.08	13.0	96.2	20.3	5.5

Organic C: It was found by difference between total and inorganic C, except for the Houghton muck in which organic C was obtained by the loss of weight after ignition for 4 hours at 600 °C.

Total Mn: 0.2 g of the finely ground soil was weighed into a platinum crucible, 5 ml of 70% HNO, added and the crucible heated on a hot plate until the residue was dry. After cooling to room temperature, 5 ml of 49% HF and 1 ml of 71% $HC10_{4}$ were added; heat was applied again and the digestion carried to dryness. This last treatment was repeated if there was evidence that the decomposition was not complete. After the crucible cooled, the residue was dissolved in 5 ml of 6N HCl, diluted to 50 ml and Mn determined by atomic absorption spectrophotometry. The Houghton muck was first ignited for 4 hours at 600 °C and then the procedure as described above was followed. All analyses were done in duplicate. Chelated Mn and Mn oxides: 1.0 g of the finely ground soil was successively extracted with 10 ml of 0.005M DTPA twice, shaking for 60 min each time and separating the supernatant by centrifugation. The sum of the Mn from both extractions was called chelated Mn to differentiate it from the DTPA extractable Mn, as defined in the Experimental Section. This denomination, however, refers to the way the Mn was extracted (chelating agent) and not to the chemical status of this Mn fraction in the soil. The soil remaining from the second extraction with DTPA was extracted twice with 20 ml of 0.1N hydroxylamine hydrochloride (pH 2) (5), for 30 min each time. The sum of Mn from both extractions was considered Mn oxides.

Other soil analysis: Soil pH was determined with a glass electrode in a 1:1 soil:water ratio. Saturation with $1N NH_4OAc$ (pH 7) (6) was used to measure the cation exchange capacity and exchangeable bases were

determined in the NH_4OAc filtrate. Texture was determined by the pipet method (8).

Experimental

Four extracting solutions for Mn were used: 0.1N HCl, 0.1N H_3PO_4 , 1N NH₄OAc (pH 7) and DTPA (0.005M diethylenetriaminepentaacetic acid, 0.01M CaCl₂ and 0.1M triethanolamine - pH 7.3). Extraction periods were 10, 30, 60 and 120 min combined with three solution:soil ratios (volume/air dry weight): 5 (25:5), 10 (20:2) and 25 (25:1), resulting in a 3 x 4 factorial arrangement. For DTPA only, a ratio of 2 (10:5) was also included since this was the one suggested in the original procedure developed by Lindsay and Norvell (1969)².

Statistical Analysis

Multiple regression was used to study the functional relationship of extractable Mn (Y) with time of shaking (X_1) and solution:soil ratio (X_2) , by fitting the data with a second order model of the type:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 + \epsilon$$
(1)

where the estimates b_i of the parameters β_i were obtained by the method of least squares. A set of estimates was calculated for each soil and extractant. For soils not showing any significant effect (except interaction) at the 5% level of significance, a first order model was used, according to:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \varepsilon$$
 (2)

To characterize the main Mn fractions and soil properties

² Development of a DTPA micronutrient soil test. Agron. Abstr., p.84.

determining the Mn extracted by each solution, models were developed at selected time-ratio combinations relating extractable Mn to the following variables: pH (X_1) , organic C (X_2) , chelated Mn (X_3) , Mn oxides (X_4) , total Mn (X_5) , milliequivalent ratio of Ca+Mg/K (X_6) and free CaCO₃ (X_7) . A modification of the stepwise regression procedure (10) was used. This system³ allows all the variables to be in the model at the begining of the regression. Variables are deleted according to a predetermined level of significance, but deleted variables can be added again to the model based also on a predetermined level of significance. The following model was used:

$$Y = \beta_0 + \sum_{i=1}^7 \beta_i X_i + \varepsilon$$
(3)

where the response variable (Y) was extracted Mn. A 5% level of significance was used to delete or add variables. Variable X_7 was used as a qualitative variable with a value of 1 for the presence and a value of 0 for the absence of CaCO₃. The data of all 12 soils were used for 0.1N HCl and H_3PO_4 and from 11 soils for DTPA and 1N NH₄OAc. Chelated Mn was not allowed to enter the model as an independent variable when developing the model for DTPA extractable Mn.

Results and Discussion

Results in Table 2 show the ranges of Mn concentrations (soil basis) extracted by the four extractants. For 0.1N HC1, 0.1N H_3PO_4 and 1N NH₄OAc (pH 7) the low values were obtained at a ratio of 5 with 10 min of shaking, while the higher ones occurred at a 25-120 min ratio-time combination. Results for DTPA varied depending on the soil

³Michigan State University Stat System. 1974. Part 12, LSSTEP Program.

considered, some yielding the lowest results at different ratio-time combinations than others. These differences were minimal in most cases. The left column for DTPA (Table 2) corresponds to a ratio of 5 with 10 min of shaking while the right column is for the same ratio with 120 min of shaking.

Soil No.	0.1N HC1	0.1N H ₃ P04	0.005M DTPA	1N NH ₄ OAc
		ppm #-		
1	32.6 - 52.7	11.0 - 50.0	1.6 - 2.4	0.52 - 2.8
2	13.0 - 36.8	4.4 - 20.3	1.4 - 2.1	0.41 - 1.0
3	20.2 - 44.6	6.8 - 26.3	8.2 - 9.8	4.7 - 7.3
4	28.4 - 59.1	5.8 - 31.3	5.4 - 7.4	2.4 - 5.8
5	3.3 - 10.1	1.9 - 6.2		
6	6.3 - 20.5	1.7 - 9.9	2.6 - 2.8	1.1 - 2.1
7	36.8 - 101	25.5 - 66.0	9.0 - 11.9	6.4 - 9.9
8	72.8 - 181	34.9 - 106	31.6 - 42.5	17.2 - 26.9
9	65.0 - 131	39.7 - 86.4	31.6 - 40.2	21.2 - 31.6
10	27.3 - 65.4	12.3 - 40.5	10.1 - 12.6	6.0 - 9.5
11	4.4 - 174	0.51 - 17.5	6.2 - 15.7	2.1 - 6.5
12	5.2 - 12.6	2.2 - 11.0	0.71 - 1.0	0.42 - 0.71

Table 2. Ranges in extractable Mn by four procedures as a result of varying solution: soil ratios and shaking times.

[#]Minimum values at a 5-10 min ratio time combination; maximum values at 25-120 min, except for DTPA whose maximum was at 5-120 min.

The complete set of results was summarized in the form of regression equations (lst. and 2nd. order models, Eq. 1 and 2) and are shown in Tables 3 to 6. In these tables the equations labelled as Average describe the response surfaces shown in Fig. 1 and were obtained by fitting the data for all soils with the 2nd. order model (Eq. 1). Except for soil 2 when extracted with 1N NH₄OAc, these models were useful in explaining variations in extracted Mm at the 1% level of significance. Some equations, however, failed to explain a sizeable part of the variation in the data, as shown by R² values smaller than 85%. This fact does not invalidate the trends considered significant by the regression but would cause error if the original data were to be reconstructed by replacing the X₁ and X₂ variables with their corresponding values.

By determining which regression coefficients are significant for a particular extractant and soil, the range in extractable Mn can be assigned to the linear and/or quadratic effects of time and ratio and/or to the interaction between both variables. The results in Table 2 show that the two acids were very effective in extracting Mn from most soils. A comparison between Fig. 1A and 1B indicates that, on the average, 0.1N HCl extracted twice the quantities of Mn extracted by 0.1N H_3PO_4 . These surfaces also show that going from a 5-10 min to a 25-120 min ratio-time combination produced a 3-fold increase in 0.1N HCl extractable Mn. In the case of 0.1N H_3PO_4 it was, on the average, a 4-fold increase which indicates that Mn extracted by this procedure is more dependent upon the time and ratio selected.

Further on in this study, it will be shown that solubilization of Mn oxides plays an important role as a source of Mn extracted by these

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Table	

Soil			,				7
No.	م	b ₁ (x10)	b2 (x10)	b ₁₁ (x10 ³)	b ₂₂ (x10 ²)	b_{12} (x10 ²)	X
							R
1	26.6	5.00 **	- 0.523	-3.15 **	0.633	0.368	88.2 **
2	9.68	3.40 **	1.53	-1.57 **	-0.717	0.317 *	98.9 **
ę	21.3	1.22 *	1.25	1	1	0.250	84.1 **
4	9.45	3.30 *	32.7 *	-1.58	-9.03 *	0.294	92.0 **
S	3.25	0.160	- 0.130		ł	0.162 *	90.2 **
9	6.95	0.161	0.210	1	ł	0.340 * +	91.9 **
7	46.8	7.27 *	-34.4	-1.83	12.18	0.0757	95.3 **
æ	79.0	12.8 *	-41.1	-4.50	16.6	0.550	93.8 **
6	81.1	8.98 *	-49.8	-2.57	18.5 *	-0.413	93.1 **
10	16.7	6.88 **	4.50	-2.89	-0.0250	0.0158	91.8 **
11	-10.95	-2.28	30.0 **		I	4.82 **	98.6 **
12	5.91	1.56 **	-4.81	-0.810*	1.52	0.0870	90.2 **
erage	24.3	4.54 **	-6.24	-1.95	3.68	0.575	96.6 **

<u>Table 4</u>. Effect of time of shaking (X_1) and solution:soil ratio (X_2) on the quantities of Mn extracted by 0.1N H₃PO₄, according to Equation (1).

Soil			19-11				7
No.	م ا	b ₁ (x10)	b2	b ₁₁ (x10 ³)	b_{22} (x10 ²)	$b_{12} (x_{10^3})$	۲ ۲
							24
	-10.1	1.46	4.16 **	-1.09	-11.2 **	8.07 **	97.1 ##
2	- 4.63	1.16 *	1.64 **	-0.473	- 4.36 **	1.36	96.2 **
e	- 0.543	0.218	1.62 **	-0.227	- 4.20 **	4.31 **	60.0 #
4	- 5.91	0.260	2.50 **	-0.220	- 5.66 **	3.27 **	** I.96
2	- 2.80	0.450	0. 899**	-0.322	- 2.56 *	0.541	85.0 **
9	- 1.60	0.140	0.626**	-0- 066	- 1.41 **	1.46 **	** I.96
7	2.46	4.05 *	3.82 **	-1.30	-10.5 **	1.78	96.2 **
8	6.24	2.01 **	5.69 **	-1.30 **	-15.5 **	16.6 **	99°9 ##
6	19.7	3.47 **	3.57 **	-2.10 **	-10.7 **	11.4 **	98.3 **
10	0.441	1.37 *	2.11 **	-0.61	- 5.60 **	5.04 **	¥¥ I.99
11	0.084	0.31	-0.159	-0.371	1.78 *	3.66 **	99°0 **
12	- 3.75	1.13 **	0.963**	-0.54 *	- 2.52 **	0.279	97.3 **
erage	- 0.056	1.35 **	2.29 **	-0.726*	- 6.03 **	4.79 **	66°3 **

two procedures. For a fixed ratio, responses to time of shaking may indicate a solubilization process that should tend to slow down as the Mn activity in the extracting solution increases. This is confirmed by the shape of the response surfaces in Fig. 1A and 1B and by the consistent negative b_{11} coefficient for all soils when using these two The fact that only three soils showed this coefficient extractants. to be significant suggests that longer shaking periods should have been used with both extractants. According to Sorensen, et al., (12), if the increase in Mn activity in the extracting solution is the limiting step in the extraction of more Mn at any fixed time, increases in ratio should produce a linear response in extractable Mn. Fig. 1A and Table 3 indicate that this may be the case for the extraction with 0.1N HC1 since only two soils showed significant b_{22} at the 5% level of significance. Results from Table 4 and Fig. 1B clearly show that factors other than Mn activity in the extracting solution are limiting the extraction by 0.1N H₃PO₄.

It is worthwhile noticing the effect of time and ratio upon Mn extraction by both extractants from the organic soil (No. 11). It was the only soil where 0.1N HCl extracted more Mn than the sum of Mn oxides and chelated Mn (Table 1). Furthermore, 0.1N HCl extractable Mn never exceeded 25% of the total Mn content of each mineral soil, but accounted for 55% of this amount from the organic soil. Increasing the time of extraction with this extractant from 10 to 120 min at any ratio produced a 2 to 3-fold increase in Mn extracted. Increasing the ratio from 5 to 25 at any shaking time produced a 12 to 13-fold increase. A similar maximum amount of Mn was extracted from soil 8 (mineral) (Table 2), but in this case while time gave a 2.2 to 2.3-fold increase, ratio only



Figure 1. Effect of shaking time and solution:soil ratio in the amounts of Mn extracted by: A. 0.1N HC1; B. 0.1N H₃PO₄; C. DTPA and D. 1N NH₄OAc (pH 7). (Average for 12 soils).

yielded a 1.1 fold increase in extractable Mn. 0.1N H₃PO₄ showed the same pattern with the organic soil as 0.1N HC1. In the best case (ratio of 25) there was a 2-fold increase in extractable Mn when increasing the shaking time from 10 to 120 min. Increasing the ratio from 5 to 25 at 10 and 120 min of shaking yielded 14 and 21-fold increases, respectively, in Mn extracted from this soil. This exponential effect of the ratio variable with both acids suggests that the total H⁺ activity per unit soil is the main driving force, probably by competing with Mn held by carboxyl groups of the organic matter (1). The pH of the 0.1N HCl extracts for all soils oscillated between 1.1 and 1.3, while those of 0.1N H₃PO₄ oscillated between 2.2 and 2.4, which is a 10-fold difference in H⁺ activity between both extractants. Since 0.1N HCl extracted 10 times as much Mn as 0.1N H₃PO₄ from the organic soil at both extremes of the range (Table 2), there is reason to believe that, at least for this soil (No. 11), Mn extraction is closely related to the H⁺ activity of the extracting solution. Differences between Mn extracted by both acids from the mineral soils do not show this degree of dependence on H⁺ activity.

With the exception of soils 8, 9 and 11, ranges for DTPA extractable Mn were of 3 ppm Mn (soil basis) or less (Table 2). The average response surface (Fig. 1C) is somewhat misleading, particularly the effect of time of shaking at a ratio of 2 (it does not include soil 11) which was caused mainly by soils 8 and 9 alone. Therefore, the soil distribution about the 12.2 ppm of Mn average for the 2-120 min ratio-time combination (Fig. 1C) is skewed, with seven soils lying below and only three soils above this average. Disregarding for a moment the results from soils 8, 9 and 11 (Table 2), a 5-fold variation in ratio and a 12-fold Effect of time of shaking (X_1) and solution:soil ratio (X_2) on the quantities of Mn extracted by DTPA, according to Equations (1) and (2). Table 5.

So11			Regre	ession Coeffic	ients		2.
No.	°م	b ₁ (x10 ²)	b ₂ (x10 ²)	b ₁₁ (x10 ⁵)	b ₂₂ (x10 ³)	b ₁₂ (x10 ⁴)	¥
							%
Ч	1.11	1.28 **	8.95 **	- 2.91	- 3.12 **	- 2.62 **	94.2 **
2	0.980	1.41 *	7.53 *	- 6.67	- 3.61 **	0.426	84.5 **
e	7.01	3.31 *	19.5 *	- 9.33	- 5.97 *	- 5.55	79.8 **
4	4.75	1.89	13.8 *	- 2.87	- 4.26 *	0.0232	88.2 **
5	1	I	1	8	ł	ł	1
9	2.77	0.310	-5.78 **	1	ł	7.28 **	79.0 **
7	8.29	3.68 **	7.91	ł	ł	- 4.66	69.0 * *
80	27.5	17.7 **	52.3 **	-58.8 *	- 9.02	-20.4 *	64.6 *
6	27.3	15.2 **	55.8 **	-41.0 *	-10.7 *	-28.8 **	95.5 **
10	8.89	3.77 *	14.4	- 6.91	- 2.24	- 5.05	89.8 **
11#	5.21	12.2 **	2.94	-16.3 *	- 1.00	-15.3 **	** 0°66
12	0.736	0.300**	-1.36 *	8	1	0.615	80.0 **
Average	7.91	4.83 **	16.1 **	-12.2 **	- 3.99 **	- 4.80 **	98.8 **
*, ** S1	gnificant at	the 5% and 1% :	level, respecti	lvely.			

Solution:soil ratio 2 not included for this equation.

Effect of time of shaking (X_1) and solution: soil ratio (X_2) on the quantities of Mn extracted by IN NH40Ac (pH 7), according to Equations (1) and (2). Table 6.

So11			Regre	ssion Coeffic	lents		. .2
No.	°م	b ₁ (x10 ²)	$b_2 (x10^2)$	b ₁₁ (x10 ⁵)	b ₂₂ (x10 ³)	b ₁₂ (x10 ⁵)	X
							26
Ч	0.100	1.01	7.48 *	1	I	8.42	74.0 **
7	D.388	0.457	4.32 **	-	I	-35.2	62.3 *
٣	5.20	1.34	-11.1	- 9.40	5.83 *	33.5	95.5 **
4	2.04	0.100	3.58	ł	ł	96.8 **	64.3 *
S	I	ł	ł	1	1	I	ł
9	1.02	-0.301	2.35 **	ł	1	25.5 *	91.0 **
7	6.07	2.41 **	- 1.75	- 7.23	5.00 *	-22.7	98.7 **
80	15.4	1.19	31.2 **	1	I	72.9	93.0 **
6	23.1	1.76	-64.4 **	7.38	33.7 **	6.47	99.2 **
10	5.39	0.481	16.5 *	1	I	-21.4	74.0 **
11	1.41	3.54 **	4.10	-13.5	-0.083	64.2 *	98.1 **
12	0.505	0.127	- 4.46	- 0.441	2.08 *	- 3.07	89.2 **
Averag	e 5.12	1.78 **	- 4.69	- 7.83	5.08 **	19.3	99.2 **
** **	Significant at	: the 5% and 1%	level, respecti	lvely.			

variation in shaking time accounted for an average 1.38 ppm variation in extractable Mn. Therefore, and for most practical purposes, results were relatively unaffected by the time and ratio variables in 8 out of 11 soils. The low R^2 values of the equations for some soils (Table 5) were probably due to experimental error, since the quantities of Mn extracted between two consecutive ratios or shaking times differed in several cases by only 5 to 10%.

Results for 1N NH₄OAc (pH 7) show that the minimum amounts of Mn extracted by this procedure were approximately half of those extracted by DTPA. This difference was reduced when considering the maximum values extracted by both procedures. With the exception of soils 8 and 11, the 1N NH₄OAc extracted approximately 75% of the Mn extracted by DTPA and above 100% in the case of soil No. 1. The exponential type of response to increases in the ratio variable (Fig. 1D) is logical, since both effects, increased ratio and larger quantities of NH⁴₄ per unit of soil, are contibuting additively in the Mn extraction.

Mn Extractability and Correlation with Plant Mn Uptake

In the previous section, the characterization of the release of Mn from soils, as affected by the shaking time and solution:soil ratio, has been discussed. This type of study is useful when the experimental conditions to maximize extractable Mn must be determined. For soil testing purposes, however, the interest lies in those conditions that give the highest correlation between extracted Mn by any procedure and plant uptake. For this purpose, the Mn extracted from the 12 soils at every time-ratio combination by each extractant was correlated with the total Mn uptake by soybeans and sorghum grown in the greenhouse

in these same soils. The complete data analysis of these two greenhouse studies is given in Parts II and III of this study. Here, only the plant data of the check pots (three replicates per soil) were used. Equations (1) and (2) were used for the regression analysis, where the response variable (Y) was now the correlation between Mn uptake and extractable Mn at each time-ratio combination. Table 7 and Fig. 2 show the equations obtained and their graphical representation, respectively. When comparing the response surfaces of Fig. 2 with those of Fig. 1 the change in the direction of the abscissas should be noticed.

Results show that the treatment combination that maximized 0.1N HCl extractable Mn (Fig. 1A) minimized its correlation with plant Mn uptake by both crops (Figs. 2A-B). While in the previous section the interaction between time and ratio was, on the average, non-significant and positive (Table 3), it is now negative and significant (Table 7). Results for 0.1N H_3PO_4 (Figs. 2C-D) were similar to those of 0.1N HCl except for a lesser degree of interaction between both variables, particularly with sorghum, and the quadratic effects being more important. The best time-ratio combination was the same for both extractants and crops: 120 min of shaking with a solution:soil ratio of 5.

Response surfaces for 1N NH₄OAc and DTPA are not shown since the overall regression for three out of the four equations was not significant even at the 15% level with either model. Reconstruction of the original data by substituting the experimental values for X_1 and X_2 into the equation of DTPA with sorghum, yields a maximum Y value of 0.75 and a minimum of 0.71. This variation was significantly explained



Figure 2. Effect of shaking time and solution:soil ratio in the correlation between 0.1N HCl extractable Mn and Mn uptake by A. Soybeans, B. Sorghum and 0.1N H₃PO₄ extractable Mn and Mn uptake by C. Soybeans and D. Sorghum.

ζ_2) in the correlation between	is (1) and (2).
. Effect of time of shaking $(\mathrm{X}_{\mathrm{I}})$ and solution:soil ratio (extractable Mn and plant Mn uptake, according to Equatio
Table 7.	

				Regres	sion Coeffici	ents		2
EXUTACTANT	urop	ം°	b ₁ (x10 ⁴)	b ₂ (x10 ³)	b ₁₁ (x10 ⁶)	b ₂₂ (x10 ⁴)	b ₁₂ (x10 ⁵)	X
								52
	Soybeans	0.792	10.8 **	- 8.99 **	ł	8	-6.87 **	98.0 **
O. IN HUL	Sorghum	0.720	11.7 **	- 8.09 **	ł	1	-7.20 **	97.1 **
	Soybeans	0.900	16.0 **	-11.8 **	- 5.04 *	2.82 *	-3.30 **	98.0 **
0.1N H3F04	Sorghum	0.922	9.20	-23.4 **	- 3.22	5.56 **	-1.24	96.0 **
	Soybeans	0.693	-4.66	- 4.21 *	2.94	1.58 *	-0.481	50.2
DIFA	Sorghum	0.765	-4.11	- 3.84 **	2.24	1.43 *	-0.711	75.3 **
	Soybeans	0.729	2.03	- 0.263	- 0.680	0.242	-1.64	57.9
IN NH4 UAC	Sorghum	0.826	-0.399	- 2.88	0.400	1.11	-1.79	65.0
*, ** Signi	ficant at t	the 5% an	d 1% level, re	espectively.				

(1% level) by the model used. However, such a small response in the correlation between extractable Mn and plant Mn uptake has no practical applications. Therefore, it may be concluded that the selection of a time of shaking and solution:soil ratio for $1N \ NH_4OAc$ and DTPA extractions is of little consequence for extractable Mn and its correlation with plant Mn uptake. In the case of $0.1N \ HCl$ and H_3PO_4 large variations in the Mn extracted at different times and ratios allowed for the selection of a treatment combination that maximized the correlation with plant uptake, and that differed from the one that maximized extractable Mn.

Extractable Mn and Soil Characteristics

The average response surfaces of Fig. 1 and results for individual soils (Tables 3 to 6) show that the shaking times and solution:soil ratios used affected the Mn extractions in different ways, depending on the extractants. In an attempt to find and explanation for these responses, a stepwise regression procedure was used. Extractable Mn at four selected time-ratio combinations, namely: 5-10 min, 5-120 min, 25-10 min and 25-120 min, was related to seven soil characteristics (Eq. 3). The basic idea underlying the use of a stepwise procedure was that each extractants would relate to a different set of variables when changing the ratio-time combination. To prevent biasing the results due to the high value of organic C and bases ratio (Table 1) of the organic soil (No. 11), this soil was excluded from the analysis.

Table 8 shows which soil characteristics explained most of the variability among soils in the Mn extracted by the four extractants at each ratio-time combination. Of the seven variables used at the

					Regres	sion Coeff:	lcients		2
Extractant	Ratio	Time		Hq	Chelated Mn	Mn Oxides	Total Mn	(Total Mn) ²	ж I
			ഛ			^b 1			м
0.1N HC1	Ś	10	-60.2	9.89*	1.28**	ł	ł	1	93.0**
=	S	120	1.14	1	1	0.554**	ł	ł	94.8**
2	25	10	-76.0	12.1 **	1.46**	1	ł	1	95.5**
=	25	120	8.19	ł	ł	0.548**	ł	1	93.4**
0.1N H ₃ PO	Ś	10	-0.982	ł	ł	0.138**	8	-	88.5**
t -	Ś	120	-0.552	ł	ł	0.193**	1	1	88.2**
=	25	10	3.39	ł	ł	0.184**	ł	1	91.4**
=	25	120	6.86	ł	1	0.332**		1	89.3
DTPA	Ś	10	2.53	1	ł	ł	-0.025	0.0001 **	93.0**
=	ŝ	120	1.04	ł	ł	ł	-0.059	0.0001**	90.8**
=	25	10	2.83	ł	ł	!	-0.034	0.0001**	93.1**
=	25	120	2.55		1	ł	-0.025	0.0001**	93.9**
IN NH, OAC	Ś	10	-1.46	ł	0.378**	ł	1	ł	95.3**
t =	ŝ	120	-1.46	ł	0.427**	ł	ļ	:	94.8**
=	25	10	-1.35	ł	0.492**	1	ł	1	95.7**
=	25	120	-1.19	1	0.555**	1	ł	1	96.3**

Main soil factors that relate to the quantities of extractable Mn by several procedures at Table 8.

begining of the stepwise procedure (Eq. 3) only one or two out of four remained in each model. These variables were significant at the 5% or 1% level except for the linear term of total Mn in the DTPA equations; this particular case will be discussed later on. The two principal variables for 0.1N HCl were chelated Mn and Mn oxides at short and long shaking periods respectively. Although significant, pH is only contributing 5 to 6% of the R^2 value in the two equations in which it was included. These two main variables may explain why soils 5 and 6 (Table 3) did not show a significant simple effect for the time variable, since both had the lowest amounts of chelated Mn and Mn oxides (Table 1). The four equations for this extractant also show that the Mn sources are the same when changing ratios at fixed shaking times, which is probably the reason why most soils did not respond to changes in ratio. Since 0.1N HCl is a powerful extracting agent for Mn (Table 2), most of the Mn from any one source should be extracted, within limits, independently of the ratio used. The limits are set by the increase in the intercept when increasing the ratio at long shaking times, while the slopes of both equations remain relatively constant (Table 8).

Results for $0.1N H_3PO_4$ show extractable Mn mainly as a function of the Mn oxides content at all ratio-time combinations. The strong effect of the interaction between time and ratio with most soils (Table 4) can now be realized by observing the changes in slope when changing one variable at a fixed level of the other one. Extractable Mn was higher when any one variable was increased at the high level of the other.

Due to the small number of points defining each equation, the number of independent variables was kept to a minimum, making no allowance for interactions or quadratic effects. Total Mn in soil was the only

variable that showed a significant relationship with DTPA extractable Mn, at all treatment combinations. A plot of these results showed a strong non-linear relation between both variables. After the 2nd order term was included in the equation, the linear term lost all its significance and explains 1% or less of the R^2 values for those equations. It was left in the equations to maintain all the terms of the polynomial. Since total Mn comprises several chemical species of very different characteristics, no explanation can be offered for the soils behavior upon changes in the time and ratio variables.

Results for 1N NH₄OAc (pH 7) extractable Mn show this variable as a function of chelated Mn at all ratio-time combinations. Chelated Mn was defined as the Mn extracted from finely ground soils by two successive extractions with 0.005M DTPA. This close relationship and similar maximum amounts of Mn extracted by DTPA and 1N NH₄OAc (Table 2) suggest that part of the Mn extracted by DTPA is in exchangeable positions. Smaller amounts of Mn extracted from most soils by the 1N NH₄OAc seem to be related to ratios and extractants concentrations. This tended to be confirmed by positive quadratic effects of the ratio (b_{22}) variable upon 1N NH₄OAc and negative ones for DTPA for all soils. Figures 1C and 1D show these effects very clearly at long shaking times.

Summary and Conclusions

The effect of 12 shaking time-solution:soil ratio combinations on the quantities of Mn extracted by 0.1N HCl, 0.1N H_3PO_4 , 0.005M DTPA and 1N NH₄OAc (pH 7) from 12 soils was studied. Effects of these variables upon extractable Mn were studied by multiple regression analysis. Extractable Mn from all soils at each time-ratio combination was then
correlated with yield data from two greenhouse studies using these same soils. Hence, the effect of both variables in the degree of correlation between extractable Mn and Mn uptake by soybeans and sorghum was obtained. To study which soil Mn fractions and soil characteristics were important in determining the quantities of Mn extracted, a stepwise regression procedure was used.

Results can be summarized as follows:

1) The time-ratio combination that yielded the largest quantities of extractable Mn by all extractants (average for 12 soils) was a solution:soil ratio of 25:1 (volume:air dry weight) and a shaking time of 120 min.

2) For 0.1N HCl and 0.1N H_3PO_4 , a ratio of 5:1 with 120 min of extraction gave the highest correlation between extractable Mn and plant Mn uptake by both crops. For most practical purposes, the correlation of 1N NH₄OAc and DTPA extractable Mn with plant Mn uptake was unaffected by the time-ratio combination used.

3) With 10 min of shaking, chelated Mn was the main variable relating to 0.1N HCl extractable Mn; at 120 min it was Mn oxides. These variables were selected at both ratios, 5 and 25. The other three extractants correlated with a single variable at all four time-ratio combinations: 0.1N H_3PO_4 with Mn oxides, 1N NH_4OAc with chelated Mn and DTPA with (total Mn)².

4) Of the four extractants used, $0.1N H_3PO_4$ was the one giving the highest correlation with plant uptake, at a ratio-time combination of 5-120 min.

5) For soil testing purposes, the use of $0.1N H_3PO_4$ with a ratiotime combination of 5-60 min is recommended for mineral soils.

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PART II

STUDIES IN SOIL MANGANESE

2. EXTRACTABLE MANGANESE AND PLANT UPTAKE

Introduction

Considerable effort has been made in the development of tests to estimate the availability of Mn in soils. This element occurs in several oxidation states and is associated with different soil fractions, namely, several types of Mn oxides, Mn associated with the organic matter, Mn related to the inorganic colloid and Mn in soil solution. A cycle for this nutrient in soils has been proposed by Ghanem, et al., (10).

The nature of this cycle has justified the use of different types of extracting solutions in an attempt to characterize the fractions which are in close equilibrium with the Mn in solution and, therefore, responsible for the replenishment of Mn extracted by a crop throughout the growing season. Reviews on this subject have been published (6, 24).

Several authors (12, 11, 3, 15) have found $0.1N H_3PO_4$, 1.5 and 3M $NH_4H_2PO_4$ extractable Mn to correlate well with Mn uptake by plants. Manganese extracted by 1N NH_4OAc has also been used with some success (1, 20) and correlated better than $0.1N H_3PO_4$ with plant uptake when the soil pH factor was included in the prediction equation (3). DTPA has been proposed as a single test for available Cu, Zn, Fe and Mn in soils (Lindsay and Norvell, 1969)¹; however a study by Dolar, et al., (8) showed that DTPA was not the best extractant for this purpose in soils of Wisconsin and they propose, instead, the use of an extraction with 1N $NH_4OAc-0.01M$ EDTA. Correlation of DTPA extractable Mn with Mn concentrations in wheat and soybeans was shown to depend on the pH of soil (20).

There have been several reports on the increased availability of Mn

¹ Development of a DTPA micronutrient soil test. Agron. Abstr., p.84.

after steam treatment of the soils (2, 21, 22), in some cases developing problems of Mn toxicity in plants. Tests performed in this laboratory (unpublished data) subjecting soil samples to a steam pretreatment have shown that the quantities of Mn extracted correlated well with plant Mn uptake.

In recent years, the incorporation of soil characteristics to the prediction equations of soil tests have been successffully used (3, 8, 6, 18). Organic matter and pH have been the variables most used.

In the investigation described herein, several soil tests for Mn are compared, including steam sterilization followed by 1N NH₄OAc extraction. Furthermore, the possiblity of including certain soil characteristics in the prediction equation of these soils tests is also explored.

Materials and Methods

Soils

Surface soil samples of 12 different soil types from Michigan and Indiana were used. The main soil characteristics have been reported previously (Part I).

Methods

Greenhouse experiment: The soil samples were air dried, screened through a one cm sieve and placed in one gallon cans lined with polyethylene bags - 3.5 kg/pot for mineral soils and 1.6 kg/pot for the organic soil (air dry weight). All soils received a basic application of 50 ppm of K and P and 10 ppm of Zn. The mineral soils received the following treatments: a) basic fertilizer application only; b) 10 ppm of Mn as $MnSO_4$ (reagent grade) and c) 20 ppm of Mn as $MnSO_4$ (reagent grade). The organic soil received 22 and 44 ppm of Mn and 110 ppm of P and K and 22 ppm of Zn. A randomized complete block design with three replications was used. After mixing the fertilizer with the soil, these were incubated for 2 weeks at 80% field capacity and then planted with 10 seeds of soybean (Glycine max, var. Hark). After emergence the plants were thinned to 3 per pot and supplemental fluorescent light was initiated to give a day length of 14 hours. Each pot was weighed daily and brought to field capacity with deionized water. To prevent uneven root distribution, N fertilizer was not added as a basic application, but rather applied when necessary, at a rate of 30 ppm of N per application. The tops were harvested from each pot when at least two plants were at blooming stage, placed in paper bags and dried at 60 °C, weighed and ground in a Wiley mill to pass a 40-mesh screen. After harvest soil samples were collected from each pot using a soil sampling probe, air dried and ground to pass a 2 mm sieve.

Plant analysis: Total Mn in plant tissue was analyzed by dry ashing according to the procedure described by White (25) and Mn determined by atomic absorption spectrophotometry.

Soil Analysis: A solution:soil ratio (volume:air dry weight) of 5 (20:4) was used for all the extractions. The lengths of extraction were 30 min for DTPA and 1N NH₄OAc (pH 7), and 60 min for 0.1N HCl, 0.1N H₃PO₄ and 1.5M NH₄H₂PO₄. For the proposed procedure 4 g of soil were subjected to 30 min of steam heat at 15 psi and then extracted with 1N NH₄OAc as indicated above. Solution:soil ratios and lengths of extraction were selected according to results obtained in Part I. In all cases Mn was analyzed in the filtrates by atomic absorption spectrophotometry.

Methods used to determine other soil characteristics mentioned in this study were given previously (Part I).

Results and Discussion

Results for total Mn uptake by soybeans are given in Table 1, together with the soil Mn extracted by each method. Extraction with 0.1N HCl gave the largest quantities of extractable Mn with the exception of the organic soil (No. 11) where steam/NH₄OAc and 1.5M $NH_4H_2PO_4$ were stronger extractants. Although Boyd (2) proposed that organic matter was the source of the Mn released by the steam treatment mineral soils 7, 8, 9 and 10 released larger amounts of Mn than the organic soil itself.

Correlation and Regression Analysis

Evaluation of the soil tests and soil factors as predictors of Mn uptake by soybeans was done using multiple regression analysis according to the following model:

$$Y = \beta_{1} + \beta_{1}X_{1} + \beta_{1}X_{1} + \beta_{2}X_{2} + \varepsilon$$
(1)

where $X_1 (X_a...X_f)$ represents the Mn extracted by the different soil tests, $X_1 = pH$, $X_2 = Ca+Mg/K$ (bases ratio using meq/100 g of soil) and the variable response (Y) is total Mn uptake. The results of this analysis are shown in Table 2. An indication of the degree of fit gained by the inclusion of X_1 and X_2 into the model is given by comparing the square of the simple correlation coefficient for any extractant with the R^2 of the complete model.

Soil reaction is known to relate negatively with soluble Mn (14) and inclussion of this variable in prediction equations has been proved

Soil Mn		n Min	Extractable Mn†					
No.	added	uptake†	HC1	DTPA	H ₃ PO ₄	NH ₄ OAc	Steam/ NH ₄ OAc	NH4H2PO4
	ppm	µg/pot			ppm (so:	il basis)		
1	0	117	45.1	1.8	13.7	1.1	5.9	17.6
	10	155	51.7	2.5	16.7	1.5	8.2	22.1
	20	145	57.5	3.3	18.0	2.0	10.0	25.3
2	0	111	27.5	2.1	7.7	1.1	6.4	9.4
	10	143	34.7	3.1	10.9	1.6	7.9	11.8
	20	204	39.2	4.1	13.1	2.0	11.6	14.5
3	0	79.4	29.4	4.2	5.1	2.6	8.4	9.3
	10	106	38.3	7.3	8.1	4.6	12.0	13.3
	20	105	42.9	10.4	9.9	6.7	15.4	17.0
4	0	72.3	38.0	2.7	5.1	1.5	5.6	11.8
	10	96.1	51.7	4.7	8.2	2.5	8.3	19.4
	20	103	58.6	6.2	8.5	2.9	10.5	25.1
5	0	7.3	5.8	0.2	2.6	0.2	1.0	2.3
	10	44.1	19.1	0.7	6.5	0.6	2.1	5.1
	20	55.1	25.5	1.2	10.5	0.9	4.1	8.3
6	0	57.4	11.6	1.2	1.7	0.7	3.4	4.8
	10	90.1	20.7	3.1	3.8	1.5	6.2	8.2
	20	110	28.1	4.2	5.2	2.1	8.8	10.5
7	0	402	55.8	7.0	35.5	4.6	36.9	42.7
	10	395	63.6	8.4	36.3	5.3	43.3	49.5
	20	440	66.0	9.4	39.6	5.9	41.5	47.6
8	0	232	102	20.0	30.3	8.7	49.4	51.5
	10	306	103	20.9	32.3	9.9	50.0	54.2
	20	336	105	22.0	32.8	10.6	53.6	56.2
9	0	363	79.6	18.9	35.6	11.5	54.4	49.2
	10	392	87.1	22.4	38.4	14.2	54.3	52.3
	20	401	87.4	23.1	40.4	14.1	58.3	54.1
10	0	231	40.8	6.5	12.9	3.6	20.5	15.1
	10	210	47.8	9.0	16.2	5.1	25.0	19.6
	20	248	51.3	9.8	17.7	5.5	28.2	21.1
11	0	59.8	8.2	8.4	0.8	2.9	22.4	29.5
	10	86.1	9.1	9.5	0.8	3.2	23.9	32.7
	20	124	11.0	10.9	1.0	3.9	29.6	37.7
12	0	80.0	10.5	0.6	4.5	0.4	2.7	4.6
	10	107	18.8	1.3	8.0	0.9	5.1	7.6
	20	150	27.0	2.7	11.1	1.8	8.3	11.1

Table 1. Mn uptake by soybeans and soil extractable Mn by each method.

+ Each result average of three replicates.

successful when using $1N \operatorname{NH}_4 \operatorname{OAc} (3)$, double acid (6) and other Mn extractants (8, 18). It is also reasonable to think that Ca^{2+} and to a lesser degree Mg²⁺ are the main divalent ion competitors of Mn²⁺ for positions on the exchange complex. Thus, including a factor accounting for this relationship seems justified -- the significant negative simple correlation of X₂ with plant uptake confirms this. The advantage of using these variables instead of others that may correlate even better with plant uptake (Part I) is that they are determined routinely in soil testing laboratories and therefore no extra analyses are necessary.

The list of the extractants in order of decreasing simple correlation with plant uptake is: H_3PO_4 > steam/NH₄OAc > NH₄H₂PO₄ > HCl > NH₄OAc > DTPA. When using the R² for the complete equations, the order becomes: H_3PO_4 > steam/NH₄OAc = NH₄H₂PO₄ > HCl > NH₄OAc = DTPA.

To study the relative contribution of X_1 and X_2 in each model, the R² delete value for each variable was included. This value gives the percentage of the variance that would be accounted for by the remaining variables, with that particular variable not being included in the equation. In this context, deletion of the X_1 variable (soil test) from any equation, would leave pH and bases ratio explaining more than 40% of the variation in the Mn uptake data. Bases ratio was more important than pH in explaining the variation of the data in the prediction equations of $NH_4H_2PO_4$, steam/NH₄OAc, NH_4OAc and DTPA -- 15% in the case of this last extractant. For HCl and H_3PO_4 , pH was more important than bases ratio. Bases ratio was not significant when included in the prediction equation of 0.1N H_3PO_4 , which is shown by the magnitude of its R² delete value. The only extractant that alone could explain most of the variation in Mn uptake by soybeans was 0.1N H_3PO_4

			 J	
Soil Test		Dential	R ²	R ²
	51mp1e		Delete	₩
	0 70(++	0 00544	<i>k</i>	6
1.5M NH ₄ H ₂ PO ₄ (x_a)	0.796**	0.805**	40.2	
рн (X ₁)	-0.34/**	-0.526**	70.9	
Bases ratio (X ₂)	-0.458**	-0.588**	6/.8	
Regression Eq.	Y = 637 + 4.7	$79X_a - 77.7X_1 -$	0.99X ₂	78.9**
Steam/1N NH ₄ OAc (X _H) 0.840**	0.806**	40.2	
pH (X ₁)	-0.347**	-0.281**	77.2	
Bases ratio (X ₂)	-0.458**	-0.529**	70.9	
Regression Eq.	Y = 389 + 4.8	88X _b - 39.5X ₁ -	0.87X ₂	79.0**
1N NH ₄ OAc (X _c)	0.747**	0.643**	40.2	
рН (X ₁)	-0.347**	-0.273**	62.1	
Bases ratio (X ₂)	-0.458**	-0.444**	56.3	
Regression Eq.	Y = 485 + 19	$2X_c - 50.1X_1 -$	0.91X ₂	64.9**
DTPA (X _d)	0.690**	0.634**	40.2	
рН (Х ₁)	-0.347**	-0.337**	59.7	
Bases ratio (X ₂)	-0.458**	-0.547**	48.9	
Regression Eq.	Y = 581 + 9.5	$95X_d - 61.9X_1 -$	1.15X ₂	64.2**
0.1N HC1 (X)	0.749**	0.692**	40.2	
рН (X ₁)	-0.347**	-0.534**	56.4	
Bases ratio (X ₂)	-0.548**	-0.244**	66.8	
Regression Eq.	Y = 710 + 2.5	92X _e - 95.0X ₁ -	0.48X ₂	68.8**
0.1N H ₃ PO ₄ (X _f)	0.919**	0.901**	40.2	
рН (X ₁)	-0.347**	-0.482**	85.2	
Bases ratio (X ₂)	-0.458**	0.055	88.6	
Regression Eq.	Y = 388 + 8.2	$29X_f - 52.2X_1$		88.6**

Table 2. Relationship of Mn uptake by soybeans (Y) with several soil Mn tests, pH and bases ratio, according to Equation (1).

** Significant at the 1% level.

Relationship Between Mn Uptake and Soil Properties

In an attempt to establish the soil Mn fractions and soil properties most important in explaining the variations of the Y variable, a stepwise regression technique was used² according to the following model:

$$Y = \beta_{0} + \sum_{i=1}^{7} \beta_{i} X_{i} + \varepsilon$$
(2)

where the variable response (Y) was Mn uptake and the seven independent variables were: pH, Ca+Mg/K, CaCO₃, organic C, chelated Mn, Mn oxides and total Mn. A 1% level of significance was selected for the deletion and addition of variables. The list of variables left in the model are shown in Table 3.

<u>Table 3</u>. Relationship between Mn uptake by soybeans and several soil characteristics.

Soil Properties	Simple Correlation	Partial Correlation	R ² Delete	R ²
			%	%
рН (Х ₁)	-0.347 **	-0.400 **	78.2	
Mn oxides (X ₂)	0.815 **	0.715 **	62.6	
Bases ratio (X_3)	-0.458 **	-0.451 **	77.1	
Total Mn (X ₄)	0.690 **	-0.522 **	74.9	
Regression Eq. $Y =$	$543 - 53.1X_{7} + 2$.26X, - 0.677X	$X_3 - 0.655 X_A$	81.7**

** Significant at the 1% level.

By the magnitude of the R^2 delete values, pH is the parameter that explain the least variation in the uptake data, in the presence of the other variables, while Mn oxides is the parameter explaining most of

² Michigan State University Stat System. 1971. LSSTEP Program, Chap.12.

the variation. Furthermore, a regression equation with Mn oxides as the only variable would account for a greater percentage of the variability of Y (66.4%) than the extraction with 1.5M $NH_{L}H_{2}PO_{L}$, 1N $NH_{L}OAc$ and 0.1N HCl as single determination, and than 1N NH, OAc and DTPA when including pH and bases ratio in the prediction equation. The strong correlation of plant uptake with Mn oxides and the fact that chelated Mn did not appear in the model as a significant variable is an indication as to why DTPA extractable Mn was not useful as a predictor of Mn uptake. This conclusion would only hold for the mineral soils studied since a recent study by Randall, et al., (18) using 20 organic soils showed DTPA to be a good predictor of Mn uptake in this type of soil. The high correlation of plant uptake with Mn oxides is in good agreement with results of other researches. According to Passioura and Leeper (17) Mn oxides in soils are not necessarily crystalline or concentrated in a few course nodules. Ross, et al., (19) reported that the soil Mn compounds that they studied were largely amorphous to X-rays due to poor crystallinity, fineness of both. Therefore high specific surfaces coupled with low degree of crystallinity may render part of this fraction available to plants through action of root exudates and modification of the pH-redox system of the root environment produced by the release of H^+ (26). Availability of higher oxides of Mn to oats has been reported (13, 16). Results by Randall, et al., (18) show hydroxylamine hydrochloride among the three best extractants out of 18 in predicting plant Mn uptake and this was the same extractant used (5) in defining the Mn oxides fraction, although the acid concentrations differed.

Simple correlation coefficients among extractants and several soil

properties are shown in Table 4. Although different procedures were used to define chelated Mn (Part I) and DTPA extractable Mn, a close relationship between both variables should be expected since the same extractant was used in both cases (Table 4). IN NH₄OAc also relates closely to chelated Mn and, therefore, both DTPA and IN NH₄OAc extractable Mn show a high correlation with each other. The high correlation between Mn extracted by steam/NH₄OAc and 1.5M NH₄H₂PO₄ can be explained by the fact that both are closely correlated to the Mn oxide fraction. The relationship between Mn oxides and steam/NH₄OAc extractable Mn indicates that this fraction may be more labile to the steam treatment than proposed by Boyd (2).

Growth Response

The results of the Mn uptake by the soybeans were shown in Table 1. The variances for the combined experiment were not homogeneous and a logarithmic transformation was necessary for the analysis of variance. The effect of the fertilizer application on each soil was studied by using orthogonal polynomials, partitioning the two degrees of freedom of the fertilizer treatment into a linear and a non-linear response (23). The results of this analysis are shown in Table 5. Based on the Mn deficiency symptoms observed in the soybeans growing in soils 3 and 4 a more significant response to the fertilizer application was expected. However, these two soils had more than 40% clay and there were delays in the germination and emergence of the soybeans plants; probably problems related to root growth and distribution did not allow for an efficient use of the applied fertilizer. No explanation can be offered for the significant response at the 5% level of soil 8, since this soil

									1	- - -	:	E
HCI	DTPA	H ₃ PO ₄	NH40Ac	Steam/ NH ₄ 0Ac	ин ₄ н ₂ Р0 ₄	Hd	Org. C	caco ₃	Bases Ratio	Chelated Mn	Mn Oxides	Mu
HC1 1.00	0.80	0.87	0.82	0.79	0.80	-0.03	-0.27	-0.37	-0.54	0.81	0.85	0.84
DTPA	1.00	0.72	0.97	0.93	0.88	-0.35	-0.01	-0.43	-0.17	0.97	0.88	0.90
н ₃ Ро4		1.00	0.80	0.85	0.83	-0.16	-0.28	-0.47	-0.58	0.73	0.84	0.72
NH40Ac			1.00	0.91	0.84	-0.37	-0.11	-0.51	-0.29	0.93	0.86	0.87
Steam/NH ₄ OAc				1.00	0.95	-0.36	-0.05	-0.47	-0.25	0.93	0.95	0.89
NH4H2P04					1.00	-0.18	-0.01	-0.30	-0.24	0.87	0.92	0.86
pH						1.00	-0.12	0.63	-0.18	-0.29	-0.24	-0.21
Organi c C							1.00	0.12	0.42	-0.02	-0.08	-0.06
caco ₃								1.00	-0.05	-0.46	-0.46	-0.43
Bases ratio									1.00	-0.17	-0.34	-0.31
Chelated Mn										1.00	0.93	0.94
Mn oxides											1.00	0.96
Total Mn												1.00

Simple correlation coefficients among extractable Mn by several procedures and soil properties.**

Table 4.

** Values larger than 0.25 significant at the 1% level.

Rates of Mn Application	Logarithm of Mn uptake (µg/pot)					
ppm			Sof	 Is		
	1	2	3	4	5	6
0	2.071	2.047	1.900	1.890	0.862	1.759
10	2.192	2.155	2.026	1.980	1.644	1.955
20	2.161	2.310	2.019	2.013	1.742	2.042
Sum of Sq.						
Linear effect	0.012	0.104**	0.022+	0.023+	1.159**	0.120**
Quadr. effect	0.011	0.001	0.009	0.002	0.235**	0.006
	7	8	9	10	11	12
0	2.605	2.366	2.560	2.363	1.777	1.903
10	2.597	2.486	2.594	2.323	1.935	2.030
20	2.643	2.526	2.603	2.394	2.092	2.176
Sum of Sq.						
Linear effect	0.002	0.038*	0.003	0.001	0.194**	0.112**
Quadr. effect	0.001	0.003	0.001	0.006	0.001	0.001

Table 5. Response in Mn uptake by soybeans to Mn fertilization as MnSO4.

+, * and ** Significant at the 10%, 5% and 1% level, respectively.





showed large amounts of extractable Mn by all the procedures used.

The determination of the critical level of Mn for the three best extractants was done by the method proposed by Cate and Nelson (4). These levels were about 12 ppm of Mn for $0.1N H_3PO_4$ and 14 ppm of Mn for steam/NH₄OAc and $1.5M NH_4H_2PO_4$ (Fig. 1). None of these extractants were able to separate soil 8 as a deficient one and as said before, no explanation can be offered for this behavior other than caused by experimental error. Except for this soil, $0.1N H_3PO_4$ was able to separate the rest of them into deficient and non-deficient, including the organic soil (48% of maximum yield), while the other two extractants did not place this last soil into the deficient group. Furthermore, the steam/NH₄OAc extraction underestimated the available Mn of soil 1 (81.2% yield) while the other two procedures did not.

Results from Table 5 show that only one soil of those that responded significantly to the fertilizer treatment had a significant quadratic effect. This would indicate that a higher maximum rate of Mn application should have been used.

Summary and Conclusions

A greenhouse experiment with 12 soils from Michigan and Indiana was used to evaluate six extractants in their ability to predict Mn uptake by soybeans. A randomized complete block design experiment with three replicates and three rates of Mn fertilization (as $MnSO_4$) namely, 0, 10, and 20 ppm of Mn for the mineral soils and 22 and 44 ppm of Mn for the organic soil was conducted. Soybeans tops were harvested at bloom stage, dry weight recorded and the tops analyzed for Mn. All statistical analyses were based on total Mn uptake data. Soil samples were taken

from each pot with the aid of a probe and extracted for Mn by the following extractants: 0.1N HCl, 0.1N H_3PO_4 , 0.005M DTPA (pH 7.3), 1N NH₄OAc (pH 7), 1.5M NH₄H₂PO₄ and steam/1N NH₄OAc. Correlation and regression techniques were used to evaluate the behavior of each extractant to study the relationships between Mn uptake and soil properties and to observe interrelations among extractants and soil properties.

The results can be summarized as follows:

1) The listing of extractants in decreasing order of correlation with Mn uptake by soybeans was: H_3PO_4 > steam/NH₄OAc > NH₄H₂PO₄ > HC1 > NH₄OAc > DTPA.

2) If pH and Ca+Mg/K were included in the prediction equation, the order was as follows: H_3PO_4 > steam/NH₄OAc = NH₄H₂PO₄ > HCl > NH₄OAc = DTPA.

3) Bases ratio was more important than pH in the prediction equations of $1.5M \text{ NH}_4\text{H}_2\text{PO}_4$, DTPA, $1N \text{ NH}_4\text{OAc}$ and $\frac{1}{4}M_4\text{OAc}$. The reverse was true for the 0.1N HCl prediction equation. The prediction equation of 0.1N H_3PO_4 showed almost no improvement when bases ratio and pH were included.

4) The Mn oxides fraction of the soils explained 66.4% of the variation of the Mn uptake data and inclusion of pH, bases ratio and total Mn in the equation raised this value to 81.7%.

5) A correlation coefficient of 0.97 was obtained between DTPA and IN NH_4OAc extractable Mn, and of 0.95 between steam/ NH_4OAc and 1.5M $NH_4H_2PO_4$. Mn extracted by the first pair of extractants was highly correlated with the chelated Mn fraction of the soils, while the second pair correlated very closely with the Mn oxides fraction.

7) The critical levels of extractable Mn in soils were 12 ppm for 0.1N H_3PO_4 and 14 ppm of Mn for steam/1N NH₄OAc and 1.5M NH₄H₂PO₄.

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PART III

STUDIES IN SOIL MANGANESE

3. MANGANESE LABILE POOL AND PLANT UPTAKE

Introduction

Extensive use of radioisotopes has been done in soil fertility studies. Most of these studies have concentrated in the macronutrients in soils, particularly P (4, 2, 9), although studies in S, Ca and N (6) have also been done. By comparison, micronutrients have received much less attention. The use of 54 Mn is particularly suited for studies about the chemistry and plant nutrition of Mn, since it is a high energy gamma emitter with a long half-life. This radioisotope has been used to study Mn distribution in plants (13), its interaction with other micronutrients (20), the fate of Mn applied to soil as MnSO₄ (16), and its interaction with clays (3).

The determination of the Mn labile pool of several soils was done by Lamm (8) who determined isotopically exchangeable Mn by laboratory procedures, by E value (18) and with the use of plants by calculating the L values (9) and by A value (7). More recently (11, 12) DTPA was used as the equilibrating solution in the determination of isotopically exchangeable Mn, Fe, Zn and Cu. All the theoretical considerations concerning the use of these values and comparisons among them have been covered extensively (10, 6, 5).

The objectives of this study were to determine the E and L-values of various soils, to assess their effectivenes as predictors of plant Mn uptake by comparison to other more commonly used Mn extraction methods, and to study the residual effect of Mn fertilization as MnSO₄.

Materials and Methods

Greenhouse experiment: The control and 20 ppm Mn treatment of the same soils used in a previous experiment (Part II) were used in this study. The soils were removed from their cans, clods were broken up and most of the root residues removed. Pots containing mineral soils were reduced to 3 kg/pot and those with the organic soil to 1.5 kg/pot. No additional Mn fertilizer was used, the rates being, therefore, 0 and 20 ppm Mn (as MnSO,) for the mineral soils and 44 ppm of Mn for the organic soil. A split-plot design was used for this experiment, with the Mn rates being layed out as randomized complete blocks with three replicates and harvests being the split-plot. Carrier free ⁵⁴Mn was added to each pot mixing 10 ml of an aqueous solution containing an activity of 0.2 μ Ci/ml with the soil on a heavy sheet of paper. Pots were taken to field capacity with water containing an equivalent of 33 ppm of N and 44 ppm of P (soil basis) and were allowed to incubate for two weeks. On April 26, they were sown with a Trudan No.2 sudangrass hybrid (Sorghum vulgare sudanense L.). After emergence pots were thinned to seven plants/pot and the use of supplemental fluorescent light was initiated. All the pots were taken twice daily to field capacity with an automatic irrigation system designed and constructed for this experiment. On May 21 the plant tops were cut 10 cm from the soil surface, placed in paper bags and dried at 60 °C. The dried tissue was weighed and then ground in a Wiley mill to pass a 40-mesh screen. On May 29 all the soils were fertilized with 50 ppm of K and N. The 2nd and 3rd harvests were done in June 4 and June 28, respectively, following the same procedure as outlined above.

Plant analysis: Duplicate 1 g samples of the ground plant tissue (except for the few cases where insufficient material was available) were counted for ⁵⁴Mn activity in a well-type sodium iodide crystal scintillation detector (Packard Auto-Gamma Spectrometer). One milliliter of the ⁵⁴Mn fertilizer solution was evaporated to dryness in a counting tube and counted with each batch of plant samples. Correction for radioactive decay was not necessary since the specific activity in plant tissue was compared with specific activity of the fertilizer counted the same day. The same plant samples were then analyzed for total Mn by dry ashing, according to the procedure of White (21). Soil analysis: The isotopic exchange study was carried out in the soil samples collected from the pots after the soybean harvest (Part II). Four-gram air dried samples were allowed to equilibrate for 72 hours (11, 12) in a rotary shaker with 20 ml of a 0.1N H_3PO_4 solution containing 0.015 μ Ci/ml. After this period the suspensions were filtered through Whatman No. 42 filter paper. A one milliliter aliquot was evaporated to dryness in counting tubes and ⁵⁴Mn activity measured in the same counter used for the plant samples. The same procedure was followed with three 20 ml blanks of the extracting solution. The Mn extracted from the soil was measured in the remaining filtrate by atomic absorption spectrophotometry.

Other soil data: The main characteristics of the soils used in this study and the results of extractable Mn by several soil tests to which reference is made in this study are given in Parts I and II. *Calculations:* L and E values were calculated according to the following formula:

L or E = B
$$\left(\frac{Sf}{S} - 1\right)$$

where L or E = Isotopically exchangeable Mn

B = Amounts of ⁵⁴Mn added (0.000333 ppm soil basis)

 $S_f = Specific activity of {}^{54}Mn$ solution added (Appendix III)

S = Specific activity of plant for L value, or specific activity of the 0.1N H_3PO_4 solution after 72 hs of shaking for E value (Appendix III).

In all cases specific activity refers to counts per minute divided by the micrograms of Mn in the plant or solution aliquots.

Results and Discussion

Sudangrass M uptake data an L values as determined by isotopic dilution techniques (10) are shown in Table 1. No correction for seedborne Mn was done (19) since its effect upon successive harvests should be negligible. Allowance for ⁵⁵Mn and ⁵⁴Mn removed in early cuttings (14) produced only minor changes in the L values of the 2nd and 3rd harvest. Results were analyzed according to a split-plot design; factor A was the fertilizer treatment for each soil and factor B was harvests. The variances for the combined experiment were not homogeneous and a logarithmic transformation of all the data was necessary for the analysis. Comparisons between means of different fertilizer treatments were done with the Tukey test, the same test was used to study the effect of harvest upon L values and Mn uptake. Critical values for these tests are not shown in the tables since they would only apply to the transformed data which were not included.

The L values increased significantly from the first to the second

			Harvest		······································	Harvest	
Soil	Ma	1	2	3	1	2	3
No.	added		L-values]	Mn uptake¶	
	ppm		mg/100g			µg/pot	
1	0	1.65a	2.67 Ъ	2.64 Ъ	71.7ab	67.9a	97.6 Ъ
	20	3.54a	3.98ab	4.70 [°] Ъc	126ab	104 a	153 [°] ь
2	0	1.46a	2.12 Ъ	2.77 c	158a	219a	323 Ъ
	20	2.21a	3.14 [°] b	3,37 Ъ	173a	200a	248a
ર	0	0.883a	1.11 в	1.37 Ъ	173a	192 a	289 Ъ
2	20	1.57 a	2.17 ^{**} b	2.77 ^{**} c	184 a	257a	409 [†] ъ
4	0	1.59a	1.78a	1.71a	40.8ab	39.0a	51.2 Ъ
	20	2.43â	3.51 [°] b	2.61âb	48.8a	52.1a	60.0a
5	0	0.227a	0.360 Ъ	0.377 Ъ	36.0a	43.3a	64.1 Ъ
2	20	1.53a**	2.21 ^{**} b	** 1.92ab	** 113a	** 119a	** 188a
6	0	0.350a	0.407ab	0.610 c	103a	96.7a	180 Ъ +
	20	1.32â	1.50â	1.63â	170â	157 a î	245'Ъ
7	0	5.05a	7.23 Ъ	8.36 b	236a	479 Ъ	774 c
	20	6.99a	7.93ab	9.15 Ъ	251a	388 Ъ	769 c
8	0	8.07a	9.74ab	11.8 Ъ	187a	365 Ъ	641 c
•	20	9.26a	11.9 Ъ	14.3 Ъ	211a	269a	633 Ъ
9	0	7.15a	7.54ab	11.3 c	308a	551 b	1216 c
,	20	7.90a	8.93ab	10.6 Ъ	354a	614 Ъ	1163 c
10	0	2.69a	3.37 Ъ	4.21 Ъ	228a	429 Ъ	722 с
	20	3.61a	4.64 [°] ъ	5.24 Ъ	216a	440 Ъ	777 с
11	0	1.96a	3.20 Ъ	3.78 Ъ	80.6a	98.2a	194 Ъ
	44	2.60a	4.02 [†] Ъ	4.04 Ъ	78.4a	132 [†] b	153 b
12	0	0.510a	0.723 Ъ	0.887 Ъ	205a	217a	309 Ъ
-	20].58a**	1.97ab	2.37 [*] b	317a	306a	493 ^{**}

Table 1. Manganese labile pool (L-values) and Mn uptake by plants.

,*,** Difference between means of fertilizer treatments significant at the 10%, 5% and 1% level, respectively, by Tukey test.

S Any two means with the same letter in the same row do not differ significantly from each other (P<.05) by Tukey test.</p>

1 Each value, average of three replicates.

harvest in most cases (Table 1). This may be due to lack of isotopic equilibrium (14, 8, 9) and/or to increases in the size of the root systems from one harvest to the next. The fact that the L values tend to stabilize, in most cases, from the 2nd to the 3rd harvest gives some basis to either explanation. Results for Mn uptake show the opposite trend. Except for the most fertile soils (No. 7, 8, 9 and 10), there were no significant increases in Mn uptake between the 1st and 2nd harvests. Between the 2nd and 3rd, however, most soils showed a significant increase in Mn uptake, probably due to the N and K fertilization just before the 2nd harvest. Although not shown in the tables, dry matter almost doubled from the 2nd to the 3rd harvest while Mn concentration dropped in most cases due to a dilution effect, in this same period. The fact that the Mn uptake increased between the last two harvests while the L values did not is in good agreement with the theoretical considerations proposed by other authors (6, 9). According to these authors, enviromental changes affecting growth but not the quantities of available nutrient should not affect the L values.

The study of the residual effect of the Mn applied in a previous experiment (Part II) using the L values results can be explained in the following way: in the unfertilized soils, the relative proportion of ⁵⁴Mn to ⁵⁵Mn uptake by the plants should favor the uptake of more ⁵⁴Mn, particularly in the Mn deficient soils, hence yielding low L values. In the fertilized soils, the proportion of ⁵⁴Mn in the plants should be lower due to a greater isotopic dilution, thus giving higher L values. It is reasonable to expect that these changes in the relative uptake of the two Mn forms is going to be significantly larger in the soils deficient in Mn that were fertilized, if this added Mn was still in

relatively available forms. Six Mn deficient soils showed significant differences for all harvests between the L values of the unfertilized and fertilized pots (Table 1). Considering that each pot sustained seven sudangrass plants it can be concluded that the applied Mn had a good residual effect. Similar results were found by other researchers (16). The L values of soils 2 and 11 were significantly different in the first two harvests, in spite of both being Mn deficient (Part II), although this significance was lost in the third harvest. No explanation can be offered for the significant differences in L values of soils 7 and 10 since both have high quantities of extractable Mn (Part II).

In order to successfully use the L value concept with this particular approach, significant differences in L values between fertilized and unfertilized soils should relate closely to significant differences in Mn uptake. Results for individual harvests (Table 1) show this relationship to be reasonably good. In evaluating these results it must be considered that with a high number of plants/pot some nutritional unbalances may have occurred even though no visual symptoms were present. It is probable that this was the reason for a lack of response in the Mn uptake from soil 2.

The average L values and Mn uptake data for the three harvests are shown in Table 2. Results for the isotopically exchangeable Mn (E value) are also shown in this table. Lopez and Graham (11, 12) used this technique to measure the Mn E values of several soils employing DTPA as the equilibrating solution. Prior studies (Parts I and II, 15) showed 0.1N H_3PO_4 to correlate better than DTPA with plant uptake; therefore, this acid was used as the equilibrating solution in this

Soil No.	Mn added	Average [§] L-values	Average§ Mn uptake	E-values	Radio- activity in solution	E-values/ total Mn	L-values/ total Mn_
	ppm	mg/100g	vg/pot	mg/100g	X	X	X
1	0	2.32	79.1	5.30	81.4	26.4	11.5
	20	4.08**	128	6.85 ^^	7.2		
2	0	2.11	233	4.91	93.1	39.0	16.7
-	20	2.91**	207	6.71**	93.5		
З	0	1.12	218	4.75	73.5	14.4	3.4
5	20	2.17**	284	6.68**	73.7		
4	0	1.69	43.7	4.88	57.0	13.8	4.8
-	20	2.85**	53.6	7.57**	59.0		
Ę	0	0.321	47.8	0.941	97.5	6.9	2.4
5	20	1.89**	140**	3.17**	98.6		
6	0	0.456	127	1.75	77.6	11.6	3.0
Ū	20	1.49**	191**	4.42**	76.9		
7	0	6.88	496	40.0	62.2	96 .9	16.7
•	20	8.02	470	41.8	61.9		
8	0	9.87	398	47.7	53.8	72.8	15.1
Ū	20	11.8	371	49.8*	53.7		
Q	0	8.66	692	45.6	57.4	81.7	15.5
,	20	9.15	710	46.8 [†]	57.3		
10	0	3.42	459	21.0	56.5	50.8	8.3
10	20	4.49*	478	23.0	56.7		
11	0	2.98	124	25.4	12.8	81.9	9.6
**	20	3.55 [†]	121	35.5*	12.5		
12	0	0.707	244	2.87	59.2	29.8	7.3
**	20	1.97	372**	6.72**	59.5		

Table 2. Effect of soil type and residual Mn fertilization upon measured parameters.

+,*,** Differences between means of fertilizer treatments significant at the 10%, 5% and 1% level, respectively, by L.S.D. test.
5 Average of three harvests.

study. Except for soils 8 and 9, there is good agreement between L and E values in their significant response to the residual effect of the Mn fertilizer and also with Mn uptake (Table 2). In this table, the column indicating the radioactivity remaining in solution shows the extent of the isotopic dilution of the tracer with the Mn in solution and in the solid phase in the determination of the E value with 0.1N H₃PO₄. Multiplying these results by their corresponding E values will give the actual quantities of Mn extracted. In two of the sandy soils (No. 2 and 5) almost all the labile pool was in solution. The opposite is true for the organic soil (No. 11). This is the only soil where the E value seems to have overestimated the Mn labile pool. With 310 ppm of total Mn (Part I), the 0.1N H_3PO_4 at equilibrium extracted only 32.5 ppm of Mn (soil basis). The isotopic dilution indicates, however, that the equilibrium was established with 82% of the total Mn, or 254 ppm of Mn (E value). If this were true, Mn availability in organic soils should be adequate when, in fact, the opposite is true (17). Therefore, for this particular soil, the L value offers a more realistic result in terms of Mn availability to plants, than the E value as measured by 0.1N H_3PO_4 . When evaluating the L and E value results, it should be kept in mind that the E value determination was done in samples taken after the soybean harvest (Part II) but prior to the sowing of the sudangrass. This results, therefore, give an indication of what the residual Mn was after the first crop. The L values, instead, give an instantaneous picture of the equilibrium situation in the soil from harvest to harvest.

Although L and E values are conceptually equivalent (10), E values were much higher than L values (Table 2). This is because both

isotopic exchanges took place in two completely different environments, one was the soil solution and the other the $0.1N H_3PO_4$ solution. By giving the L and E values as a percentage of total Mn in the unfertilized soils (Table 2), the relative strength of the soil solution-plant system and the $0.1N H_3PO_4$ system can be effectively compared. Results for the E values as a percentage of total Mn clearly show the big differences that exist among soils in the type of Mn compounds present.

The correlation coefficients of E and L values with sudangrass Mn uptake are given in Table 3. Extractable Mn by six other extractants was reported previously (Part II); here only its correlation with plant uptake is reported. Allextractants show an increase in the correlation between both variables in the succesive harvests probably due to a better sampling of the soil volume by the roots.

Codil toot		Harvests		Average	America P ²
Soll test	1	2	3	Harvest	Average R
					z
0.1N HC1	0.457	0.563	0.639	0.608	37.0
DTPA	0.482	0.625	0.715	0.674	45.4
0.1N H ₃ PO ₄	0.641	0.749	0.815	0.794	63.0
1N NH ₄ OAc	0.587	0.713	0.808	0.771	59.4
Steam/NH ₄ OAc	0.564	0.732	0.808	0.773	59.8
1.5M NH4H2PO4	0.416	0.576	0.656	0.615	37.8
E value	0.488	0.675	0.746	0.708	50.1
A value	0.542				
A value		0.616			
A value			0.762		
Avge. A value				0.703	49.4

Table 3. Simple correlation coefficients between Mn uptake by sudangrass and several soil tests for Mn.**

** All correlation coefficients significant at the 1% level.

The list of the different tests in order of decreasing simple correlation with the Mn uptake for the average of the three harvests is: $H_3PO_4 > steam/NH_4OAc > NH_4OAc > E$ value > A value > DTPA > $NH_4H_2PO_4 >$ HCl.

Inclusion of pH and Ca+Mg/K ratio in the prediction equation of each soil test increased greatly the usefulness of all of them, as shown by the R^2 values in Table 4. In fact, for any soil test, the R^2 delete value indicates that 52.7% of the variation in the uptake data is explained by pH and bases ratio alone. This is a larger percentage than that reported for soybeans (Part II). The R^2 delete for any variable indicates which percentage of the variation would be explained by the remaining variables if that particular variable were deleted from the model. In this context, pH is more important than the soil test in the prediction equation of 0.1N HC1, DTPA, A value and 1.5M $NH_{L}H_{2}PO_{L}$ and more important than bases ratio in all the equations. This last variable contributes to explain between 5 and 13% of the variation in the different equations with the exception of those for 0.1N HCl and 0.1N H_3PO_4 . The lack of significance of this variable in the prediction equation of $0.1N H_3PO_4$ was also reported previously, (Part II).

The relationships among E and L values with other soil tests and soil characteristics are given in Table 5. Both values (E and L) are highly correlated with each other; this indicates that $0.1N H_3PO_4$ can be used as the equilibrating solution for determining E values in mineral soils. Mn oxides, steam/NH₄OAc and 1.5M NH₄H₂PO₄ are the soil characteristic and soil tests that correlate best with both, E and L values. Other interrelationships not included in this table were given

Soll Test Simple Partial X delete wegression pH (X ₁) 0.1N HC1 (X 0.608 0.635** 52.7 $1427 + 3.62$ pH (X ₁) -0.563 -0.743** 52.7 $1427 + 3.62$ bases ratio (X ₂) -0.334 -0.270* 69.5 $1427 + 3.62$ bH (X ₁) -0.563 -0.537** 59.5 $1410 + 10.9$ bases ratio (X ₂) -0.334 -0.537** 59.5 $1410 + 10.9$ bases ratio (X ₂) -0.334 -0.537** 59.5 $1410 + 10.9$ bases ratio (X ₂) -0.334 -0.537** 59.5 $1410 + 10.9$ bases ratio (X ₂) -0.334 -0.537** 59.5 $1410 + 10.9$ bases ratio (X ₂) -0.334 -0.645*** 52.7 $Y = 1410 + 10.9$ bases ratio (X ₂) -0.334 -0.240*** 52.7 $Y = 1427 + 5.94$ bases ratio (X ₂) -0.334 -0.642*** 52.7 $Y = 1427 + 5.94$ bases ratio (X ₂) -0.334 -0.496*** 70.5		Correlation	coefficients	-2		ی 2
\mathbf{x} x	Soll Test	Simple	Partial	k delete	kegression equations	×
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				*		~
pH (\mathbf{X}_1)a-0.563-0.743**37.0 $\mathbf{Y} = 1427 + 3.62$ Bases ratio (\mathbf{X}_2)0.6740.626**52.7 $\mathbf{Y} = 1981 + 18.0$ pH (\mathbf{X}_1)0.1N H ₃ PO ₄ (\mathbf{X}_c)0.6740.626**52.7 $\mathbf{Y} = 1981 + 18.0$ Bases ratio (\mathbf{X}_2)0.334-0.563-0.645**52.7 $\mathbf{Y} = 1981 + 18.0$ Bases ratio (\mathbf{X}_2)0.334-0.563-0.645**52.7 $\mathbf{Y} = 1410 + 10.9$ pH (\mathbf{X}_1)0.1N H ₄ PO ₄ (\mathbf{X}_c)0.7730.729**52.7 $\mathbf{Y} = 1410 + 10.9$ Bases ratio (\mathbf{X}_2)0.7730.729**52.7 $\mathbf{Y} = 1410 + 10.9$ pH (\mathbf{X}_1)0.7730.729**52.7 $\mathbf{Y} = 1410 + 10.9$ PH (\mathbf{X}_1)0.7730.729**52.7 $\mathbf{Y} = 1427 + 5.94$ Bases ratio (\mathbf{X}_2)0.7730.729**52.7 $\mathbf{Y} = 1427 + 5.94$ PH (\mathbf{X}_1)0.7710.701**52.7 $\mathbf{Y} = 1427 + 5.94$ PH (\mathbf{X}_1)0.7730.729**52.7 $\mathbf{Y} = 1427 + 5.94$ Bases ratio (\mathbf{X}_2)0.7730.701**52.7 $\mathbf{Y} = 1427 + 5.94$ PH (\mathbf{X}_1)0.6628**52.7 $\mathbf{Y} = 1427 + 5.94$ Bases ratio (\mathbf{X}_2)0.7710.701**52.7 $\mathbf{Y} = 1427 + 5.94$ Bases ratio (\mathbf{X}_2)0.7710.701**52.7 $\mathbf{Y} = 1427 + 5.94$ Bases ratio (\mathbf{X}_2)0.7710.701**52.7 $\mathbf{Y} = 1427 + 5.94$ Bases ratio (\mathbf{X}_2)0.6150.621**60.7 $\mathbf{Y} = 1427 + 5.10$ <td>IN HCI (X)</td> <td>0.608</td> <td>0.635**</td> <td>52.7</td> <td></td> <td></td>	IN HCI (X)	0.608	0.635**	52.7		
Bases ratio (χ_2) -0.334 -0.270* 69.5 pH $(\chi_1)^b$ -0.563 -0.674 0.626** 52.7 pH $(\chi_1)^b$ -0.563 -0.645** 50.7 Y = 1981 + 18.03 Bases ratio (χ_2) -0.334 -0.537** 59.5 Y = 1410 + 10.93 pH $(\chi_1)^a$ -0.334 -0.794 0.820** 52.7 Y = 1410 + 10.93 pH $(\chi_1)^a$ -0.334 -0.040 84.4 55.1 Y = 1427 + 5.94. pH $(\chi_1)^a$ -0.563 -0.642** 65.2 Y = 1427 + 5.94. pH $(\chi_1)^a$ -0.563 -0.642** 62.2 Y = 1427 + 5.94. Bases ratio (χ_2) -0.334 -0.496** 70.5 IN NH,OAC (χ_2) -0.334 -0.496** 70.5 PH $(\chi_1)^a$ -0.563 -0.642** 62.2 Y = 1418 + 28.4. Bases ratio (χ_2) -0.334 -0.496** 70.5 IN NH,OAC (χ_2) -0.334 -0.621** 60.9 Y = 1418 + 28.4. pH $(\chi_1)^a$ -0.563 -0.621** 60.9 Y = 1418 + 28.4. Pases ratio (χ_2) -0.334 -0.621** 60.7 Y = 1674 + 3.19. pH $(\chi_1)^a$ -0.563 -0.713** 50.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.334 -0.621** 60.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.334 -0.621** 60.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.334 -0.621** 60.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.334 -0.621** 60.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 50.2 Y = 1674 + 3.19. Pases ratio (χ_2) -0.334 -0.620** 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.334 -0.620** 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 50.2 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 50.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 50.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 50.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.728* 70.7 Y = 1674 + 3.19. Pases ratio (χ_2) -0.563 -0.718** 70.7 Y = 1674 + 3.19.7 Y = 160.7 Y = 160.7 Y = 160.7 Y = 160.7	I (X,) ^a	-0.563	-0.743**	37.0	$Y = 1427 + 3.62X_{2} - 249X_{3} - 0.875X_{3}$	71.8**
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	x_2 ises ratio (x_2)	-0.334	-0.270*	69.5	9 T 8	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	TPA (X,)	0.674	0.626**	52.7		
Bases ^t ratio (x_2) -0.334 -0.537** 59.5 0.1N H ₃ PO ₄ (x_1) 0.794 0.820** 52.7 PH (x_1) 84.4 Bases ratio (x_2) -0.334 -0.040 84.4 Steam/NH ₄ OAc (x_d) 0.773 0.729** 52.7 PH (x_1) 9.0.773 0.729** 52.7 PH (x_1) -0.334 -0.496** 70.5 Bases ratio (x_2) -0.334 -0.496** 70.5 IN NH ₄ OAc (x_d) 0.771 0.701** 52.7 PH (x_1) -0.334 -0.496** 70.1 IN NH ₄ OAc (x_d) 0.771 0.701** 52.7 PH (x_1) -0.563 -0.642** 60.9 PH (x_1) 9.771 0.701** 52.7 PH (x_1) -0.334 -0.496** 70.1 I.5M NH ₄ H ₂ PO ₄ (x_f) 0.615 0.623** 60.7 PH (x_1) 9.0.713** 70.1 I.5M NH ₄ H ₂ PO ₄ (x_f) 0.615 0.628** 52.7 PH (x_1) 9.0.703 0.700** 52.7 PH (x_1) 9.1791 + 5.107 PH (x_1) 9.0.703 0.700** 52.7 PH (x_1) 9.0.703 0.700** 52.7 PH (x_1) 9.0.563 -0.718** 50.2 PH (x_1) 9.0.703 0.700** 52.7 PH (x_1) 9.1674 + 3.197 Pases ratio (x_2) -0.334 -0.420** 70.7	H (X,) ^D	-0.563	-0.645**	50.7	$Y = 1981 + 18.0X_{L} - 250X_{1} - 2.06X_{2}$	72.6**
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$xes^{T}ratio(x_{2})$	-0.334	-0.537**	59.5	7 7 0	
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	(X) (X)	0.794	0.820**	52.7		
Bases ratio (x_2) -0.334 -0.040 84.4 Steam/NH ₄ OAc (x_d) 0.773 0.729** 52.7 PH (x_1) -0.563 -0.642** 62.2 Y = 1427 + 5.94. Bases ratio (x_2) -0.334 -0.496** 70.5 IN NH ₄ OAc (x_e) 0.771 0.701** 52.7 PH (x_1) -0.563 -0.621** 60.9 Y = 1418 + 28.4. Bases ratio (x_2) -0.334 -0.443** 70.1 I.5M NH ₄ H ₂ PO ₄ (x_f) 0.615 0.628** 52.7 PH (x_1) -0.334 -0.713** 41.8 Y = 1791 + 5.10. Bases ratio (x_2) -0.334 -0.713** 52.7 PH (x_1) -0.563 -0.713** 52.7 PH (x_1) -0.334 -0.514** 60.7 Bases ratio (x_2) -0.334 -0.713** 41.8 Y = 1791 + 5.10. Bases ratio (x_2) -0.334 -0.713** 52.7 A-values (Avge.) (x_g) 0.703 0.700** 52.7 PH (x_1) Bases ratio (x_2) -0.334 -0.621** 60.7 Bases ratio (x_2) -0.334 -0.621** 60.7 PH (x_1) -0.334 -0.713** 41.8 Y = 1791 + 5.10.7 Pases ratio (x_2) -0.334 -0.713** 41.8 Y = 1791 + 5.10.7 Bases ratio (x_2) -0.334 -0.713** 70.1	I (X,) 4 c	-0.563	-0.745**	65.1	$Y = 1410 + 10.9X_{0} - 194X_{1}$	84.5**
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$xes^{T}ratio(X_{2})$	-0.334	-0.040	84.4	T C	
pH $(x_1)^4$ a -0.563 -0.642** 62.2 Y = 1427 + 5.94; Bases ratio (x_2) -0.334 -0.496** 70.5 -1418 + 28.4; pH (x_1) 0.771 0.701** 52.7 Y = 1418 + 28.4; pH (x_1) -0.563 -0.642** 60.9 Y = 1418 + 28.4; Bases ratio (x_2) -0.334 -0.443** 70.1 -0.615 0.628** 52.7 0.1 1.5M NH ₄ H ₂ PO ₄ (x_f) 0.615 0.628** 52.7 0.1 -0.513** 41.8 Y = 1791 + 5.103 pH $(x_1)^4$ -0.563 -0.713** 41.8 Y = 1791 + 5.103 bases ratio (x_2) -0.334 -0.563 -0.713** 52.7 0.521** 60.7 Bases ratio (x_2) -0.334 -0.521** 60.7 Y = 1674 + 3.193 pH (x_1) -0.334 -0.563 -0.718** 52.7 Y = 1674 + 3.193 pH (x_1) -0.334 -0.620** 70.7 Y = 1674 + 3.193	ceam/NH,OAc (X,)	0.773	0.729**	52.7		
Bases ratio (X_2) -0.334 -0.496** 70.5 IN NH ₄ OAc (X_2) 0.771 0.701** 52.7 pH (X_1) -0.563 -0.621** 60.9 Y = 1418 + 28.43 Bases ratio (X_2) -0.334 -0.443** 70.1 1.5M NH ₄ H ₂ PO ₄ (X_F) 0.615 0.628** 52.7 pH (X_1) -0.563 -0.713** 41.8 Y = 1791 + 5.103 pH (X_1) -0.334 -0.521** 60.7 Bases ratio (X_2) -0.334 -0.521** 60.7 A-values (Avge.) (X_g) 0.703 0.700** 52.7 pH (X_1) -0.334 -0.511** 60.7 Bases ratio (X_2) -0.334 -0.521** 60.7 h values (Avge.) (X_g) 0.703 0.700** 52.7 pH (X_1) -0.334 -0.503 -0.718** 50.2 pH (X_1) -0.334 -0.6420** 70.7 PH (X_1) -0.334 -0.6420** 70.7 PH (X_1) -0.334 -0.6420** 70.7 PH (X_2) -0.420** 70.7 PH (X_2) -0.334 -0.6420** 70.7	I (X,) ⁴ ^d	-0.563	-0.642**	62.2	$Y = 1427 + 5.94X_3 - 180X_1 - 1.26X_3$	77.8**
IN NH ₄ OAC (X ^a) 0.771 0.701** 52.7 PH (X ₁) $= 0.563 = -0.621** 50.9$ Y = 1418 + 28.43 Bases ratio (X ₂) $= -0.334 = -0.443** 70.1$ 1.5M NH ₄ H ₂ PO ₄ (X _F) 0.615 0.628** 52.7 PH (X ₁) $= -0.563 = -0.713** 41.8$ Y = 1791 + 5.10 Bases ratio (X ₂) $= -0.334 = -0.521** 60.7$ A-values (Avge.) (X _g) 0.703 0.700** 52.7 PH (X ₁) $= -0.563 = -0.718** 50.2$ Y = 1674 + 3.19 Bases ratio (X ₂) $= -0.334 = -0.420** 70.7$	$xes^{T}ratio(X_{2})$	-0.334	-0.496**	70.5	7 T D	
pH (X_1^4) = 0.563 -0.621** 60.9 Y = 1418 + 28.43 Bases ratio (X_2) -0.334 -0.443** 70.1 = 1418 + 28.43 I.5M NH ₄ H ₂ PO ₄ (X_F) 0.615 0.628** 52.7 = 1791 + 5.103 pH (X_1) = -0.563 -0.713** 41.8 Y = 1791 + 5.103 Bases ratio (X_2) -0.334 -0.521** 60.7 = 0.713** 50.2 Y = 1674 + 3.193 pH (X_1) = -0.563 -0.718** 50.2 Y = 1674 + 3.193 Bases ratio (X_2) -0.334 -0.622** 50.2 Y = 1674 + 3.193 Bases ratio (X_2) -0.334 -0.420** 70.7 = 1674 + 3.193	NH, OAc (X_)	0.771	0.701**	52.7		
Bases ¹ ratio (X_2) -0.334 -0.443** 70.1 1.5M NH ₄ H ₂ PO ₄ (X_f) 0.615 0.628** 52.7 pH (X_1) -0.563 -0.713** 41.8 Y = 1791 + 5.10 Bases ratio (X_2) -0.334 -0.521** 60.7 A-values (Avge.) (X_g) 0.703 0.700** 52.7 pH (X_1) -0.334 -0.663 -0.718** 50.2 Y = 1674 + 3.19 Bases ratio (X_2) -0.334 -0.420** 70.7	I (X,) e	-0.563	-0.621**	60.9	$Y = 1418 + 28.4X_{2} - 179X_{1} - 1.16X_{3}$	76.0**
1.5M NH ₄ H ₂ PO ₄ ($\mathbf{X}_{\rm F}$) 0.615 0.628** 52.7 pH ($\mathbf{X}_{\rm I}$) ⁴ - 0.563 -0.713** 41.8 Y = 1791 + 5.103 Bases ratio ($\mathbf{X}_{\rm Z}$) -0.334 -0.521** 60.7 A-values (Avge.) ($\mathbf{X}_{\rm S}$) 0.703 0.700** 52.7 pH ($\mathbf{X}_{\rm I}$) 0.703 0.700** 52.7 Y = 1674 + 3.193 Bases ratio ($\mathbf{X}_{\rm Z}$) -0.334 -0.420** 70.7	$ses^{t}ratio(X_{2})$	-0.334	-0-443**	70.1	7 T D	
pH $(x_1)^4 - 4 = 1$ Bases ratio (x_2) -0.563 -0.713** 41.8 Y = 1791 + 5.103 A-values (Avge.) (x_2) -0.334 -0.521** 60.7 A-values (Avge.) (x_3) 0.703 0.700** 52.7 pH (x_1) -0.563 -0.718** 50.2 Y = 1674 + 3.193 Bases ratio (x_2) -0.334 -0.420** 70.7	SM NH, H, PO, (X,)	0.615	0.628**	52.7		
Bases ^t ratio (X ₂) -0.334 -0.521** 60.7 A-values (Avge.) (X ₂) 0.703 0.700** 52.7 pH (X ₁) g -0.563 -0.718** 50.2 Y = 1674 + 3.19 Bases ratio (X ₂) -0.334 -0.420** 70.7	I (X,) ⁴ ² ⁴ ¹	-0.563	-0.713**	41.8	$Y = 1791 + 5.10X_{e} - 233X_{1} - 1.50X_{2}$	71.4**
A-values (Avge.) (X) 0.703 0.700** 52.7 pH (X ₁) -0.563 -0.718** 50.2 Y = 1674 + 3.19 Bases ratio (X ₂) -0.334 -0.420** 70.7	x_2 ises ratio (x_2)	-0.334	-0.521**	60.7	7 7 7	
pH (X ₁) ⁸ -0.563 -0.718** 50.2 Y = 1674 + 3.19 Bases ratio (X ₂) -0.334 -0.420** 70.7	-values (Avge.) (X_)	0.703	0.700**	52.7		
Bases ^t ratio (X ₂) -0.334 -0.420** 70.7	I (X,) ⁸	-0.563	-0.718**	50.2	$Y = 1674 + 3.19X_{2} - 219X_{1} - 1.10X_{3}$	75.9**
	x_2 ises ratio (X ₂)	-0.334	-0.420**	70.7	ч I	
E-values (X_) 0.708 0.685** 52.7	-values (X_)	0.708	0.685**	52.7		
pH (X_1) ^{II} -0.563 -0.665** 54.9 Y = 1585 + 0.56	I (X,) I	-0.563	-0.665**	54.9	$Y = 1585 + 0.562X_{h} - 199X_{h} - 1.51X_{h}$	74.9**
Bases ⁺ ratio (X ₇) -0.334 -0.550** 64.0	$xses^{-}ratio(X_{\gamma})$	-0.334	-0.550**	64.0	7 T II	

** Significant at the 1% level.

Soil tests and soil properties	Average L value	E value
0.1N HC1	0.891**	0.716**
DTPA	0.880**	0.882**
0.1N H ₃ PO ₄	0.894**	0.797**
1N NH ₄ OAc	0.864**	0.840**
Steam/NH ₄ OAc	0.934**	0.973**
1.5M NH4H2PO4	0.938**	0.953**
pH	-0.152	-0.293**
Organic C	-0.104	0.024
CaCO ₃	-0.387**	-0.402**
Bases ratio	-0.356**	-0.167
Chelated Mn	0.895**	0.902**
Mn oxides	0.939**	0.944**
Total Mn	0.860**	0.862**
E value	0.922**	

Table 5. Simple correlation coefficients among several soil tests and soil characteristics.

** Significant at the 1% level.

previously (Part II).

The determination of the critical L and E values below which response to Mn fertilization can be expected were obtained by the method proposed by Cate and Nelson (1) and are shown in Figures 1A and 1B. These critical values are about 3.2 mg Mn/100 g for the L value and 7.0 mg/100 g for the E value determined with $0.1N H_3PO_4$. Lack of response in the Mn uptake from soil 2 misplaces it, although it has a low L value. As said before, this lack of response may have been caused by some factor other than Mn, particularly since soybeans growing in this soil showed a significant increase in Mn uptake upon fertilization




(Part II). Soil 11 is also misplaced due to its lack of response. Here, probably the organic matter transformed the Mn into unavailable forms, since again, soybean responded to Mn fertilization in the prior study. The comments mado above apply to the E value figure of soil 2. Results for the organic soil (No. 11) were certainly overestimated by this procedure, and it would not be of application to organic soils when using $0.1N H_3PO_4$ as the equilibrating solution.

The critical level for $0.1N H_3PO_4$ extractable Mm as determined by the Cate and Nelson procedure was 14 ppm of Mn (soil basis). This was the best predictor of Mn uptake by sudangrass whether used alone or with the inclusion of pH in its prediction equation.

Summary and Conclusions

To study the residual effect of Mn fertilization, the soils with 0 and 20 ppm of applied Mn (as $MnSO_4$) that had been previously cropped with soybeans were sown to sudangrass. Prior to the sowing, soil samples were taken from each pot and carrier free ⁵⁴Mn was mixed with the remaining soil. Isotopically exchangeable Mn (L value) was calculated by measuring the ⁵⁴Mn in the plants at each of 3 harvests. E values were obtained by equilibrating soil samples with 0.1N H₃PO₄ containing a known amount of ⁵⁴Mn. Soil extractable Mn by six extractants was reported in Part II. The results were used in the correlation with Mn uptake by the sudangrass together with the L and E values.

Results can be summarized as follows:

1) It was shown that Mn applied as MnSO₄ has a good residual effect, since three successive harvests of sudangrass differed significantly in their Mn uptake between fertilized and unfertilized pots. This happened in six out of eight soils known to be deficient in this nutrient.

2) The L and E values were useful parameters in predicting Mn uptake response due to the residual effect of Mn fertilization. The exception was for E value with the organic soil, in which case the Mn labile pool was greatly overestimated.

3) The listing of soil tests in decreasing order of correlation with the average Mn uptake (3 harvests) by sudangrass was: H_3PO_4 > steam/NH₄OAc > NH₄OAc > E value > A value > DTPA > NH₄H₂PO₄ > HC1[~]

4) Inclusion of pH and bases ratio in the prediction equation of

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the soil tests improved markedly the R^2 values of these equations. The prediction equation of 0.1N H_3PO_4 accounted for 84.5% of the variation in the Mn uptake data.

5) The critical levels of Mn in soil as determined by L value, E value and 0.1N H_3PO_4 were 32, 70 and 14 ppm of Mn respectively.

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APPENDIX

			Yield		1	in Content	
Soil	Mn	1	Replicatio	n	I	Replication	n
No.	added	1	2	3	1	2	3
			g/pot			ppm	من منہ برن ک رہے ہے ا
1	0	4.90	4.68	4.48	24.3	25.5	25.6
	10	4.68	4.92	4.70	31.5	31.6	34.8
	20	5.00	4.15	5.28	35.1	29.1	27.2
2	0	5.60	5.00	4.12	26.4	20.9	21.7
	10	4.85	4.65	5.05	25.7	36.4	27.3
	20	5.00	4.98	7.35	41.6	27.7	40.4
3	0	7.10	5.90	6.45	14.8	12.7	9.83
	10	8.80	5.25	5.35	16.8	16.6	17.3
	20	8.90	7.50	4.70	19.2	11.7	16.1
4	0	6.35	6.70	6.75	12.3	11.2	11.7
	10	6.62	8.00	8.15	12.4	14.0	11.6
	20	7.90	6.78	7.42	14.3	14.2	13.5
5	0	0.620	0.751	0.583	11.6	12.7	9.76
	10	1.80	1.55	1.25	33.5	27.3	26.8
	20	1.22	1.48	1.50	38.4	42.6	37.8
6	0	6.45	4.80	5.35	9.47	11.4	10.6
	10	7.65	4.73	7.55	12.1	15.9	13.9
	20	5.80	5.28	6.50	25.3	14.3	18.6
7	0	6.40	6.08	6.25	58.0	63.4	72 .9
	10	7.50	6.25	6.62	57.5	59.2	58.5
	20	7.35	7.40	6.15	60.3	63.1	66.9
8	0	7.60	4.70	5.60	42.7	42.8	34.3
	10	7.05	6.52	7.45	45.1	43.9	42.4
	20	7.00	7.00	7.50	50.0	51.8	39.8
9	0	9.27	8.88	9.90	39.9	40.2	36.6
	10	9.75	7.70	7.40	42.8	49.2	51.6
	20	10.3	7.72	8.75	42.1	45.6	48.4
10	0	8.38	8.35	8.80	19.9	37.0	27.1
	10	10.9	4.70	7.80	29.9	23.8	32.8
	20	8.10	6.95	8.68	25.8	31.9	37.9
11	0	7.20	8.40	5.82	8.08	8.30	9.05
	10	8.32	7.38	6.80	13.5	11.0	10.3
	20	9.60	8.83	7.05	14.3	15.7	14.1
12	0	3.50	3.55	3.70	17.2	23.8	27.2
	10	3.85	3.32	3.58	29.8	31.5	28.7
	20	4.00	3.70	4.10	36.6	44.8	33.9

Table II-1. Soybean yield and Mn content as affected by soil type and Mn fertilizer.

		···	Yield			Mn Content	
Soil	Mn	-	Replicatio	n	_	Replicatio	n
No.	added	1	2	3	1	2	3
			g/pot			ppm	
1	0	2.40	2.60	2.60	23.5	33.2	27.8
	20	2.35	3.12	3.02	42.9	41.8	48.2
2	0	4.08	3.88	3.10	39.2	44.0	46.5
	20	3.25	3.72	2.82	53.5	54.4	50.6
3	0	4.60	4.50	3.10	35.3	55.1	35.3
	20	4.88	4.86	4.60	44.5	33.3	37.7
4	0	2.68	3.75	4.40	10.0	12.7	10.9
	20	4.58	2.95	4.82	10.0	12.5	13.2
5	0	1.82	3.68	2.42	13.8	11.4	16.9
	20	2.55	4.38	1.90	35.7	35.0	49.8
6	0	4.10	3.22	3.52	27.0	27.5	31.4
	20	4.80	3.85	5.05	29.0	40.8	42.2
7	0	2.12	3.00	2.92	92.1	93.7	79.9
	20	2.15	2.82	2.70	93.9	100	99.9
8	0	4.78	3.32	2.70	54.0	46.2	55.5
	20	3.95	3.90	3.15	49.9	70.9	50.3
9	0	3.68	4.10	2.82	90.6	83.7	87.6
	20	4.05	5.22	3.75	85.8	72.0	90. 5
10	0	4.05	3.75	3.52	58.2	72.8	49.5
	20	3.40	4.05	3.55	65.3	57.2	55.0
11	0	3.88	3.65	4.42	30.5	19.8	11.6
	20	4.92	4.85	4.85	11.9	12.6	23.8
12	0	3.57	3.80	3.52	58.2	57.7	53.4
	20	4.55	2.80	4.50	80.6	77.3	81.8

Table III-1.	Sudangrass yield and Mn content as affected by soil type
	and Mn fertilizer (lst harvest).

			Yield			Mn Conten	t
Soil	Mn		Replicatio	n		Replicati	on
No.	added	1	2	3	1	2	3
			g/pot			ppm	
1	0	3.40	3.10	3.35	21.3	21.8	19.0
	20	2.80	3.80	4.25	31.4	29.8	26.4
2	0	4.50	4.65	3.40	52.8	51.2	53.6
	20	2.85	4.15	4.30	49.6	56.3	52.5
3	0	3.65	3.45	3.85	64.5	53.5	44.9
	20	4.10	3.26	4.55	67.6	65.3	61.7
4	0	2.85	6.15	4.00	7.0	8.5	11.2
	20	3.68	2.50	3.88	17.7	17.8	12.0
5	0	1.72	2.60	2.10	18.4	20.1	21.9
	20	2.28	2.35	2.05	56.9	53.3	49.4
6	0	3.30	3.60	4.10	26.9	31.1	21.8
	20	4.00	3.60	4.20	40.6	39.4	39.5
7	0	2.82	3.90	4.10	158	141	108
	20	3.05	3.75	3.78	105	106	119
8	0	5.62	5.38	5.49	71.3	65.2	62.7
	20	4.18	2.52	4.65	77.8	89.2	55.3
9	0	4.50	4.40	4.75	139	130	96.4
	20	3.58	4.68	5.82	111	142	134
10	0	4.60	4.10	4.85	102	95.7	87.9
	20	4.65	4.45	5.05	96.9	86.0	96.1
11	0	6.50	6.40	5.22	17.0	17.9	13.3
	20	4.80	6.65	7.40	25.7	23.3	15.7
12	0	2.15	2.32	2.30	94.6	89.6	104
	20	3.55	2.15	2.20	121	100	124

Table III-2.	Sudangrass yield and Mn content as affected by soil type
	and Mn fertilizer (2nd harvest).

			Yield			Mn Content	t
Soil	Mn		Replicatio	on		Replicatio	on
No.	added	1	2	3	1	2	3
	- <u> </u>		g/pot			ppm	
1	0	6.60	4.60	7.28	18.0	18.7	12.1
	20	5.90	0.72	8.70	29.3	25.5	10.0
2	0	7.30	7.00	7.82	45.8	45.9	39.9
	20	5.92	4.85	7.25	32.6	45.0	45.7
3	0	4.92	6.58	7.95	60.2	46.7	33.2
-	20	6.25	9.28	8.42	76.2	41.8	43.3
4	0	5.00	5.40	9.25	9.0	9.5	6.2
-	20	6.80	3.75	10.9	7.7	12.8	7.3
5	0	3.85	4,50	6,08	12.5	14.5	13.0
•	20	4.58	6.70	5.45	35.6	33.8	31.7
6	0	5.45	6.20	7.98	28.5	30.7	24.3
-	20	6.90	7.25	6.70	36.0	35.6	34.1
7	0	7.12	7.00	7.55	108	114	99.6
	20	5.25	7.42	8.20	134	113	93.3
8	0	7.98	9.52	9.38	59.9	78.8	74.1
	20	6.12	8.50	9.35	93.8	84.3	65.2
9	0	12.3	9.82	9.38	119	125	102
	20	8.30	10.8	10.2	131	109	122
10	0	6.00	8.20	8.18	118	91.3	86.4
	20	8.45	8.70	9.82	96.3	89.7	75.0
11	0	10.3	9.65	9.20	26.8	14.8	17.8
	20	7.58	8.25	7.35	20.7	21.8	16.6
12	0	4.02	5.20	4.72	68.9	62.0	69.4
	20	5.38	4.40	5.78	98.1	95.3	92.2

Table III-3.	Sudangrass yield and Mn content as affected by soil type
	and Mn fertilizer (3rd harvest).

Table III-4. Results of 55Mn and 54Mn analysis of sudangrass samples at each harvest.

So11	Rep.	Mn	1	st Harvest		21	nd Harvest		3г	d Harvest	
No.	No.	added	Mn content	Radio- activity	S f	Mn content	Radio- activity	s f	Mn content	Radio- activity	s f
			μ8	cpm	cpm	р.	cpm	cpm	9n	cpm	cpm
-1	1	0	27.4	205	329090	23.5	115	322596	17.7	76.7	265095
	2	0	31.0	200	324650	19.6	82.4	325891	20.8	54.2	263739
	e	0	28.3	171	329026	18.7	62.4	322596	14.3	53.6	265095
	-1	20	53.9	170	327276	31.5	92.2	323899	35.4	72.1	263739
	2	20	46.1	112	329090	28.1	66.2	322042	33.7	52.0	263739
	e	20	40.1	166	329090	27.7	80.8	323899	24.8	52.9	263739
4	Ч	0	47.5	385	329090	56.0	340	323899	54.8	218	265059
	2	0	49.9	424	327276	50.8	273	322596	58.0	222	260755
	Ś	0	47.3	295	327276	63.3	266	323736	47.2	135	263685
	Ч	20	58.6	273	329026	43.1	167	322042	32.3	110	283617
	2	20	56.4	253	328202	52.1	177	323736	52.7	123	260755
	e	20	44.9	268	328202	63.0	196	322596	48.8	119	265429
Ś	1	0	33.3	411	324650	65.5	682	323736	73.8	436	263685
	7	0	64.4	701	329026	48.2	474	323736	59.9	371	260755
	Ś	0	34.9	506	329026	42.6	381	326595	38.5	294	283617
	Ч	20	44.6	297	329090	62.4	318	323736	80.3	294	283617
	7	20	32.4	241	328202	60.7	308	325891	56.5	178	265429
	ς.	20	37.6	257	327276	60.9	288	322042	59.7	180	265095
ø	Ч	0	12.1	96.9	328202	7.71	48.3	323736	10.6	70.2	283617
	7	0	12.8	74.3	327276				10.6	44.8	265429
	'n	0	10.6	72.8	324650	12.0	74.7	323899	7.0	37.9	259416
	Ч	20	10.7	55.2	327276	18.7	63.8	322596	8.8	27.7	259416
	7	20	11.9	45.6	327276	20.9	49.1	322596	17.0	59.8	283617
	e	20	13.0	61.8	329090	11.4	43.7	323736	9.4	34.1	265095
10	Ч	0	14.6	623	324650	18.5	634	326595	16.3	422	265429
	7	0	14.9	717	329090	20.2	622	326595	19.8	448	263739
	m	0	19.1	1016	324650	23.5	628	326595	16.4	363	263739

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Soil	Rep.	Ma	1,	st Harvest		2r	d Harvest		3г	d Harvest	
No.	No.	added	Min content	Radio- activity	s _f	Mn content	Radio- activity	sf	Mn content	Radio- activity	Sf
			μg	cpm	cpm	81	cpm	cpm	р 18	cpm	cpm
	-	20	1 67	375	320000	54.7	303	376505	5 07	213	259416
) (1	1.24		060670					747	
	2	20	40.3	261	324650	36.7	201	325891	40.3	186	C60C9Z
	ო	20	47.1	301	329026	55.0	223	326595	36.6	144	260755
11	1	0	28.6	776	327276	25.8	596	322042	33.9	422	259416
	7	0	27.4	897	329026	32.1	807	323736	28.1	569	265429
	e	0	31.6		329026	21.8	704	322042	32.1	509	263739
	Ч	20	30.9	292	329090	42.7	315	323899	39.4	277	259416
	7	20	41.1	343	329090	39.95	274	322042	45.5	236	260755
	ო	20	44.3	323	329026	43.6	317	323899	39.2	186	283617
12	Н	0	99.4	223	327276	174	274	326595	136	151	263685
	2	0	111	196	329090	158	200	323899	130	120	265429
	e	0	88.5	235	328202	98.9	167	322042	114	129	263685
		20	98.1	187	328202	102	147	322596	155	162	263685
	7	20	119	178	329090	94.4	131	323736	129	110	265429
	Ś	20	116	162	329026	111	140	323899	108	105	259416
13	Ч	0	62.5	80.5	329090	73.5	84.2	323899	64.6	57.6	259416
	2	0	46.8	63.4	328202	69.9	66.0	325891	98.2	64.4	260755
	e	0	58.6	83.5	329026	70.4	90.5	326595	103	71.5	263685
	Ч	20	52.1	63.8	327276	73.8	76.9	323736	106	72.7	265429
	2	20	85.4	92.0	329026	94.4	74.3	323899	106	63.8	259416
	Ś	20	47.1	59.4	329090	50.9	47.4	325891	98.0	53.0	263685
14	1	0	92.8	137	329090	133	174	322042	160	130	263739
	7	0	87.6	146	328202	132	180	322596	164	151	263739
	ო	0	93.9	138	329026	107	172	322596	127	116	263685
	1	20	88.6	120	329090	111	146	325891	148	119	263685
	2	20	74.6	113	327276	153	184	322042	128	109	259416
	ო	20	95.8	124	329090	135	149	322596	154	124	263739

Table III-4. continued

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So11	Rep.	Æ		st Harvest		5	nd Harvest		3r	d Harvest	
No.	No.	added	Mn content	Radio- activity	sf	Mn content	Radio- activity	s f	Mn content	Radio- activity	sf
			βη	cpm	cpm	81	cpm	cpm	βr	cpm	cpa
15	1	0	58.1	226	324650	100	351	323736	175	376	263685
	7	0	74.2	257	329090	98.9	300	325891	117	238	265095
	m	0	45.9	238	328202	98.3	305	322596	105	221	265429
	Ч	20	71.3	189	329026	111	246	322042	112	187	260755
	7	20	57.3	160	328202	78.7	178	325891	111	161	265095
	e	20	59.6	229	328202	96.2	243	325891	88.3	187	283617
16	1	0	33.9	146	329026	19.6	80.0	323899	30.8	68.1	260755
	7	0	17.4	89.6	328202	21.0	53.0	326595	17.4	45.7	265095
	ო	0	11.2	113	369090	12.5	51.0	325891	23.1	49.2	260755
	Ч	20	13.5	60.4	329090	26.1	55.0	322596	26.2	48.4	263685
	7	20				26.5	71.7	322596	26.3	62.1	265429
	m	20	22.6	95.8	329090	17.4	60.8	322042	20.3	48.4	265095
17	1	0	66.1	2076	329090	86.1	1932	326595	72.5	1035	259416
	2	0	64.6	904	329090	86.1	676	326595	69.5	518	259416
	ო	0	52.4	1392	324650	103	1601	326595	83.3	810	260755
		20	87.6	683	324650	112	697	326595	116	478	263739
	7	20	71.5	675	324650	85.4	452	325891	109	369	260755
	ę	20	86.6	584	324650	103	529	326595	94.3	343	265429

Table III-4. continued

