MANGANESE TOXICITY IN AN ACID SOIL.

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SUMMARY.

The occurrence of manganese toxicity in French bean gown on an acid soil (referred to as the Dagun soil) is reported.

The manganese content of the plants in the field varies with the pH of the soil, reaching 3,000 ppm at pH 4.4 Healthy plants contained between 200 ppm and 1,000 ppm manganese, and values greater than 1,000 ppm may be regarded as indicating manganese toxicity.

The amount of exchangeable manganese in the soil is not a reliable criterion for predicting manganese toxicity, but if the pH is low and the easily reducible manganese high, the soil can be regarded as suspect.

French bean is a good indicator plant for excessive manganese in the soil.

A pot trial indicated that the excessive uptake of manganese by French bean grown on the Dagun soil can be controlled by applying lime to raise the pH to about 5.4.

Some evidence is presented that pineapples grown on the Dagun soil and peanuts grown on certain other soils suffer from manganese toxicity.

INTRODUCTION.

Manganese toxicity in plants grown on strongly acid soils rich in manganese has been reported by various authors. Lohnis (1951) described experiments with French beans (*Phaseolus vulgaris*) and other crops in the Netherlands. Sherman and Fujimoto (1946) found up to 3,800 ppm manganese in affected lettuce plants in Hawaii. Somers and Shive (1942) studied the iron and manganese contents of soybeans and concluded that a relationship existed between the ratio of soluble iron to soluble manganese and the occurrence of injury in the soybeans. Parberry (1943) reported that beans grown in certain soils in New South Wales were affected by excess manganese, and found the effects to be more marked when associated with magnesium deficiency.

OCCURRENCE IN QUEENSLAND.

The main soil type in Queensland which has given rise to manganese toxicity problems occurs in the south-east of the State, near Dagun, which is situated on the edge of the Mary River Valley. It will be referred to in this paper as the Dagun soil. This soil is used mainly for the growing of pineapples and French beans. In work to be described, beans were selected as the indicator crop, but pineapples are also affected by the disorder.

The soil type is developed from a jasper, which occurs in the district interbedded with cherts and shales of Devonian age. Deposits of manganiferous ores occur in various parts associated with the jaspers, and these have been mined for manganese. According to W. C. Burns (unpublished data, 1951), the manganese was originally deposited with the sediments of the enclosing formations in a relatively deep water environment. Compaction and induration resulted in the formation of haematitic coloured shales, together with manganiferous radiolarian jaspers and cherts. Subsequent major strike faulting caused shattering of these rocks, and facilitated the leaching of the manganese minerals, either to fill open fractures in the shales or to cement and replace shattered cherts and jaspers. This resulted in the formation of localised deposits rich in manganese. The manganese remaining in the rocks and passing to the soil after weathering has been of sufficient concentration to cause manganese toxicity problems.

The area receives predominantly summer rainfall, with a moderately dry winter. Gympie, about 10 miles from Dagun, receives an average annual rainfall of 45·43 inches, distributed as follows:—

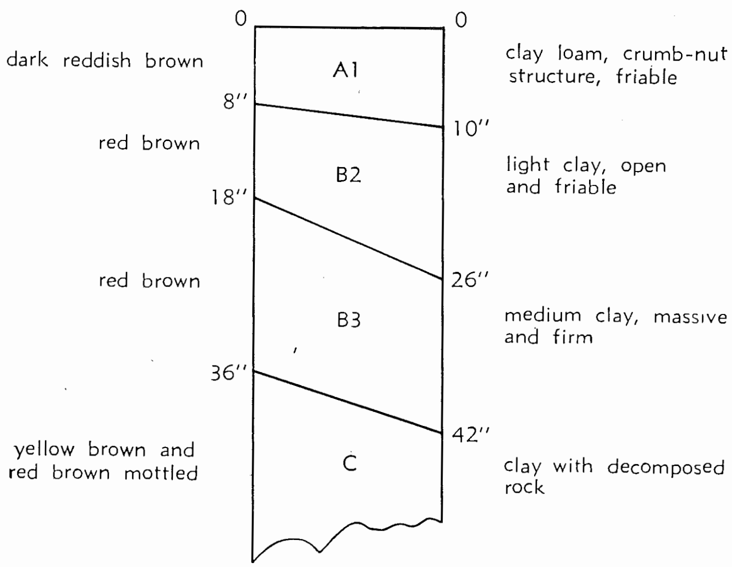
January-March	19·28 in.
April-June	8·94 in.
July-September	5·74 in.
October-December	11·46 in.

The rainfall for Dagun might be assumed to be a little higher but similarly distributed. The low winter rainfall is unreliable, so that irrigation is necessary for a winter crop of beans and is used by most farmers.

In summer, both temperature and humidity are high, while in winter, frosts may be severe. Most of the bean crops, however, are grown at an elevation sufficient to escape serious frost damage.

THE SOIL SERIES.

In the virgin state the soil, which belongs to the great soil group "Kratznosem", is a dark reddish brown clay loam on the surface, fairly high in organic matter, with a good crumb structure. It has been designated the Dagun Series. The profile description of the virgin soil is:—



Steep slopes are used for cultivation. This has been practised for a number of years; consequently in many parts the structure of the surface soil has deteriorated and erosion has reduced the depth of the soil. The organic matter content has also been considerably reduced and aeration is now poor because of these factors.

The greatest change in the properties of the soil as a result of cultural practices has been in its reaction. The pH value (soil to water ratio 1:2·5) of the surface horizon in the virgin soil is approximately 6·0, while that of the cultivated area is now as low as 4·2 in some portions. Part of this increase in acidity is due to cultivation practices and part to the heavy fertilizer applications (mainly sulphate of ammonia) which are used for pineapples.

SYMPTOMS OF MANGANESE TOXICITY.

These are almost identical with those described by Lohnis (1951) and with colour plates illustrated by Wallace (1951). Beans grown on the very acid parts of the area are stunted and show severe marginal and interveinal chlorosis in the leaves. In extreme cases, the leaves are crinkled and exhibit necrotic spotting. Very little flowering then occurs and practically no fruit is set. Less severely affected plants may recover somewhat as they approach mtaurity, but the yield of pods is poor.

PLANT ANALYSIS.

Analysis of unthrifty plants offers some proof that excessive manganese uptake is the cause of the trouble. The plants were digested with perchloric, nitric and sulphuric acids, and the manganese determined colorimetrically after oxidation to permanganate with potassium periodate, using the method of Willard and Greathouse (1917). The colours were read in a Lumetron photoelectric colorimeter using an M515 filter and 1 cm. cells.

Affected plants were found to contain up to 3,000 ppm manganese on a dry-matter basis. Healthy plants, on the other hand, varied between 200 and 1,000 ppm. Some values for manganese in the whole plant, and the soil pH at which the plants were grown, are given in Table 1.

Table 1.

PLANT GROWTH IN RELATION TO SOIL pH AND MANGANESE CONTENT OF PLANT.

Soil pH.	Mn in Plant (ppm).	Plant Growth.
4·4	3000	Very poor
4·5	2400	Poor
4·8	1200	Fair. Some chlorosis
4·9	800	Good
5·0	1100	Fair. Some chlorosis
5·9	260	Good

Fig. 1 illustrates the relationship between manganese in the plant and soil pH, and demonstrates the influence of pH on manganese uptake by beans.

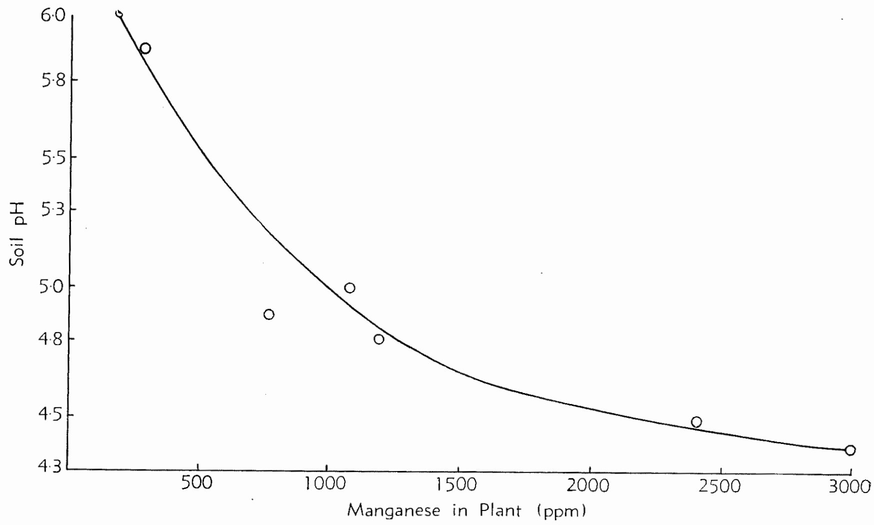


Fig. 1.

Correlation Between Manganese in Plant and Soil pH.

SOIL ANALYSIS.

Manganese in the soil can exist in varying degrees of oxidation, the forms being in dynamic equilibrium with one another. The oxidation-reduction status is affected by several factors, of which pH and organic matter are the most important. The bivalent manganous ion is oxidised by soil organisms to manganic forms of higher valency when the pH is greater than 5·5; the reverse can also occur, the higher oxides being reduced either by biological processes or by reaction with organic matter. Leeper (1947) pointed out that the reduction with organic matter is the more likely at lower pH values, because of the rapid increase in the oxidizing powers of the higher oxides as the pH falls.

The manganous form is usually regarded as being available to the plant, and Piper (1931) maintained that the amount of manganous manganese present in the soil is an indication of likely deficiency in the plant. Leeper (1935, 1947) laid emphasis on the higher oxides, and considered it important to examine the oxidation-reduction state of the manganese. He divided the manganic oxides (the formula for these being empirically written as MnO_2) into highly reactive forms, which could be easily reduced by quinol, and the less active forms which could react with sodium thiosulphate. The remainder of the higher oxides of manganese in the soil is regarded as inert. That portion of the active manganic oxides which can be reduced with quinol he referred to as the "easily reducible manganese".

The manganous form in the soil is usually termed exchangeable manganese, and is determined by extraction with a neutral salt. Ammonium acetate is commonly used, but Heintze (1938) used calcium nitrate, and this method was followed by Lohnis (1951). Leeper (1935), investigating manganese deficiency in soils, preferred to determine the "easily reducible manganese", because some soils could not maintain a supply of the exchangeable form but plants were still healthy when grown on them. He used a 0·2% solution of quinol in normal ammonium acetate as the extractant. Later Jones and Leeper (1951) used a less drastic method of extracting the easily reducible manganese, and obtained a better correlation with the occurrence of manganese deficiency in plants. They treated the soil with 0·05% quinol in 50% alcohol, centrifuged, and then extracted the reduced manganic oxides from the soil with 0·5 M calcium nitrate. Sherman (1942) adapted Leeper's original method and determined water soluble, exchangeable and easily reducible manganese to give an indication of the manganese status of the soil.

Most of these methods have been applied to neutral or alkaline soils as a means of testing for manganese "deficiency", but their usefulness with acid soils as a means of testing for manganese "toxicity" is doubtful.

The problem was approached first with a view to correlating soil pH with plant growth, and next with a view to predicting the uptake of manganese by plants by determination of the exchangeable and the easily reducible manganese. Fig. 1 demonstrates a relationship between plant manganese and soil pH, and Table 2 compares the pH of surface soils taken from various parts of the affected area with the observed growth of beans.

Table 2.

pH OF SURFACE SOIL AND OBSERVED GROWTH OF BEANS.

Soil pH.	Plant Growth.
4·4	Very chlorotic
4·7	Very chlorotic
4·7	Chlorotic
4·9	Very chlorotic
4·9	Fair. Some chlorosis
5·1	Good
5·7	Good. A few plants affected
6·1	Good

Dolomite had been applied on the area from which the pH 5·7 sample was taken, and uneven distribution of the dolomite probably accounts for the few affected plants. These figures indicate that at a pH of greater than 5·0 good growth can be expected. If the pH is less, the plants will probably show symptoms of toxicity.

Exchangeable manganese was determined by extraction with neutral N ammonium acetate for 30 minutes, following the method of Sherman, McHargue and Hodgkiss (1942). Good correlation between pH and exchangeable manganese was obtained. The results are given in Table 3 and represented graphically in Fig. 2.

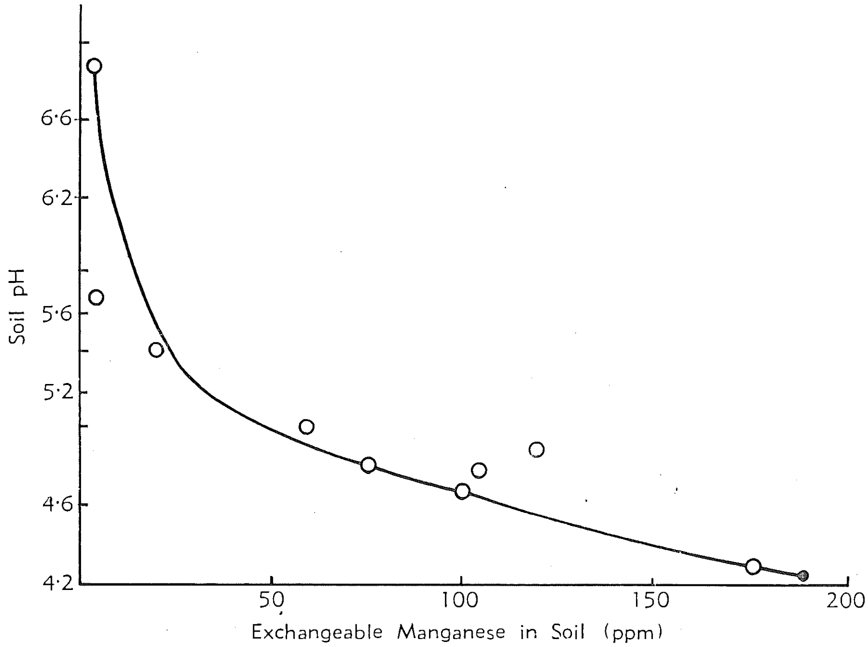


Fig. 2.

Correlation Between Exchangeable Manganese in Soil and pH.

The sharp drop in the amount of exchangeable manganese when the soil pH varies from 4·9 to 5·4 is consistent with the figures given in Table 2.

The easily reducible manganese was determined by extracting the soil with 0·2% quinol in N ammonium acetate solution. Large amounts were extracted from all samples, even when the pH was quite high. The method of Jones and Leeper (1951) was also used for a few samples, but high values were still obtained at different pH levels. The results are given in Table 3.

The inference is that the Dagun soil has a large reserve of active manganese, which can be reduced to the exchangeable form when conditions are favourable. From the ratio of exchangeable to easily reducible manganese it appears that only a relatively small fraction is reduced at any one time. For this soil type the amount of exchangeable manganese indicates to some extent whether or not the plant will take up an excess of this element.

Table 3.

EXCHANGEABLE AND EASILY REDUCIBLE MANGANESE IN DAGUN SOIL.

Soil pH.	Exchangeable Manganese.	Easily Reducible Manganese (0·2% Quinol).	Easily Reducible Manganese (Jones & Leeper).
	ppm	ppm	ppm
4·3	175	2080	
4·4	105	2600	1720
4·5	104	3400	
4·5	74	2550	1620
4·7	100	2180	1470
4·9	120		
5·0	62		
5·4	20	2700	
5·7	2	2750	1680
6·9	2		

Leeper (1947) has shown the easily reducible fraction of the active manganese to be important for assessing the status of soils which are deficient in manganese, but its importance for the Dagun soil with a toxicity problem is doubtful. Areas of the Dagun soil with reaction values of 5·5 or higher contain large amounts of reducible manganese, which does not appear to affect the beans grown on them. It would seem that this fraction of the manganese is not available to the plant.

It is interesting to record here some further analytical data relating to the active manganese content of soils from four other districts. Values for these are given in Table 4.

Table 4.

ACTIVE MANGANESE CONTENT OF VARIOUS FARM SOILS.

District.	Soil pH.	Exchangeable Manganese.	Easily Reducible Manganese.	Comments.
		ppm	ppm	
Brookfield ..	6·3	2	940	
Maryborough 1...	5·7	6	14	
Maryborough 2...	7·5	2	38	
Coolabunia 1. ..	4·3	200	520	Poor peanut growth
Coolabunia 2. ..	4·8	10	1360	Fair peanut growth
Coolabunia 3. ..	5·3	46	450	Good peanut growth
Beaudesert ..	6·0	0·5	80	Responded to applications of Mn

The poor growth of peanut (*Arachis hypogea*) on a soil from Coolabunia is probably due to manganese toxicity. The soil from Brookfield could give rise to toxicity problems should the reaction be allowed to become very acid.

Pot Trial.

To demonstrate the effect of lime on plant growth and on exchangeable manganese of the soil, a pot trial was set up using a sample of Dagun soil with a reaction value of pH 4·2. Lime was added to raise the pH to 5·0 (2 tons/acre) for one treatment, and to 6·0 (4 tons/acre) for the second treatment. It was expected that the pots treated with the lower level of lime would grow plants partly affected by the disorder and with a medium uptake of manganese. Four replications were used, making 12 pots in all. Each pot contained 25 lb. of soil.

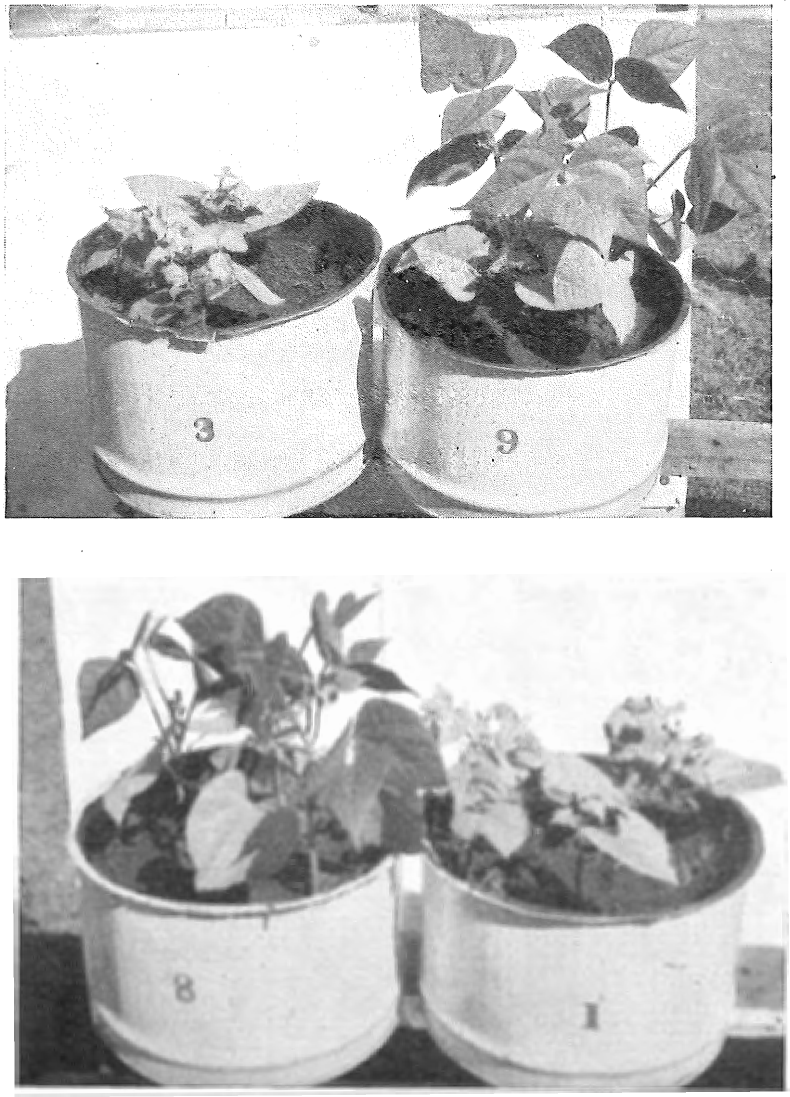


Fig. 3.

Effect of pH on Plant Growth. Pot 3, pH 4.2; Pot 9, pH 5.1; Pot 8, pH 5.9; Pot 1, pH 4.2.

Precipitated chalk was used as the source of lime. It was mixed with the soil, and water added to keep the pots at a little under field capacity. When the soil pH had reached equilibrium (about 10 days) French dwarf bean seed (variety Brown Beauty) was planted. Fertilizer was added at the same rate as that used by most bean farmers in the Dagun district—8 cwt. of 5 : 14 : 2 mixture per acre applied in the rows. Three plants were grown in each pot.

Good growing conditions were experienced, and the plants in the no-treatment plots were showing typical symptoms within 14 days of germination. At this stage, all the plants in the other pots were healthy. Flowering commenced 5½ weeks after germination, but the plants in the treated pots were the only ones to set fruit. At this stage, the control plants were very severely affected. They had small leaves, with the usual characteristics, and were only 4–5 in. high. The plants growing in soil at pH 5·1 were no different in appearance from those at pH 5·9. The photographs illustrating the affected and healthy plants (Fig. 3) were taken when the plants were five weeks old.

Eight weeks after germination all plants were cut off at ground level, and any soil adhering to them brushed off. They were dried in a vacuum oven at 60°C. The soils were sampled at the same time and extracts prepared for analysis within a few days. The analyses carried out are given in Tables 5 and 6. Figures for plant analysis are given on a dry-matter basis. The dry weights of the plants in the treated pots are significantly higher than those in the untreated pots at the 1% level.

Table 5.

Soil Analyses in Pot Trial.

Pot No.	Treatment.	pH.	Exchangeable Manganese.	Easily Reducible Manganese.	Exchangeable Iron.
			ppm	ppm	ppm
1	Control	4·2	168	2030	13
2	Control	4·2	154	2270	12
3	Control	4·2	152	2330	9
4	Control	4·2	152	2370	7
5	2 tons $CaCO_3$/acre	5·1	6	2340	18
6	2 tons $CaCO_3$/acre	5·1	6	2060	13
7	2 tons $CaCO_3$/acre	5·2	16	2040	13
8	2 tons $CaCO_3$/acre	5·0	13	2340	18
9	4 tons $CaCO_3$/acre	5·8	10	2340	14
10	4 tons $CaCO_3$/acre	5·9	8	2380	15
11	4 tons $CaCO_3$/acre	5·9	5	2000	17
12	4 tons $CaCO_3$/acre	5·9	8	2000	18

Table 6.

PLANT ANALYSES IN POT TRIAL.

Pot No.	Plant No.	Treatment.	Dry Weight.	Total Mn.	Total Fe.	Fe/Mn.
			gm.	ppm	ppm	
1	1	Control	1·4	4300	1160	0·27
	2	Control	0·8	3800	800	0·21
	3	Control	1·6	6700	1630	0·24
2	1	Control	1·6	6200	1330	0·21
	2	Control	1·6	5800	820	0·14
	3	Control	1·2	4000	1650	0·41
3	1	Control	2·0	5400	850	0·15
	2	Control	1·1	5800	1000	0·17
	3	Control	1·4	5000	1100	0·22
4	1	Control	1·2	5100	2250	0·44
	2	Control	1·7	5400	1850	0·39
	3	Control	1·2	5700	1820	0·32
5	1	2 tons $CaCO_3$/acre	5·1	250	1670	6·6
	2	2 tons $CaCO_3$/acre	4·0	270	1220	4·5
	3	2 tons $CaCO_3$/acre	2·8	300	2160	7·2
6	1	2 tons $CaCO_3$/acre	3·0	260	1670	6·4
	2	2 tons $CaCO_3$/acre	2·0	180	800	3·3
	3	2 tons $CaCO_3$/acre	2·7	200	820	4·1
7	1	2 tons $CaCO_3$/acre	2·1	200	780	3·9
	2	2 tons $CaCO_3$/acre	3·9	160	860	5·3
	3	2 tons $CaCO_3$/acre	6·2	280	740	2·6
8	1	2 tons $CaCO_3$/acre	2·4	390	1510	3·8
	2	2 tons $CaCO_3$/acre	2·4	330	1460	4·4
	3	2 tons $CaCO_3$/acre	3·2	310	910	2·2
9	1	4 tons $CaCO_3$/acre	2·4	110	940	8·5
	2	4 tons $CaCO_3$/acre	3·2	330	1440	4·3
	3	4 tons $CaCO_3$/acre	1·2	340	2100	6·2
10	1	4 tons $CaCO_3$/acre	3·8	130	1780	13·6
	2	4 tons $CaCO_3$/acre	3·1	260	810	3·1
	3	4 tons $CaCO_3$/acre	2·4	180	890	4·9

Table 6—continued.
PLANT ANALYSIS IN POT TRIAL—*continued.*

Pot No.	Plant No.	Treatment.	Dry Weight.	Total Mn.	Total Fe.	Fe/Mn.
11	1	4 tons $CaCO_3$/acre	3·4	140	2220	15·4
	2	4 tons $CaCO_3$/acre	1·6	150	730	4·8
	3	4 tons $CaCO_3$/acre	2·0	140	1630	11·6
12	1	4 tons $CaCO_3$/acre	3·6	180	1580	8·7
	2	4 tons $CaCO_3$/acre	4·5	170	780	4·5
	3	4 tons $CaCO_3$/acre	1·7	90	780	8·6

DISCUSSION.

Manganese Values.

The uptake of manganese by the affected plants was surprisingly high—much higher than had been obtained in preliminary work—while the uptake from the soil in the limed pots was quite low. The figures for exchangeable manganese in the soil correlate well with the manganese in the plant, but the easily reducible manganese, as had been found before, remained at a high level.

The plants in the pH 5·1 series of pots were quite normal, and the figures for exchangeable manganese in this series of pots are low. However, some previous samples taken in the field had yielded higher amounts of exchangeable manganese at this pH value, and beans growing at this pH were affected. It is apparent that near the critical pH, exchangeable manganese can vary depending on some factor other than acidity.

Iron Values.

Iron was determined colorimetrically using o-phenanthroline (Sandall 1944, p. 271). Exchangeable iron in the soil was determined on the same extract as was used for manganese, and the values for the treated pots are significantly higher than those for the untreated pots at the 5% level. The number of replications, however, was small, and more analyses will be required before much weight can be given to this difference. The results for total iron in the plant are very variable and do not correlate with plant growth.

The relationship between iron deficiency and manganese toxicity has been discussed by several authors, but conflicting results are reported. Most writers state that symptoms of manganese toxicity are different from those of iron deficiency, while some report that plants injured by manganese excess responded to the application of ferrous salts. Mulder and Gerretsen (1952) summarized the papers which deal with this problem.

Sideris and Young (1949) reported that pineapples grown on manganiferous soils in Hawaii became very chlorotic, presumably due to excess manganese uptake, and that healthy leaf colours could be restored by spraying with ferrous salts.

Pineapples grown on acid areas of the Dagun soil behave similarly. It is necessary for farmers to spray with ferrous sulphate as often as 10 times a year to maintain good leaf colour, which is evidence of manganese-induced iron deficiency.

The analytical results for the pot trial do not show any relationship between iron deficiency and manganese toxicity in the plant, possibly because the figures are for total amounts of these elements present, rather than for the soluble fraction. Somers and Shive (1942) considered the ratio of soluble iron to soluble manganese to be important, and claimed that for good growth the ratio should be about 2·0. The ratios of iron to manganese given in Table 4 depend too much on the absolute amounts of manganese present to be of much value.

CONCLUSIONS.

For practical purposes, the excessive uptake of manganese by beans grown on the Dagun soil can be controlled by the application of lime in sufficient quantity to raise the pH to about 5·4.

The use of soil analysis to predict when the manganese uptake is likely to be injurious depends on a consideration of soil pH, and of exchangeable and easily reducible manganese. It appears that the value for exchangeable manganese will vary somewhat even in the same soil type and at the same pH. However, if the pH is low and the easily reducible manganese high, the soil can be considered as suspect.

Plant analysis is more reliable than soil tests as a means of predicting toxicity, and it would appear that a final proof can be obtained by the growth of French bean as an indicator plant, because the symptoms are so characteristic. Values greater than 1,000 ppm (dry-matter basis) of manganese in bean plants indicate manganese toxicity.

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