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THE CHEMICAL CHARACTERISTICS
AND EFFECT OF CALCIUM CARBONATE
ON THE MANGANESE STATUS OF FIVE
ACID ORGANIC SOILS

Thesis for the Degree of M. S.

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THE CHEMICAL CHARACTERISTICS AND EFFECT
OF CALCIUM CARBONATE ON THE MANGANESE
STATUS OF FIVE ACID ORGANIC SOILS

By

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INTRODUCTION

The importance of an adequate supply of calcium in organic soils has long been recognized as essential for optimum crop yields. However, specific information regarding rates of application of calcium required to bring about optimum conditions in acid organic soils is limited.

It is important to recognize not only the beneficial effects of calcium, applied in the form of lime (calcium carbonate) in optimum amounts but also possible detrimental effects associated with overliming.

Soil reaction (pH) is generally considered as a practical measure of the lime needs of an organic soil. It has been observed, however, that crops growing on organic soils with similar soil reaction vary in the degree of response from lime applications. In extreme cases fair crops of onions have been produced on soils with a low pH and on other organic soils with the same pH a crop failure would result. Soil reaction, therefore, does not appear in all cases, to be the only criterion by which the lime requirement of an organic soil can be based.

While the need for lime is recognized as a recommended soil management practice, the addition of excessive amounts of lime to a soil should be avoided in order to prevent the inducing of certain micro-nutrient element deficiencies,

notably manganese. Manganese, iron and aluminum availabilities are highest in the soil reaction range from intensely acid (pH 3.0 - 3.9) to strongly acid (pH 4.6 to 5.1).

It is important that these micro-nutrient elements are in optimum amounts in the soil, thus preventing a deficiency when too little is present or a toxicity when they are present in excess. The former condition commonly occurs on soils too heavily limed, whereas the latter condition frequently arises when the soils are too acid and in need of lime.

The following study was instituted to investigate a number of factors that might be associated with the causes of variation in the response of different acid organic soils to lime applications.

REVIEW OF LITERATURE

In many respects the properties of organic soils have been reported to be similar to those of mineral soils (37). Organic soils possess, as do mineral soils, the property of ionic exchange (19, 24). The difference is one of degree, peat soils containing more absorbed cations than do mineral soils.

On the other hand, striking inherent differences were found between these soils. Peat soils, containing comparatively large amounts of calcium were often found distinctly acid in character (38), differing in this respect from mineral soils.

Wilson and Staker (37), investigating the ionic exchange of peat soils found that organic soils differed quite widely in the content of exchangeable hydrogen, had a high absorptive capacity for cations and to contain large amounts of replaceable cations in comparison with the amounts usually found in mineral soils. An inverse correlation was observed between the degree of acidity and replaceable cations. Little relationship between the total exchange capacity and pH was found to exist and exchange capacity was not necessarily a function of the pH (1).

Hissink (12) stated that the object of liming was primarily to bring calcium into the clay humus fraction of

the soil (lime absorption) and thereby increase the amount of calcium per 100 parts of humus and the degree of base saturation. Beneficial changes in soil structure and soil reaction also resulted. Lime not adsorbed either remained in the carbonate form or was rapidly transformed into this form.

Hissink (13) working with lime additions on organic soils found a relationship between the three values: pH, the degree of saturation of the base exchange complex and milligrammequivalents of bases present.

Wilson and Staker (37) and Gedroiz (10) have pointed out that calcium is the predominant exchangeable cation on the base exchange complex.

Gedroiz (10) reported that the order of relative magnitude of the proportions in which cations occur in most soils is Ca, Mg, K and Na, according to the decreasing energy of absorption. It has been shown (5, 7, 25) that an excessive concentration of calcium ions tends to decrease the absorption of other nutrient ions.

Moser (23) studying the calcium nutrition of plants at various pH levels below neutrality found good correlation of plant growth with calcium concentration. With three types of plants, soybeans, lespedeza and sorghum, it was found that pH was a minor factor in comparison to the supply of available calcium. Increasing the supply of available calcium

resulted in increases in plant growth and the absorption of the other nutrient elements.

Davis and Brewer (5) pointed out that comparatively large quantities of calcium are essential to plant growth. They found that normal absorption of other ions depended on a certain minimal quantity of calcium ions, the amount varying with the plant studied.

Harmer (14) stated that the annual harvesting of good yields of crops from muck land resulted in the gradual removal of considerable amounts of lime in the form of calcium and magnesium compounds in those crops. If the muck was well supplied with lime, this removal had little or no effect on the pH or the productivity of the soil. Most crops will grow normally with proper fertilization with the muck soil reaction down as low as 4.6. However, he stated the range in adaptable muck soil reaction for onions was between 5.0 and 6.6.

Davis (4) has used lime at the ratio of 4 to 10 tons per acre to correct extreme conditions of acidity. He stated that the amount used depended upon the acidity and type of muck and considered a pH of 5.0 to 6.0 as ideal for most crops that would be grown on muck soils, with the exception of cranberries and blueberries. He also found that the pH of the muck is in part correlated with micro-nutrient element needs.

Pierre and Allaway (26) mentioned that a decrease in solubility of manganese and iron may occur as the hydrogen ion concentration of the soil decreases, but it is difficult to distinguish between an unavailable form resulting from reaction and inability of the plant to utilize them as a result of excess calcium in the plant. Piper (27) has shown that the solubility of manganese is intimately controlled by the soil reaction and by the oxidation-reduction equilibrium.

Sherman and Harmer (34) have shown that neutral and alkaline conditions favor the formation of manganic manganese and acid conditions of manganous manganese. Strong reducing agents are capable of reversing the oxidative equilibrium. In general, as the manganous ion decreases in the soil, the easily reducible MnO_2 increases and, as the manganous ion increases, MnO_2 decreases. They have stated that in alkaline soils at least 3 p.p.m. of exchangeable manganese must be present for satisfactory crop production. In order to maintain an adequate level of the exchangeable fraction this must be supplemented by at least 100 p.p.m. of easily reducible manganese.

Mann (18) studied the effect of additions of calcium and magnesium carbonates on the water solubility of manganese in two acid soils. He found that the solubility of manganese was rapidly decreased by both carbonates as the soil reaction

became less acid and only a trace of water soluble manganese was detected at pH 7.0. He also found that increasing dressings of the carbonates of calcium and magnesium steadily decreased the amount of manganese in the crop until near neutrality the plant exhibited typical symptoms of manganese deficiency.

Lynd and Turk (17) found that lime proved highly beneficial to crop growth, but definite injury occurred when the lime requirement of the soil was exceeded. They found that a marked decrease in exchangeable manganese in the soil resulted from increased rates of lime.

Funchess (9) observed that applications of lime to acid soils decreased the amount of replaceable manganese. The lime-induced chlorosis reported by Gilbert, McLean and Hardin (11) was accompanied by a low manganese content of plants growing on limed soils, as compared with those growing on more acid soils. Harmer (14) stated, however, that although it is true that those mucks which show a need for manganese generally have a fairly high pH, occasionally alkaline mucks do not require manganese. Russell (32) stated that soils on which manganese deficiency exists are generally reclaimed peats rich in organic matter and made alkaline by lime.

Davis (4) found when the pH of the soil reached 6.5 or above, manganese in the form of manganese sulfate, was required by a number of crops, such as onions, celery, spearmint, lettuce, table beets, potatoes, carrots, peas, beans, sudan grass and oats.

The work of Prince and Toth (30) revealed that exchangeable manganese decreased with increasing lime application and pH. They based this difference in exchangeable manganese due to the exchange between the adsorbed manganese and calcium ions in the solution. The result is a precipitation of the former cation as insoluble manganese hydroxide which may be oxidized to MnO_2 .

McHargue (20) reported that manganese in the plant is connected with carbon assimilation, and in this respect the higher concentration of manganese in the leaves and the lower concentrations in the roots of various plants is interesting. Remington and Shiver (31), in examining a number of different vegetables found from three to eight times as much manganese in the leafy parts as in the roots.

The availability of manganese and iron are affected in much the same manner, but as shown by the work of Willis and Carrero (39) the solubility of iron and the amount available to plants cannot be taken as a certain determinant of the efficiency of iron.

Mann (18) working with soybeans grown on heavily limed soils also concluded that the solubility of iron and manganese in soils, the iron and manganese contained in plants and the chlorotic plants that resulted is not associated with a deficiency of iron, but is specifically due to a deficiency of manganese.

Although apparently not as common an occurrence as aluminum toxicity, manganese toxicity has been reported by a number of investigators. Jacobson and Swanback (16) stated that a definite correlation was established between reaction of the soil and manganese content of the plant materials, viz., the higher the acidity, the greater the percentage of manganese found in the plant material, until a toxic amount resulted. Blair and Prince (1) found with slight exception, the manganese content of the crop decreased as the amount of lime applied to the soil increased. Emmert (8) increased the manganese content of lettuce by adding sulfuric acid to the soil and obtained a chlorosis and reduced growth which he attributed to manganese toxicity. The occurrence of soluble manganese in an acid soil may be one of the causes of toxicity in such soils as exhibit toxic effects according to McHargue (21).

Harmer (14) has also shown that the addition of sulfur to alkaline mucks is oxidized to form sulfuric acid in the

soil which permanently lowers the pH and increases the availability of the phosphate, manganese and boron compounds present in an unavailable condition in the alkaline muck.

Most of the evidence as to what causes the injurious effects of acid soil on plants supports the view that it is due to toxic amounts of soluble aluminum or manganese and in some cases to a combined effect of the two. In most instances, however, aluminum has been found to be the toxic principle (22, 29).

Crist (3) found that applications of lime greatly reduced the intake of iron and aluminum by the plant. Hardenburg (15) reported that there is some indication that the iron and aluminum in lettuce tissue decreased with increasing pH values of the soil.

Truog (36) concluded the main harmful influence of soil acidity on certain plants is due to its influence in preventing these plants from getting, at a sufficiently rapid rate, the calcium as the carbonate or bi-carbonate. Calcium is needed to neutralize and precipitate certain acids in the plants themselves, which are probably largely by-products, produced as a result of certain vital reactions in the growth of the plants. If calcium in these forms is not furnished at a sufficiently rapid rate, then the rate of these reactions is lowered accordingly as is also the rate of plant growth.

PROCEDURE

Five acid organic soils were obtained from the following locations in Michigan during October and November, 1950, from the upper 12 inches of the soil profile.

Soil Number 1 - Trebish Farm, Livingston County

2 - Anderson Farm, Lapeer County

3 - Vicinity of Capitol Airport, Ingham County

4 - Schoenfeld Farm, Lapeer County

5 - Norton Farm, Clinton County

The soils were dried to an apparent optimum moisture content and each soil was sieved through a 1/4 inch screen. The soil was uniformly mixed and a ten-gram sample of each soil was dried over night at 115° C. to determine the moisture content.

Determinations of pH were made on duplicate samples at the previously determined moisture percentages by the glass electrode method.

Lime was added to the soil in two-ton increments resulting in soil treatments varying from 2 to 12 tons per acre. Each treatment was replicated three times. An unlimed treatment was included in each case.

A basic treatment of 2000 pounds of 3-9-18 fertilizer and 100 pounds of copper sulfate per acre was added to all the treatments of the five soils.

The addition of copper to organic soils with a pH of 6.5 or lower is very important for maximum crop production of a number crops. Besides resulting in increased yields to many crops, it has been reported to improve the color and quality of onions, carrots, lettuce and spinach (14).

The soil, lime, fertilizer and copper sulfate were thoroughly mixed and placed in one gallon jars.

On January 19, 1951, the jars were seeded 3/4 to 1 inch deep with Brigham's Yellow Globe, a medium maturing variety of onions.

Prior to seeding, the seeds were treated with "Arasan" to prevent damage from soil borne organisms.

The onions in each pot were thinned to four onions per pot.

The soils were maintained at optimum moisture conditions by periodically bringing the jars up to weight with distilled water. Notes were recorded and photographs taken of the plants to show the differences that developed.

The onions were harvested on June 21, 1951. Air dry weights of the tops and bulbs were recorded.

The untreated soils were chemically analyzed for the following constituents: Exchangeable calcium, magnesium, potassium, sodium, manganese and iron, and total iron, aluminum and manganese. In addition the following properties

were determined: pH, exchangeable hydrogen, total exchange capacity, exchangeable cations (total bases) and per cent base saturation.

The lime requirement for each soil was determined.

Exchangeable and easily reducible manganese and pH were determined on the soils after treatment with calcium carbonate and following the harvesting of the onions.

Total manganese determinations were made on oven-dried tissue from the tops and the bulbs of the onions to investigate the relationship of the amount of manganese present in the plants and the amount available to the plants at the various soil reactions obtained after liming; and to see what effect, if any, this had on the growth and yield of the plants.

METHODS OF CHEMICAL ANALYSIS

Base Exchange Capacity Determination (33)

Place 5 grams of air dry soil in a 300 ml. flask and add 250 ml. of neutral N ammonium acetate solution. Shake at intervals from 1/2 hour to 1 hour, and then pour into a funnel fitted with a number 42 filter paper. Allow to drain; then leach with an additional 100 ml. of 0.1 N ammonium acetate. After the soil in the funnel has finished draining, leach the soil slowly with 200 ml. of 10 per cent NaCl.

Place the salt filtrate in a Kjeldahl flask, add 20 ml. of 2 N NaOH and distill into 50 ml. of 4 per cent boric acid solution. Titrate distillate with 0.1 N HCl using brome cresol green as the indicator.

Note: After the soil has been leached with 0.1 N ammonium acetate solution, it must be washed with an indefinite amount of distilled water and 85 to 90 per cent ethyl alcohol until all the occluded ammonia has been removed. To check for absence of ammonia add 1 drop of Nessler's reagent to 3 drops of the leachate. Compare the color obtained against a color chart for ammonia. A very pale yellow color indicates approximately 1 part per million of ammonia present.

Determination of Total Bases (2)

Extract the soil by the same procedure used in the determination of the base exchange capacity.

Collect the filtrate and evaporate to dryness on a hot plate. Transfer the residue to a porcelain evaporating dish and gently ignite over a meeker burner for a few minutes and then at full red heat for 10 minutes. After cooling, add a calculated excess of 0.2 N HCl, warm the solution and rub the bottom of the dish with a rubber policeman. Add 5 drops of methyl red indicator. The solution should be red. Back titrate with 0.1 N NaOH. Calculate the milliequivalents of soil bases per 100 grams of soil.

Per cent Base Saturation

From the base exchange capacity and total base determinations the per cent base saturation may be determined in the following manner:

$$\frac{\text{Total bases}}{\text{Base Exchange Capacity}} \times 100 = \text{per cent base saturation}$$

Exchangeable Hydrogen

From the base exchange capacity and the total base determinations of a soil, the exchangeable hydrogen may be calculated in the following manner:

$$\text{Base Exchange Capacity} - \text{total bases} = \text{Exchangeable hydrogen}$$

The Determination of Calcium, Sodium and Potassium by the
Flame Photometer (35)

Preparation of Solution A

Extract the soil by the same procedure used in the determination of the base exchange capacity.

Collect the filtrate and evaporate nearly to dryness. Pour into a 100 ml. volumetric flask. Cool, dilute to 100 ml. and label as solution A.

Pipette 50 ml. of solution A into a 100 ml. volumetric flask, add 10 ml. of 250 p.p.m. lithium chloride solution, and dilute to 100 ml. The solution is now ready for the determination of calcium, sodium and potassium.

Calcium

Warm up the flame photometer using the blue photocell for at least one-half hour prior to its use. Locate the position of the calcium line on the wave length scale with a solution containing 60 p.p.m. calcium in the form of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. With the location established, reset the machine for the indirect method of determination, using 25 p.p.m. lithium in the form of the chloride as the internal standard. Set the 60 p.p.m. calcium solution containing 25 p.p.m. lithium at 100 and check one point on the curve to be sure that the machine is working satisfactorily. A 30 p.p.m. calcium solution should read 50 scale divisions

when the 60 p.p.m. calcium solution is set at 100. Pour unknowns in the funnel of the flame photometer and record scale readings.

Sodium

Locate the position of the sodium line on the wave length scale using a solution containing 20 p.p.m. sodium in the form of sodium chloride. With the location established, reset the machine for the indirect method of determination using 25 p.p.m. lithium as the internal standard. Set the 20 p.p.m. sodium solution containing 25 p.p.m. lithium at 100, and check one point on the curve. A 10-p.p.m. sodium solution should read 52 scale divisions when the 20 p.p.m. sodium solution is set at 100. Pour unknowns into the funnel of the flame photometer and record scale readings. Read p.p.m. sodium from curve.

Potassium

Remove the blue photocell from the photometer and replace with the red photocell. Locate the position of the potassium line on the wave length scale with a solution of 60 p.p.m. potassium in the form of potassium chloride. With the location established, reset the instrument for the indirect method of determination, using 25 p.p.m. lithium in the form of the chloride as the internal standard. Set the 60-p.p.m. potassium solution containing 25 p.p.m.

lithium at 100, and check one point on the curve. A 30-p.p.m. potassium solution read 43 scale divisions when the 60-p.p.m. K solution is set at 100. Four unknowns into the funnel of the flame photometer and record scale reading. Read p.p.m. from the standard curve.

Determination of Magnesium (6)

In this method for the determination of magnesium, it was found that a 10 ml. aliquot of the sample and 10 ml. of sodium hydroxide with a concentration of 200 grams per liter, proved best for magnesium determinations on the organic soils used in this study.

Since these soils are not particularly high in magnesium, a smaller aliquot than 10 ml. did not contain sufficient magnesium to get an accurate test with Thiazol Yellow. 10 ml. of sodium hydroxide with a concentration of 200 grams per litre was also required rather than a concentration of 100 grams per litre in order that the required volume could be maintained and that the color could be developed.

The procedure outlined by Drosdoff and Hearpass (6) was followed with the above modifications.

Determination of Total Manganese (40)

Weigh a 2-5 gram sample into an ignition crucible. Ignite over night at 500 to 600° C. Add 3-5 cc. of concentrated HNO_3 to the ash and boil for 1 minute. Add about 25 ml. of water and filter. Wash with hot water until it is free from nitrates (test filtrate with diphenylamine).

Evaporate the filtrate to a volume of 10-40 cc., then add 1 cc. HNO_3 , 10 drops of H_3PO_4 and 2-3 drops of H_2SO_4 (helps the color to develop faster), and 1 cc. of periodic acid solution (30 grams per 100 cc. of water).

Heat until the full color develops, then transfer to a volumetric flask and bring up to volume (usually 100 cc.). Read the per cent transmission in a photolometer or photoelectric colorimeter, using filters 401 and 398 in combination for the photolometer and for the photoelectric colorimeter a filter of 530 mμ (millimicrons) wave length for color comparison.

Exchangeable Manganese (34)

Add 250 ml. of neutral normal ammonium acetate solution to flask containing the soil. Shake frequently and filter. Return soil to original flask for extraction with ammonium acetate-hydroquinone solution. Evaporate the filtrate to dryness and ignite over an open flame.

Dissolve the residue in dilute HNO_3 and determine manganese by the periodate method.

Easily-Reducible Manganese Dioxide (34)

Add 250 ml. of neutral normal ammonium acetate solution containing 0.3% hydroquinone to flask containing soil from which exchangeable manganese has been removed. Shake contents of flasks frequently and filter in the same manner as for the determination of exchangeable manganese. Add 10 ml. (1-1) of H_2SO_4 and 10 to 20 ml. of concentrated HNO_3 to filtrate and evaporate to dryness by boiling vigorously. The HNO_3 must be in excess so that, when liquid approaches dryness, it will foam, due to escaping nitrogen oxides and thus prevent spattering. It is essential that all hydroquinone be destroyed. Residue after evaporation should be a translucent mass. Dissolve residue in 25 to 50 ml. (1-4) of H_2SO_4 and determine manganese as previously described.

Exchangeable Iron (35)

Iron is determined colorimetrically as the ferrous ortho-phenanthroline complex. For the determination of exchangeable iron the soil is extracted with the same amount and concentration of ammonium acetate that has been previously described, and evaporated nearly to dryness on

a hot plate. Wash into a 25 ml. volumetric flask, add 0.5 ml. 5 per cent solution of hydroxylamine hydrochloride and 1 ml. 0.20 per cent solution ortho-phenanthroline in 25 per cent alcohol. Mix and add a 60 per cent ammonium acetate solution to obtain complete color development. Dilute to volume. Prepare a set of standards simultaneously and read on a photoelectric colorimeter, using a filter of 530 mμ wave length for color comparison. The color should be read within 1 hour after its development.

Total Iron and Aluminum (26)

Ignite a 2-5 gram sample in an ignition crucible at 500-600° C. over night.

Dissolve ash in 3-5 cc. of HNO_3 and dilute to a volume of 250 cc. If the extract is known to be low in phosphorus add about 0.5 gram of $(\text{NH}_4)_2 \text{HPO}_4$ before making the dilution.

Add a few drops of thymol blue and then NH_4OH until the solution just turns yellow. Run in 0.5 ml. of concentrated HCl and follow with 25 ml. of 25% ammonium acetate solution and stir. Let stand at room temperature until precipitate settles (about 1 hour). Filter and wash 10 times with hot 5 per cent NH_4NO_3 solution. Ignite and weigh as iron and aluminum phosphate.

Pipette a 50 ml. aliquot from the original 350 ml. into a 200 ml. beaker and evaporate to a volume of approximately 20 ml. Oxidize the iron by adding KMnO_4 (1 + 1000) until a very faint permanganate color persists. Add 5 ml. of 10 per cent NH_4CNS solution and titrate with dilute TiCl_3 solution to disappearance of red color. This will give the amount of iron present.

Convert this amount of iron to FePO_4 and subtract it from the total amount of FePO_4 and AlPO_4 obtained on ignition, precipitation and weighing; this will give the amount of AlPO_4 present. Both iron and aluminum phosphate can be converted to per cent iron and aluminum by specified factors.

Lime Requirement Determination (41)

A buffered solution of the following composition was prepared: Para-nitrophenol, 8 grams; calcium acetate 40 grams; and sodium hydroxide, 1.2 grams. The mixture was made up to 1 liter with distilled water. The pH of the resulting solution was then adjusted to 7 at 25° C. with a few drops of dilute HCl or pellets of NaOH as required.

Twenty cubic centimeters of the buffered solution were added to a measured 2 gram sample of 40 mesh air-dried soil in a 50 cc. glass beaker. The mixture was shaken gently and let stand 30 minutes prior to reading the pH with a glass electrode.

Organic Matter and Total Ash

A 5 gram sample of soil is weighed into a weighed flat bottomed dish of about 40 cc. capacity (platinum or fused silica) which has previously been ignited. The dish with sample is then placed in an electric muffle furnace and slowly ignited at 500 to 600° C. over night. Allow to cool in a desiccator and weigh. The loss in weight is due to the loss of volatile constituents, which in peat and muck analysis is taken as the content of organic matter. Calculate the percentage of organic matter and total ash in the sample correcting for moisture content in case the sample taken was not water-free.

EXPERIMENTAL RESULTS

Table 1. Some chemical characteristics of five acid organic soils used in the investigation.

Soil	pH	Milliequivalents per 100 grams of air dry soil			Per cent base saturation
		Exchangeable hydrogen	Total exchange capacity	Exchangeable cations	
1	3.6	65.2	81.78	16.6	20.3
2	3.7	62.5	80.42	17.9	22.3
3	4.0	62.4	84.71	22.3	26.3
4	4.3	40.8	74.46	33.6	45.2
5	5.0	12.9	71.55	58.7	82.0

As shown by the data in Table 1, the five acid organic soils differed quite widely in the content of exchangeable hydrogen.

Each soil was found to possess a high absorptive capacity for cations and contained a large amount of replaceable bases.

A positive relationship was found to exist between pH, milligram equivalents of bases and per cent base saturation. An inverse correlation existed between the pH of the soils and the milligram equivalents of exchangeable hydrogen. As indicated in Tables 1 and 2 percentage base saturation was found to be closely related to the calcium content of the soils.

No relationship between pH and total exchange capacity was noted.

Table 2. Exchangeable cations and organic matter and ash contents of five acid organic soils.

Soil	Per cent		Milliequivalents					
	Organic matter	Ash	per 100 grams of air dry soil					
			Ca	Mg	K	Na	Mn	Fe
1	91.0	9.0	13.6	1.2	0.3	1.4	.009	.015
2	93.2	6.8	14.3	1.2	0.4	1.2	.004	.010
3	90.9	9.1	15.4	2.1	0.4	1.5	.005	.017
4	91.6	8.4	25.9	2.5	0.3	1.5	.009	.009
5	87.6	12.4	44.9	2.6	1.3	2.2	.013	.011

For each of the five soils calcium was found to be the predominant exchangeable cation. In general, the cations appeared in the following order of decreasing magnitude --- calcium, magnesium, sodium, potassium, iron and manganese.

The organic matter content varied from 93.2 per cent in soil number 2 to 87.6 per cent in soil number 5 and the ash contents of these two soils were 6.8 per cent and 12.4 per cent respectively.

As shown in Table 2, soil number 5 contained the largest amount of exchangeable cations.

Table 3. Per cent total iron, aluminum and manganese in the five organic soils under investigation.

Soil	Per cent		
	Fe	Al	Mn
1	0.22	0.32	.0056
2	0.16	0.26	.0025
3	0.19	0.28	.0027
4	0.30	0.33	.0044
5	0.43	4.70	.0113

As indicated in Table 3, the order of magnitude in which the above three elements occurred in the soils was aluminum, iron and manganese. The percentages of the three elements did not vary to any marked degree between soils, with the exception of soil number 5 which contained the largest amounts of all three of the elements, and was particularly high in aluminum.

Table 4. Lime requirements of the soils as determined by Woodruff's method (41).

Soil	Tons per acre*				
	1	2	3	4	5
Lime requirement	13.1	13.1	12.5	11.2	7.5

*500,000 pounds per acre basis.

Lime requirement is defined as the amount of lime required to bring the soil to pH 7.

As shown in Table 4 there was a general decrease in the lime requirement of the five organic soils as the pH increased from 3.6 in soil number 1 to 5.0 in soil number 5.

Table 5. The effect calcium carbonate additions on the pH of five acid organic soils.

Treatment*	Replication	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
		pH	pH	pH	pH	pH
0	1	3.5	3.5	4.2	4.4	4.9
	2	3.6	3.6	4.0	4.4	4.8
	3	3.6	3.6	4.1	4.4	4.9
2	1	4.2	4.1	4.3	5.2	5.1
	2	4.1	4.3	4.9	5.1	5.0
	3	4.1	4.3	4.7	5.2	5.0
4	1	4.7	4.9	5.3	5.5	6.0
	2	4.6	5.0	5.3	5.5	6.1
	3	4.3	5.1	5.2	5.6	5.8
6	1	4.3	5.7	5.7	6.0	6.2
	2	4.3	5.4	5.8	6.2	6.2
	3	4.7	5.6	5.3	6.0	6.2
8	1	5.1	6.0	6.5	6.6	6.4
	2	4.9	6.0	6.4	6.7	6.8
	3	5.2	6.1	6.4	6.6	6.7
10	1	5.2	7.1	7.0	7.0	6.9
	2	5.5	7.0	6.8	7.2	6.9
	3	5.2	6.8	6.8	6.3	7.0
12	1	5.6	7.3	7.3	7.2	7.0
	2	5.5	7.0	7.2	7.0	7.1
	3	5.6	6.8	6.8	7.3	7.0

*Tons of CaCO_3 per acre.

It has been shown in Tables 4 and 5 that a positive correlation existed for soils 2, 3 and 4, between the amount

of lime required to raise the soil pH to 7, as calculated by Woodruff's lime requirement method, and that obtained by actual liming. A negative correlation existed for soils 1 and 5.

With the exception of soil number 1, all the soils were raised to pH 7 with the addition of 10 to 12 tons of lime per acre.

It is evident from data presented in Table 5 that soil number 1 had a greater buffer capacity than the other soils. It has been stated (37) that the buffer capacity is closely related to soil reaction and to both ash and calcium content.

Table 6. The manganese status of the five organic soils under investigation.

Soil	pH	Parts per million			Total manganese
		Exchangeable manganese	Easily reducible manganese	Inert manganese oxides	
1	3.6	25.0	18.5	18.7	56.2
2	3.7	3.5	3.7	17.3	25.0
3	4.0	3.7	3.5	20.3	26.5
4	4.3	8.7	2.5	32.8	44.0
5	5.0	15.0	8.7	88.8	112.5

The manganous-manganic equilibrium of the five organic soils is shown in the above table. The exchangeable manganese

varied considerably in the five soils. This was due to both the difference in the amounts of total manganese that each soil possessed and also to the difference in soil reactions. The high pH values favored the oxidation of the available manganese to the unavailable manganic form.

The amount of easily reducible manganese for each of the five organic soils was relatively small, but was highest in soil numbers 1 and 5 which also contained the largest amounts of total manganese.

There was a relatively small amount of manganese fixed as inert MnO_2 in soil number 1 due to its intensely acid character. However, the manganese fixation was considerably greater for soil numbers 3, 4 and 5.

Table 7. The effect of calcium carbonate on the exchangeable and easily reducible manganese in five acid organic soils.

Tons CaCO ₃ per acre	pH					p.p.m. of exchangeable manganese					p.p.m. of easily reducible manganese				
	soil number					soil number					soil number				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
0	3.6	3.6	4.1	4.4	4.9	25.0	3.5	3.7	6.7	15.0	12.5	3.7	2.5	2.5	8.7
2	4.1	4.2	4.8	5.0	5.0	17.5	5.0	5.0	6.2	13.7	6.2	3.5	2.5	2.5	33.7
4	4.5	5.0	5.3	5.5	6.0	15.0	3.7	3.7	3.7	1.2	5.0	2.5	8.7	1.2	25.0
6	4.8	5.6	5.8	6.1	6.2	10.0	2.5	1.2	2.5	3.7	5.0	2.5	3.7	5.0	13.7
8	5.0	6.0	6.4	6.6	6.6	5.0	1.2	0.0	1.2	1.2	12.5	2.5	3.7	6.2	20.0
10	5.3	7.0	6.9	7.0	6.9	0.0	0.0	0.0	0.0	2.5	8.7	2.5	3.7	1.2	-
12	5.6	7.0	7.1	7.2	7.0	0.0	0.0	0.0	0.0	0.0	6.2	2.5	1.2	1.2	15.0

The influence of calcium carbonate addition on the exchangeable and easily reducible manganese status is shown in the data presented in Table 7.

The exchangeable manganese decreased in the five soils with increasing calcium carbonate applications and pH. It has been reported (14) that neutral and alkaline conditions favor the formation of manganic manganese while acid conditions favor the formation of manganous manganese. Thus, the available manganous manganese in these soils has been converted to the unavailable manganic manganese with increased applications of calcium carbonate.

It has been stated (14) that in alkaline soil at least 3 p.p.m. of exchangeable manganese must be present for satisfactory crop production.

From these data it is observed that the exchangeable or manganous manganese becomes deficient (less than 3 p.p.m.) at approximately pH 5.5. As the pH was raised beyond this value the p.p.m. of exchangeable manganese fell off rapidly. At the neutral point there was no available manganese present.

In a general way the data have shown that the easily reducible manganese increased as the exchangeable manganese decreased.

From the data presented in Table 6 a positive relationship was found between the total manganese in the soil and the amount of active manganese (exchangeable and easily reducible MnO_2) available for plant use.

A positive relationship between the total soil manganese of the 5 acid organic soils and exchangeable manganese is shown in Figure 1. The p.p.m. of exchangeable manganese increased with increasing percentages of total manganese. Although soil number 5 possessed the highest percentage of total manganese it still contained less exchangeable manganese than soil number 1 which had less total manganese. This condition might be considered due to the conversion of the available manganous manganese to the unavailable manganic manganese induced by unfavorable soil reaction.

Table 8. The effect of calcium carbonate applied to acid organic soils on the total manganese + in the tops and bulbs of the onions.*

Treatment															
Tons CaCO ₃ per acre		Soil 1		Soil 2		Soil 3		Soil 4		Soil 5					
	pH	tops	bulbs	pH	tops	bulbs	pH	tops	bulbs	pH	tops	bulbs			
0	3.6	**	**	3.6	-	-	4.1	125	50	4.4	175	22	4.9	375	50
2	4.1	1125	100	4.2	338	38	4.8	63	31	5.0	169	22	5.0	173	28
4	4.5	625	83	5.0	200	22	5.3	61	25	5.5	31	12	6.0	50	19
6	4.8	330	53	5.6	75	13	5.8	31	3	6.1	19	7	6.2	31	-
8	5.0	225	38	6.0	25	9	6.4	19	6	6.6	13	7	6.6	25	16
10	5.3	94	28	7.0	75	13	6.9	19	6	7.0	13	4	6.9	22	13
12	5.6	44	25	7.0	22	3	7.1	13	6	7.2	13	6	7.0	25	13

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*Dried for 48 hours at 80-85° C.

**Tissue analyzed for total iron, aluminum and manganese.

+ Data expressed in parts per million on an oven-dried basis.

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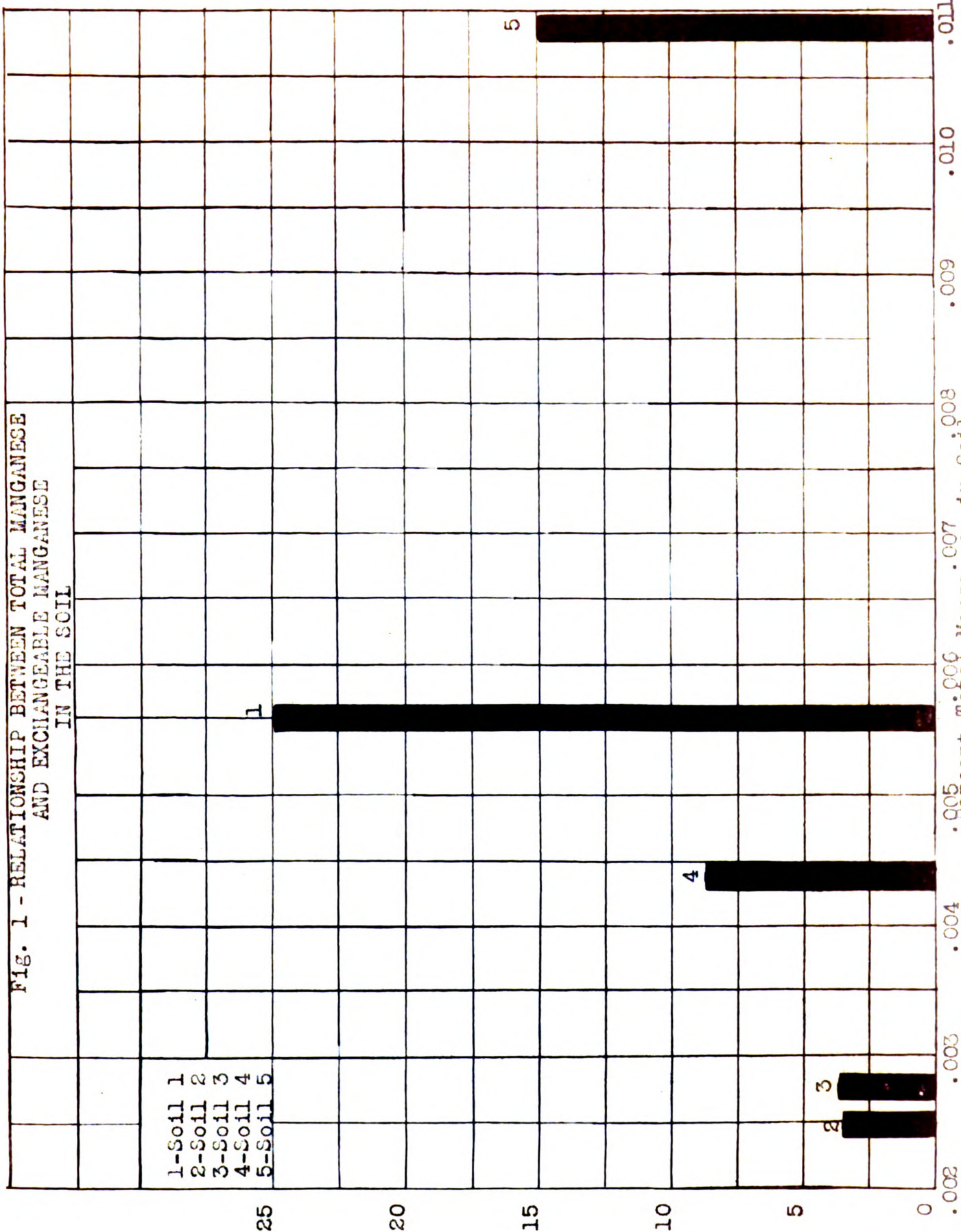
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Fig. 1 - RELATIONSHIP BETWEEN TOTAL MANGANESE
AND EXCHANGEABLE MANGANESE
IN THE SOIL



p.p.m. of Exchangeable Manganese in Soil

As shown in Table 8, the p.p.m. of manganese decreased in both the tops and the bulbs with increasing calcium carbonate applications and pH. At the lower pH values, 4.0 - 4.6, the manganese in the tops and the bulbs was in the ratio of approximately 10:1. At the higher pH values this ratio was considerably smaller. At pH 7.0 the ratio was approximately 2:1 for those plants growing on soils 3, 4 and 5. In every case the total manganese was greatest in the leaves of the plant.

A comparison of data in Tables 6 and 8 shows a positive relationship between the total manganese in the soils and the total manganese in the plant tissue. A positive relationship is also evident between the exchangeable manganese in the soil and the total manganese in the plant tissue, as shown in Tables 6 and 8 (Fig. 2).

As shown in Table 6, soil number 5 was highest in total manganese. However, the onions harvested from soil number 1, which contained half the amount of total manganese found in soil number 5, had the greatest percentage of manganese in both tops and bulbs of the onion plants. This difference is accounted for by the difference in pH of the two soils. Soil number 5 had a higher pH value and less exchangeable manganese available for plant use. This relationship is shown in Tables 6 and 8.

The higher amounts of manganese in the plant tissue from soil number 2 which contained less total and exchangeable manganese than soil number 4, is attributable to a possible antagonistic effect of calcium since soil number 4 contained nearly twice the amount of exchangeable calcium.

Table 9. The effect of calcium carbonate on the content of total iron, aluminum, and manganese in the plant tissue from soil number 1.

Tons of CaCO_3 per acre	pH	Per cent			Grams
		Fe	Al	Mn	Yield of onion bulbs
0	3.6	.17	2.6	.04	0.33
2	4.1	.03	0.3	.12	145.00

As shown from the data contained in Table 9, aluminum was present in the plant tissue in the largest amount both before and after the addition of calcium carbonate. However, the percentage of aluminum decreased considerably in the plant tissue as did the iron, after the calcium carbonate had been added; conversely, however, the per cent manganese increased in the plant tissue.

The yield of onion bulbs increased as the percentage iron and aluminum decreased in the plant tissue with increased calcium carbonate and pH.

FIG. 2 - RELATION BETWEEN EXCHANGEABLE MANGANESE IN THE SOIL AND TOTAL MANGANESE IN THE ONION TOPS

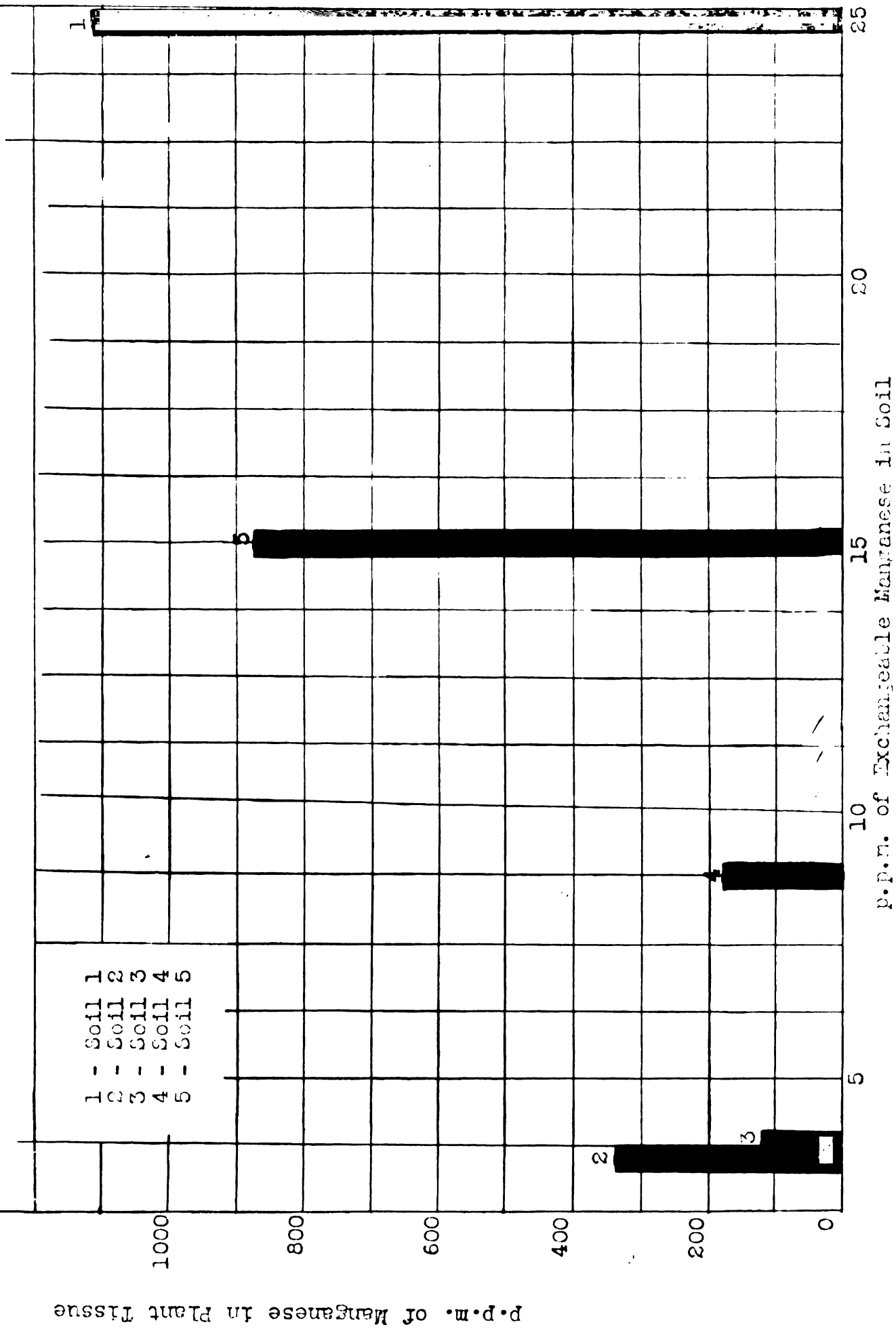


Table 10. The effect of calcium carbonate applications on five organic soils on the yield of onions grown in the greenhouse.

Tons of CaCO ₃ per acre	Yield - grams per pot														
	Soil 1			Soil 2			Soil 3			Soil 4			Soil 5		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
0	0.31	0.23	.45	0.36	0.22	0.00	174	160	165	241	232	162	210	156	213
2	153	140	142	180	174	170	200	175	222	196	206	242	201	162	178
4	158	162	126	172	179	166	202	210	220	202	200	204	200	205	174
6	170	163	158	166	140	118	198	186	204	201	206	198	204	202	164
8	124	156	164	94	122	103	122	154	176	180	205	177	130	145	148
10	147	172	122	62	29	47	90	23	132	168	129	126	176	174	167
12	147	139	152	27	31	51	59	82	96	152	129	144	128	122	160

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Table 11. Analysis of variance of yield data of onion bulbs.

Source of Degrees Variance Freedom	Sum of squares					Mean squares				
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Total	20	64904	90958	52063	21442	13130				
Repli- cations	2	619	139	2639	96	1113	309.5	69.5	1344.5	48
Treatment	6	62173	38233	46398	13626	8379	10363	14105.5	7016.3	2271
Error	12	2107	2725	2476	7720	3638	175.6	227.0	206.3	303.1

Table 11 (continued).

Source of Variance	Degrees Freedom	F				
		Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Total						
Repli- cations						
Treatment		59.01**	64.7**	37.8**	3.53*	4.56*
Error						

**Significant at 1% level

*Significant at 5% level

Table 18. The effect of calcium carbonate applied to five acid organic soils in the greenhouse on the yield of onion bulbs, and on the exchangeable and easily reducible manganese in the soils.

Tons of CaCO ₃ per acre	Mean yield- grams per pot					p.p.m. exchangeable manganese					p.p.m. Easily reducible manganese				
	Soil 1	2	3	4	5	Soil 1	2	3	4	5	Soil 1	2	3	4	5
0	0.33	0.19	166	212	203	25.0	3.5	3.7	8.7	15.0	13.5	3.7	2.5	2.5	8.7
2	145	175	201	217	180	17.5	5.0	5.0	6.2	13.7	6.2	3.5	2.5	2.5	33.7
4	149	172	213	202	192	15.0	3.7	3.7	3.7	1.2	5.0	2.5	8.7	1.2	25.0
6	164	141	196	202	190	10.0	2.5	1.2	2.5	3.7	5.0	2.5	3.7	5.0	13.7
8	168	108	151	187	140	5.0	1.2	0.0	1.2	1.2	12.5	2.5	3.7	6.2	20.0
10	151	46	103	161	172	0.0	0.0	0.0	0.0	2.5	8.7	2.5	3.7	1.2	-
12	146	37	79	143	159	0.0	0.0	0.0	0.0	0.0	6.2	2.5	1.2	1.2	15.0
L.S.D.															
1% level	33.1	37.6	35.8	-	-										
5% level	23.6	26.8	25.5	55.2	31.0										

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As shown from Tables 10 and 12 a high degree of significance has been obtained between treatments of soil numbers 1, 2 and 3 and significance at the 5 per cent point for soil numbers 4 and 5.

The yield of onion bulbs and lime application is shown in Table 12. The yield of the onion bulbs on soil number 1 was increased with the addition of calcium carbonate up to the 3 ton calcium carbonate treatment. Additional calcium carbonate decreased the yield of onion bulbs. The exchangeable manganese was also shown to decrease with increased calcium carbonate addition.

The yield of onion bulbs on soil numbers 2, 3 and 4 were increased with calcium carbonate additions of 2, 4 and 2 tons respectively. The exchangeable manganese also decreased in these soils with increased additions of calcium carbonate.

The p.p.m. of exchangeable manganese present in the soils at maximum yields were 5.3, 5.0, 3.7, 6.2 and 15.0 for soils 1, 2, 3, 4 and 5 respectively.

It is shown from these data that maximum yields on soil numbers 1, 2 and 3 were obtained when 5.0 to 3.7 p.p.m. of exchangeable manganese was present in the soil. The pH values were 3.6, 3.7 and 4.0 for soil numbers 1, 2 and 3 respectively. As the pH increased to 4.3 and 5.0 for soil

numbers 4 and 5 the p.p.m. of exchangeable manganese also increased and maximum yields were obtained at 6.3 and 15.0 p.p.m. of exchangeable manganese. It is evident from these data that maximum yields on soils of an intensely acid character (pH 3.0 - 3.9) required less exchangeable manganese than soils with pH values less acid in reaction.

From these data 4 to 5 p.p.m. of exchangeable manganese appeared optimum in intensely acid soils to give maximum yields; and 6 to 14 p.p.m. of exchangeable manganese was optimum in strongly acid conditions (pH 4.6 - 5.1) to give maximum yields.

Figures 4 to 8 show the effect of increased calcium carbonate addition on the onions of the five soils during their period of growth. A different growth curve was obtained for each soil. With the exception of soil number 5, all the soils responded to the addition of calcium carbonate. These growth curves are reflected in figure 3 showing the relation between the yield of onion bulbs and pH.

The bulbs decreased in size with increased calcium carbonate addition after the optimum amount of calcium had been reached. As shown in Figure 3 the highest yields were obtained between the pH range of 4.2 to 5.3. From Table 8 it is seen that a marked decrease in the p.p.m. of manganese

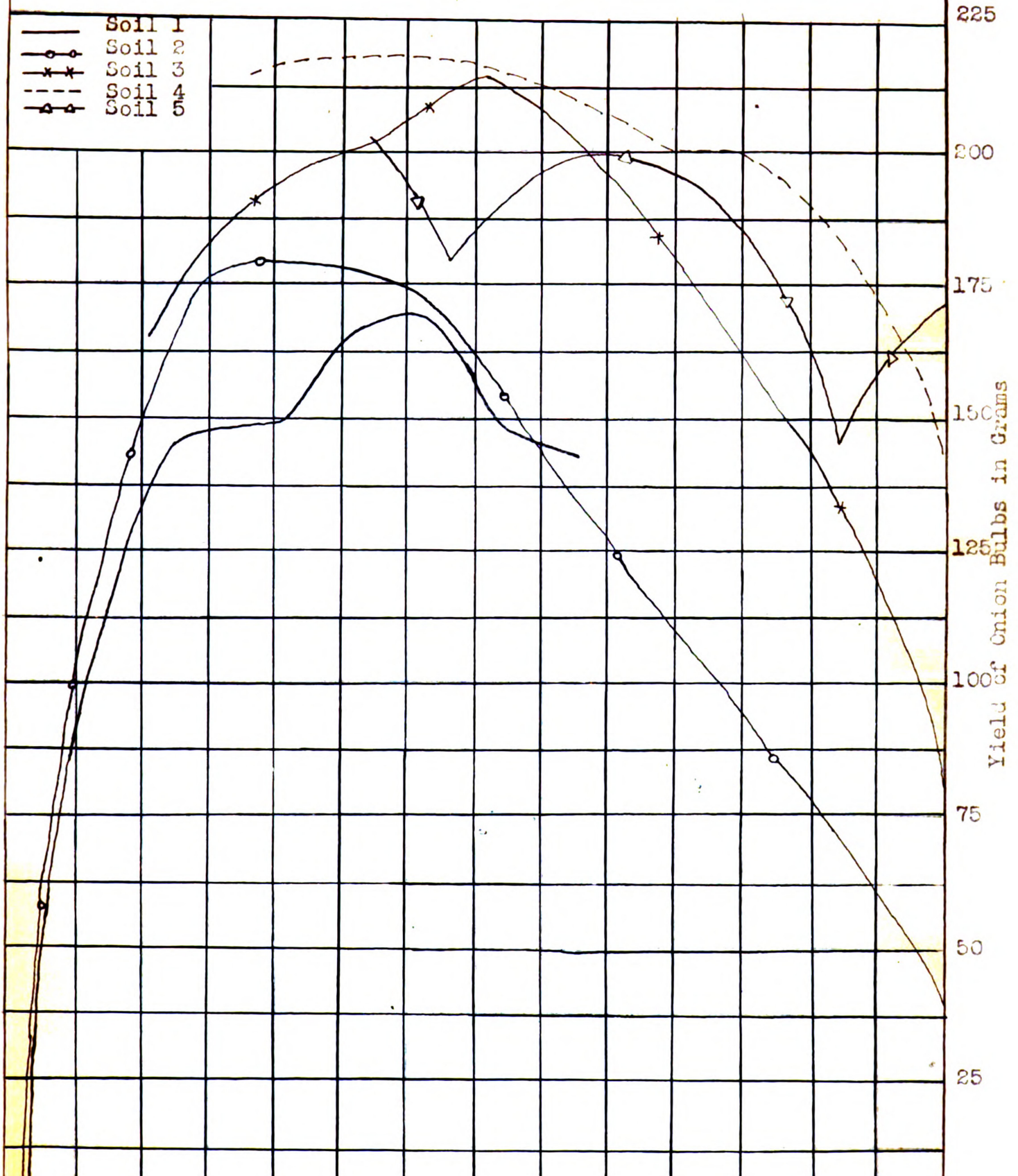
in the onion bulbs occurred as the soil pH approached neutrality, and a definite manganese deficiency resulted. This was observed in the early stages of growth. The tips of the plants developed a light yellow color, later died and in some cases fell off. As shown in Table 8 the onion plants that received the 6, 8, 10 and 12 ton calcium carbonate treatments contained very little manganese in their bulbs. The small amounts of manganese in the onion bulbs and the symptoms that occurred during their early and late stages of growth indicated that a deficiency of manganese was a contributing factor towards the low yields obtained from the heavier limed treatments.

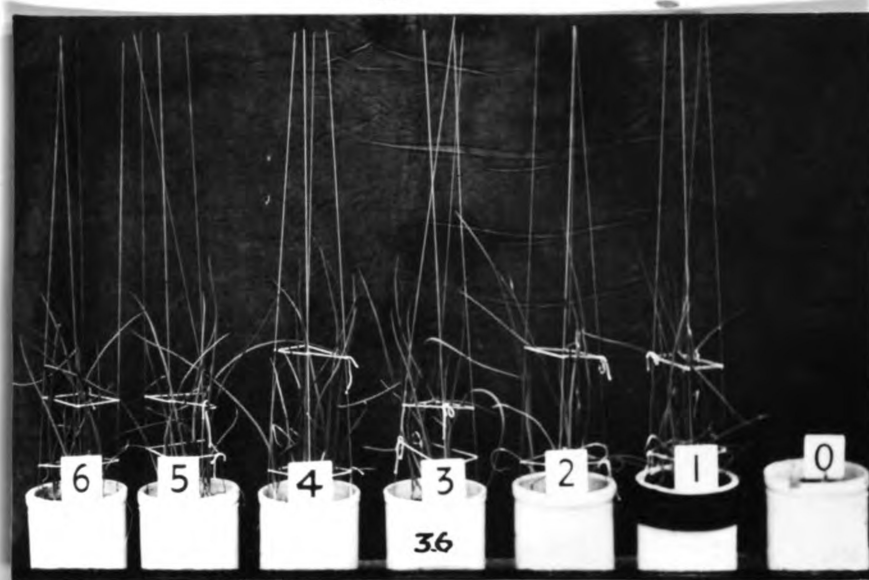
Table 13. The optimum pH values at which the highest yields were obtained from the 5 organic soils and the p.p.m. of manganese contained in the onion bulbs.

Soil	pH	Tons of calcium carbonate required to raise soil reaction to optimum pH	p.p.m. of total manganese in onion bulbs
1	5.0	8	33
2	4.2*	2	38
3	5.3	4	25
4	5.0	2	22
5	4.9	0	50

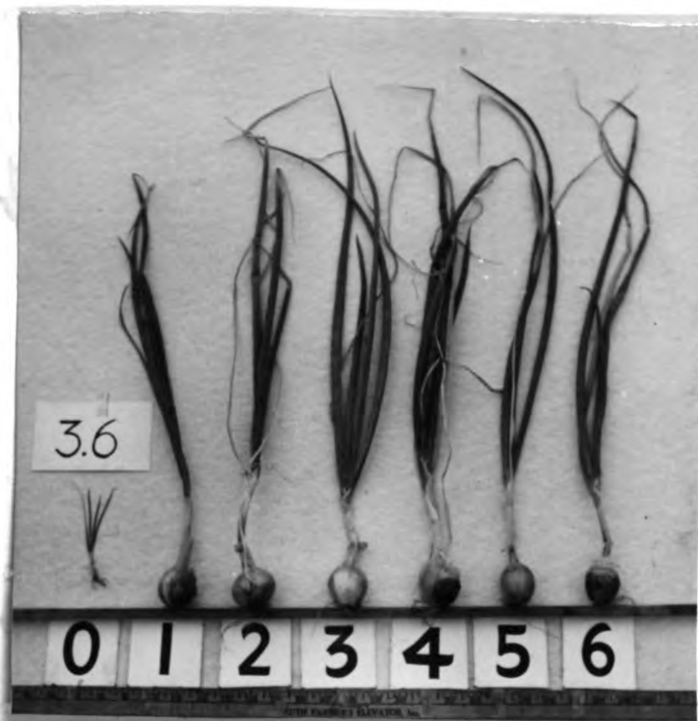
*There was little difference in yield between the 2 ton and 4 ton calcium carbonate treatments.

Fig. 3-RELATIONSHIP BETWEEN YIELD OF
ONION BULBS AND pH



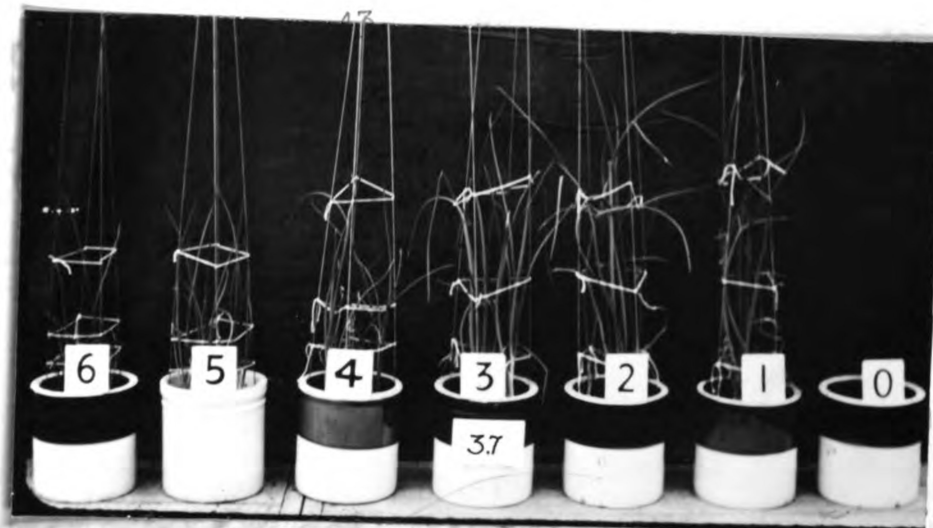


Soil 1. Growth of onions 14 weeks after date of planting.

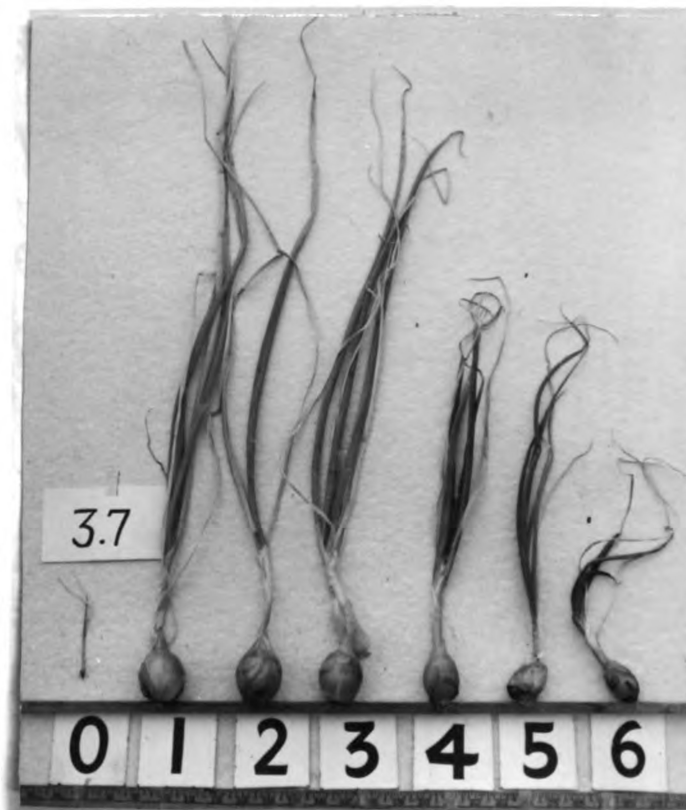


Soil 1. Onions approximately 6 months after date of planting.

Fig. 4 - The effect of lime on the growth of onions of soil number 1 (pH 3.6). 0 - no lime; 1 - 2 tons; 2 - 4 tons; 3 - 6 tons; 4 - 8 tons; 5 - 10 tons; 6 - 12 tons.

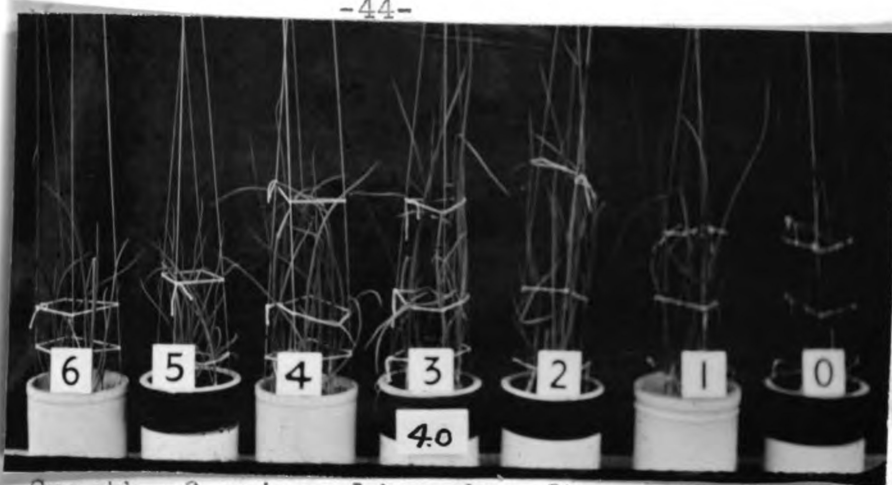


Soil 2. Growth of onions 14 weeks after date of planting.

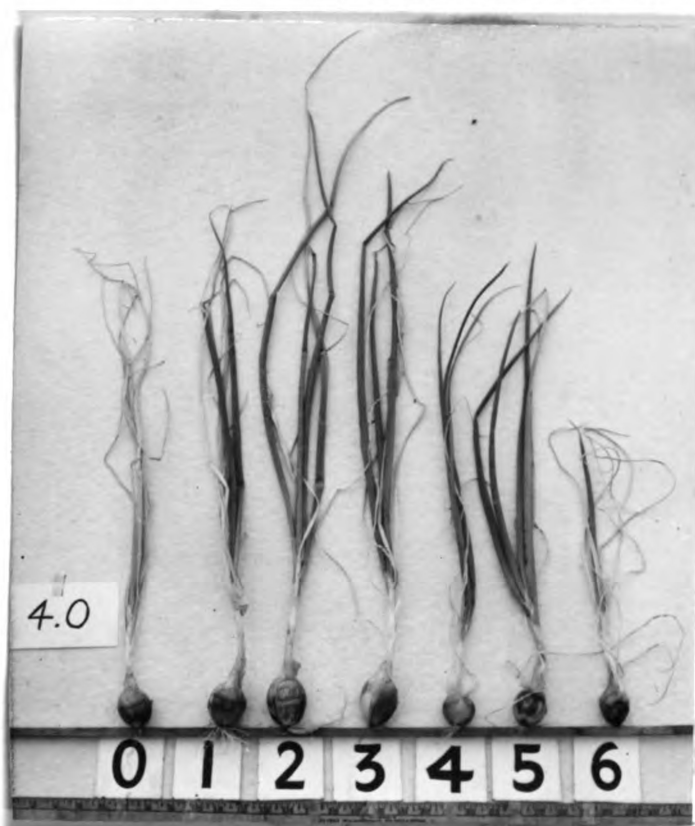


Soil 2. Onions approximately 6 months after date of planting.

Fig. 5 - The effect of lime on the growth of onions of soil number 2 (pH 3.7). 0 - no lime; 1 - 2 tons; 2 - 4 tons; 3 - 6 tons; 4 - 8 tons; 5 - 10 tons; 6 - 12 tons.

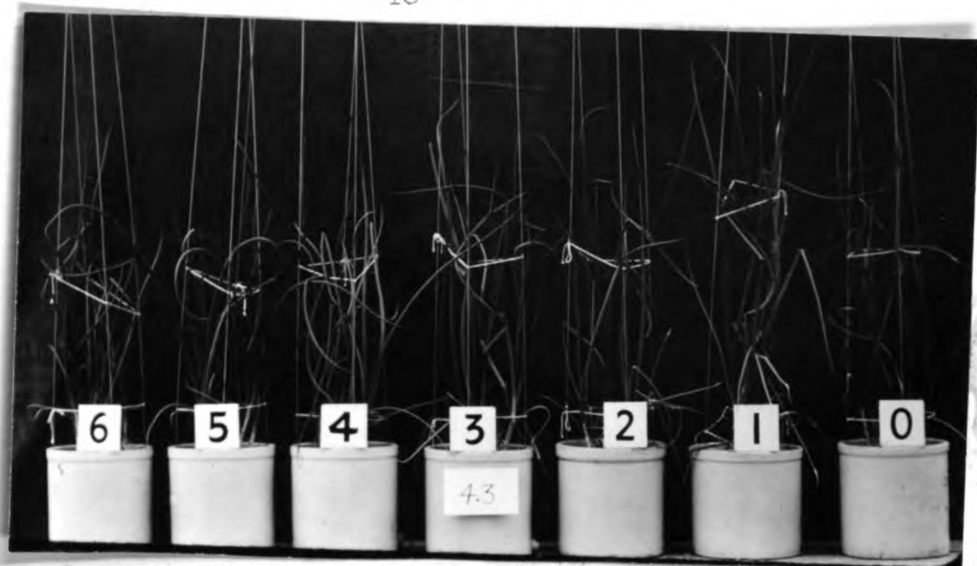


Soil 3. Growth of onions 14 weeks after date of planting.

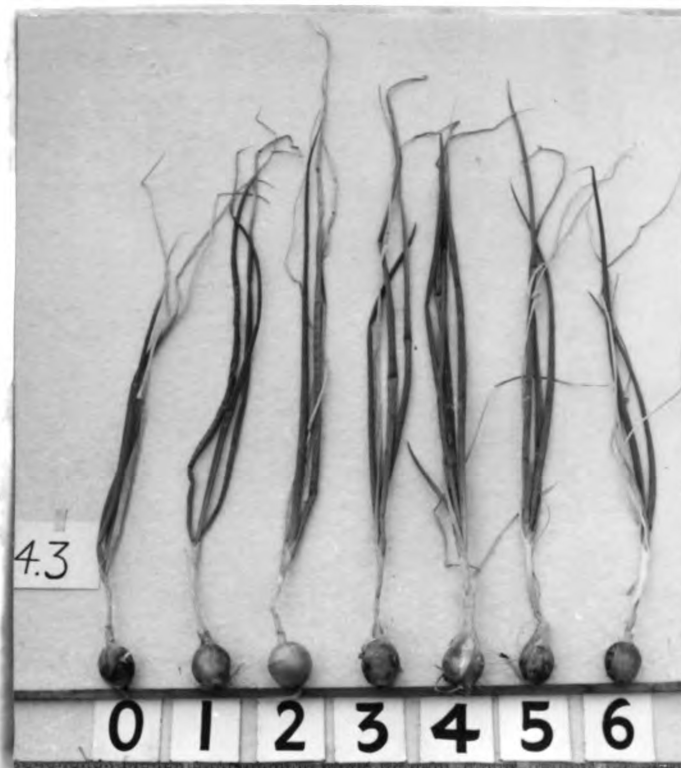


Soil 3. Onions approximately 6 months after date of planting.

Fig. 6 - The effect of lime on the growth of onions of soil number 3 (pH 4.0). 0 - no lime; 1 - 2 tons; 2 - 4 tons; 3 - 6 tons; 4 - 8 tons; 5 - 10 tons; 6 - 12 tons.

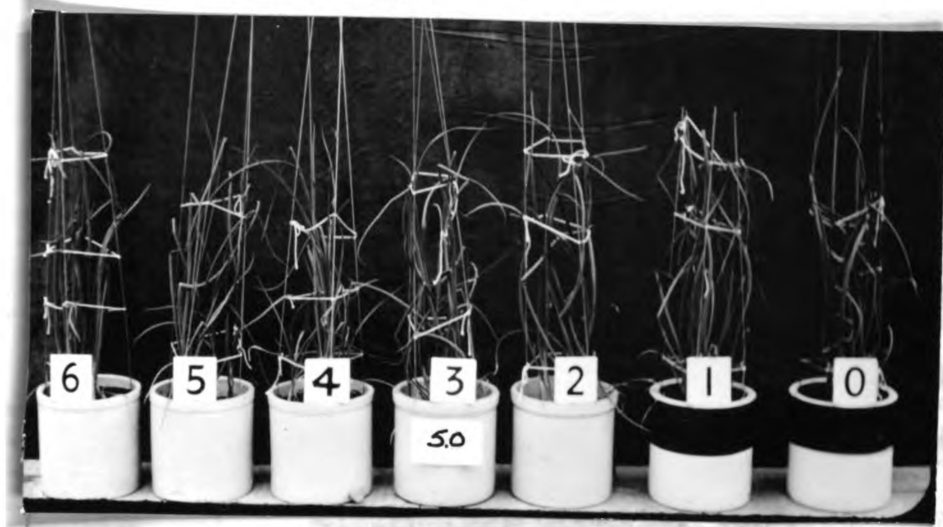


Soil 4. Growth of onions 14 weeks after date of planting.

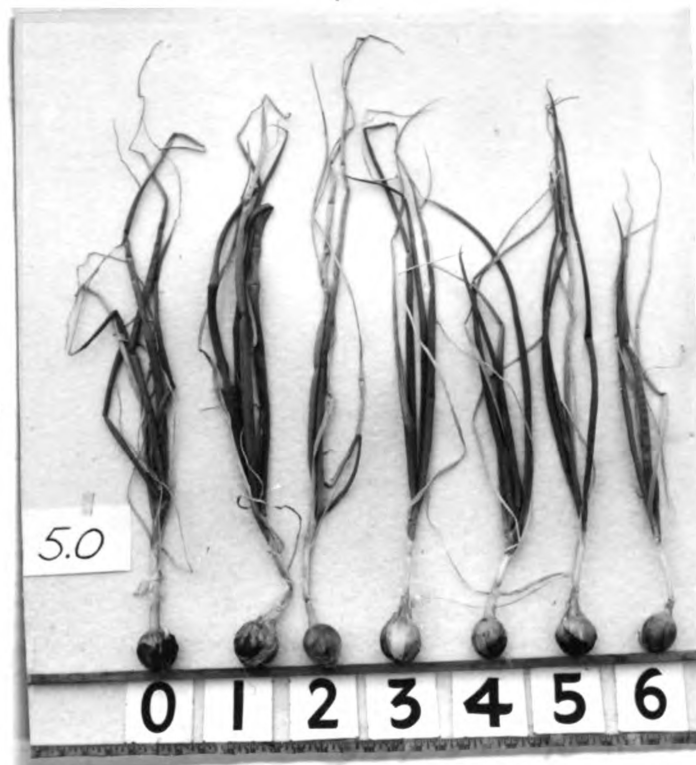


Soil 4. Onions approximately 6 months after date of planting.

Fig. 7 - The effect of lime on the growth of onions of soil number 4 (pH 4.3). 0 - no lime; 1 - 2 tons; 2 - 4 tons; 3 - 6 tons; 4 - 8 tons; 5 - 10 tons; 6 - 12 tons.

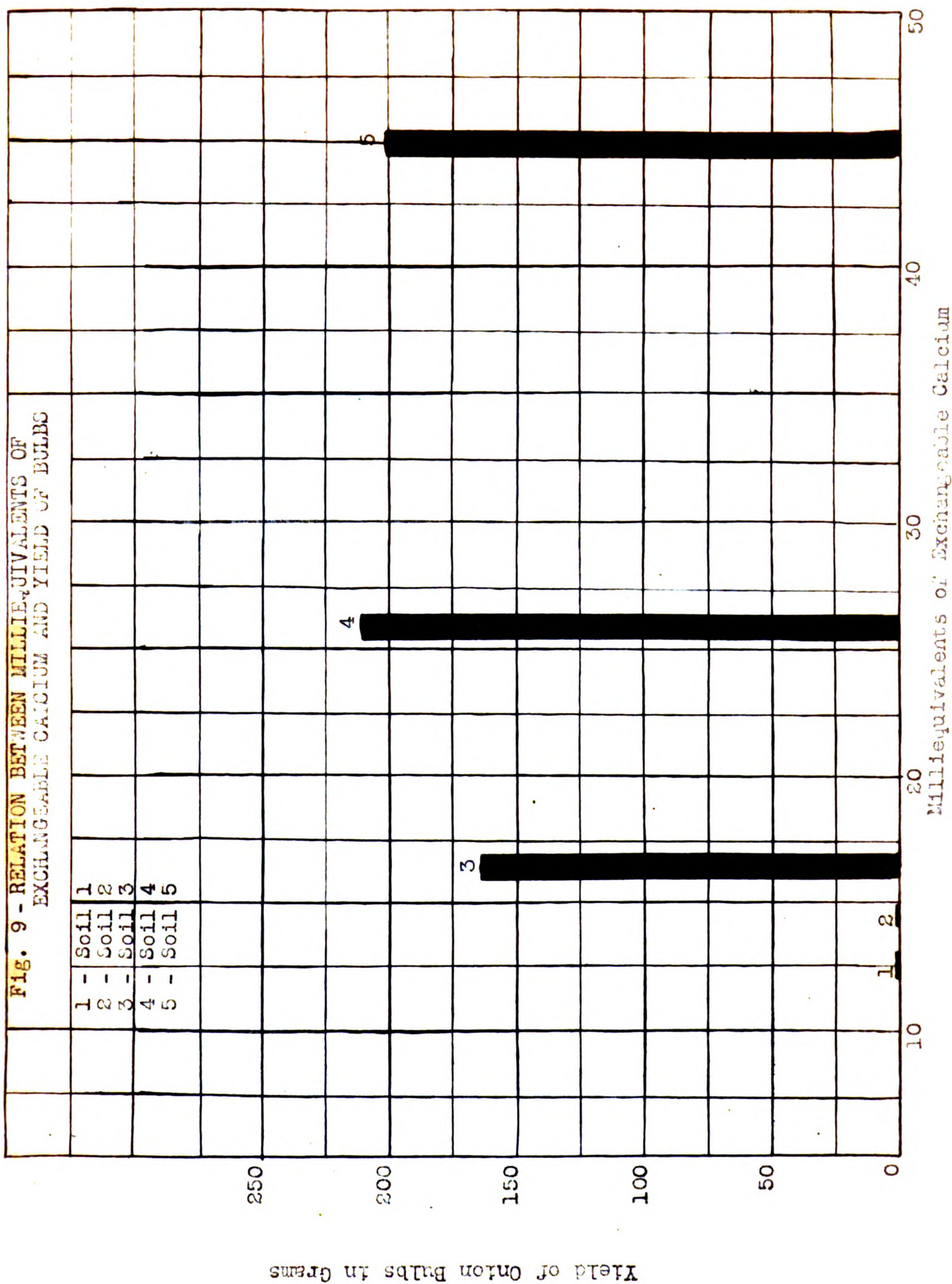


Soil 5. Growth of onions 14 weeks after date of planting.



Soil 5. Onions approximately 6 months after date of planting.

Fig. 8 - The effect of lime on the growth of onions of soil number 5 (pH 5.0). 0 - no lime; 1 - 2 tons; 2 - 4 tons; 3 - 6 tons; 4 - 8 tons; 5 - 10 tons; 6 - 12 tons.



DISCUSSION

The experimental results presented have shown that the possible factors affecting the response of different acid organic soils to lime application are numerous.

The lime requirement as determined by Woodruff's method (41) agreed closely with the actual amount of calcium carbonate required to raise the pH of soils 2, 3 and 4 to 7.0, but failed to correlate with soils 1 and 5. This lack of relationship was possibly due to the greater buffer capacities of these two soils if the amount of calcium carbonate that is required to bring the soils to any higher pH value may be used as a measure of buffer capacity. High acidity and a low content of bases are associated with high buffer capacities as measured with a base.

The per cent base saturation and total exchange capacity are perhaps better criteria than pH for estimating lime needs on organic soils. The base exchange capacities of the five organic soils used in this study did not vary to any marked degree and thus it was possible to make a good comparison in their lime requirements.

The importance of optimum base saturation was shown by the yields obtained on the unlimed treatments of the five organic soils.

Percentage base saturation was found to be closely related to the calcium content of the soils and it was found (Fig. 9) that the yields obtained on the unlimed treatments were a function of the milliequivalents of exchangeable calcium present. The yields increased with increased amounts of exchangeable calcium up to the point where additional calcium inhibited increased yields. It has been pointed out (5) that comparatively large quantities of calcium are essential to plant growth and that normal absorption of other ions depended on a certain minimal quantity of calcium ions. However, from the results obtained in this study and from the work of others (9, 11, 17, 18, 30) the addition of excessive amounts of calcium to the soil have resulted in decreased availabilities of many micro-nutrient elements especially manganese and iron.

The manganese status of the five organic soils was found to vary considerably as shown by the data presented in Table 6. There was relatively small amounts of manganese fixed as inert oxides in soil 1, due to its intensely acid character. However, the fixation of manganese was considerably higher for soils 4 and 5. This resulted from a decrease in acidity which favored the oxidation to the manganic form.

The amount of easily reducible manganese was relatively small in all soils but was highest in soils 1 and 5 which also contained the largest amounts of total manganese.

The larger amounts of exchangeable and easily reducible manganese in soils 1 and 5 accounted for the greater quantities of total manganese contained in the onion tissue harvested from these soils.

Sherman (14) has stated that in any alkaline soil at least 3 p.p.m. of exchangeable manganese must be present for satisfactory crop production and in order to maintain an adequate level of the exchangeable fraction this must be supplemented by at least 100 p.p.m. of easily reducible manganese. In acid soils, however, the optimum level of exchangeable manganese can be much lower, with the amount depending on the degree of acidity.

From the data presented in Table 6 it was shown that the total manganese for every soil with the exception of soil 5 to be less than 100 p.p.m. and much of this was present in the inert form.

No manganese deficiency existed in the plant tissue, however, where no calcium carbonate was applied. It appears, therefore, that sufficient manganese was available to the plant although there was a small amount of easily reducible manganese in the soil. With continued cropping, however, this small reserve of manganese would eventually become depleted and additional manganese would be required, usually applied to the soil as manganese sulfate.

The exchangeable manganese decreased in the five organic soils with increased calcium carbonate applications and pH. In part, the exchangeable manganese was dependent upon the total manganese in the soil, as shown in Fig. 1. This relationship, however, was associated with the pH of the soil. At low pH values the quantity of exchangeable manganese was a function of the total soil manganese and increased proportionately with the increase in total soil manganese. At higher pH values, however, there was less exchangeable manganese present in soil number 8 even though it contained the largest percentage of total manganese. High pH values favor the formation of the unavailable manganic manganese while acid conditions favor the formation of the available manganous form. It has been stated (30) that the difference in exchangeable manganese is due to the exchange between the absorbed manganese and calcium ions in the solution. The result is a precipitation of the former cation as insoluble manganese hydroxide which may be oxidized to MnO_2 .

A relationship was evident between total manganese in the plant tissue and total soil manganese. Soil numbers 1 and 5 contained the highest percentages of total soil manganese and the plant tissue harvested from these two soils was also the highest in total manganese. This

relationship, however, is influenced by pH, since the exchangeable manganese available for plant use was predominantly governed by the pH of the soil.

In a general way the data have shown that the easily reducible manganese increased as the exchangeable manganese decreased with increased calcium carbonate applications and pH.

From the results obtained all of the soils had sufficient total manganese to supply adequate amounts of exchangeable manganese if the pH values were maintained at strongly acid conditions, however, such a soil reaction would not be conducive to good plant growth. Additions of sulfur to alkaline mucks have permanently lowered the pH and increased the availability of manganese present in the unavailable condition, manganic manganese.

It has been shown (14) that in alkaline soil at least 3 p.p.m. of exchangeable manganese must be present for satisfactory crop production. From these data it is observed that the exchangeable or manganous manganese becomes deficient (less 3 p.p.m.) at approximately pH 5.5. As the pH was increased beyond this point the p.p.m. of exchangeable manganese fell off rapidly.

In every case the total manganese was found to be greatest in the leaves of the plants. The ratio of manganese in the leaves to that of the bulbs was approximately

10:1 at the lower pH values for soils 1, 2 and 4 as compared to 2:1 at the higher pH values for soils 1, 3, 4 and 5. This shows that most of the manganese is translocated to the tops of the plant where it probably aids in chlorophyll synthesis.

From the analytical data of the onion tissue harvested from the non-limed treatment of soil number 1, pH 3.6, it has been shown that iron and aluminum were present in such quantities as to be toxic to the plant. The addition of two tons of calcium carbonate to soil number 1 decreased the amounts of iron and aluminum in the plant tissue, as shown in Table 9, and the subsequent onion yields were increased from .33 grams to 115 grams respectively. Crist (3) and Mardenburg (15) found that applications of lime greatly reduced the intake of iron and aluminum by the plant. From the results obtained, manganese does not appear to be the toxic micro-nutrient element since it was actually present in smaller quantities in the plant before the addition of calcium carbonate than afterwards. The increased manganese content subsequent to calcium carbonate addition is converse to the other results obtained with manganese availability. It is known, however, that an excess amount of aluminum has caused a reduction in the absorption of all materials (22).

The reduced quantities of soluble aluminum in the soil after the addition of calcium carbonate offers a possible explanation for the difference in manganese content of the plant tissue before and after calcium carbonate addition.

Aluminum toxicity or a combined toxicity of aluminum, iron and possibly manganese appears to account for the low yields obtained from the unlimed treatments of soil numbers 1 and 2 which had pH values of 3.6 and 3.7 respectively. As shown in Figures 4 and 5 the onion plants were dwarfed and the roots produced few branches.

As shown from the data in Table 12 calcium carbonate significantly increased the yields of onions on soils 1, 2 and 3 (1% level) and at the 5 per cent level between calcium carbonate treatments on soils 4 and 5. The unlimed treatment on soil number 5 gave significantly higher yields over the limed treatments and this was the only soil that did not respond to calcium carbonate addition. Soil number 5 was 82 per cent base saturated before liming, apparently increased additions of calcium carbonate decreased the absorption of the micro-nutrient elements and especially manganese as shown in Table 8.

Although there was no direct correlation between the yield of onion bulbs and manganese content there appeared to be a definite trend in this direction.

With the exception of the unlimed treatments (check treatments) of soils 1 and 2 the heavily limed treatments gave the lowest yields and they also contained the lowest amounts of manganese; however, some of the treatments that also gave high yields contained low amounts of manganese.

Results have shown, Table 23, that the highest yields for the five soils were obtained between pH 4.20 and 5.3 and the optimum pH approximated 5.0. The manganese content in the onion bulbs obtained from the soils with the highest yields ranged between 22 and 50 p.p.m.

The data have shown that it is important to recognize not only the beneficial effects of calcium, applied in the form of lime (calcium carbonate) in optimum amounts but also possible detrimental effects associated with overliming. While the need for lime is recognized as a recommended soil management practice, the addition of excessive amounts of lime to a soil should be avoided in order to prevent the inducing of certain micro-nutrient element deficiencies, notably manganese.

SUMMARY

This study was instituted to determine the effects of calcium carbonate addition on the manganese status of five acid organic soils and to investigate a number of factors that might be associated with the causes of variation on the response of different acid organic soils to lime applications.

Five organic soils of varying acidity were obtained from different locations in Michigan. The soils were dried to an apparent optimum moisture content and each soil was sieved through a 1/4 inch screen. Determinations of pH were made on duplicate samples at a previously determined moisture content by the glass electrode method. Lime was added to the soil in 2 ton increments resulting in soil treatments varying from 2 to 12 tons per acre. Each treatment was replicated three times. An unlimed treatment was included in each case.

A basic treatment of 2,000 pounds of 3-9-18 fertilizer and 100 pounds of copper sulfate per acre was added to all the treatments of the five soils.

On January 19, 1951, the jars were seeded 3/4 to 1 inch deep with Brigham's Yellow Globe, a medium maturing

variety of onions. The onions were harvested on June 21, 1961. Air dry weights of the tops and bulbs were recorded.

The untreated soils were chemically analyzed for the following constituents: Exchangeable calcium, magnesium, potassium, sodium, manganese and iron, and total iron, aluminum and manganese. In addition the following properties were determined: pH, exchangeable hydrogen, total exchange capacity, exchangeable cations and per cent base saturation. The lime requirement for each soil was determined. Exchangeable and easily reducible manganese and pH were determined on the soils after treatment with calcium carbonate and following the harvesting of the onions.

Total manganese determinations were made on oven-dried tissue from the tops and the bulbs of the onions.

The following observations were made from the investigation:

1. The per cent base saturation and total exchange capacity are perhaps better criteria than the pH value for estimating lime needs on the organic soils investigated.

2. Percentage base saturation was found to be closely related to the exchangeable calcium content of the soils.

3. The yields of the unlimed treatments increased with increased exchangeable calcium up to the point where additional calcium inhibited increased yields.

4. The exchangeable manganese decreased in the five organic soils with increased calcium carbonate applications and pH.

5. There was a positive relationship between exchangeable manganese and total manganese in the soil in strongly acid conditions, however, this relationship did not hold at higher pH values.

6. There was some indication of relationship between total manganese in the plant tissue and total manganese in the soil, however, this relationship was in part dependent on the amount of exchangeable manganese present in the soil which varied with pH.

7. In a general way the easily reducible manganese increased as the exchangeable manganese decreased with increased calcium carbonate applications.

8. All five soils had sufficient total manganese to supply adequate amounts for good plant growth, but under a continuous cropping system additional manganese would be required.

9. In every case the total manganese was found to be greatest in the leaves of the plants.

10. At intensely acid pH values (3.0-3.9), the iron and aluminum were present in the plant tissue in sufficient amounts to be toxic to the plants.

11. The addition of calcium carbonate decreased the amounts of iron and aluminum in the plant tissue.

12. A high significance between treatments was obtained with addition of calcium carbonate on soils 1, 2 and 3 with pH values of 3.6, 3.7 and 4.0 respectively. It was not advantageous to lime soils 4 and 5 which had pH values of 4.3 and 5.0 respectively.

13. Although there was no direct correlation between the yield of onion bulbs and manganese content there appeared to be a definite trend in this direction.

14. The highest yields for the five soils were obtained between pH 4.2 and 5.3 and the optimum pH approximates 5.0. The manganese content of the onion bulbs which gave the highest yields ranged between 22 and 50 p.p.m.

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