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# The Development of Soluble Manganese in Acid Soils as Influenced by Certain Nitrogenous Fertilizers

By

M. J. FUNCHESS

Associate Agronomist

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# THE DEVELOPMENT OF SOLUBLE MANGANESE IN ACID SOILS AS INFLUENCED BY CERTAIN NITROGENOUS FERTILIZERS.*

By

M. J. Funchess

Associate Agronomist, Alabama Polytechnic Institute

## Introduction

In the spring of 1913 a series of plots on the Alabama Experiment Station Farm was devoted to a field study of the rate of nitrification of dried blood, cotton seed meal, and calcium cyanamid. The amount of fertilizer applied to the several plots was sufficient to supply seventy-seven pounds of nitrogen per acre. An attempt was made to prevent leaching on small areas of some of these plots by protecting them against rainfall with covers during the winter of 1915-1916. During the period, it was noticed that a brown crust had accumulated under some of the covers on the fertilized plots. Nitrate determinations made on this brown soil crust showed a nitrate content as high as 4959 p. p. m. of nitrates with an average of 2269 p. p. m. as the result of six determinations.

Soil taken from beneath these covers and used in a pot experiment with corn in the green house, proved to be less productive than unfertilized soil which contained only a normal amount of nitrates. In a similar experiment with sorghum as the plant indicator, the plants made little growth and finally died on the high nitrate soil. On the other hand, pots to which lime had been added made a vigorous growth and developed normally. The work suggested that this acid soil, when carrying a high nitrate content, contained some substance which was injurious to plants, and that liming reduced or prevented the injury.

An effort was made to determine the nature of the basic material in the extract of this soil, but lack of time prevented the completion of the work. Enough progress was made, however, to show that the extract

*The writer hereby expresses his appreciation of the faithful and efficient assistance rendered by S. A. Wingard and F. W. Parker in the prosecution of the work here reported.

from the high nitrate soil gave quite a precipitate with hydroxides.

This work was actively resumed in the fall of 1916. On October 21, the plots were prepared and fertilized as usual, a part of the fertilized plots again being covered to protect them from rainfall. The characteristic brown crust again appeared on the surface beneath the covers; and during a rather long rainless period the entire surface of some of the plots showed the brown incrustation. From this crusted surface, a bulk supply of soil was collected and taken to the laboratory for a study of the water soluble constituents therein. Continuing the work which had been started in the spring, water extracts of the high nitrate soil were analyzed, and were found to contain but little chlorides or sulphates, but enormous amounts of nitrates. Iron and aluminum were present in mere traces, or absent; but in every instance where the nitrate content of the soil was high, a large amount of manganese was found. On the contrary, in no case was a large amount of soluble manganese found in the soil from these plots, if the nitrate content was low. It was apparent, then, that there was some correlation between nitrate production and the development of soluble manganese in this acid soil. And since soluble manganese in appreciable quantities is toxic to plants, it was apparent, further, that it was the soluble manganese that was causing the injury to corn and sorghum in the pot experiments before mentioned.

It is the aim of this paper to report the work done in the effort to show whether or not soluble manganese is the cause of injury to plants grown in these soils, and if the process of nitrification is the cause of the development of soluble manganese.

## Review of Literature

A search through the literature shows that, while a large amount of work has been done with soluble manganese salts added to soils, but little study has been made of the water soluble compounds of manganese normally appearing in soils. Heretofore, the studies have been made chiefly on the assumption that there was a deficiency of such soluble compounds, and that, by their application, plant growth might be increased. Reviews of the literature bearing on this phase of the subject have been made by Kelley (8),* Skinner (18),

(*) Reference is made by No. to "Literature Cited" P. 41.

and others, and will not be taken up here. Suffice it to say that the results obtained by various experimenters are quite conflicting; some obtaining beneficial results, others negative results, and still others injury. Most workers are agreed, however, that application of soluble manganese compounds in amounts much greater than 50 pounds per acre are likely to cause injury, even where smaller amounts have produced increased yields.

With regard to the presence of water soluble manganese in soils, Kelly and McGeorge (9) report the analysis of 12 Hawaiian soils representing a very wide range, including normal and abnormal types. Of the 12 soils studied, 3 had more than 20 p. p. m. of soluble $Mn_3O_4$, while only two had less than 5 p. p. m. Drying these soils at 100° C. increased the solubility of manganese in 9 of the 12 soils; and drying at 250° C. produced an increase in 11 of the 12 samples. The maximum solubilities in the soils dried at 100° C. were 161.1 and 180.5 p. p. m. respectively.

In an unproductive soil on which legumes failed, Newell (13) found considerable quantities of manganese compounds soluble in water. Examinations of the extracts made from this soil showed that it contained about twice as much manganese as calcium, and it was suggested that the occurrence of such compounds contributed largely to the sterility of this soil.

De Sornay (4) states that Boname found that the nitric acid formed through nitrification, combined in the absence of a base, with manganese. While DeSornay's own work showed a considerable solubility of manganese in 2 per cent nitric acid, not more than a trace of manganese was dissolved by water, using the same methods of extraction in each case.

In a discussion of the effect of manganese phosphate on plants, Truog (20) states that "water extracts of acid soils often contain considerable amounts of manganese. When these soils are limed, scarcely no manganese is found in the water extract. Since manganese may greatly affect chlorophyll formation especially of clover and alfalfa, it seems possible that in some cases one of the reasons why soil acidity is injurious to clover and alfalfa is the presence of considerable manganese in the soil solution and hence in a condition to enter the plants in considerable amounts. The variable deportment of manganese in its chemistry makes it seem all the more probable that in certain cases the effect of soil acidity may be partly due to the manganese in solution."

## Experimental

### *Soil and Solution Cultures.*

All the pot culture work here reported was done in 2-gallon pots, in the green house. The pots were filled to within about one inch of the top with the soil to be used, after the soil had been thoroughly composited. No attempt was made to maintain a given water content in the pots, but tap water was added from time to time as the need was indicated. A part of the solution cultures was grown in pint jars, and a part in ordinary tumblers. The manner of setting up the tumbler cultures was essentially that of McCool (12).

### Manganese Determinations.

The manganese determinations were made by the ammonium persulphate method, as described by Hillebrande (7). The standard used contained one p. p. m. of Mn. The comparisons were made in tall form Nessler cylinders.

### Preparation of Soil Extracts

Bulk soil extracts were obtained by leaching approximately 20 pounds of soil until about 2 liters of percolate were obtained. However, these ratios were not exactly maintained. In some cases where a very concentrated solution was obtained, more than 2 liters were passed through the pot of soil. The leaching was usually done in a 2-gallon pot provided with a covered opening in the bottom; or in an inverted aspirator bottle, the bottom of which had been broken out. In either case, little difficulty was experienced in securing clear extracts.

### Preliminary Pot Experiments on Soil with a High Nitrate Content

As stated in the introduction, preliminary work with the sandy soil from the Alabama Experiment Station Farm carrying a very high nitrate content gave disappointing yields of corn in pots in the green house, while sorghum made little or no growth under the same conditions. From a bulk supply of the soil with a high nitrate content, duplicate pots were prepared and treated as follows:

Series 1 received no treatment; series 2 was limed; series 3 and 4 were thoroughly leached. After leaching, series 3 received no further treatment, while series 4 received nitrate of soda sufficient to replace the nitrate nitrogen removed by the leaching. As soon as the soil from the pots had dried sufficiently to permit planting, the several series were planted to sorghum. When the plants were about 2 inches high, the number was reduced to 8 plants per pot. The sorghum was harvested when some of the plants were in head, and the green weights taken. One pot of each series is shown in Plate I, fig. 1, and the average weights of the crops are given in Table I.

TABLE I.—*The Effect of leaching, lime, etc., on the Growth of Sorghum in Acid Soil with a High Nitrate Content.*

| TREATMENT | Green weight of sorghum: grams |
|---|---|
| Checks, no treatment | 55.5 |
| Limed, 18 gr. per pot | 263.5 |
| Leached | 75.5 |
| Leached, $NO_3$ equivalent returned as $NaNO_3$ | 278.0 |

The plants in the check pots showed a very unhealthy color as soon as they came up. After being thinned nearly all the plants in the check pots died. For about 5 or 6 weeks the surviving plants retained the unhealthy color, the tips and margins of the leaves showing the injury most clearly. Later, these plants seemed to overcome the initial injury, and made a satisfactory growth. The plants in the limed pots made a rather poor growth for a short time, after which they grew rapidly. In the leached pots the plants made a normal growth, but appeared to lack nitrogen. The fourth series which had been leached and treated with sodium nitrate in sufficient quantity to return the nitrate nitrogen removed, made a very satisfactory growth throughout.

This work was in part repeated, using small jars of about 2 pounds capacity as the containers. Similar soil with a high nitrate content was used. The unleached soil proved to be so toxic that all plants died after a few days. The duplicate jars were replanted, and again all but one plant died. The soil that had been thoroughly leached produced normal plants, both root and top. Liming this soil in a large measure removed the toxic body, although the root development was not so good as in the leached series. In still another series the soil was leached before planting, and the leachings slowly returned to the pots in the water applied to the growing plants. The plants in this series grew about as well as those in the limed series.

In all cases above discussed, each extract from the high nitrate soil had a very high concentration of manganese. The extracts contained not more than traces of iron, and very small amounts of aluminum. The data obtained justify the conclusion that the toxic body in this soil is easily removed by leaching; or is made non-toxic by the addition of lime. That the infertility is not due to the concentration of the soil solution is shown by the yields obtained from the pots to which nitrate of soda was returned to replace the nitrates leached out. Since manganese was the only unusual constituent found in quantity in the extracts, it was apparent that the infertility was due to this element, or to some soluble organic compound.

## Experiments to Determine the Cause of the Infertility of the Soil with a High Nitrate Content

Since thorough leaching of the soil carrying a high nitrate content greatly reduced its toxicity, the leachings from this soil should contain the substance responsible for the low productive power of the soil. In order to test this, the following methods were used: Pint jars were fitted with paraffined corks, through which five holes had been bored with a small cork borer. After the jars had been prepared and treated as indicated in Table II, germinated oat seedlings were inserted in the holes in the corks, and held in place by a wrapping of cotton. The cultures were then so placed in the laboratory as to receive maximum light. At the end of about three weeks, the plants were taken down, carefully air dried and weighed. The data so obtained are given in Table II.

TABLE II.—*The Effect of Dilution and of Precipitation, on the Toxicity of a Soil Extract Containing a High Concentration of $NO_3$ and Mn. Weight in Grams of Air Dry Roots and Tops.*

| Nature of Solution | Untreated | | | Precipitated | | |
|---|---|---|---|---|---|---|
| | Root | Top | Total | Root | Top | Total |
| Tap water | .110 | .125 | .235 | --- | --- | --- |
| Soil extract | .020 | .158 | .178 | .024 | .111 | .135 |
| Soil extract 50 per cent dist. water 50 per cent | .054 | .178 | .232 | .107 | .180 | .287 |
| Soil extract 25 per cent, dist. water 75 per cent | .091 | .158 | .249 | .134 | .198 | .332 |
| Soil extract 10 per cent, dist. water 90 per cent | .166 | .221 | .387 | .382 | .181 | .563 |
| Second leaching | .186 | .197 | .383 | --- | --- | --- |

When this soil extract was made alkaline with NaOH, a voluminous precipitate came down, which precipitate gradually darkened on standing. The precipitate was filtered out and $HNO_3$ added to slight acidity. Sufficient c. p. $CaCO_3$ was added to bring the extract back to the neutral point. In the last three columns of the table are given the yields of oats from the solutions so treated. On account of the wick-like action of the cotton wrapping around the seedlings, salts accumulated around some of the seedlings to such an extent as to become very injurious. In spite of this defect in the method used, the soil extract from which the elements precipitated by NaOH had been removed, proved to be a much better medium for growth than the original extracts of similar dilution.

A chemical examination of the second leaching from this soil showed that practically all of the manganese had been removed in the first extract. This second leaching was used as a medium for growth, with the results shown in the last line of Table II.

The evidence presented thus far shows that the brown crusted soil under discussion contains a very large amount of nitrates and soluble manganese; that this soil is a poor medium for plant growth; that leaching removes, in a large measure, the toxic body; that the water extract of this soil is highly toxic to seedling plants; and that the use of an active base markedly improves both soil and extract.

To obtain further evidence as to the cause of the toxicity of the extract of this soil, another supply of extract was obtained, and the culture method described by McCool was used. If the toxic body present were organic in nature, in all probability the extract would be improved by treating it with carbon black, as suggested by the work of Scheiner (16). In this work washed carbon black was used at the rate of 10 grams per liter and filtered out.

Again, the extract was distilled in an effort to determine if any volatile toxic bodies were present. The distillation was done in the following manner: 500 cc. of the extract was placed in a Jena flask connected with a glass condenser, and distilled until the distillate amounted to 485 cc. Both the residue and the distillate were then made to 1,000 cc with distilled water. Still another portion of the extract was evaporated to dryness, burned to a red heat in a porcelain dish, the mineral residue taken up with HCl, and evaporated to dryness on the water bath. A little water was added, and the salt again evaporated to dryness, after which the dish was heated at about 100° C. until no trace of free acid could be detected. This salt was then taken up with distilled water and made to volume. The extract that was precipitated was made alkaline with NaOH, the precipitate filtered out and $H_2SO_4$ added until the solution was slightly acid. Then a slight excess of c. p. $CaCO_3$ was added to bring the solution back to neutral. The sorghum cultures grown in these solutions were started May 15, and taken down June 5, 1917. The data are set forth in Table III, and photographs are given in Plate I, fig. 2.

TABLE III.—*The Effect of Carbon Black, Distillation, Precipitation, and Ignition on the Toxicity of a Soil Extract Containing a High Concentration of $NO_3$ and Mn.*

| Culture Medium | Av. air dry wt. of | | |
|---|---|---|---|
| | Roots | Tops | Total |
| Distilled water | .032 | .039 | .071 |
| Soil extract 50 per cent, dist. water 50 per cent, precipitated | .086 | .159 | .245 |
| Soil extract 25 per cent, dist. water 75 per cent, precipitated | .058 | .115 | .173 |
| Volatile part of soil extract 50 per cent, dist. water 50 per cent | .031 | .040 | .071 |
| Non-volatile part of soil extract 50 per cent, dist. water 50 per cent | .024 | .056 | .080 |
| Soil extract 50 per cent, dist. water 50 per cent, plus carbon black | .037 | .085 | .122 |
| Soil extract ashed, 50 per cent, dist. water 50 per cent | .029 | .057 | .086 |
| Dist. water plus carbon black | .038 | .034 | .067 |
| Soil extract 50 per cent, dist. water 50 per cent | .023 | .046 | .069 |
| Soil extract 25 per cent, dist. water 75 per cent | .021 | .039 | .060 |

A study of Table III along with the photograph on Plate I, fig. 2, shows that by far the best growth was obtained from the solution that had been precipitated with caustic soda, with the carbon black treated solution ranking second. The effect of carbon black was much more pronounced on top than on root development. The duplicates in this culture failed to agree, one making twice as much root as the other. The effect of separating the extract into volatile and non-volatile parts is best seen in the photograph, since the root weight fails to give a correct idea of the toxicity of the two separates. In such cases as this, it has been found that the short, stumpy roots developed are very woody, and are much heavier than is indicated by their appearance. Ashing the extract reduced the toxicity as indicated by appearance but not as indicated by the weight of roots produced. The fact that the more dilute extract gave poorer results than the more concentrated in each case where a comparison is afforded cannot be explained.

While the evidence is not conclusive, consideration of both the data and the photograph, indicates very strongly that the cause of the toxicity of this extract is inorganic rather than organic. On account of the results obtained with carbon black, the experiment was repeated with slight variations. The ashing of the solution, the separation into volatile and non-volatile parts, and the treatment with carbon black were made in the way already described. In this instance, the precipitation was done by adding to the extract a small amount of calcium oxide and shaking vigorously for about twenty minutes, after which the solution was left over night. It was then filtered and $CO_2$ led in until the extract gave no reaction with phenolphthalein. The portion treated with calcium chloride was given enough c. p. $CaCl_2$ to make a N/20 solution. The second leaching was obtained immediately after the first. The data obtained and the treatments given are found in Table IV.

TABLE IV.—*The Effect of Carbon Black, Distillation, Ignition, and Precipitation, on Plant Growth in a Toxic Soil Extract*

| Nature of Solution | Av. wt. root and top from | | | |
|---|---|---|---|---|
| | Peas | | Sorghum | |
| | Tops | Roots | Tops | Roots |
| Tap water | .2949 | .0921 | .0450 | .0181 |
| Soil extract | .1594 | .0640 | .0402 | .0075 |
| Volatile part of soil extract | .2327 | .1129 | .0382 | .0206 |
| Non-volatile part of soil extract | .3047 | .1244 | .0505 | .0128 |
| Soil extract and carbon black | .2250 | .0903 | .0471 | .0096 |
| Soil extract and $CaCl_2$ | .3458 | .1065 | .0443 | .0106 |
| Soil extract precipitated with Ca $(OH)_2$ | .3796 | .1358 | .0538 | .0177 |
| Soil extract ash | .2893 | .1164 | .0335 | .0107 |
| Second leachings | .3340 | .1214 | .0415 | .0103 |

Photographs of the peas and sorghum are shown in Plate II, figs. 1 and 2. Tap water was used in the extraction of the soil, and as a check in the cultures. The concentrated extract contained manganese equivalent to 255 p. p. m. $MnSO_4$, and the second leaching contained the equivalent of 17 p. p. m. The cultures grew from September 3 to September 19, 1917.

In the untreated soil extract, neither the peas nor the sorghum developed scarcely any roots, the growth of lateral roots being almost completely inhibited. The short, thickened roots were much darker than the normal. The volatile part of the soil extract proved to be a splendid medium for the growth of sorghum,—very much better than the non-volatile part. Exactly opposite results were obtained with peas, the volatile part producing less root and top than the non-volatile part. The tops of the peas grown on the non-volatile part, however, were almost white at the time the photograph was taken, and some of the leaves had dead margins. The tops of the sorghum plants were similarly affected under the same conditions. Highly bleached plants were also produced by the extract ash. Carbon black slightly improved the extract as shown by root and top development of both the plants grown, though the tops were yellow in both cases. Calcium chloride added in sufficient amount to make a N/20 solution, increased root and top development for both plants, though the peas were benefitted more than the sorghum as can be readily seen from the plant weights and the photographs. In presence of calcium chloride both plants produced tops of a normal green color.

The extract ash produced neary twice as much growth of peas as did the untreated extract; but for sorghum, little improvement was affected by ashing.

The results of this experiment appear to show that the toxic body in this extract is organic, at least in part. But special attention is called to the use of tap water in this case. The unexpected results obtained from the non-volatile part of the extract, and the extract ashed, both of which were made to volume with tap water, warranted a careful examination of the tap water used; and it was found to carry a very considerable quantity of calcium bicarbonate in solution. Since the untreated extract was highly toxic, the toxic body should have been found in either the volatile or the non-volatile part; but in this case, both separates supported a very fair growth, quite in disagreement with the results reported in Table III, where sorghum was also used as the plant indicator. It was suggested that the results obtained might be due to the bicarbonate of calcium carried in the tap water, which served to a certain extent as an antidote to the manganese in the soil extract.

In the effort to determine whether or not the salts in the tap water were responsible for the good root and top growth in the non-volatile part, and in the ashed part of the soil extract, another test was made, using a soil extract containing manganese equivalent to 204 p. p. m. of manganese sulphate. Unfortunately, a severe storm smashed a laboratory window and blew some of the plants from the containers, making it impossible to get the complete record. Notes on root and top development had been made previous to the accident, however, and these are here given.

Boiling the extract or heating it to 80°C., had little or no effect on the toxicity. The volatile part supported a good growth of roots, and a fair growth of tops. And, in agreement with the results given in Table IV., the non-volatile part made to volume with tap water produced a good growth of both roots and tops. On the other hand, the non-volatile part made to volume with distilled water produced a fair amount of tops, but root development was almost completely inhibited.

This experiment was again repeated, with modifications, using a soil extract containing 60 p. p. m. of Mn. The results are shown in Table V.

TABLE V.—*The Effect of Distilled Water vs. Tap Water, on the Toxicity of a Soil Extract Containing* 60 *p. p. m. Mn.*

| Culture Medium | Peas Wt. of air dry | | Sorghum Wt. of air dry | |
|---|---|---|---|---|
| | Roots | Tops | Roots | Tops |
| Tap water | .1209 | .3005 | .0251 | .0344 |
| Distilled water | .1318 | .2118 | .0105 | .0269 |
| Soil extract, untreated | .0550 | .3819 | .0050 | .0286 |
| Volatile part of soil extract | .1267 | .1986 | .0230 | .0304 |
| Non-volatile part of extract made to volume with distilled water | .0758 | .3497 | .0051 | .0208 |
| Non-volatile part of extract made to volume with tap water | .1626 | .3402 | .0210 | .0310 |
| Extract evaporated, ignited, dissolved, made to volume with dist. water | .0525 | .3125 | .0063 | .0255 |
| Extract evaporated, ignited, dissolved, made to volume with tap water | .1686 | .3566 | .0238 | .0340 |
| Extract plus 2 gm. $CaCO_3$ per liter | .1556 | .2971 | .0306 | .0399 |

The data given in Table V fully confirm the suggestion that the salts in the tap water used* in the previous experiments were responsible for the reduced toxicity of the soil extract which had been concentrated and again made to volume with tap water. The photographs shown on Plate III, figs. 1 and 2, show conclusively that concentrating the soil extract and making it back to volume with distilled water, had no effect on the toxicity of the solution; but when tap water was used, both roots and tops grew very well indeed. Similar results were obtained by evaporating the extract to dryness, igniting, and dissolving the residue in acid, as previously explained. When made to volume with distilled water, the toxicity was not reduced; but when made to volume with tap water, both roots and tops grew well. It should be stated, however, that in each of the tap water dilutions, the plants produced yellow tops. The untreated extract and the cultures made to volume with distilled water produced tops with a normal green color, but root growth was almost completely inhibited. Neither the sorghum nor the peas made lateral roots more than a few millimeters long. In the photograph, none of the sorghum roots in these cultures can be seen, but the stubby pea roots may be seen in tumblers No. 3 and 5. The soil extract to

*Five hundred cc of the tap water used in this experiment required 3.3 cc. of N/5 HCl to titrate, using methyl orange as the indicator.

which a little calcium carbonate was added produced nearly as good peas and sorghum as did the extract which had been reduced and made to volume with tap water, or ashed, and made to volume in a similar manner. The distillate of the soil extract was slightly better as a medinum for growth than distilled water made in the same glass still used in distilling the soil extract.

Evidence that the amount of manganese found in the several soil extracts used was sufficient to cause great injury to plants is here given. To the distillate of a toxic soil extract with a high manganese content, manganese sulphate was added to equal the manganese content of the original extract. Both roots and tops of plants died in this culture. In two other instances, soil extracts containing but traces of manganese, and capable of supporting a very satisfactory growth of sorghum, have been made extremely toxic through the addition of manganese sulphate at the rate of 200 p. p. m. These results are not surprising in view of the fact that McCool (12) has shown that a solution of N/4000 $MnCl_2$ (18 p. p. m.) is injurious, and N/2000 $MnCl_2$ (36 p. p. m.) prevents root growth of pea seedlings, using distilled water as the solvent.

One of the most interesting experiments tending to show the inorganic nature of the toxic body in our soil extracts is given in Table VI. The soil extract used contained 15.8 p. p. m. of aluminum, and 80 p. p. m. of manganese. The cultures grew from Dec. 8th to Dec. 29th, 1917.

The culture solution to which 3 cc. of N/1 NaOH were added was slightly alkaline to litmus and to phenolphthalein; but those to which less than 3 cc. were added, gave no reaction with these indicators. The cultures which received lime were treated with an excess of CaO, and vigorously shaken for about 20 minutes, after which the solution was left undisturbed for several hours. The excess calcium hydroxide was then carbonated. In all of the previous experiments, the compounds precipitated by alkaline hydroxides were filtered out; but in this case, the precipitate was left in the culture medium. Special attention is called to the fact that partial precipitation proved very much more effective in reducing the toxicity of this extract than various degrees of dilution. In fact, the dilutions used were not high enough to materially reduce the toxicity toward root development. With 50 per cent soil extract and 50 per cent distilled water, or with 25 per cent soil extract and 75 per cent distilled water, the solutions were toxic enough to seriously reduce root growth. On the other hand, with approximately 50 per cent or 75 per cent of the manganese precipitated, good root growth was obtained. Reduced toxicity of the cultures in which a part of the manganese precipitated is probably due to the antidotal action of the potassium salts formed in the culture medium. See Table VI for the data, and Plate IV, figs. 1 and 2 for the photographs of these cultures.

TABLE VI.—*The Effect of Precipitation and of Dilution on the Toxicity of a Soil Extract Containing* 15.8 *p. p. m. of Al., and* 80.0 *p. p. m. of Mn. in Solution.*

| Culture Medium | Av. air dry weight of | |
|---|---|---|
| | Roots | Tops |
| Tap water | .137 | .234 |
| Distilled water | .109 | .189 |
| Soil extract | .088 | .222 |
| Soil extract plus 0.6 cc. N/1 NaOH | .145 | .317 |
| Soil extract plus 1.2 cc. N/1 NaOH | .157 | .269 |
| Soil extract plus 1.8 cc. N/1 NaOH | .162 | .293 |
| Soil extract plus 2.4 cc. N/1 NaOH | .144 | .259 |
| Soil extract plus 3.0 cc. N/1 NaOH | .179 | .317 |
| Soil extract plus CaO | .170 | .318 |
| Soil extract 75 per cent, dist. water 25 per cent | .097 | .279 |
| Soil extract 50 per cent, dist. water 50 per cent | .093 | .276 |
| Soil extract 25 per cent, dist. water 75 per cent | .119 | .317 |
| Second leaching | .154 | .267 |

Even though a good top growth was obtained, there was practically no root development in the untreated soil extract. The addition of 0.6 cc. N/1 NaOH reduced the toxicity slightly; but this amount was not as effective as 1.2 cc. Beyond this point, increased amounts of alkali were not proportionately effective. Tests made on these culture solutions after the plants were taken out, showed that only a part of the manganese had been precipitated. This experiment strongly indicates the protective action of the sodium and the calcium salts formed with a part of the acid radicle formerly held by manganese and aluminum. Considering both the precipitation and the dilution cultures, it would appear that the amount of soluble manganese in soil relative to the amount of other soluble bases, is more important than the actual amount of soluble manganese. The work further indicates that precipitated manganese compounds are not toxic to pea roots, since many of the roots were buried in the precipitate in the container, at the time the experiment was discontinued; and there was no injury to these, so far as could be judged by external appearances.

The writer believes that the evidence given is sufficient to justify the conclusion that the toxicity of the soils and soil extracts studied was due chiefly to inorganic compounds and that manganese is the element responsible for the toxicity observed. And since but small amounts of sulphates and chlorides were usually found, manganese nitrate is believed to be the specific form in which the soluble manganese occurs.

### Does Nitrification Develop Soluble Manganese? Studies on Alabama Soils

In order to throw light on this question the following experiments were performed, using two different soils. One of the soils was taken from a plot on the Experiment Station Farm which had received annual application of sulphate of ammonia, and is very sour. It is designated "soil from plot 4" in the table. The other soil was taken from the plots described earlier in this paper and is designated "soil from nitrification plots"; this soil is but moderately sour. From each of these soils, three sets of pots were prepared, each treatment being made in duplicate on each soil. One set of pots was planted to sorghum on the day that the treatments were applied; the second set of pots was planted about seven weeks later; and the third set was left unplanted. The pots of this last set were leached after 95 days, the leaching filtered through a Pasteur-Chamberland filter, and analyzed. The treatment given, the crop yields, and the analyses of the extracts, are given in Table VII. Photographs of the pots are shown on Plate V, figs. 1 and 2.

TABLE VII.—*The Effect of Nitrogenous Fertilizers on the Development of Soluble Manganese, and on Plant Growth. Early Planted Crops Only. $NO_3$ Mn., and Green Weights of Sorghum in Grams.*

| Series | TREATMENT | Soil from plot 4 — Analysis of leaching from uncropped pots: $NO_3$ | Mn | Green weight of crop | Soil from nitrification plots — Analysis of leaching from uncr'p'd pots: $NO_3$ | Mn | Green weight of crop |
|---|---|---|---|---|---|---|---|
| 1 | None | 1.092 | .0039 | 20.0[2] | 1.432 | .0341 | 21.5 |
| 2 | Lime, 18 grms. | 1.867 | trace | 104.5 | 1.012 | trace | 106.0 |
| 3 | Am. sulphate, 4.3 grm. | 1.239 | .0372 | Dead | 1.015 | .0843 | 1.0 |
| 4 | Am. sulphate and lime | 12.424[1] | trace | 321.5 | 3.661 | trace | 373.0 |
| 5 | Dried blood, 7 grms. | 2.335 | .0237 | 31.5 | 2.118 | .0880 | 28.5 |
| 6 | Dried blood, and lime | 3.350 | trace | 330.5 | 4.470 | trace | 425.0 |

[1]Apparently there was an error in this determination.
[2]One pot omitted from average, since it was evidently abnormal.

The soil from plot 4 is a yellow rather heavy one, inclined to run together and puddle when wet. According to the Veitch method, the lime requirement is about 4,000 pounds per acre. In this experiment ammonium sulphate was nitrified but little in the unlimed pot. However, the water soluble manganese recovered by leaching was nearly ten times as great as from the unfertilized pot. Dried blood was nitrified to some extent, and the soluble manganese recovered was about seven times as great from the untreated pot. The other soil used is of a rather coarse sandy nature and leaches very readily. By the Veitch method, the unfertilized plot has a lime requirement of about 1200 pounds per acre. In this soil ammonium sulphate was not nitrified; and seemed to retard nitrification in the unlimed pots. On the other hand, dried blood was nitrified to a moderate degree, under the same conditions. Both the ammonium sulphate and the dried blood caused a very considerable increase in the soluble manganese in the unlimed pots.

Considering the plant growth, it will be seen that in both soils the addition of ammonium sulphate proved highly detrimental to sorghum in the unlimed pots. In fact, all the plants died soon after they came up. Without lime, dried blood produced but very little better growth than did the untreated soil. From the limed pots, only traces of manganese were recovered; and the growth of sorghum in these was very satisfactory. The increased nitrification cannot be the cause of the increased yields in the limed pots, since in the sandy soil lime apparently retarded nitrification in the unfertilized pots, but increased the plant growth five fold. The manganese leached from the unlimed fertilized pot of the sandy soil is quite sufficient to cause the poor growth obtained, as can be seen from the following considerations. The optimum water content of this soil is probably about 10 per cent. On this basis the water content of the approximately 20 pounds of soil per pot would be about 1,000 cc. Assuming that the manganese recovered in the leachings existed in the soil in readily soluble form, and calculating the manganese as sulphate, the concentration of the soil solution would be above 280 p. p. m. While the amount of manganese leached from the plot 4 soil is not as great as that obtained from the nitrification plot soil, still the amounts obtained are sufficient to cause injury to plants, according to the assumptions above. Repeated leachings from this soil continued to show manganese, even after about 7 liters had been percolated, and it is doubtful if all the soluble manganese could be removed by a much more thorough leaching than this.

Most of the pots used in the above work were planted to cow peas on June 17, and harvested August 25, 1917. In the early stages of growth, the plants in the pots to which ammonium sulphate or dried blood had been added, were yellow, and had a very unhealthy appearance. Later, all plants took on a healthy green color, and made a good growth, all pots yielding about alike. At harvest time, it was found that the root system of the plants in the unlimed fertilized pots was very poorly developed, and had a scant development of tubercles. Aside from this, there was little or no apparent injury to peas, as judged by final weights of tops produced. This result with cow peas is in strong contrast with sorghum in these same pots, and with cow peas in the field. In all probability, however, these plants with poor root growth would have made a poor showing under field conditions in time of drought.

After the cow pea harvest, the pots used in this work were left undisturbed in the green house until September 24, 1917, at which time, 5 grams of ammonium sulphate and 6 grams of dried blood were applied, respectively, to those pots which had received these substances in the previous treatment. No further addition of lime was made. On October 16, one set of pots was planted to oats, and the other, to crimson clover. A good stand of oats was obtained, but the clover came up very slowly in the unlimed, fertilized pots. On Nov. 17, all clover plants in the unlimed pots to which ammonium sulphate had been added were dead; and the unlimed dried blood treated pots carried very poor plants, some of which were dying. Of the limed pots, only those fertilized with ammonium sulphate produced unhealthy plants. All remaining clover plants were removed and English peas planted on November 17. Both the oats and the peas were harvested and weighed green on January 7, 1918. At this time, all of the peas on the unlimed pots fertilized with sulphate of ammonia were dead. Some plants in the limed pots of the sulphate of ammonia series, and the unlimed dried blood series, had such poor root development that the entire root growth was pulled out in cutting the plants with a knife. The lateral roots were mere stubs, not more than a fourth of an inch long in some instances. Oats failed on the unlimed sulphate of ammonia series, and were very poor on the unlimed dried blood series. In the limed series, with nitrogenous fertilizer, a very good growth was made. The average green weight of peas and of oats is given in Table VIII.

TABLE VIII.—*The Effect of Nitrogenous Fertilizers on the Growth of Oats and Peas, in Soil from "Plot 4" Alabama Experiment Station Farm.*

| TREATMENT | Av. green wt. in grams | |
|---|---|---|
| | Oats | Peas |
| None | 8.9 | 9.9 |
| Lime | 17.8 | 13.4 |
| Am. sulphate, 5 grms. | 2.1 | Dead |
| Am. sulphate, 5 grms., and lime | 62.8 | 10.9 |
| Dried blood, 6 grms. | 7.2 | 6.8 |
| Dried blood, 6 grms., and lime | 65.6 | 14.6 |

Oat plants pulled from the unlimed fertilized pots showed severe root injury similar in appearance to that obtained with plants taken from the field, where the addition of dried blood was causing crop failure.

A further study of the influence of nitrogenous fertilizers on the development of soluble manganese was made, using the following methods. One hundred gram portions of acid soils collected from various places in Alabama, were weighed into tumblers; and to each sample was added .1 gram of ammonium sulphate in solution. Distilled water was then added to the estimated optimum, and the tumblers set away in a dark closet. From time to time, distilled water was added to restore that lost by evaporation. Solutions were obtained for analysis by washing the 100 grams of soil into a jar with 500 cc of distilled water, the jar thoroughly shaken at short intervals and then allowed to settle, after which the supernatent extract was filtered through a Pasteur-Chamberland filter. The soils were incubated from June 15 to August 1, 1917. The data so obtained are given in Table IX.

TABLE IX.—*The Influence of Ammonium Sulphate on the Development of Soluble Manganese in Acid Soils. $NO_3$ and Mn. in p. p. m. of Air Dry Soils.*

| Soil No. | $NO_3$ in soil at | | Mn in soil at | |
|---|---|---|---|---|
| | Start | End | Start | End |
| 15 | trace | 200.0 | trace | 5.0 |
| 39 | trace | 25.0 | trace | 7.5 |
| 41 | trace | 130.0 | trace | 11.0 |
| 42 | trace | 130.0 | trace | 11.0 |
| 44 | trace | 100.0 | trace | 7.5 |
| 45 | trace | 43.0 | None | 6.5 |
| 46 | trace | 55.0 | trace | 4.5 |
| 47 | trace | 150.0 | None | 17.5 |
| 48 | trace | 55.0 | None | 6.0 |
| 49 | trace | 24.0 | None | 4.5 |
| 50 | 4.4 | 300.0 | 3.0 | 10.0 |
| 51 | 7.3 | 90.0 | None | 8.0 |
| 52 | 5.3 | 90.0 | trace | 7.5 |
| 53 | 4.0 | 55.0 | trace | 10.0 |
| 54 | trace | 9.0 | trace | 3.0 |
| 55 | trace | 150.0 | trace | 13.5 |
| 56 | trace | 24.0 | trace | 6.5 |
| 57 | 12.4 | 210.0 | None | 13.0 |
| 58 | 3.7 | 200.0 | trace | 7.5 |
| 59 | trace | 240.0 | trace | 40.0 |
| 60 | trace | 5.5 | trace | 3.0 |
| 61 | 13.6 | 1100.0 | trace | 92.5 |
| 62 | 3.0 | 100.0 | trace | 13.5 |
| 63 | 3.9 | 90.0 | None | 8.0 |
| 64 | trace | 13.0 | trace | 5.0 |
| 65 | 7.2 | 60.0 | trace | 19.5 |
| 66 | trace | 650.0 | trace | 13.5 |
| 67 | trace | 85.0 | None | 12.5 |
| 68 | 6.0 | 875.0 | None | 8.0 |
| 69 | trace | 50.0 | trace | 12.5 |
| 70 | 5.6 | 55.0 | 2.0 | 30.0 |
| 71 | 2.5 | 5.0 | trace | 7.0 |
| 72 | trace | 30.0 | None | 9.0 |
| 73 | 4.7 | 150.0 | trace | 12.5 |
| 74 | trace | 2.5 | None | 4.5 |
| 75 | 3.0 | 4.0 | 20.5 | 10.0 |
| 76 | trace | 38.5 | trace | 6.5 |
| 77 | 2.5 | 4.0 | 2.5 | 15.0 |
| 78 | trace | 100.0 | 6.0 | 14.0 |

As shown in Table IX, the addition of ammonium sulphate to these acid soils caused an increase in the soluble manganese in each of the soils, with the exception of number 75. In several of the soils, ammonium sulphate was nitrified so poorly that it seemed worth while to repeat the experiment; and this was done as far as the supply of soils at hand would permit. The method used was changed somewhat, in that dried blood was used in this instance at the rate of .1 gram for 50 grams of soil. The solution for analysis was obtained by leaching the soil on a filter paper held in a large funnel, until 100 cc of leachings were obtained. In case extracts were turbid, a little calcium nitrate was added to clear the solution. This was done, where necessary, after part of the extract had been analyzed for nitrates. A treated and an untreated portion was used in this experiment, to determine if the unfertilized soil developed soluble manganese. The soils were incubated at laboratory temperature from August 13 to November 20, 1917. The results obtained by this method are to be found in Table X.

TABLE X.—*The Effect of Nitrification of Dried Blood on the Development of Soluble Manganese in Acid Soils. $NO_3$ and Mn. in p. p. m. of Air Dry Soil.*

| Soil No. | Soil untreated | | Soil, +.1gm dried blood | |
|---|---|---|---|---|
| | $NO_3$ | Mn | $NO_3$ | Mn |
| 1[1] | 66.0 | None | 380.0 | 8.0 |
| 2[1] | 376.0 | 4.2 | 860.0 | 25.0 |
| 20 | 80.0 | None | 480.0 | 13.0 |
| 21 | 160.0 | None | 720.0 | 63.0 |
| 31 | 120.0 | None | 400.0 | 5.8 |
| 41 | 100.0 | None | 720.0 | 43.6 |
| 45 | 75.0 | None | 300.0 | None |
| 47 | 120.0 | None | 880.0 | 23.0 |
| 48 | 100.0 | None | 640.0 | 38.6 |
| 51 | 300.0 | None | 360.0 | 53.8 |
| 53 | 120.0 | None | 800.0 | 77.5 |
| 54 | 140.0 | None | 500.0 | 9.5 |
| 56 | 100.0 | None | 500.0 | 14.5 |
| 60 | 200.0 | None | 400.0 | 2.1 |
| 62 | 160.0 | None | 520.0 | 42.0 |
| 64 | 60.0 | None | 440.0 | 14.5 |
| 69 | 50.0 | None | 480.0 | 30.0 |
| 70 | 132.0 | None | 480.0 | 6.4 |
| 72 | 55.0 | None | 630.0 | 11.5 |
| 76 | 46.0 | None | 450.0 | 44.5 |

[1]Sample No. 1 is Plainfield sand, and sample No. 2 is Marshall silt loam, both of which were kindly furnished by E. Truog of the Wisconsin Agricultural Experiment Station.

An inspection of Table X shows clearly that the addition of dried blood caused an increase in the soluble manganese in each of the soils, with the exception of No. 45. The amounts made soluble in soils No. 21, 41, 48, 51, 53, 62, and 76 are probably sufficient to cause serious injury to most plants. Calculating the manganese as nitrate, and assuming the acre foot of soil 6 inches deep to weigh two million pounds, the manganese recovered from several of these soils is equivalent to more than 200 pounds per acre, an amount that has been found by a number of investigators, to be great enough to injure crops. In the unfertilized soils, only the Marshall silt loam from Wisconsin gave any manganese in the extract. The evidence here given seems to warrant the conclusion that the acids developed in the nitrification of dried blood may dissolve manganese in large quantities in the absence of active bases. Further, it appears that sulphate of ammonia may increase the solubility of manganese without increasing the amount of nitrates in a soil. On the other hand, the data show that a very considerable degree of nitrification of the organic matter occurring in soils, does not bring manganese into solution, as indicated by the methods used. Again, when rapid nitrification causes the solution of some manganese, not more than 20 per cent of the nitrates recovered were in the form of manganese nitrate, assuming all of the manganese to be in nitrate form.

## Studies on Soils from Plots 31 and 32, Tier 4, of the Pennsylvania Experiment Station

Through the courtesy of Prof. J. W. White, a small quantity of soil was obtained from plots 31 and 32, tier 4, of the rotation experiments at the Pennsylvania Experiment Station. Plot 31 receives 48 pounds of nitrogen and plot 32 receives 72 pounds, in the form of sulphate of ammonia. The acidity of these two soils according to White (21) is roughly proportional to the amount of sulphate of ammonia that has been applied. The soil on plot 32 has become so acid that crops have begun to fail in recent years. To show whether or not soluble manganese would be developed in these two soils, the same method described above was employed, using 100 grams of soil and .1 gram of dried blood and sulphate of ammonia, respectively, per tumbler.

After incubation from August 13 to November 23, 1917, the soil was leached as described above. As soon as the first leaching was completed the containers were replaced by others and a second leaching obtained. The soil was then air dried and again leached. The treatments and the analyses of the extracts are given in Table XI.

TABLE XI.—*The Effect of Dried Blood and Sulphate of Ammonia on the Development of Soluble Manganese in Soils from the Pennsylvania Experiment Station. Mn. and $NO_3$ in p. p. m. of Air Dry Soil.*

| TREATMENT | Soil from plot 31 | | | | | Soil from plot 32 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mn in Leaching | | | $NO_3$ in Leaching | | Mn in Leaching | | | $NO_3$ in Leaching | |
| | 1 | 2 | 3 | 1 | 2 | 1 | 2 | 3 | 1 | 2 |
| Dry checks | 17.0 | 5.4 | 3.2 | 18.0 | 1.7 | 33.5 | 11.0 | 6.2 | 29.0 | trace |
| Dist. water | 12.2 | 2.0 | 1.2 | 140.0 | 2.2 | 54.0 | 13.4 | 7.1 | 210.0 | 8.2 |
| Dried blood | 46.2 | 3.9 | 2.9 | 430.0 | 2.7 | 89.0 | 12.0 | 8.6 | 370.0 | 6.8 |
| Am. sulphate | 45.0 | 4.8 | 2.0 | 160.0 | 2.0 | 115.0 | 14.0 | 6.7 | 110.0 | 10.0 |

In the first leachings, the air dry soil from plot 31 gave up 17 p. p. m. and soil from plot 32, 33.5 p. p. m. of manganese. Incubation of these soils with distilled water for three months resulted in a decrease in the soluble manganese in soil from plot 31, while there was quite an increase in the amount recovered from soil from plot 32. In each soil incubation with dried blood produced approximately 2.5 as much soluble manganese as was found in the dry checks; and very notable increases in the nitrate content. Soil from plot 31 nitrified ammonium sulphate to a certain extent, with an increase in the soluble manganese equal to that produced by dried blood. On the other hand, ammonium sulphate retarded nitrification in the soil from plot 32, but caused an enormous increase in the solubility of the manganese. Qualitative tests showed the presence of traces of iron and small amounts of aluminum in some of the extracts. However, the amount of aluminum present was not nearly as great as the manganese.

The amount of chlorides found in the soil extracts was very small; and of those examined for sulphates, where dried blood was the source of nitrogen, only minute quantities of sulphate were found. The conclusion seems justified, therefore, that the manganese recovered was in the form of nitrate, in the dried blood treated soils; and as nitrate or sulphate in the soil to which ammonium sulphate was applied. The evidence presented indicates that the addition of certain nitrogenous fertilizers to acid soils from the Pennsylvania plots may increase the infertility of these plots by bringing into solution relatively large quantities of manganese.

In order to study the toxicity of the extracts of the Pennsylvania soils, the following methods were used: Eight hundred gram portions of the soil were weighed out and treated with one gram of dried blood, and 0.8 gram of ammonium sulphate, respectively, and thoroughly mixed. Each portion of soil was then placed in a percolator, the required amount of distilled water added, and incubated at 28°C. from October 12 to December 29, 1917. Each peroclator was then leached with distilled water until 1600 cc. had passed through the 800 gms. of soil contained. Samples of the air dry soil were also leached to make possible a comparison of the extracts of the original soil with those of the same soil that had been treated. Pea cultures were set up in the usual way and permitted to grow from Jan. 5 to Jan. 26, 1918. A photograph of all cultures grown in the extract of the soil from plot 32 is shown in Plate VI, fig. 1, and the complete data is presented in Table XII.

TABLE XII.—*The Effect of KOH and $CaCO_3$ on the Toxicity of Water Extracts of the Soil from Plots 31 and 32, Penn. Exp. Station. Air Dry Weight of Pea Roots and Tops, in Grams.*

| Source of culture medium | Treatment of culture medium | Partial Composition P. P. M. | | | Average weight of | |
|---|---|---|---|---|---|---|
| | | Ca | Mn | $NO_3$ | Roots | Tops |
| Tap water | ---- | --- | --- | ---- | .1769 | .2486 |
| Distilled water | ---- | --- | --- | ---- | .1249 | .1395 |
| Extract, plot 31, initial condition | ---- | --- | 12.0 | 9.5 | .1486 | .2607 |
| Extract, plot 31, plus dried blood | ---- | 60.2 | 22.0 | 200.0 | .1521 | .2281 |
| Extract, plot 31, plus dried blood | 1.0 gm. $CaCO_3$ | --- | 22.0 | 200.0 | .1491 | .1862 |
| Extract, plot 31, plus dried blood | 1.0 gm. $CaCO_3$ plus $CO_2$ | --- | 22.0 | 200.0 | .1689 | .2500 |
| Ext. plot 31, plus am. sulphate | ---- | 77.3 | 42.5 | 110.0 | .1596 | .2180 |
| Ext. plot 31, plus am. sulphate | 1.0 gm. $CaCO_3$ | --- | 42.5 | 110.0 | .1734 | .2282 |
| Ext. plot 31, plus am. sulphate | 1.0 gm. $CaCO_3$ plus $CO_2$ | --- | 42.5 | 110.0 | .1725 | .1946 |
| Extract, plot 32, initial condition | ---- | 22.0 | 21.0 | 18.0 | .1391 | .1892 |
| Ext. plot 32, incubated, no fert. | ---- | 36.1 | 37.5 | 100.0 | .1150 | .1990 |
| Ext. plot 32, plus am. sulphate. | 1 cc N/1 KOH | --- | 37.5 | 100.0 | .1860 | .2610 |
| Ext. plot 32, incubated, no fert. | 2 cc N/1 KOH | --- | 37.5 | 100.0 | .2033 | .2569 |
| Ext. plot 32, plus am. sulphate | ---- | 41.4 | 42.5 | 53.7 | .0997 | .3172 |
| Ext. plot 32, plus am. sulphate | 2 cc N/1 KOH | --- | 42.5 | 52.7 | .2025 | .2839 |
| Ext. plot 32, plus am. sulphate | 4 cc N/1 KOH | --- | 42.5 | 53.7 | .1927 | .3045 |
| Ext. plot 32, plus am. sulphate | 1.0 gm. $CaCO_3$ | --- | 42.5 | 53.7 | .1967 | .2499 |
| Ext. plot 32, plus am. sulphate | 1.0 gm. $CaCO_3$ plus $CO_2$ | --- | 42.5 | 53.7 | .2059 | .2630 |
| Extract, plot 32, 2nd leaching | ---- | --- | --- | ---- | .1645 | .2656 |

The soil from plot 31 nitrified dried blood much more efficiently than ammonium sulphate. However, ammonium sulphate caused nearly twice as much manganese to go into solution as did the dried blood. Ammonium sulphate retarded nitrification in the soil from plot 32, but increased the amount of manganese in the solution. Incubation of this soil without fertilizers of any kind, increased the amount of soluble manganese from 21 to 37 p. p. m. of solution.

In every case, the peas grown in the untreated soil extracts showed a tendency to bleach; the untreated extract from plot 32 produced plants that were almost white. Those extracts to which calcium carbonate was added made a good growth of both roots and tops; but even here, bleached leaves were found, and the entire foliage was of a lighter green color than that of plants grown in the solution to which caustic potash had been added. According to McCool (12), such bleaching is a characteristic effect of manganese. Had these cultures received direct sunlight, instead of the subdued light from glazed windows, it is very probable that the injury to the tops would have been much more severe.

As shown in Table XII, the extract of the soil from plot 31 which had been incubated with dried blood contained 22 p. p. m. of Mn., and 200 p. p. m. of $NO_3$. The original air dry soil from plot 32 gave an extract with 21 p. p. m. of Mn., and 18 p. p. m. of $NO_3$. With the same manganese content, these two extracts differed widely in toxicity. Each supported a fair root growth; but the tops of the peas grown in the extract from plot 32 were highly abnormal in development, and were almost white. Since these extracts contained widely different amounts of nitrates, it was thought possible to explain the difference in toxicity on the basis of the difference in calcium content. Therefore, after the cultures were taken down, quantitative calcium determinations were made on these, and on several other untreated extracts. And the less toxic extract with the high nitrate content, was found to contain 60.2 p. p. m. of Ca., while the more toxic extract contained only 22.0 p. p. m. of Ca. Incubated with sulphate of ammonia, soil from plots 31 and 32 gave extracts with identical amounts of manganese. But the extract from plot 31 was not nearly so toxic toward pea roots as was the extract from plot 32. The difference in the calcium content of the two extracts again offers an explanation as to the cause of the difference in toxicity. These data in a large measure confirm the suggestion that it is the relative amount of soluble manganese, rather than the total, that determines the toxicity of a soil, or of its extract.

Considering in detail the extracts of the soil from plot 32, a photograph of which is given in Plate V, fig. 1, it will be seen that the extract of the original soil produced abnormal, bleached tops, but a fair development of roots. However, the addition of a little caustic potash to this extract removed the toxicity toward both roots and tops. Incubated with sulphate of ammonia, soil from plot 32 gave an extract that was extremely toxic. Here again, the tops were almost white, and made practically no growth. The roots grew but little after being placed in the solutions, lateral root development being almost completely suppressed. The toxicity of this extract was completely removed by the addition of caustic potash. In each case the manganese precipitated from the extracts was left in the tumblers in which the plants grew. By a close inspection of the photograph on Plate VI, fig. 1, the black precipitate may be seen in the bottom of the tumblers, 3, 4, 6, and 7. The precipitated manganese, with roots growing in it, is very clearly shown in the photograph on Plate VI, fig. 2. Insoluble manganese has no toxic effect whatever, since many roots were growing normally, even where several inches of root were embedded in the precipitated manganese. In so far as can be judged by the methods used, it would appear that the infertility of the sour plots in the Pennsylvania rotation experiments owe their infertility, in a large measure, to the presence in the soil solution of relatively large amounts of manganese.

### Does Sulfofication Develop Soluble Manganese?

When sulphur is added to an unsterilized soil and incubated, a part of the sulphur is oxided to sulfuric acid. The result of such oxidation is to increase the acidity of acid soils. Ames and Boltz (1) found a decided increase in the water soluble acidity of soils to which sulphur had been added. Shedd (16) found that the addition of large amounts of sulphur enormously increased the acidity of the soil, even where lime had been applied at the rate of 4,000 pounds per acre. Where large amounts of sulphur had been added, plants either failed to germinate, or made but little growth if there was any germination.

In view of the fact that our work indicated an increase in the solubility of manganese due to the use of dried blood or ammonium sulphate, it was thought worth while to study the influence of sulfofication on the development of soluble manganese in acid soils. In this experiment the same methods were used as in the study of the effect of dried blood, 0.1 gm. of sulphur being used to each 100 gms. of air dry soil. The soils were incubated at room temperature from Nov. 16, 1917, to Jan. 30, 1918. They were then leached as previously explained and manganese determinations made. The data so obtained are set forth in Table XIII.

TABLE XIII.—*The Effect of Sulphur on the Development of Soluble Manganese in Acid Soils.*

| Source of Soil | Treatment | Mn in p. p. m. of air dry soil |
|---|---|---|
| Plainfield sand, Wis. | None | None |
| Plainfield sand, Wis. | 0.1 gm. sulphur | 54.0 |
| Marshall silt loam, Wis. | None | trace |
| Marshall silt loam, Wis. | 0.1 gm. sulphur | 54.0 |
| Plot 31, Penn. Agr. Exp. Sta. | None | 26.0 |
| Plot 31, Penn. Agr. Exp. Sta. | 0.1 gm. sulphur | 182.0 |
| Plot 32, Penn. Agr. Exp. Sta. | None | 84.0 |
| Plot 32, Penn. Agr. Exp. Sta. | 0.1 gm. sulphur | 168.0 |
| Thomasville, Ala. | None | None |
| Thomasville, Ala. | 0.1 gm. sulphur | 160.0 |
| Leroy, Ala. | None | None |
| Leroy, Ala. | 0.1 gm. sulphur | 40.0 |
| Boaz, Ala. | None | None |
| Boaz, Ala. | 0.1 gm. sulphur | 38.0 |
| Clanton, Ala. | None | None |
| Clanton, Ala. | 0.1 gm. sulphur | 52.0 |
| Tanner, Ala. | None | None |
| Tanner, Ala. | 0.1 gm. sulphur | 104.0 |
| Oxford, Ala. | None | None |
| Oxford, Ala. | 0.1 gm. sulphur | 68.0 |
| Oxford, Ala. | 0.2 gm. sulphur | 168.0 |
| Plot 4, Ala. Exp. Sta.[1] | None | 3.6 |
| Plot 4, Ala. Exp. Sta. | 0.1 gm. sulphur | 33.6 |
| Plot 4, Ala. Exp. Sta. | 0.2 gm. sulphur | 39.6 |
| Plot 4, Ala. Exp. Sta. | 0.1gm. sul. 1gm. $CaCO_3$ | None |
| Plot 8, Ala. Exp. Sta.[2] | None | None |
| Plot 8, Ala. Exp. Sta. | 0.1 gm. sulphur | 28.0 |
| Plot 8, Ala. Exp. Sta. | 0.2 gm. sulphur | 54.0 |
| Plot 8, Ala. Exp. Sta. | 0.1gm. sul., 1gm.$CaCO_3$ | None |

[1]From source of nitrogen test.
[2]From rotation experiments.

All of the soil extracts were tested for sulphates, and it was found that each soil to which sulphur was added contained much more sulphates than the untreated soil. However, quantitative determinations were not made. The oxidation of sulphur increased the amount of soluble manganese in each of the soils used; and in several the amount made soluble was relatively large. In both of the soils from Pennsylvania and in three of the soils from Alabama, above 100 p. p. m. of manganese were made soluble. The smallest amount found in the treated soils was 28 p. p. m. Calcium carbonate added at the rate of 1 per cent completely prevented the solution of manganese. The results indicate that soils in need of sulphur fertilization should be well limed, unless already supplied with lime, if injury from sulphur application is to be avoided. Further, it is believed that these results explain the sterility of Shedd's soil to which large amounts of sulphur were applied. Manganese, aluminum, or iron, in the form of sulphate, very probably cause sterility, rather than free sulfuric acid.

## The Toxicity of Field Soils to Which Different Nitrogenous Fertilizers Have Been Applied

As stated in the introduction, 16 plots on the Alabama Experiment Station Farm have been devoted to a field study of the rate of nitrification of dried blood, cottonseed meal, and calcium cyanamid, beginning in the spring of 1913. The area occupied by these plots is very uniform, and is nearly level. The surface soil is very sandy and has a low water capacity. The subsoil is a yellow sandy clay with a much higher water capacity than the surface soil. Soluble salts are very readily lost from this soil by leaching, as shown by unpublished results.

The fertilizers given these plots are in sufficient amounts to furnish nitrogen at the rate of 77 pounds per acre. All fertilizer has been applied broadcast, and either disked or plowed in. Since 1915, applications have been made in both spring and fall.

Each crop is grown continuously on the same set of plots. With the exception of the first year, one-half of each plot has been fallowed both winter and summer. A winter cover crop of oats has been planted on the cropped ends of all plots most of the years.

All of the summer crops made a fair response to the nitrogenous fertilizers during the years 1913-15. The summer of 1916 was so extremely unfavorable that little was made on any of the plots.

During the late winter and early spring of 1916, it was noticed that a brown crust had formed on the surface of some of the highly fertilized plots, which crust contained an enormous amount of nitrates. Pot experiments previously described indicated that this brown crusted soil contained some material that was toxic to plants. In order to get as much information as possible on the cause of this toxicity, the plots were carefully planted in 1917, both the fallowed and the cropped ends being planted. The spring was comparatively dry thus affording conditions favorable for salt accumulation.

At the end of the growing season all of the crops were harvested and weighed green. The corn and sorghum were cut near the ground, while the cotton and cow peas were pulled, both root and top being weighed. The yields obtained are set forth in Table XIV.

TABLE XIV.—*Yield of Crops from Plots Treated with Different Forms of Nitrogenous Fertilizers. Green Weight of Crops in Pounds.*

| Treatment of Plot | Crops | | | |
|---|---|---|---|---|
| | Sorghum | Corn | Peas | Cotton |
| Dried blood | 12663 | 11718 | 5481 | 126 |
| Cotton seed meal | 16821[1] | 17693 | 9576 | 2520 |
| None | 12663 | 5733 | 5985 | 1764 |
| Calcium cyanamid | 17514[1] | 15876 | 8631 | 4662 |

[1]These sections of the sorghum plot received dried blood. In 1913, only the first section was fertilized. The entire plot was unfertilized in the fall of 1916.

Considering the effect of the different forms of nitrogen, it will be seen that dried blood produced the poorest yields with each crop. The highest yield of corn and peas was obtained from the plot treated with cotton seed meal, while cotton yielded best on the plot fertilized with calcium cyanamid. The brown surface crust before mentioned has never been noted on the unfertilized plot, nor on the plots treated with calcium cyanamid. The nitrate content of these plots is usually much lower than that of the plots receiving cotton seed meal or dried blood. Of the crops fertilized with cotton seed meal, cotton was the only one that was seriously injured in the field. Each crop fertilized with dried blood suffered very seriously from some cause. The damage on the dried blood sections was much greater on the ends that had been in fallow for several years, than on the ends that had been continuously cropped, with the exception of the plot in cotton, in which case the entire plot failed. The condition of each crop on the end of the plots previously fallowed and previously cropped, is clearly shown in the photographs on Plates VII, VIII and IX. A possible explanation of the different yielding powers of the fallowed and the cropped ends of the plots is that toxic salts accumulated in the fallowed section. At times during previous seasons, the fallowed plots frequently accumulated more than 100 p. p. m. of nitrates, while the other end of the same plot, carrying a crop, usually had less than 10 p. p. m. at the same time. It should be stated, however, that such differences usually disappeared with the coming of heavy winter rains. Even in such instances, it is possible that the readily soluble salts may have been, in part at least, brought back to the surface soil in the capillary water during the dry weather of spring.

It is difficult to explain the much greater injury to crops on the plots fertilized with dried blood than on those where cotton seed meal is the source of nitrogen. The nitrate content of the plots to which cotton seed meal is added has been, usually, slightly higher than in the dried blood treated plots. It has been suggested that a part of the nitric acid developed through the nitrification of the cotton seed meal may be neutralized by the calcium and potassium compounds in the meal itself, and hence less manganese is rendered soluble.

Examination of the roots of plants which were making poor growth showed that the roots were brown or nearly black, and in many cases, practically dead. Cotton plants shed most of their leaves, and finally most of them died outright. The leaves of sorghum and corn seemed to be affected alike.. The tips and margins of the leaves turned yellow and usually died. So many of the sorghum plants died that by summer, the stand was very poor. The corn plants had a purplish color, similar to that described by Kelley (19).

In the fall of 1917 the first tier of plots in this section was prepared as usual and planted on October 20. One or two rows of the following crops were planted across each section: Rye, wheat, oats, crimson clover, bur clover, narrow leaf vetch, hairy vetch, and rape. On December 24, 1917, specimen plants from the plots fertilized with dried blood and with calcium cyanamid were dug with a hand trowel, placed in covered jars, and taken to the laboratory to be photographed. The plants were taken up and handled as nearly alike as possible. The condition of the root and top is clearly shown in Plates X, XI and XII. The roots of all plants fertilized with dried blood were unhealthy, poorly developed, and appeared to be practically dead. The absence of root hairs is shown by the dearth of soil adhering to the roots. The few roots produced by bur clover were all dead at the time the plants were photographed. Rape, crimson and bur clover had been so severely injured that scarcely enough plants could be found for photographic purposes; while wheat, rye, oats, and the vetches were still living, but making no growth.

An examination of the plants in the plot to which cotton seed meal was applied showed that there was some injury to plant roots in this plot, but not nearly so much injury as was found on the plot fertilized with dried blood.

Water soluble manganese has been recovered from the plots fertilized with cotton seed meal or dried blood, but none has been found in the plots treated with calcium cyanamid. Apparently calcium cyanamid has a sufficient basic tendency to prevent the development of soluble manganese in this soil. The fact that the lime requirement of the plots fertilized with dried blood and with calcium cyanamid is 2568 and 856 pounds per acre, respectively, supports this view.

## Discussion

It is believed that the work here presented offers further explanation of the cause of infertility of acid soils. Regarded in a broad way, it may be stated that the results emphasize the importance of sufficient active bases in the soil to prevent the solution of such compounds as manganese and possible aluminum, iron, etc. This view is substantiated by the fact that soil extracts which are toxic, apparently, because of the presence of soluble manganese, may be made non-toxic by the addition of either calcium, sodium, or potassium hydroxide. Such toxic extracts may be greatly improved by the precipitation of only a part of the soluble manganese, the corresponding salts of the added bases probably serving as an antidote to the salts of manganese remaining in solution. According to this view, non-productive acid soils may owe their infertility to the presence in the soil solution of salts of certain bases which are injurious to plant growth, rather than to the actual acidity of the soil. Support for this view may be found from the fact that corn, cotton, cow peas, velvet beans, soy beans, peanuts, and sorghum have been grown on a set of plots on the Alabama Experiment Station Farm, the soil of which has nearly twice as high a lime requirement as have the plots from which most of our soil extracts were obtained for the work here given. The more acid soil receives moderate fertilization and is productive, while the less acid plots are heavily fertilized with nitrogenous fertilizers, and are rapidly becoming non-productive. In other words, productivity seems to be more dependent upon the nature of the salts in the soil solution, than on the actual acidity of the soil. (a) In this connection, it would be very interesting to know the solubility of the manganese in the soil solution of the variously treated plots of the rotation experiment at the Pennsylvania Station. For the soil on these plots, White has attempted to set an acidity limit beyond which clover fails. Is it actual acidity, or is it soluble manganese that prevents the growth of clover, after the lime require-

(a) Since the completion of this manuscript, a paper by B. L. Hartwell and F. R. Pember (Jour. Am. Soc. Agr., v. 10, No. 1) has come to hand in which a very similar view has been advanced, based on studies on soluble aluminum in acid soils of Rhode Island. These writers state that "A moist acid soil upon which most kinds of plants were unable to exist was kept intimately mixed for about two weeks with acid phosphate added at the extraordinary rate of 28 tons per acre, after which lettuce was planted. This crop could not exist on the unphosphated soil supplied only with nutrients, but the soil treated with acid phosphate produced a maximum crop, even more than when lime replaced the phosphate. It was shown that for a considerable time at least, the large amount of acid phosphate greatly increased the acidity, and yet a crop which usually responds markedly to liming had made its maximum growth on a very acid soil without the addition of any lime. The solubility of the aluminum in dilute acetic and carbonic acids had been markedly reduced by the phosphate, just as it doubtless would be by lime or by a mixture of the two."

"Determinations of the amount of what may be called active aluminum may prove to be as desirable as acidity determinations, and the lime requirement of a soil may be due to the need for lime to precipitate toxic aluminum quite as much as to neutralize acidity."

ment approximates a certain amount per acre? Again, does sorrel invade acid soils because it grows well under such conditions? White (22) has shown that lime greatly benefits this plant, and that it is found on the very sour plots 32 because other plants failed and there is no competition. Since sorrel is not an acid loving plant, but still grows where clover and other crops fail, apparently, it is the tolerance of manganese, more than the tolerance of acidity which permits this plant to grow under such conditions.

In his discussion of the variations in yields from the acid plots at Pennsylvania, White (21) says the variations may be due to "increasing amounts of organic acids which in the absence of sufficient basic material accumulate from year to year and exert an increasing 'toxic' effect on plant growth. The resultant effect may be physical, chemical, physiological, or bacteriological." Studies on soils from Pennsylvania and from Alabama indicate strongly that the toxicity of the soils used is due chiefly to soluble manganese, with possibly aluminum playing a small part. Precipitation of the manganese from the water extract of these soils is all that is necessary to make such extracts very satisfactory mediums for plant growth. Further, there is little indication that the toxicity of the Alabama soil extracts is due to any form of organic matter. Extracts from our soils have been ashed in several experiments with little or no indication of benefit, except where the ash was taken up with tap water. Nor has carbon black effected any marked improvement in such extracts. Boiling in the open, or under a reflux condenser failed to reduce the toxicity. The distillate from the soil extracts proves to be as good medium for plant growth as ordinary distilled water. These tests are deemed to be sufficient to show that the toxic body is inorganic, rather than organic. Of the unusual inorganic elements found, manganese was present in greatest quantity, and is very probably the chief cause of toxicity.

The data presented on the previous pages puts special emphasis on the toxicity of manganese soluble in the soil solution of acid soils. However, the possibility of the occurrence of soluble aluminum and iron under such conditions has not been disregarded, since it has been shown that under certain conditions quite appreciable amounts of aluminum, with usually less amounts of iron occur in the water extracts of acid soils. Connor et al (3) have shown that acid soils of the Kankakee region of Indiana contained relatively large amounts of water soluble aluminum, and small amounts of iron. The soils studied appeared to support a vigorous nitrification , with aluminum as the base, in part at least, uniting with the nitric acid formed. The aluminum nitrate thus produced was thought to account for the barrenness of the soils in question. A water extract of these soils was found to be about as toxic as a solution carrying aluminum nitrate and nutrient salts to approximate the composition of the soil extract. The addition of various chemicals which would precipitate the aluminum, removed the toxicity of such extracts.

Ruprecht and Morse (15) found considerable amounts of water soluble iron and aluminum in soil that had been continuously fertilized with ammonium sulphate; further, treatment of the soil with ammonium sulphate increased the solubility of these compounds, showing that use of this nitrogenous fertilizer on acid soils may cause injury to crops through the solution of such elements even though no nitrification takes place.

In the writer's work on the soils from the Alabama Experiment Station Farm, not more than traces of iron was found; and in many instances, only traces of aluminum were present. One of the very concentrated extracts used early in the work had less than one-tenth as much soluble aluminum as manganese; while a recent extract contained 15.8 p. p. m. of aluminum and 80 p. p. m. of manganese. The extracts from plot 32 of the Pennsylvania Experiment Station contaned mere traces of iron, and but little more than traces of aluminum. On the other hand, under various treatments this soil has been found to contain from 75 to more than 100 p. p. m. water soluble manganese. Since normal soils have been shown by Robinson (14) to contain very much more aluminum than manganese, it would appear that the manganese compounds found in soils are more readily soluble than aluminum. It is conceivable, however, that in time the small amounts of manganese may be exhausted,* and that soluble aluminum and iron be found in soils where now, chiefly manganese goes into solution.

The occurrence of soluble manganese in a soil extract is a strong indication of acidity. But not all acid soils contain soluble manganese. From our work, it appears that rapid nitrification, or the use of a fertilizer which is acid in nature, are the chief causes for the solubility of this element. Slow nitrification of the relatively inert soil organic matter causes but little development of soluble manganese, as shown by data in Table IX. In neutral soils, soluble manganese is rarely found; and under basic conditions, the writer has never found a trace of this element soluble in water. Soluble manganese added to a very acid soil may be quite largely removed by leaching, even after standing for some days. But if calcium carbonate be added to an acid soil, soluble manganese applied is rapidly removed from solution, calcium being found instead. An acid soil so treated in our laboratory contained but a trace of soluble manganese after six days, and none after thirteen days.

The field work of Skinner and Reid (19) is interesting in this connection. On acid soil of the Arlington Farm, an application of 50 pounds per acre of manganese sulphate caused decreased yields of wheat corn, cowpeas and potatoes; with rye, variable results were obtained. After continuing the experiment for five years, systematic liming of the soil was begun. When sufficient lime had been applied to completely counteract the acidity, each crop except potatoes yielded best on the manganese treated area. In all probability, the decreased yields attributable to the use of manganese sulphate before liming, were due to the fact that this compound remained unchanged in the acid soil, and proved toxic to the crops grown; on the other hand, it is very doubtful if the increased yields obtained after liming should be attributed to manganese sulphate as such. With the establishment of basic conditions, the soluble manganese added would very likely be precipitated in a relatively insoluble condi-

*As an average of determinations made on duplicate samples of soil from the plots used in our field work, there were 262.5 p. p. m. of Mn., and 51.3 p. p. m. of Ca., soluble in hydrochloric acid, the digestion being made according to the A. O. A. C. method.

tion, with the formation of a corresponding amount of calcium sulphate. The increased productiveness then, may have been due to the precipitated manganese compounds, or to the stimulating action of calcium sulphate, or to the sulphur applied. In discussing these results, Skinner and Reid state that "The action of manganese in decreasing the oxidation in the soil while acid is in harmony with the decreased yield, and its action in increasing the oxidation of the neutralized soil is in harmony with the increased yield. The action of manganese in the acid soil was probably to stimulate the life processes in the soil, acting on the organic matter in such a way as to produce changes which resulted in a lessened crop-producing power, while its action in the neutralized soil was such as to stimulate oxidation and other biological processes, acting on the organic soil constituents and producing changes favorable to the growing plants."

Skinner and Reid's view as to increased oxidation due to manganese sulphate applied to a basic soil is substantiated by the work of Greaves (5) who, working with a soil which was clearly basic from the analysis given, found that moderate amounts of manganese sulphate stimulate ammonification. Brown (2) has published the results of similar studies, with results similar to those obtained by Greaves, with respect to ammonification. However, the data obtained by Brown in his studies on nitrification would seem to indicate that his soil was acid, since there was little or no nitrification of ammonium sulphate in four weeks.

In discussing the peculiar soils of Hawaii, Kelley (9) states that "In Hawaii the growth of certain crops is enormously influenced by the mere burning of small accumulations of brush and undergrowths of Guava and lantana. The effect on cotton on the uplands of Oahu produced by these small fires may represent the difference between success and failure. The color and vigor of the crop on these small areas dotted here and there over a field attract attention. Other crops are affected similarly." Again he says "A field plowed for the first time, although the soil be thoroughly pulverized and reduced to a state of fine tilth, usually will not support plant growth satisfactorily. The farmers of Hawaii have found it necessary to areate newly plowed lands for a period of several months before planting the first crop. It has been observed, however, that excellent growth of crops is obtained on the small spots where brush was burned and without the continued areation above referred to. Heat, therefore, seems to accomplish in the soil effects similar to those brought about by areation. The application of fertilizers produces no such effects." Since heating by burning brush on Hawaiian soils seemed to accomplish the same results as aeration, Kelley made a study of the effect of heating on the solubility of the constituents of soils; and found that in most soils, heating increased the amount of soluble manganese. Also it is of special interest to note his results on the unheated soils. Working with both normal and abnormal types, he reports water soluble manganese, iron, and aluminum in each of the unheated soils.

While no definite statement was made as to the acidity of the soils used, it is evident that each was acid, else these water soluble compounds were not likly to have been found. In all probability, water soluble iron, aluminum, and manganese found in these soils would be sufficient to account for poor plant growth. Kelley states that his samples No. 416 and 417 are representative of a type of soil abundant in the islands. Soil No. 416 was taken from cultivated land, and No. 417 from a near-by sod. Since these sod lands are nonproductive when first put under cultivation, it is interesting to note that much more manganese and iron, and approximately equal amounts of aluminum were recovered from the sod land. The point is stressed that cultivation and aeration reduce the solubility of manganese. With regard to productivity, aeration and heating by the burning of brush seem to accomplish the same beneficial results. The results reported above suggest that the increased fertility found where brush was burned on these soils was due to the alkaline ash which would tend to precipitate manganese, iron, and aluminum, rather than to any direct effect of the heating.

From ammonification and nitrification studies on these soils Kelley (11) concludes that while both the cultivated and the uncultivated support ammonification, only the cultivated soils support a vigorous nitrification.

Kelley says "Some of the inert virgin soils appear to contain soluble substances which inhibit nitrification. Sterilization in the autoclave affected both cultivated and uncultivated soil in such way as to render them practically equal in regard to subsequent ammonification and brought about conditions toxic to nitrification in each instance; similar effects were produced by heating to still higher temperatures."

Working with soils from the Pennsylvania plots, Given (6) found at the end of 7 days, that the acid soil from plot 32 had produced the greatest amount of ammonia from dried blood. This result was confirmed by repeated experiments. Further studies showed the soil from plot 32 incapable of supporting more than a very feeble nitrification.

White (23) has shown by laboratory studies on the acid soils from the Pennsylvania plots that nitrification of organic substances proceeds at a very slow rate, and that ammonium sulphate is not at all nitrified.

Both Greaves (5) and Brown (2) have shown that ammonification may proceed after the addition of considerable amounts of manganese salts to soils; but Brown's work indicates that the nitrifying organisms are rather sensitive to manganese compounds. In view of the fact that soluble manganese has been found in the soil from Pennsylvania; and manganese, aluminum, and iron in the Hawaiian soils, it seems probable that these compounds in solution may be responsible, in a large measure, for the reduced, or inhibited, nitrification in these soils. This view is not necessarily in conflict with the observations that nitrification does take place in acid field soils carrying a large amount of such elements in solution. In times of drought, the writer has often noted that there was a large accumulation at the surface of the salts contained in soils. At times, nearly the entire nitrate and soluble manganese content of our plot soil has been found in the top inch of soil. To substantiate this view the following is given. In November, 1917, the surface soil from about 5 square feet was scraped from one plot, to a depth of about one-half inch. A water extract of this soil contained 200 p. p. m. of manganese, and 1200 p. p. m. of nitrates. Another sample taken from this area, after the first had been removed, gave an extract with 10 p. p. m. of manganese, and 225 p. p. m. nitrates. Pea cultures grown in these extracts produced .064 and .091 grams of roots, and .164 and .314 grams of tops, respectively.

White presents data showing that similar conditions may obtain in the soil studied by him. During these periods of dry weather, when the salts are largely concentrated at the surface, nitrification may proceed in the deeper layers of the soil; again, with the coming of a rain, these salts are largely washed down into the deeper layers of the soil, to be again returned to the surface, with the return of dry weather. In laboratory work, where the water content is kept nearly constant, there is little chance for this movement of the salt into zones, and hence, retarded, or even inhibited nitrification results.

While the data given in Tables IX and X show that incubating acid soils with either dried blood or sulphate of ammonia tends to bring manganese into solution, it sould be remembered that our soils contained initially, but little soluble manganese. It is not surprising, therefore, that dried blood was nitrified to a considerable extent. On the other hand, several of the soils used failed to nitrify ammonium sulphate. It is probable that manganese brought into solution by this compound, acted as the agent inhibitory to nitrification.

To make a practical application, our work indicates that unfertilized acid soils supporting a slow rate of nitrification, develop but little soluble manganese. On the other hand, if such soils be liberally fertilized with nitrogenous fertilizers, the acids produced therefrom may bring into solution sufficient quantities of manganese to cause serious injury to crop plants. The use of lime in connection with high fertilization becomes imperative, then, if full benefit is to be derived from such fertilization. Whether or not plowing under of large crops of leguminous plants would produce results similar to those obtained with certain fertilizers, is a point that cannot be answered at present.

## Summary

1. Acid soil on the Alabama Experiment Station Farm has been shown to be injured by the use of dried blood as a fertilizer. It is indicated that cotton seed meal may also cause injury in time; as yet, little injury has resulted from its use.

2. In pot experiments, dried blood and ammonium sulphate produced almost complete sterility in two different soils from the Experiment Station Farm. Lime added to these soils not only prevented injury, but promoted a very vigorous plant growth.

3. Soil which has been made highly unproductive by heavy applications of dried blood, still supports nitrification under field conditions.

4. The infertility of this soil is attributed to the pres-

ence of manganese in the soil solution, rather than to organic toxic bodies.

5. When dried blood is the source of nitrogen, soluble manganese is believed to be due to the action of nitric acid developed by nitrification.

6. When ammonium sulphate is the source of nitrogen, nitrification is apparently unnecessary in order to increase the amount of soluble manganese in acid soils.

7. Reduced growth appears to be due chiefly to the injury to plant roots, from the direct action of manganese, rather than to reduced or altered oxidation of soil organic matter.

8. A part of the injury may also be due to the effect of manganese on the foliage. Plants with bleached leaves are frequently found in both soil and water cultures when soluble manganese is present.

9. Relatively large amounts of manganese were recovered from the soil obtained from the Pennsylvania Experiment Station. Water extracts of this soil were highly toxic to seedling plants.

10. When the manganese was precipitated from these extracts they supported a vigorous plant growth.

11. Apparently, the relative amount of soluble manganese is of more importance, within certain limits, than is the total amount. The presence of considerable amounts of calcium salts in an extract reduces the toxicity of manganese.

12. Precipitataion of a part of the manganese by means of bases is much more effective in reducing toxicity than is dilution. Calcium, sodium, and potassium hydroxides were found to be very effective when used in this way.

13. A large number of acid soils from Alabama contained soluble manganese, after incubation with dried blood or ammonium sulphate. Soluble manganese has not been found in any of the basic soils, or in any of the acid soils which had been thoroughly limed.

14. The products of sulfofication appear to be very effective in dissolving manganese in acid soils.

15. It is believed that this work throws light on the conflicting results obtained by different workers who have used manganese as a fertilizer. Manganese salts applied to basic soils would rapidly be changed, the manganese going out of solution. When applied to acid soils, the manganese salt would persist as such, and heavy aplications would likely cause injury.

16. Work on several phases of this usbject is being continued.

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## PLATE I.

Fig. 1.—Sorghum grown in soil with a high content of $NO_3$ and Mn.

(1) Untreated.
(2) Limed.
(3) Leached.
(4) Leached and, $NO_3$ equivalent returned as $NaNO_3$.

Fig. 2.—Sorghum grown in water extract of soil with a high content of $NO_3$ and Mn.

(1) Distilled water.
(2) Soil extract diluted 50 per cent, precipitated with NaOH.
(3) Soil extract diluted 75 per cent, precipitated with NaOH.
(4) Distillate of soil extract diluted 50 per cent.
(5) Non-volatile part of extract diluted 50 per cent.
(6) Soil extract treated with carbon black, diluted 50 per cent.
(7) Soil extract evaporated, ignited, dissolved, diluted 50 per cent.
(8) Distilled water treated with carbon black.
(9) Soil extract diluted 50 per cent.
(10) Soil extract diluted 75 per cent.

PLATE I


Fig. 1

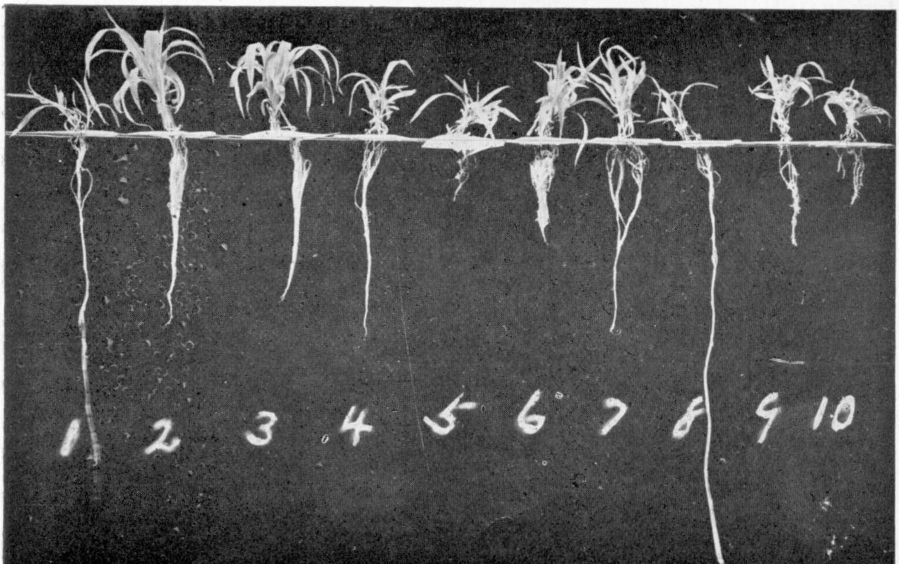



Fig. 2

PLATE II

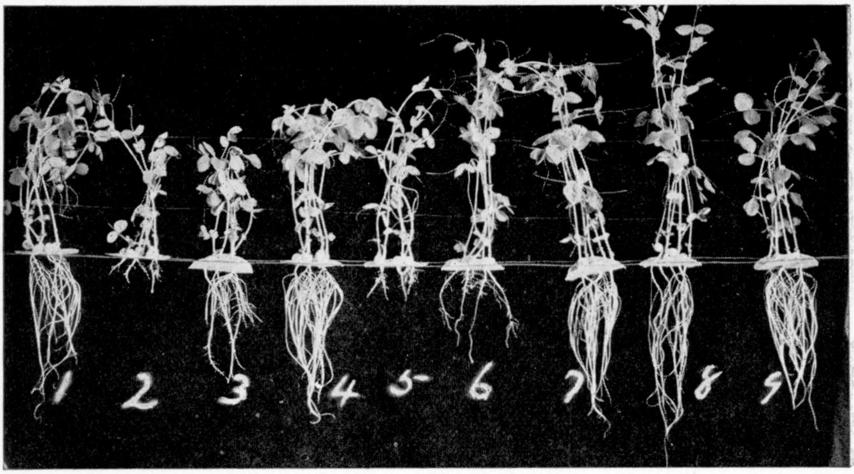



Fig. 1

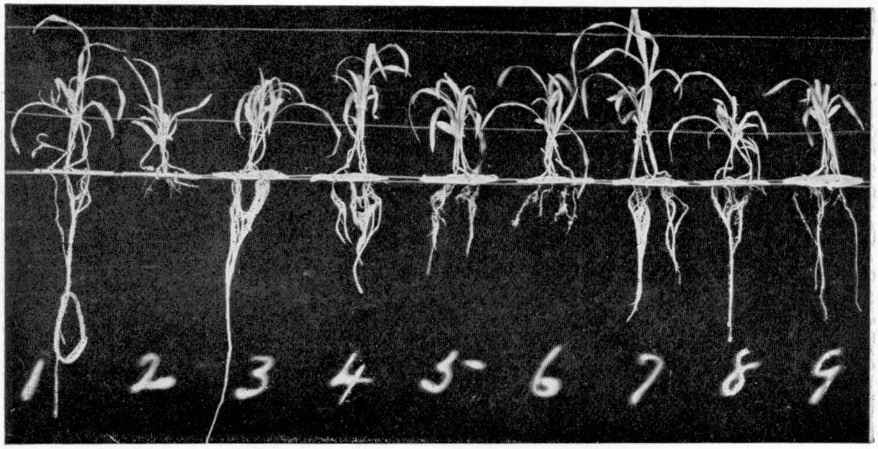



Fig. 2

## PLATE II.

Peas and sorghum grown in water extract of soil scraped from the surface of plot C1, which plot was very infertile due to the application of dried blood. The extract contained a large amount of nitrates and soluble manganese.

Treatment for figs. 1 and 2:

(1) Tap water.

(2) Soil extract untreated.

(3) Distillate of soil extract.

(4) Non volatile part of soil extract.

(5) Soil extract treated with carbon black.

(6) Soil extract with $CaCl_2$ to make a N/20 solution.

(7) Soil extract precipitated with $Ca(OH)_2$.

(8) Soil extract evaporated, ignited, dissolved in HCl, and neutralized.

(9) Soil extract. Second leaching.

## PLATE III.

Peas and sorghum grown in water extract of soil scraped from area fertilized with dried blood. The extract contained manganese equivalent to 203 p. p. m. of manganese sulphate.

Treatments for figs. 1 and 2:

(1) Tap water.

(2) Distilled water.

(3) Soil extract untreated.

(4) Distillate from soil extract.

(5) Soil extract concentrated, made to volume with distilled water.

(6) Soil extract concentrated, made to volume with tap water.

(7) Soil extract ashed, dissolved, made to volume with distilled water.

(8) Soil extract ashed, dissolved, made to volume with tap water.

(9) Soil extract treated with two gms. calcium carbonate per liter.

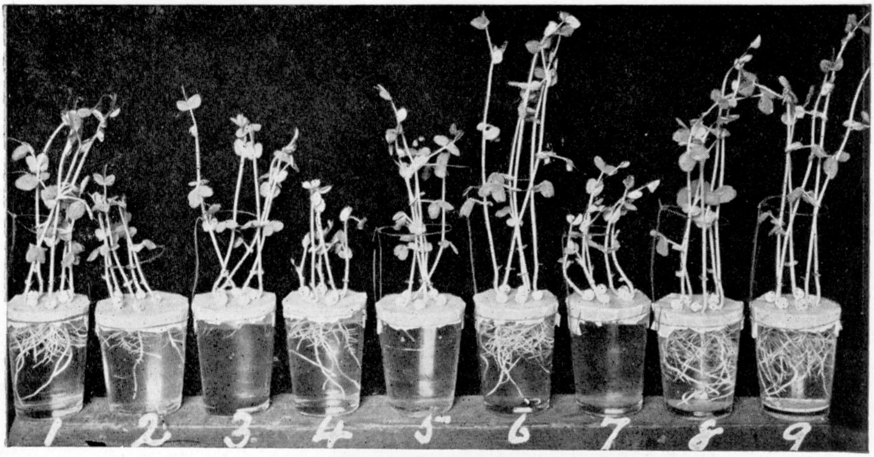



Fig. 1

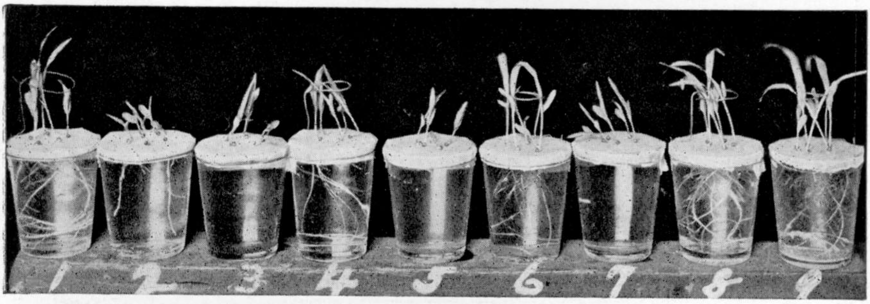



Fig. 2

PLATE IV

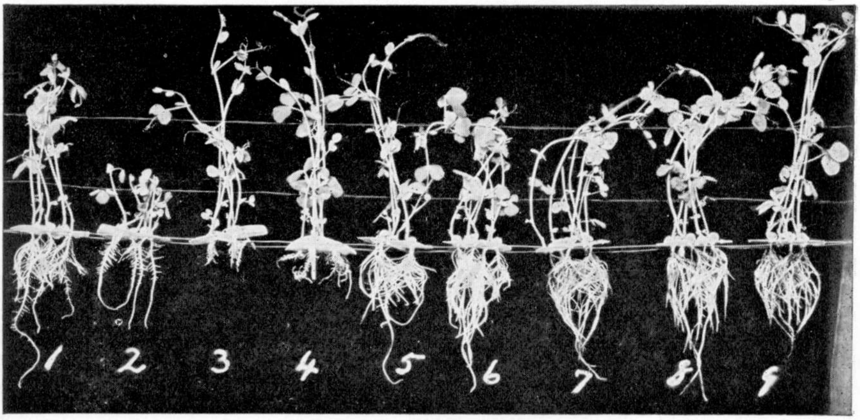



Fig. 1

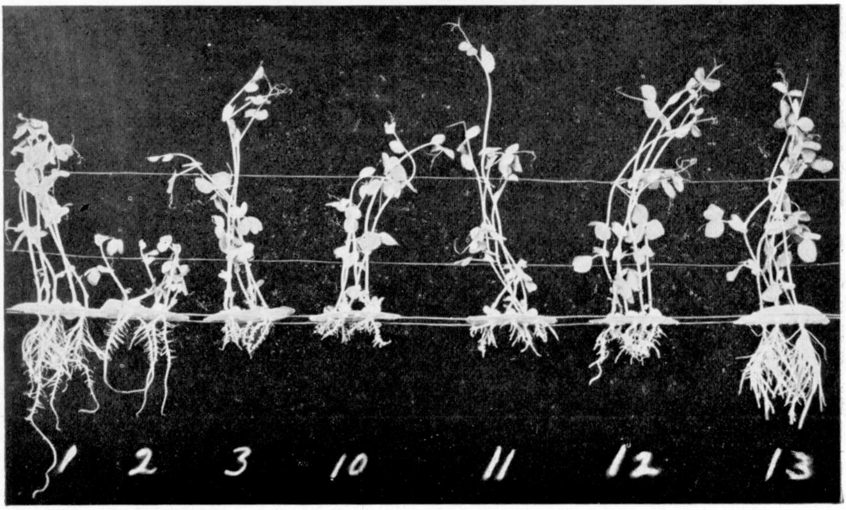



Fig. 2

## PLATE IV.

Peas grown in soil extract containing 15.8 p. p. m. of Al., and 90.0 p. p. m. of Mn.

Fig. 1.—

(1) Tap water.
(2) Distilled water.
(3) Soil extract untreated.
(4) Soil extract plus 0.6 cc N/1 NaOH.
(5) Soil extract plus 1.2 cc N/1 NaOH.
(6) Soil extract plus 1.8 cc N/1 NaOH.
(7) Soil extract plus 2.4 cc N/1 NaOH.
(8) Soil extract plus 3.0 cc N/1 NaOH.
(9) Soil extract, second leaching.

Fig. 2.—

(1) As in fig. 1.
(2) As in fig. 1.
(3) As in fig. 1.
(10) Soil extract 75 per cent, distilled water 25 per cent.
(11) Soil extract 50 per cent, distilled water 50 per cent.
(12) Soil extract 25 per cent, distilled water 75 per cent.
(13) Soil extract, second leaching, as (9) in fig. 1.

## PLATE V.

Fig. 1.—Soil from nitrification plots.
(1) Untreated.
(2) Limed.
(3) Ammonium sulfate, 4.3 grams.
(4) Ammonium sulfate, 4.3 grams, limed.
(5) Dried blood, 7.0 grams.
(6) Dried blood, 7.0 grams, limed.

Fig. 2.—Soil from plot 4, source of nitrogen test.
(1) Untreated.
(2) Limed.
(3) Ammonium sulfate, 4.3 grams.
(4) Ammonium sulfate, 4.3 grams, limed.
(5) Dried blood, 7.0 grams.
(6) Dried blood, 7.0 grams, limed.

Fig. 1

Fig. 2

PLATE VI

Fig. 1

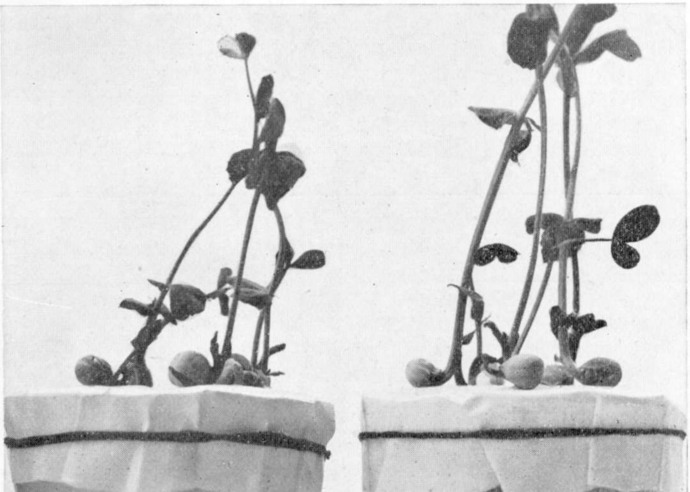


Fig. 2

## PLATE VI.

Fig. 1.—Peas grown in extract of soil from plot 32, Pennsylvania rotation experiments.

(1) Extract plot 32, original condition.
(2) Extract plot 32, incubated without fertilizer.
(3) As (2), plus 1 cc N/1 KOH.
(4) As (2), plus 2 cc N/1 KOH.
(5) Extract plot 32, incubated with ammonium sulphate.
(6) As (5), plus 2 cc N/1 KOH.
(7) As (5), plus 4 cc N/1 KOH.
(8) As (5), plus 1 gram $CaCO_3$.
(9) As (5), plus 1 gram $CaCO_3$, plus $CO_2$.
(10) Extract plot 32, second leaching.

Fig. 2.—Cultures (5) and (7), fig. 1.

On left, untreated extract.

On right, extract plus 4 ccN/1 KOH per 500 cc extract. Note the extensive root development, and the precipitated manganese in the bottom of the tumbler.

## PLATE VII.

Fig. 1.—Corn growing on plot fertilized with dried blood, nitrification plots.

Fig. 2—Corn growing on plot not fertilized. The photographs in fig. 1 and fig. 2 were taken on areas not more than 40 feet apart.

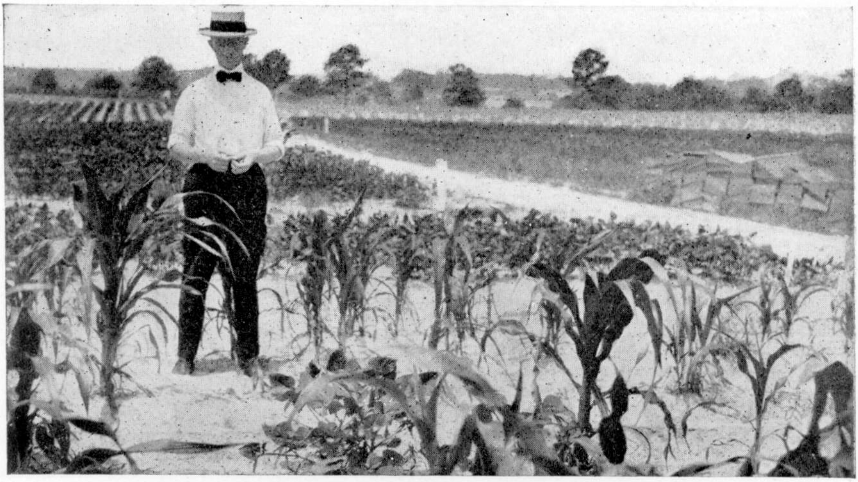


Fig. 1

Fig. 2

PLATE VIII

Fig. 1

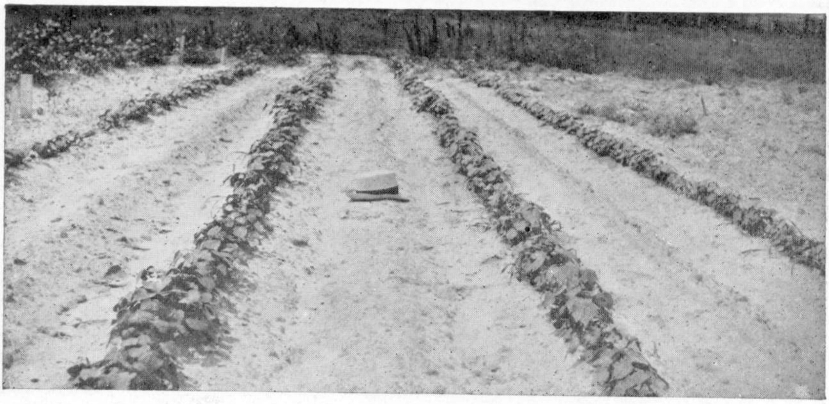


Fig. 2

## PLATE VIII.

Fig. 1.—In the foreground, cotton on the plot fertilized with dried blood. In the background, cotton on the plot fertilized with cotton seed meal. Cotton was the only crop that was notably injured on the plots fertilized with cotton seed meal.

Fig.—Cotton growing on the unfertilized plot. Note that it is making a better growth than on the plots fertilized with dried blood or cotton seed meal.

## PLATE IX.

Fig. 1.—Sorghum, corn, and cowpeas growing on the areas fertilized with dried blood.

In right foreground, sorghum on end of plot previously in crops. On left, sorghum on end of plot previously in fallow.

In right middle ground, corn on end of plot previously in crops. On left, corn on end of plot previously in fallow.

In far background, peas on end of plot previously in crops; on left, peas on end of plot previously in fallow.

Fig. 2.—

In the foreground, a near view of the peas shown in fig. 1. In the background, the cotton plot is shown. Note that the entire plot is bare, with the exception of a few scattered, badly stunted plants.

Fig. 1

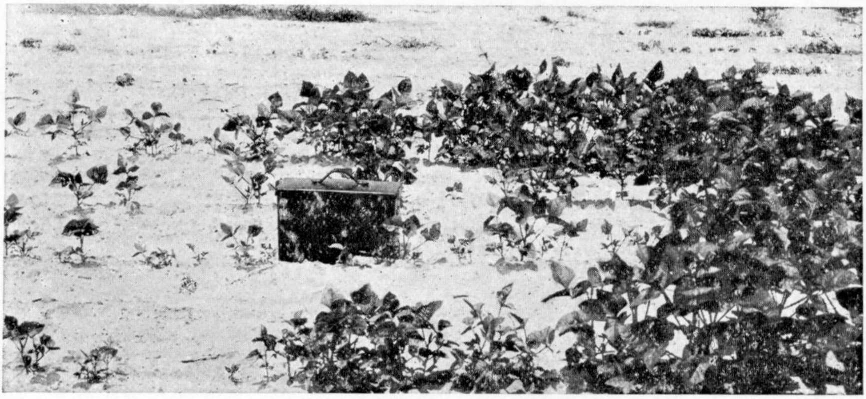
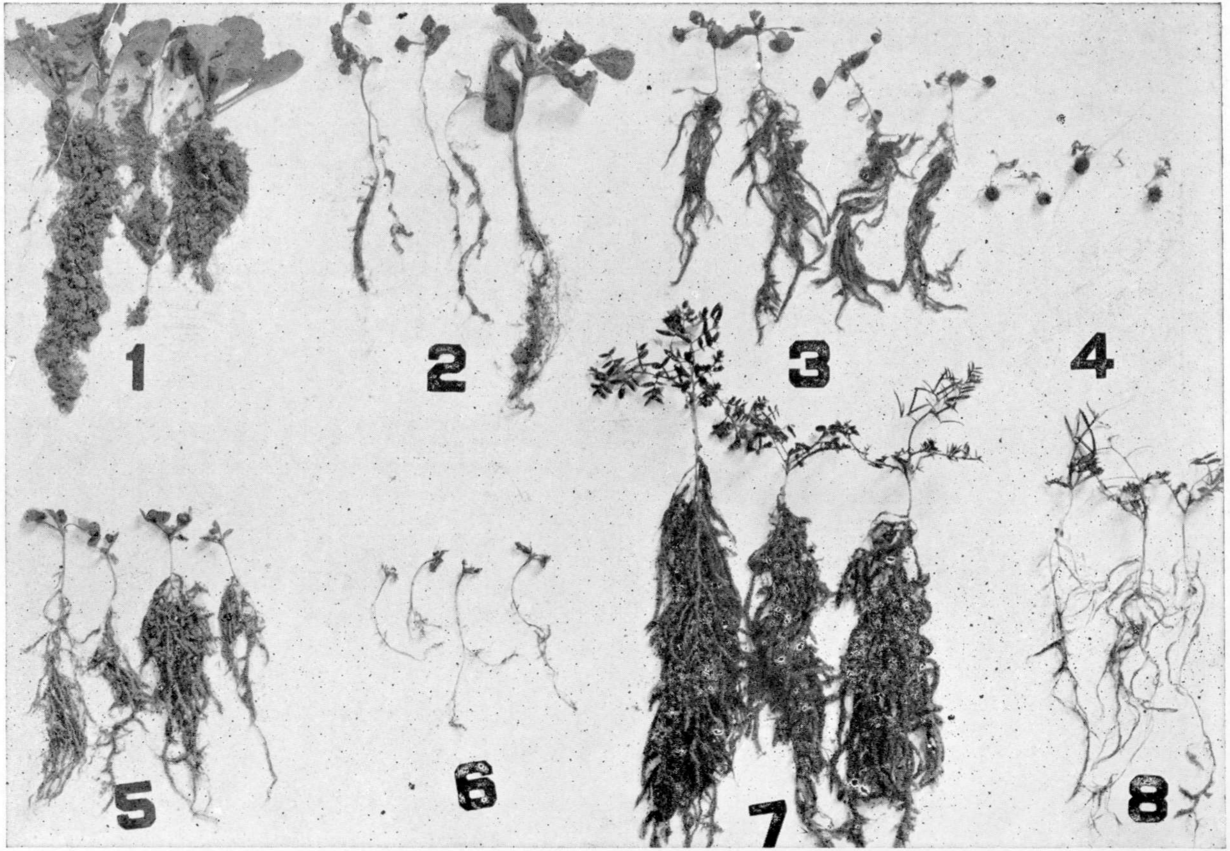


Fig. 2

PLATE X



## PLATE X.

Fig. 1.—Showing a comparison of plants taken from field plots fertilized with calcium cyanamid and with dried blood.

(1) Rape from plot fertilized with calcium cyanamid.
(2) Rape from plot fertilized with dried blood.
(3) Bur clover from plot fertilized with calcium cyanamid.
(4) Bur clover from plot fertilized with dried blood.
(5) Crimson clover from plot fertilized with calcium cyanamid.
(6) Crimson clover from plot fertilized with dried blood.
(7) Hairy vetch from plot fertilized with calcium cyanamid.
(8) Hairy vetch from plot fertilized with dried blood.

## PLATE XI.

Fig. 1.—Showing a comparison of plants grown on field plots fertilized with calcium cyanamid and with dried blood.

(1) Narrow leaf vetch grown on plot fertilized with calcium cyanamid.

(2) Narrow leaf vetch grown on plot fertilized with dried blood.

(3) Wheat grown on plot fertilized with calcium cyanamid.

(4) Wheat grown on plot fertilized with dried blood.

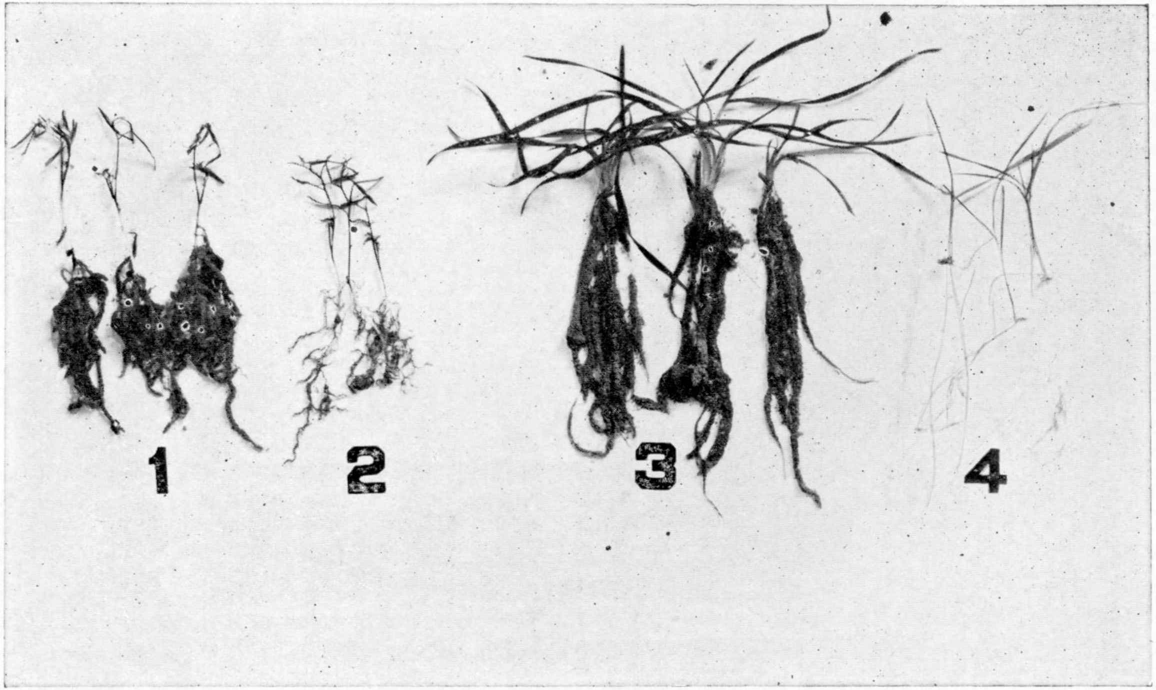
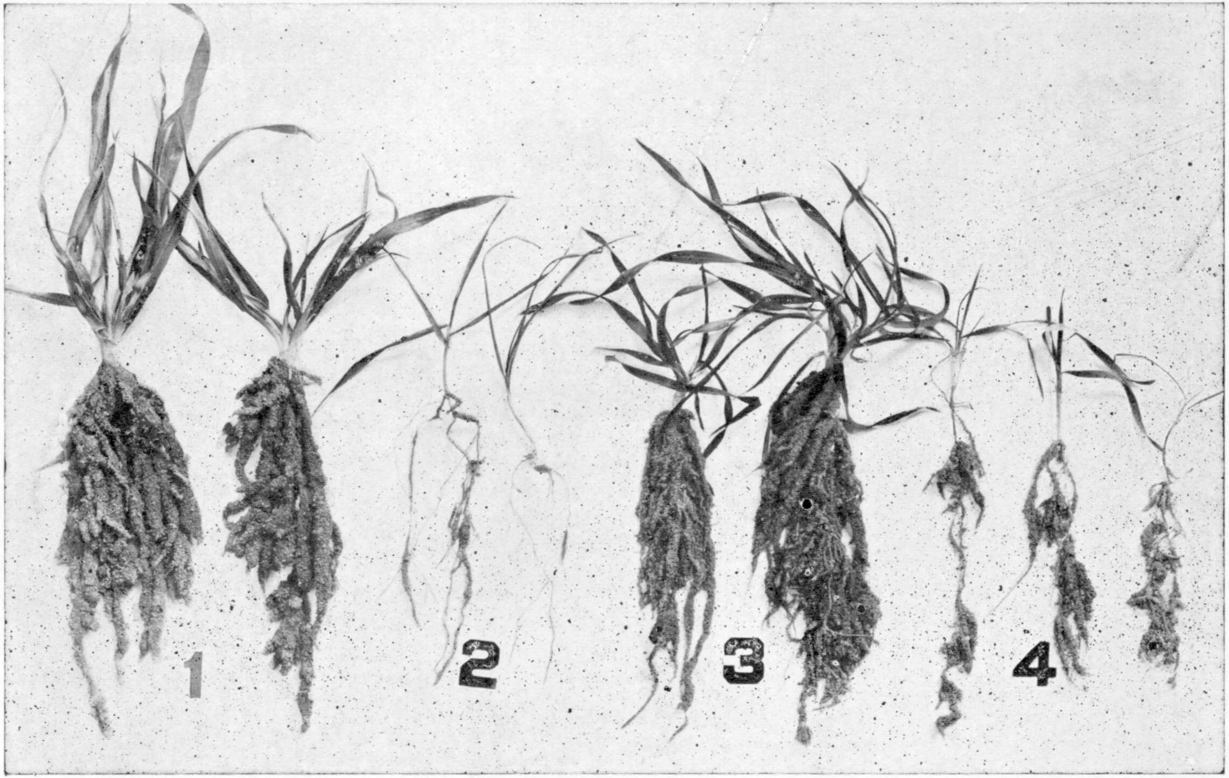



PLATE XI

PLATE XII



## PLATE XII.

Fig. 1.—Showing a comparison of plants grown on field plots fertilized with calcium cyanamid and dried blood.

(1) Oats from plot fertilized with calcium cyanamid.
(2) Oats from plot fertilized with dried blood.
(3) Rye from plot fertilized with calcium cyanamid.
(4) Rye from plot fertilized with dried blood.