# Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.







No. 42



Contribution from the Bureau of Soils, Milton Whitney, Chief. April 3, 1914.

## (PROFESSIONAL PAPER.)

## THE ACTION OF MANGANESE IN SOILS.<sup>1</sup>

. By J. J. SKINNER and M. X. SULLIVAN,

Assisted by J. H. BEATTIE, F. R. REID, and H. WINCKELMANN, Scientists in Soil Fertility Investigations.

The effect of manganese on soils and crop yields is a question of much interest and has caused considerable comment for the last few years. Practically no work on its use as a fertilizer has been reported as done in this country, and only a limited number of tests are reported in foreign literature.

The present paper embodies the results of a series of experiments upon the effect of manganese salts in soils. These results it is believed throw some light on the action of manganese.

The quantity of manganese differs considerably, but it occurs in small amounts in practically all soils. It has been found in a number of soils in rather large quantities. In Wolff's<sup>2</sup> tables are mentioned four soils, each of a distinct type, where the manganese expressed as manganese dioxide varies from 0.042 per cent in a humus soil to 0.135 per cent in a loamy soil. More recently Kelley<sup>3</sup> has reported some pineapple soils that contain in some cases less than 0.1 per cent and others as high as 9.74 per cent  $Mn_3O_4$ . Robinson,<sup>4</sup> of the Bureau of Soils, has examined 26 American soils and found each to contain manganese, varying in amounts from 0.01 to 0.51

<sup>2</sup>Wolff, E., Aschen-Analysen, von Land und Forstwirthschaftlichen Producten. 2, 16 (1870-1880).

<sup>4</sup> Sullivan, M. X., and Robinson, W. O., Manganese as a fertilizer. Cir. 75, Bureau of Soils, U. S. Department of Agriculture (1912).

25873°-14-1

<sup>&</sup>lt;sup>1</sup> This study of the action of manganese in soils has been made from various viewpoints and has accordingly involved otherwise separate lines of investigation. The cultural tests, including the growth of plants in pots and solution cultures, together with the oxidation effects on plant roots, were made by Mr. Skinner and Mr. Beattie, while the field experiments were executed by Mr. Winckelmann. The oxidation and catalytic experiments on the field soils were made by Dr. Sullivan and Mr. Reid. The experiments demanded close cooperation between the various workers to produce the results obtained.—OSWALD SCHREINER, Scientist in charge.

<sup>&</sup>lt;sup>8</sup>Kelley, W. P., The influence of manganese on the growth of pineapples. Press Bul. 23, Hawaii Expt. Sta. Jour. Ind. and Eng. chem. 1, 533 (1909).

Note.—The results given in this bulletin throw considerable light on the effect of this catalytic fertillzer in various soils. Manganese as a fertilizer is comparatively unknown and untried in this country, so that discussion of its action is necessarily scientific, yet of great interest to those growers whose technical training induces them to experiment with new substances to increase or control crop production,

per cent MnO, the average content being 0.071 (instead of 0.20 per cent given in the circular).

This element is universally found in plants, frequently in relatively large quantities, exceeding often that of the related element iron. In the ash of beech leaves was found in one case 11.25 per cent Mn.O. and only 1.07 per cent Fe<sub>2</sub>O<sub>3</sub>.<sup>1</sup> Manganese has been found in the various organs: young shoots and leaves are especially rich in the element.<sup>2</sup> The conifers have a higher per cent than have leaf-bearing trees. One case has been reported where 35 per cent was found in the ash of pine needles and 41 per cent in the ash of pine bark.<sup>3</sup> Kelley 4 has reported the analysis of a large number of plants grown on two different soils. The ash of these vary in manganese content from a trace in the case of wheat straw to 1.70 per cent Mn<sub>3</sub>O<sub>4</sub> in pineapple leaves grown on normal soil. Of plants grown on soil high in manganese content, the analysis showed the ash of wheat straw to contain 0.22 per cent and pineapple leaves to contain 2.41 per cent, the highest quantity being in the leaves of Waltheria americana, which contained 8.70 per cent Mn<sub>2</sub>O<sub>4</sub>. While manganese is found universally distributed in plants and exists in most soils, it is recognized that it does not serve directly in a plant-food capacity. Plants have been raised in water cultures to perfection in the absence of any added manganese. Nevertheless, manganese salts have been frequently recommended in soil work for the increase of crop production, either as soil amendment or fertilizer, although its action is neither well understood nor its effects on crop yield very definitely determined, the results in the literature being often contradictory. Its recent prominence as a catalytic fertilizer makes a knowledge of its action in soils of considerable interest.

## REVIEW OF EARLIER EXPERIMENTS WITH MANGANESE IN SOIL CULTURE.

The study of the effect of manganese on growth has been made almost entirely in foreign countries. The application of manganese compound in soil culture has given widely different results. In some cases there were beneficial actions, in others harmful, and in a large number of the experiments the results were negative.

Of the various forms of manganese, the sulphate and chloride have been used most by investigators. Nagaoka<sup>5</sup> working with the culture of rice in frames in paddy fields found that manganese sulphate added at the rate of 25 kilos of  $Mn_3O_4$  per hectare (about 20 pounds

<sup>1</sup> Wolff, E., loc. cit., 1, 121.

<sup>&</sup>lt;sup>2</sup> Pichard. Comp. rend., 126, 550 (1898).

<sup>&</sup>lt;sup>3</sup> Schroder, T., Forstchemische und pflanzenphysiologische Untersuchungen, Thorand, 1878.

<sup>&</sup>lt;sup>4</sup> Kelley, W. P., The function and distribution of manganese in plants and soils. Bul. 26, Hawaii Expt. Sta. (1912).

<sup>&</sup>lt;sup>5</sup> Nagaoka, M., On the stimulative action of manganese upon rice. Bul. Col. Agr. Tokyo, 5, 469 (1902-3); 6, 135 (1904-5); 7, 77 (1906-1908).

#### ACTION OF MANGANESE IN SOILS.

per acre) caused an increased growth of 37 per cent; that the production with smaller amounts of the manganese fertilizer increased uniformly up to 25 kilos per hectare; but with additions larger than this there were no correspondingly larger increases. There was a residual effect, the second year showing an increase of 8 per cent. The third year the experiment was repeated on the same plots and an increase of 15 per cent only was secured where two years before the same application of manganese gave an increase of 37 per cent. The fourth year manganese in the form of sulphate, chloride, and carbonate in amounts of 25 kilos per hectare were used on these plots. Manganese sulphate and chloride this time depressed the yield; the carbonate caused no change. It is stated that the plots had become acid, due to the continued application of manganese, and that the weather conditions of the last year were unfavorable to the growth of rice.

K. Aso<sup>1</sup> has also shown that manganese increases the production of rice. The work was conducted in large plots in the paddy field of the Tokyo College Experiment Station. Manganese chloride was used in amounts of 25 kilos of  $Mn_3O_4$  per hectare. The first year there was an increase of 41.8 per cent, yet with continuous culture and an application of the manganese before each crop the increase for the second and third years did not exceed 3 per cent. He attributes the small increase secured the second and third years to the fact that the plot the year before produced a large crop and left the soil in an acid condition. An application of lime made the plot more productive.

T. Katayama<sup>2</sup> made some experiments with barley, using manganese in the form of sulphate. The work was done in large pots holding 8 kilos of soil. The soil had received no fertilizer for five years and was in a deteriorated condition. A general fertilizer was applied to all the pots. The manganese sulphate was applied in amounts from 0.01 per cent to 0.10 per cent as a top dressing.<sup>3</sup> He secured appreciable increases by using the salt at the rate of 0.01 per cent; amounts higher than this caused a decrease. Iron sulphate plus manganese also gave stimulation when used in amounts of 0.01 per cent.

S. Kakehi and K. Baba<sup>4</sup> found that manganese carbonate increased the growth of barley and peas. Their experiments were conducted in pots, using soil which had received a general manuring. The manganese was applied at the rate of 0.01 per cent. The stimulation

<sup>&</sup>lt;sup>1</sup>Aso, K., On the practical application of manganese chloride in rice culture. Bul. Col. Agr. Tokyo, 6, 131 (1904-5). On the continuous application of manganese chloride in rice culture. Bul. Col. Agr. Tokyo, 7, 449 (1906-1908).

<sup>&</sup>lt;sup>2</sup>Katayama, T., On the degree of stimulating action of manganese and iron salts on barley. Bul. Col. Agr. Tokyo, 7, 91 (1906–1908).

<sup>&</sup>lt;sup>3</sup> These amounts seem excessive, corresponding approximately to an application (the larger one) of 2 tons per acre-foot.

<sup>&</sup>lt;sup>4</sup>Kakehi, S., and Baba, K., Observations on stimulation of plant growth. Bul. Col. Agr. Tokyo, 7, 455 (1906–1908).

was greater with peas than with barley. Manganese sulphate used in the same manner caused a stimulation in the growth of wheat.

Voelcker<sup>1</sup> at the Woburn Experimental Station, England, made experiments in pots to study the effect of the different compounds of manganese on wheat and barley. The chloride, sulphate, phosphate, and nitrate of manganese stimulated growth in both wheat and barley. The stimulation was greatest with barley. The iodide and carbonate had a detrimental effect. The oxides were harmful to both cereals. The surface of the soil in these pots was stiff and hard and turned dark, which indicated excessive oxidation.

Fukutome<sup>2</sup> secured results showing that the joint application of manganese chloride and ferrous sulphate had a beneficial effect on the growth of flax, while each alone in the proportion of 0.4 grams to 8 kilos of soil had but little effect.

A continuous culture experiment <sup>3</sup> with wheat and maize was conducted at Suessola, Italy, using manganese dioxide with manure. In some years there was an increase and in others a decrease.

Namba<sup>4</sup> effected increases by the use of manganese sulphate in amounts of 0.1 and 0.2 gram to 8 kilos of soil with the culture of onions. He secured an increase of 59 and 38 per cent, respectively. Amounts as high as 0.5 gram in a pot of 8 kilos of soil depressed growth considerably. Gregoire, Hendrick, and Carpiaux <sup>5</sup> worked on the action of manganese sulphate on potatoes on a rich soil without securing any beneficial action. Loew <sup>6</sup> working with pots secured very little stimulation with tobacco and only a slight increase with potatoes. He also found that manganese chloride decreased the yield of millet, where the manganese was applied the previous year to another crop.

Loew and Honda<sup>7</sup> obtained an interesting result with young cypress trees (*Cryptomeria japonica*), which received manganese sulphate as a top dressing in monthly applications for one year and a half. The organic production was doubled compared with the control trees. Manganese proved beneficial to vine culture and the culture of trees in general.

Ray and Pradier<sup>8</sup> fertilized apricot trees with manganese, which increased vegetation and produced larger fruit.

Bertrand <sup>9</sup> secured beneficial effects with oats, using manganese sulphate in field plots in amounts of 45 pounds per acre. In more

<sup>&</sup>lt;sup>1</sup> Voelcker, Jour. Royal Agr. Soc., 64, 348 (1903); 65, 306 (1904).

<sup>&</sup>lt;sup>2</sup> Fukutome, Y., On the influence of manganese salts on flax. Bul. Col. Agr. Tokyo, 6, 137 (1904-5).

<sup>&</sup>lt;sup>3</sup> Italo Giglioli. Annali scuola agricoltura Portici. Ser. 2, p. 159 (1901).

<sup>&</sup>lt;sup>4</sup> Namba, L., On the behavior of onion to stimulants. Bull. Col. Agr. Tokyo, 7, 635 (1906-1908).

<sup>&</sup>lt;sup>5</sup> Bul. Agricole, Bruxelles, 23, 388 (1907).

<sup>&</sup>lt;sup>6</sup> Loew, O., On the treatment of crops by stimulating compounds. Bul. Col. Agr. Tokyo, 6, 161 (1904-5).
<sup>7</sup> Loew, O., and Honda, S., Ueber den Einfluss des Mangans auf Waldbäume. Bul. Col. Agr. Tokyo, 6, 125 (1904-5).

<sup>&</sup>lt;sup>8</sup> Ray, G., and Pradier, G., Nitrate d'uranium et sulfate de manganèse, leur emploi avantageux en arboriculture fruitière. L'Engrais, 24, 1029 (1909).

<sup>&</sup>lt;sup>9</sup> Bertrand, G., Compt. rend. 141, 1255 (1905).

recent <sup>1</sup> work with pot experiments, manganese sulphate increased the yield of peas, barley, and radish. Oats were increased 9.5 per cent with 60 kilos per hectare. Rape, lupine, and alfalfa were also stimulated. The best results were obtained by using 30 to 50 kilos of the dried sulphate per hectare. Quantities as great as 100 kilos gave less favorable results.

The work of N. Strampelli,<sup>2</sup> G. Salomoni,<sup>3</sup> G. Bellini,<sup>4</sup> G. Paris,<sup>5</sup> and others, has demonstrated the beneficial action of the various manganese compounds on wheat and other cereals when used, alone and in combination with general fertilizers, in small amounts not exceeding 50 kilos per hectare. Bernardini <sup>6</sup> showed that considerable increases were obtained in the yield of wheat and corn by the use of manganese chloride.

Sutherst<sup>7</sup> working with corn in pots secured beneficial results from the use of manganese sulphate, chloride, and dioxide. The dioxide was more stimulating than the other forms used. In v. Feilitzen's <sup>8</sup> work with oats on a poor moor soil, to which a general fertilizer was added, manganese sulphate used at the rate of 10 kilos per hectare had no beneficial effects.

Rousset <sup>9</sup> reports some experiments made by Stoklasa, with beets, who secured an increase in yield by an addition of manganese salts. Grégoire, Hendrick, and Carpiaux <sup>10</sup> applying manganese sulphate found a decrease in yield, but the sugar content of the beets was higher. The amounts used varied from 10 to 50 kilos per hectare.

Pfeiffer and Blanck<sup>11</sup> conducted some pot and field experiments with oats and beets in which they secured an increased yield, using manganese sulphate, carbonate, and nitrate. Andoward<sup>12</sup> found that manganese carbonate applied at the rate of 270 pounds per acre increased the yield of wheat and kidney beans and decreased the yield of carrots and potatoes.

A number of other experiments with manganese salts have been made. Many of these tests have proved beneficial, while a great many other experimenters have secured negative results. The results seem to vary according to the circumstances. Not only the mode of application but the manures used influence the results.

<sup>12</sup> Andoward, A. and P., Action des engrais de manganèse sur la vegetation. L'Engrais, 26, 915 (1911).

<sup>&</sup>lt;sup>1</sup> Bertrand, G., Manganese as a catalytic fertilizer. Orig. Com. 8th Intern. Congr. Appl. Chem., 15, 39 (1912).

<sup>&</sup>lt;sup>2</sup> Atti del VI Congresso internationale di chimica applicata., 6, 14 (1907).

<sup>&</sup>lt;sup>3</sup> Manganese elo voiluppo delle piante. Staz. sper. agr. Ital., 40, 97 (1907).

<sup>4</sup> Agricoltura Senese, 31, 14. (1907.)

<sup>&</sup>lt;sup>5</sup> Giornale di Viticollura edi Euologia, 14, No. 1 (1906).

<sup>&</sup>lt;sup>6</sup> Bernardini, Funzione del manganese nella concimazione. Staz. sper. agr. Ital., 43, 217 (1910).

<sup>&</sup>lt;sup>7</sup> Sutherst, M., Manganese compounds as fertilizer for maize. Transvaal Agr. Jour., 6, 437 (1908).

<sup>&</sup>lt;sup>B</sup>v. Feilitzen, Stimulating effect of manganese salts on crops. Jour. Landw., 55, 289 (1907).

<sup>&</sup>lt;sup>9</sup> Rousset, An. Sci. Agron., 3. Ser. 4. II, 81 (1909).

<sup>10</sup> Grégoire, Hendrick and Carpiaux, Bul. Agr. (Brussels), 23, 388 and 764 (1907.)

<sup>&</sup>lt;sup>11</sup> Pfeiffer and Blanck, Beitrag zur Frage über die Wirkung des Mangans auf das Pflanzenwachstum. Landw. Vers. Sta., 77, 33 (1912).

Repeated applications of small amounts in the form of top-dressing seem more favorable than a single application of the same amount of manganese salts at the time of manuring before the seed is sown. The stimulative action also seems to differ greatly with the character of the soil. Leidreiter,<sup>1</sup> working with oats, mustard, beets, and potatoes, found manganese to have a beneficial effect. Similar results were obtained with beans with small amounts of manganese; large amounts, however, were injurious. Manganese showed best effects on humus soils, next on clay soils, and least on sandy soils; this, however, varied to a certain extent with the kind of plant and the form of the manganese. Labergerie<sup>2</sup> found manganese less effective in wet soils than dry, also found that manganese chloride was more effective when used with potassium sulphate.

A very extensive experiment was made by Uchiyama<sup>3</sup> on the action of manganese with different manurial mixtures on two soils having widely different characteristics. A variety of crops were grown, including the cereals, legumes, and vegetables. Each crop was stimulated by the treatment, the increase varying from 5 to 60 per cent. The legumes were most benefited. Repeated applications as top-dressing throughout the period of growth gave better results than other methods of applying the substance. The amount of manganese salts gave best results when applied at the rate of 20 to 50 kilos per hectare. In these experiments it was found that the manganese, when applied with fertilizers that have a neutral reaction and to soils that were neither acid nor alkaline, had a better effect than when there was an acid or alkaline condition.

Takeuchi<sup>4</sup> found that leguminous and coniferous plants were stimulated more by manganese than were grasses. Barley and other grains were least stimulated.

Kelly's <sup>5</sup> work at the Hawaii experiment station showed that some plants were less affected by manganese than others. He worked with a soil that was very high in manganese. Pineapples were seriously injured. Corn, peanuts, beans, cowpeas, and a number of the other legumes were also more or less injured. Sugar cane was not so much affected. Certain weeds, cotton, and a number of the truck crops were unaffected.

The results of experiments with manganese as a fertilizer have been variable. In general the effect has been a beneficial one. In many cases, however, growth has either been retarded, or there has been no action. This may be due to certain soil conditions. Few

<sup>8</sup> Buls. 23, 26, 28, Hawaii Expt. Sta.

<sup>&</sup>lt;sup>1</sup> Leidreiter, P., Behavior of manganese in the soil toward some agricultural plants. Inaug. Diss. Rostock. (1910). Biedermann's Zentr., **40**, 531.

<sup>&</sup>lt;sup>2</sup> Labergerie, Semaine Agr. Paris, 26, 331 (1907).

<sup>&</sup>lt;sup>2</sup> Uchiyama, Influence of stimulating compounds upon the crops under different conditions. Bul. Imp. Centr. Agri. Exp. Sta., Japan, 1, No. 2, 37 (1907).

<sup>&</sup>lt;sup>4</sup> Takeuchi, Difference of susceptibility of plants to stimulation. Jour. Col. Agr., Tokyo, 1, 207 (1909).

of the investigators, however, have given detailed description of the composition and character of the soil. A good deal of evidence has been secured by Kelly<sup>1</sup> and others which tends to show that the effect, whether beneficial or harmful, is an indirect one. The results show in a general way that manganese is beneficial to certain trees and leguminous crops and is harmful to root crops. It also seems that manganese is not stimulating to growth when applied to an acid soil.

## EXPERIMENTS WITH MANGANESE SALTS IN POTS.

The effect of manganese salts was tested on soils in paraffined wire pots according to the method described in Circular 18 of the Bureau of Soils. Wheat was the plant used as the test crop. The soil was weighed out in pans and treated with the various manganese salts in different amounts and allowed to stand in a moist condition for a week before planting. Five pots were used for each treatment and six wheat plants grown in each pot. The wheat was grown in the greenhouse for a month and then was cut and the weight of the green plant taken. Five pots of untreated soil were included in the experiment as a check. The increase or decrease in weight of the treated plants over the untreated was taken as the effect of the manganese.

The soil used in this experiment was a sandy loam, which was unproductive in the field, and did not respond well to general fertilizers. Five manganese salts were worked with, each in five different concentrations, namely 10, 25, 50, 100, and 250 parts per million of Mn. The salts tested were the chloride, sulphate, nitrate, carbonate, and dioxide of manganese. The salts were dissolved or suspended in water and applied to the soil. It was thoroughly mixed by sifting and after one week was put in the pots and planted to wheat. The wheat came up uniformly and grew well. Table 1 gives the relative growth due to the various treatments. The growth in the untreated soil is taken as 100 and the figures, therefore, represent relative green weight. The plants grew from September 30 to November 6.

TABLE 1.—Effect of manganese on	growth of wheat plants in an unproductive sandy loam
soil.	Untreated taken as 100.

Manganese (parts per million).	MnCl <sub>2</sub> .	MnSO4.	Mn (NO <sub>3</sub> ) <sub>2</sub> .	MnCO <sub>3</sub> .	MnO <sub>2</sub> .
0	100	100	100	100	100
10 25	119 129	122     121	116 121	111 119	$\begin{array}{c}108\\104\end{array}$
50	131	101	101	100	110
100	115	122	100	91	111
250	103	116	103	89	104

Each of the manganese salts caused a stimulation in growth in this soil. The degree of stimulation, however, varied with the salt and with the amount. Manganese chloride and sulphate seem to have had the most effect, the chloride causing the greatest improvement. There was an increase in this case of 31 per cent when 50 parts per million were used. Smaller amounts caused a corresponding increase. Amounts larger than 50 parts per million were not so beneficial. With manganese sulphate there was an increase of 22 per cent in amounts of 10 to 100 parts per million. The result with 50 parts per million would seem to be abnormal or inaccurate, since there is shown only an increase of 1 per cent, while with 25 and 100 parts per million the increase was 21 and 22 per cent, respectively. Again, 250 parts per million was not as effective as smaller amounts.

Where manganese nitrate was used the largest improvement was with 25 parts per million, which gave an increase of 21 per cent. Amounts larger than 25 parts per million caused no appreciable increase. There was a similar effect in the case of manganese carbonate. The largest increase here was 19 per cent with 25 parts per million. Ten parts per million increased growth 11 per cent. Quantities higher than 50 parts per million were harmful. The dioxide was the least effective of the manganese salts. While there was no harmful action with any of the amounts used, the largest increase was only 11 per cent where 100 parts per million were used.

This experiment was repeated with the same soil at a later time. The test was conducted in the same way as the one just described. The same salts were used in the same concentrations. This time the plants grew from November 17 to December 20. There were increases with each salt. Again the chloride and sulphate caused the largest increases, and the dioxide the least. The best growth was secured with 25 to 50 parts per million of the manganese, this being true with each of the salts.

These two experiments seem to indicate that manganese in small quantities is beneficial on this soil. The chloride and sulphate gave largest increases. Twenty-five to 50 parts per million of the element, Mn, which is  $12\frac{1}{2}$  to 25 pounds per acre, to a depth of 6 inches, gave the largest growth. Applications higher than this gave no correspondingly larger increases and in some cases were even harmful.

Another soil was worked with in a similar manner as the poor sandy loam just discussed. This was a clay loam soil from Pennsylvania, and was a productive field soil. The soil had been manured and well cultivated for a number of years. A four-year crop rotation had been practiced. The soil at the time the sample for this work was taken was growing a good crop of wheat. The relative green weights obtained in this experiment are given in Table II. The plants grew from January 5 to February 6.

**TABLE II.**—Effect of manganese on growth of plants in a productive loam soil. (Untreated equals 100.)

Manganese (parts per million).	MnCl <sub>2</sub> ,	MnSO4.	$Mn(NO_3)_2$ .	MnCO3.	MnO <sub>2</sub> .
$\begin{array}{c} 0\\ 10\\ 25\\ 50\\ 100\\ 250 \end{array}$	$     \begin{array}{r}       100 \\       103 \\       100 \\       101 \\       102 \\       97     \end{array} $	100 99 102 100 98 98	$     \begin{array}{r}       100 \\       104 \\       105 \\       100 \\       97 \\       98     \end{array} $	100     101     100     103     98     100	100 103 99 100 102 99

By an examination of the table it is seen that there is no appreciable increase with any of the manganese salts. There is a slight increase in some cases and frequently a slight depression. The slight differences may be due to experimental errors; at least it seems fair to conclude that manganese has no beneficial effect on this loam soil, which is already productive.

Investigators have invariably found that the action of manganese was different on different soils. The beneficial effects secured in most of the experiments were when the manganese was applied to a deteriorated soil. This was especially so in the work of Katayama<sup>1</sup> and Kakehi and Baba,<sup>2</sup> who secured large increases. On the other hand, Grégoire, Hendrick, and Carpiaux,<sup>3</sup> among others who worked with manganese on a rich soil, noticed no beneficial action.

## MANGANESE IN AQUEOUS EXTRACTS OF SOILS.

Further studies were made on manganese salts in the aqueous extracts of good and poor soils. The effect on growth was noted and the oxidizing power of the plant roots in the solution as influenced by manganese salts received especial attention.

Some interesting work has been done with the action of manganese in aqueous solutions. Aso<sup>4</sup> found that manganese stimulated growth of radish, barley, wheat, and peas in nutrient solution when added in amounts of 20 parts per million. He showed that the plants grown in solution containing manganese yielded a juice which has a more powerful oxidizing power than the plants without manganese. A yellowing of the leaves of the manganese plants occurred and the roots turned dark. Bertrand <sup>5</sup> had observed that the ash of oxidizing enzymes contain manganese and that in the presence of manganese the oxidizing effect of these enzymes is greatly increased.

25873°-14-2

<sup>&</sup>lt;sup>1</sup> Bul. Col. Agr. Tokyo, 7, 91 (1906-1908).

<sup>&</sup>lt;sup>2</sup> Bul. Col. Agr. Tokyo, 7, 455 (1906-1908).

<sup>&</sup>lt;sup>3</sup> Bul. Agr. (Brussels), 23, 388 and 764 (1907).

<sup>&</sup>lt;sup>4</sup>Aso, K., On the physiological influence of manganese compounds on plants. Bul. Col. Agr., Tokyo, **5**, 177 (1902–3).

<sup>&</sup>lt;sup>5</sup> Compt. rend., **124**, 1032 (1897).

Loew and Sawa<sup>1</sup> grew barley plants in a 0.1 per cent  $MnSO_4$  solution. An injurious action was observed in this dilution, and after several days a change in color from green to yellow was evident. The reactions for the oxidizing enzymes were more intense with the manganese plants than the control plants, which accounts for the fading or bleaching out of the chlorophyl. In discussing the stimulation by manganese Loew suggests that manganese increases the oxidizing power of oxidizing enzymes, and thus aids in destroying injurious compounds as fast as they are formed, or checking their formation.

Brenchley <sup>2</sup> made some water culture experiments with manganese sulphate. In solution of 100 parts per million barley was injured, the roots turned dark, and the leaves appeared diseased. Even with 10 parts per million the barley was injured, but not so badly as in the stronger solution. Concentrations less than 1 part per million caused stimulation. Manganese was found in the leaves of the plant.

Voelcker<sup>3</sup> working with wheat in water cultures found that manganese iodide produced a thin delicate root development, a peculiarity which was accentuated in a stronger solution. Manganese dioxide gave a good growth, with a wealth of finely branched roots which were not noticed in the untreated.

Schreiner, Sullivan, and Reid <sup>4</sup> have shown that the oxidation of soils was increased by the addition of manganese, that soils, though having similar amounts of manganese, varied greatly in oxidizing power, and that oxidation in soils depended on the form of the manganese as well as the amount. The form of the organic matter of the soil also controls the oxidizing power. The oxidative power of the manganese salts was increased by some organic acids and decreased by others.

Schreiner and Reed <sup>5</sup> studied the oxidizing power of plants growing in soil solutions. They found that the oxidizing power of the plant was greater in extracts of productive soils than in extracts of unproductive soils. In one experiment the oxidizing power of plants growing in distilled water was compared with that in an extract of a poor soil and of a good soil. Putting the distilled water at 100, the relative oxidation in the poor soil extract was 72 and in the good soil extract 286. In another experiment a poor sandy loam was compared with a rich garden soil. When the oxidation of the plants in

<sup>&</sup>lt;sup>1</sup> Loew, O., and Sawa, S., On the action of manganese compounds on plants. Bul. Col. Agr., Tokyo, 5, 161 (1902-3).

<sup>&</sup>lt;sup>2</sup> Brenchley, The influence of copper sulphate and manganese sulphate upon the growth of barley. Ann. Bot., 24, 571 (1910).

<sup>&</sup>lt;sup>3</sup> J. Royal Agr. Soc. Eng., 65, 313.

<sup>&</sup>lt;sup>4</sup> Schreiner, O., Sullivan, M. X., and Reid, F. R., Studies in soil oxidation. Bul. 73, Bureau of Soils, U. S. Dept. Agr. (1910).

<sup>&</sup>lt;sup>6</sup> Schreiner, O., and Reed, H. S., The rôle of oxidation in soil fertility. Bul. 56, Bureau of Soils, U. S. Dept. Agr. (1909).

distilled water was taken as 100, the poor soil extract was 103 and the good soil extract 275. It was also pointed out that treating the poor soil extract with an absorbent agent benefited oxidation, that the presence of toxic organic substances in solution was deleterious to the oxidizing power of plants, and that the oxidizing power of the plants, especially in the presence of chemicals which promoted oxidation, was able to alleviate the toxicity of such solutions.

In more recent work harmful organic compounds have been found in soils and isolated.<sup>1</sup> The harmfulness of some of these soil compounds are overcome by fertilizers which promote root oxidation. Other harmful organic compounds have been worked with in this laboratory which are overcome by fertilizers which check root oxidation.<sup>2</sup>

## CULTURAL AND OXIDATION METHODS.

In order to study the oxidation by manganese and its effect on soil improvement, aqueous extracts of soils were used as culture solutions. The aqueous extract was made by stirring 2 parts of soil with 5 parts of distilled water for 3 minutes and filtering after 30 minutes through a Pasteur-Chamberland filter tube. It has been found that soil extracts prepared in this manner possess a plantproducing power similar to that of the soil from which they were made. That is, fertile soils give extracts which promote good plant growth and infertile soils give extracts which grow poor plants. The effect of manganese salts was studied by adding the substance to the soil extract. The water used in making soil extracts was distilled water, further purified by treating with carbon black and filtering.<sup>3</sup>

Salt-mouth bottles having a capacity of 250 c. c. were used as containers of the solution and served as culture jars in which to grow the plants.

Wheat was used in these experiments. The seeds were germinated on floating perforated aluminum plates, according to the method described in Bulletin 70 of this bureau. The seedlings were transferred from the germinating plates to the cultures when they were about an inch high, or just when the first true leaf was beginning to emerge from its sheath. Ten wheat plants were used in each culture. They are held in place by a cork which has had triangular wedges cut from its circumference. These wedges are truncated at their inner angle and are held in place by a rubber band around the cork.

<sup>&</sup>lt;sup>1</sup>Schreiner, O., and Shorey, E. C., The isolation of harmful organic substances from soils. Bul. 53, Bureau of Soils (1909). Chemical nature of soil organic matter. Bul. 74, Bureau of Soils, U. S. Dept. Agr. (1910).

<sup>&</sup>lt;sup>2</sup>Schreiner, O., and Skinner, J. J., Organic compounds and fertilizer action. Bul. 77, Bureau of Soils, U. S. Dept. Agr., (1911).

Buls. 36 and 70, Bureau of Soils, U. S. Dept. Agr.

In each treatment two cultures containing 20 wheat plants were used. Comparison was made with an equal number of plants growing in an untreated portion of the soil extract under the same conditions. At the end of two weeks the green weight of each culture was taken. In addition the oxidizing power of the plants subjected to various treatments was determined.

The method used to determine the oxidizing power of the roots in these solutions is the one described by Schreiner and Reed in Bulletin 56 of the Bureau of Soils. One hundred milligrams of aloin were added to each 250 c. c. culture jar. Aloin is a yellow powder and when dissolved in water gives a pale yellow solution, which is changed by oxidation to a deep red wine color. The aloin was added to the solution the last day of the cultural experiment; that is, after the plant had grown for two weeks. It remained in the solution and was subjected to oxidation by the plant roots for 12 hours before a comparison of the various treatments was made. The intensity of color of the solution was estimated by means of a Schreiner colorimeter. The untreated soil solution was used as the standard for comparison. It is sometimes difficult to make comparisons where there is a wide difference in the degree of oxidation. When this was the case the solutions were arranged in the order of their apparent color intensity, and the weakest colored solution was used first as a standard, being compared with the second weakest. Number 2 was then compared with the third weakest. In turn the third solution can be used as a standard against the next strongest, and so on. In this way the necessity of comparing a solution strongly tinged with yellow against a solution which has a deep red color is avoided. Finally, all readings were reduced to the basis of the untreated soil solution as the standard.

### EFFECT OF MANGANESE IN EXTRACTS OF UNPRODUCTIVE SOILS.

The first experiments were made with the poor sandy loam soil, which responded to manganese when tested in pots. Extracts were made of the soil, in the manner described above, and wheat plants were grown in the extracts with additions of manganese in several forms. The manganese was added at the rate of 50 parts per million of the element Mn. The chloride, sulphate, nitrate, and carbonate were used. The plants grew from May 11 to May 22. Two cultures were run with each treatment. Aloin was added to the solution the last day of the experiment and the oxidizing power of the plants taken. The comparative growth and oxidation is given in Table III.

**TABLE III.**—Effect of manganese (50 parts per million) on growth and oxidation in extracts of a poor sandy loam soil. (Untreated extract taken as 100.)

Treatment.	Relative growth.	Relative oxidation.
Extract untreated. Extract+MnCl2. Extract+MnSO4. Extract+Mn(NO3)2. Extract+Mn(NO3)2.	114     116     108	100 116 140 200 196

There was an increased oxidation power of the plant roots in the manganese cultures. Each of the salts caused an increase in oxidation and also an increase in the growth. The manganese chloride increased oxidation 16 per cent and growth 14 per cent. The sulphate increased oxidation 40 per cent and growth 16 per cent. The nitrate increased oxidation 100 per cent and growth 8 per cent. The carbonate increased oxidation 96 per cent and growth 11 per cent. It should here be noted in connection with the last two compounds that root oxidation is also greatly increased by nitrates and by alkaline conditions, as shown by Schreiner and Reed.<sup>1</sup> The high oxidation here noted is therefore the summation of the effects of manganese and nitrate or carbonate, respectively.

The greatest amount of oxidation in the solutions containing the different salts of manganese does not give the largest increase in growth. This suggests that the oxidation in the solutions containing the nitrate and carbonate in the amounts of 50 parts per million was perhaps too great for the best growth in this culture medium.

Another experiment with this soil extract was made using several concentrations of manganese sulphate, namely, 10, 30, and 50 parts per million. Two cultures were run in each treatment. The experiment continued from February 9 to February 19. The results are given in Table IV.

 TABLE IV.—Effect of manganese sulphate on oxidation and growth of wheat in extracts of a poor sandy loam. (Untreated taken as 100.)

Treatment.	Relative growth.	Relative oxidation.
Extract untreated. Extract + manganese 10 parts per million. Extract + manganese 30 parts per million. Extract + manganese 50 parts per million.	$100 \\ 114 \\ 119 \\ 124$	100 133 173 210

As seen in the table, the oxidation and growth increased as the amount of manganese in the solution increased. This experiment was repeated, the plants growing from February 25 to March 13. The results were very similar to those in the first test. With 10 parts per million, manganese oxidation was increased 35 per cent and growth 3 per cent. With 30 parts per million, manganese oxidation was increased 48 per cent and growth 19 per cent. With 50 parts per million, manganese oxidation was increased 45 per cent and growth 12 per cent.

Subsequent experiments with other poor soils were made, the results of which are similar to the one recorded above. One of these tests was with a poor clay loam from Maryland. Manganese sulphate was added to the soil extract in amounts of 10, 30, and 50 parts per million. There was considerable improvement in growth and an increase in the oxidizing power of the plants following the manganese treatment. The relative growth was for the untreated 100; manganese 10 parts per million, 132; manganese 30 parts per million, 111; and manganese 50 parts per million, 105. The relative oxidation was, respectively, 100, 133, 133, and 160.

A similar test was made with a sample of poor Collington sandy loam. The manganese was added at the rate of 20 parts per million, manganese in the form of chloride, sulphate, nitrate, carbonate, and dioxide being used. The results of the action of these various compounds on this soil extract are shown in Table V. The experiment was made from November 22 to December 6.

**TABLE V.**—Effect of manganese (20 parts per million) on growth and oxidation of wheat in extracts of poor Collington sandy loam. (Untreated extract = 100.)

	Treatment.	Relative growth.	Relative oxidation.
$\begin{array}{l} Extract + MnCl_2.\\ Extract + MnSO_4.\\ Extract + Mn(NO_3)_2.\\ Extract + MnCO_3.\\ \end{array}$		$102 \\ 110$	100 102 100 280 233 271

The chloride and sulphate showed practically no increase in oxidation or in growth in this soil solution. The other salts of manganese increased oxidation considerably and also the growth. Where the nitrate was used, oxidation was increased 180 per cent and growth 10 per cent. With the carbonate, oxidation was increased 133 per cent and growth 8 per cent. With dioxide, oxidation was increased 171 per cent and growth 10 per cent.

The effect of manganese on an extremely poor lawn soil is reported in the next experiment. The soil used was very unproductive. The natural vegetation is stunted and attempts at lawn making had failed. The water extract of this soil is a poor medium for plant growth, but is much improved by treatment with carbon black, which acts as an absorbent. A chemical examination of the soil showed it to contain dihydroxystearic acid and picoline carboxylic acid, both of which are harmful to plants. An experiment with this soil extract was started April 2 and run until April 16. The manganese chloride, sulphate, nitrate, and carbonate were used in two concentrations, 20 and 50 parts per million. The results of this test are given in Table VI.

 TABLE VI.—Effect of manganese on growth and oxidation of wheat plants in extract of a poor lawn soil. (Untreated extract = 100.)

Treatment.	Relative growth.	Relative oxidation
$\begin{array}{l} \textbf{Extract untreated.} \\ \textbf{Extract+MnCl_2 20 parts per million.} \\ \textbf{Extract+MnCl_2 50 parts per million.} \\ \textbf{Extract+MnSO_4 50 parts per million.} \\ \textbf{Extract+MnSO_4 50 parts per million.} \\ \textbf{Extract+Mn(NO_3)_2 20 parts per million.} \\ \textbf{Extract+Mn(NO_3)_2 50 parts per million.} \\ Extra$	120 113 124 131 120 119 152	$\begin{array}{c} 100\\ 136\\ 150\\ 130\\ 166\\ 114\\ 115\\ 175\\ 200\\ \end{array}$

Manganese considerably increased oxidation and growth of the wheat in this soil solution, as shown by the table. The effect of each salt was quite marked and the beneficial action is greater with this soil than any previously reported. This experiment was repeated, but with only the manganese chloride and sulphate. The plants grew from April 16 to April 28. Manganese sulphate in amounts of 20 parts per million increased oxidation 33 per cent and growth 21 per cent; with 50 parts per million oxidation was increased 50 per cent and growth 20 per cent. With manganese chloride in amounts of 20 parts per million oxidation was increased 30 per cent and growth 22 per cent; with 50 parts per million oxidation was increased 66 per cent and growth 21 per cent. In this experiment, as in the preceding, manganese in the solution greatly increased the oxidation and consequently made the solution a much better medium for the growth of plants.

The experiments with these poor soil solutions indicate that the manganese, by increasing oxidation, has overcome their harmful properties. Treating the extracts of poor soils with carbon black is beneficial to growth and increases oxidation. Whatever increases root oxidation enables the plant to offset more or less the ill effects of injurious substances. Thus the harmfulness of dihydroxystearic acid is overcome by nitrate fertilizers and others which tend to increase root oxidation.<sup>1</sup> Dihydroxystearic acid interferes greatly with the normal root oxidation and nitrates stimulate this oxidation. The presence of other toxic organic substances in solution have been shown to be extremely deleterious to the oxidizing power of plants. This oxidizing power of the plants, especially in the presence of nitrates,

<sup>&</sup>lt;sup>1</sup>Schreiner, O., and Skinner, J. J., Some effects of a harmful organic soil compound. Bul. 70, Bureau of Soils, U. S Dept. Agr (1910).

was able to alleviate the toxicity of such solutions.<sup>1</sup> The oxidizing power of plants grown in extracts of productive soils is greater than that of plants grown in extracts of unproductive soils. Harmful organic compounds upon proper conditions suffer change in the soil. This change may occur under conditions of thorough aeration and oxidation, which is promoted by thorough tillage and good drainage and also by the addition of substances to increase oxidation in the soil. This seems to be a function of manganese. Its addition to extracts of soils of low fertility increases the oxidation, and by so doing may change the organic material of the solution and make it a better medium for plant growth.

## EFFECT OF MANGANESE IN EXTRACTS OF PRODUCTIVE SOILS.

The next experiments are concerned with the action of manganese in good soils where harmful conditions are necessarily at their minimum or entirely wanting. One of the soils tested was the Hagerstown loam from a productive plot in the experimental field of the Pennsylvania experiment station. The soil is naturally productive and in the field has been subjected to a four-year rotation. When tested in pots, this soil did not respond to manganese.

An extract of the soil was made in the usual way and wheat seedlings grown. Manganese chloride, sulphate, and nitrate were used in concentrations of 10 and 25 parts per million. Two cultures were used in each treatment. The experiment was run from December 9 to December 23. The results are given in Table VII.

 TABLE VII.—Effect of manganese on growth and oxidation in extracts of a productive loam soil. (Untreated extract = 100.)

Treatment.	Relative growth.	Relative oxidation.
Extract untreated Extract+MnCl <sub>2</sub> , 10 parts per million. Extract+MnCl <sub>2</sub> , 25 parts per million. Extract+MnSO <sub>4</sub> , 10 parts per million. Extract+MnSO <sub>4</sub> , 25 parts per million. Extract+MnSO <sub>4</sub> , 25 parts per million. Extract+Mn(NO <sub>3</sub> ) <sub>2</sub> , 10 parts per million. Extract+Mn(NO <sub>3</sub> ) <sub>2</sub> , 25 parts per million.	90	100 98 97 100 102 101 100

As seen in the table, there was no increased oxidizing power of the plant roots in the manganese cultures. The oxidation in the untreated solution was very good, as might have been expected in this highly fertile soil, and the addition of manganese produced no additional oxidation by the plants. The growth was not increased. In several instances it was decreased. Only in one treatment, and that with the nitrate, was the growth as good as in the untreated solution.

<sup>&</sup>lt;sup>1</sup> Schreiner, O., and Reed, H. S., The rôle of oxidation in soil fertility. Bul. 56, Bureau of Soils, U. S. Dept. Agr. (1909).

The effect of manganese was also tested in the extract of Sassafras sandy loam taken from a productive field. In this test the manganese was used in concentrations of 20 parts per million. The chloride, sulphate, nitrate, carbonate, and dioxide were used. The experiment ran from November 12 to November 27. The results are given in Table VIII.

 TABLE VIII.—Effect of manganese on growth and oxidation in productive Sassafras sandy loam. (Untreated = 100.)

Treatment.	Relative growth.	Relative oxidation.
$\begin{array}{l} \textbf{Extract untreated.} \\ \textbf{Extract+MnCl}_{2}. \\ \textbf{Extract+MnSO}_{4}. \\ \textbf{Extract+Mn(NO_{3})_{2}.} \\ \textbf{Extract+Mn(NO_{3})_{2}.} \\ \textbf{Extract+MnO}_{3}. \\ \textbf{Extract+MnO}_{2}. \end{array}$	79 90	100 125 106 120 150 200

The effect of the various manganese salts on this good soil was to increase the oxidation by the plants; the growth, however, was even decreased. The experiment was repeated with the same soil and same manganese salts. The plants grew from December 1 to December 14. The results are given in Table IX.

 TABLE IX.—Effect of manganese on growth and oxidation in productive Sassafras sandy

 loam.
 (Untreated = 100.)

Treatment.	Relative growth.	Relative oxidation.
$\begin{array}{l} Extract untreated\\ Extract+MnCl_2.\\ Extract+MnSO_4.\\ Extract+Mn(NO_3)_2.\\ Extract+MnCO_3.\\ Extract+MnO_2.\\ \end{array}$	100 82 90 95 90 92	100 106 100 116 140 150

Again it is shown that manganese is not beneficial to this good soil. In both experiments the oxidation by the plants was increased by addition of the salts. Other experiments were made with this soil, using varying amounts of several salts of manganese. The action, however, was similar to those recorded above. There was no stimulation of growth with any of the salts varying in amount from 5 to 100 parts per million. In each of the tests with this soil the plants were affected, and after 10 days' growth the tips became yellow and the leaves showed indications of drying up. These effects are the result of excessive oxidation and probably show the cause of the harmfulness of manganese in this and certain other good soils. The oxidizing power of plants in these productive soils was already good, and they needed nothing to stimulate this function. When manganese was added the oxidation was increased and became even too great, thus causing a harmful action. The experiments with the different soils recorded above were made at different times of the year and, as the action of the manganese and growth of the plants might be influenced by some climatic conditions, an experiment was next made in which both poor and good soils were simultaneously tested. Six soils of different character were selected.

Three of these soils were very poor and unproductive and three were good productive soils. Soils Nos. 1, 2, and 3 are unproductive. Soil No. 1 is a sandy clay collected from a park where the lawn was very poor. No. 2 is a sandy loam soil from a cultivated field. No. 3 is a clay loam taken from under a tree, where repeated attempts to grow a lawn had failed.

Soils Nos. 4, 5, and 6 are productive soils taken from fields which were growing good crops. No. 4 is a loam, No. 5 a sandy loam, and No. 6 a silt loam.

Extracts were made and plants grown in each at the same time. Manganese in the form of chloride and sulphate were used in amounts of 20 and 50 parts per million of the element manganese. The experiment was conducted from April 5 to April 19. The results are given in Table X. The growth and oxidation are compared with the untreated soil extract in each case.

	Unproductive soils.						Productive soils.					
Treatment.	1	1 2		2	3		4		5		6	
	Sandy	z clay.	Sandy loam.		Clay loam.		Loam.		Sandy loam.		Silt loam.	
	Growth.	Oxidation.	Growth.	Oxidation.	Growth.	Oxidation.	Growth.	Oxidation.	Growth.	Oxidation.	Growth.	Oxidation.
Extract untreated	100	100	100	100	100	100	100	100	100	100	100	100
Extract+MnCl <sub>2</sub> , 20 parts per million Extract+MnCl <sub>2</sub> , 50 parts	126	142	102	111	112	180	99	180	90	125	106	150
per million	119	156	101	118	122	190	76	175	93	156	76	132
Extract+MnSO <sub>4</sub> , 20 parts per million	130	135	114	120	114	130	94	130	96	142	100	100
Extract+MnSO <sub>4</sub> , 50 parts per million	137	172	107	130	108	127	98	135	88	160	83	114

**TABLE X.**—Effect of manganese on oxidation and growth in unproductive and productive soil extracts. Results expressed in relative oxidation and growth. (Untreated = 100.)

The results of this test substantiate those of previous experiments. The effect of the manganese on the unproductive soils was to increase the oxidation and growth. There was an increase with both salts of manganese and both concentrations. This, however, is reversed in the case of the productive soils. The oxidation is increased with each of the solutions, while the growth was depressed. The effect of excessive oxidation was noticeable; the leaves were yellow at the tips and appeared bleached. The natural processes of oxidation in the productive soils were good, and the addition of manganese caused excessive action, and thus injured the culture as a medium for growth. The life processes in the unproductive soils were probably bad, and the addition of this substance aided the needed function and therefore overcame its bad qualities and made it a better medium for plant growth.

In relation to the beneficial effect of manganese on poor soils by stimulating root oxidation where oxidation is naturally poor, and the harmful effect by causing additional oxidation by plant roots in good soils where the oxidation processes are already good, it is interesting to note the effect of different fertilizers, which increase or check oxidation on the action of organic compounds. Quinone, which has been shown to be toxic to wheat seedlings in a former research,<sup>1</sup> is an oxidizing substance. Its harmful effect is partly overcome by potash salts, which check oxidation processes. On the other hand, those harmful soil organic compounds that have reducing properties—that is, are themselves readily oxidized—such as vanillin and dihydroxystearic acid, have an inhibiting effect on root oxidation and on root growth generally, and their harmful effects are overcome by fertilizers such as nitrate, which increase root oxidation to the greatest extent.

## EXPERIMENTS WITH MANGANESE IN THE FIELD.

The tests with manganese sulphate made at the department farm at Arlington, Va., were laid out in the spring of 1907 and are a part of a larger experiment, which includes the testing of a number of other compounds and fertilizers. Five crops are concerned in each treatment. The crops grown were wheat, rye, corn, cowpeas, and potatoes.

Describing only the manganese plots in this series, it should be said that these consisted of two parallel strips of land, each 1 rod wide and separated by a 3-foot path. Each strip is divided into 5 plots of 1 square rod, with  $2\frac{1}{2}$ -foot paths separating the plots. One strip or series of 5 plots is treated with manganese sulphate, the other strip is not treated and serves as a control or check. The five different crops are grown on both the treated and untreated plots, which lie side by side in the two strips.

The soil on which these experiments were made is a silty clay loam, low in organic matter. The physical condition of the soil is rather poor. Great care had to be practiced in cultivation to keep the soil in a good physical condition. The ground on which the manganese experiments were made is level and has surface drainage. The soil throughout these manganese plots and their controls is uniform, so

<sup>&</sup>lt;sup>1</sup> Schreiner, O., and Skinner, J. J., Organic compounds and fertilizer action. Bul. 77, Bureau of Solls, U. S. Dept. Agr. (1911).

the results secured should not be considered as unduly influenced by irregularities due to nonuniformity of the soil in different plots. The soil is inclined to be of an acid nature.

The manganese sulphate was applied at the rate of 50 pounds per acre. The untreated and treated plots received the same cultivation. The corn, cowpeas, and potatoes were planted in the spring of each year and harvested in the fall. The wheat and rye were planted in the fall and harvested the next July. This experiment has now run for six years, each crop on the same plot each year. That is, continuous culture of one crop on the same plot was practiced. The manganese was applied each year after the ground was broken and the land was cultivated before planting.

## EFFECT OF MANGANESE SULPHATE ON WHEAT.

Manganese sulphate was applied to the plot, 1 square rod, in September, 1907, at the rate of 50 pounds per acre shortly before it was planted to wheat. The crop was harvested in July of the following year and the soil was plowed and again prepared for wheat planting in September. The manganese sulphate was applied to the same plot each year before planting. The results of five years are given in Table XI. The weight of the unthrashed straw and grain only was taken. The first column gives the year. The second and third columns give the yields of the manganese and untreated plots in pounds per square rod. The yields of the two plots are calculated to pounds per acre and given in the fourth and fifth columns. The last column gives the increase or decrease of the manganese plot from the untreated plot in pounds per acre.

	Yield of squar	crop per e rod.	Calculated yield per acre.			
Year.	Manganese sulphate.	Untreated.	Manganese sulphate.	Untreated.	Increase or decrease of manganese plot.	
1908 1909 1910 1911 1911 1912	Pounds. 27 23 22 21 15	Pounds. 31 26 25 25 25 24	Pounds. 4, 320 3, 680 3, 520 3, 360 2, 400	Pounds. 4,960 4,160 4,000 4,000 3,840	Pounds. - 640 - 480 - 480 - 640 - 1,440	

 TABLE XI.—Showing the effect of manganese sulphate on wheat grown in soil treated five

 successive years.

In each year the manganese caused a decrease in yield. As shown in the last column in the table, the decrease in 1908 was 640 pounds per acre; in 1909 and 1910 the decrease was 480 pounds; in 1911 it was 640 pounds; and in 1912 it was 1,440 pounds. Some pot experiments were made in the greenhouse, using this silty clay loam soil. Wheat was grown in soil in paraffined wire pots. Manganese sulphate was used at the rate of 25, 50, and 100 pounds per acre. Five pots were used for each treatment, six plants in each pot. The wheat grew in the greenhouse for one month, from January 5 to February 6, when it was cut and the green weight of the plants taken. The manganese caused no material difference in growth.

The green weight was the same in the soil treated with manganese at the rate of 25 and 50 pounds per acre as in the check. Manganese at the rate of 100 pounds per acre caused a decrease; only 2 per cent, however. There was no stimulation of growth in any case.

## EFFECT OF MANGANESE SULPHATE ON RYE.

The result of the five-year test of manganese sulphate on plots of 1 square rod planted to rye are given in Table XII. Like the wheat, the rye was planted in September and harvested the next July. The manganese sulphate was applied each year at the rate of 50 pounds per acre, shortly before the crop was planted. Five years' results have been secured. The arrangement of the table is similar to that of Table XI. The increase or decrease in pounds per acre due to manganese is given in the last column. The weight of the unthrashed straw and grain is given.

In 1908 there was a decrease in the manganese plot of 1,120 pounds per acre. The next year, 1909, there was an increase of 480 pounds per acre; in 1910 there was a decrease of 320 pounds; in 1911 there was an increase of 320 pounds, and in 1912 an increase of 480 pounds per acre.

		crop per e rod.	Calculated yield per acre.		
Year.	Manganese sulphate.	Untreated.	Manganese sulphate.	Untreated.	Increase or decrease of manganese plot.
1908	Pounds. 26 29 10 25 17	Pounds. 33 26 12 23 14	Pounds. 4,160 4,640 1,600 4,000 2,720	Pounds. 5,280 4,160 1,920 3,680 2,240	$\begin{array}{c} Pounds. \\ -1,120 \\ + 480 \\ - 320 \\ + 320 \\ + 480 \end{array}$

 TABLE XII.—Showing the effect of manganese sulphate on rye grown on soil treated five

 successive years.

The results are somewhat inconsistent, some years there being an increase from the manganese and in others a decrease. There is no apparent reason for this. The decrease in 1908, the first year of the treatment, was very large. In the following years the differences were more moderate.

## EFFECT OF MANGANESE SULPHATE ON CORN.

Six years' results have been secured with corn. The manganese was applied in the spring of 1907, before the planting of corn. The ground, as in the other test, was thoroughly prepared, and the crop was cultivated throughout the growing season. Manganese sulphate was applied each year at the rate of 50 pounds per acre.

Table XIII gives the yields of stover and grain for the manganese and the check plots. The first column gives the year of growth, the second and third the yields for the manganese plot. The fourth and fifth columns give the yields for the untreated plot. The results have been calculated to pounds per acre of stover and bushels per acre of shelled corn. In making the calculations from pounds per square rod to bushels per acre, 56 pounds was taken as the weight of a bushel of shelled corn. These results are given in columns 6, 7, 8, and 9. The last two columns give the increase or decrease of stover and grain per acre on the manganese plot.

TABLE XIII.—Effect of manganese	sulphate on cor	orn grown on soil treated six succe	essive
	years.		

	Yield per square rod.				Calculated yield per acre.						
Year.		Manganese sulphate. Untreated.		Manganese sulphate. Untre		eated.	Increase or decrease of manganese plot.				
	Stover.	Grain.	Stover.	Grain.	Stover.	Grain.	Stover.	Grain.	Stover.	Grain.	
1907 1908 1909 1910 1911 1912	Pounds. 65 21 19 27 25 17	Pounds. 14 18 6 8 7 3	Pounds. 57 26 27 39 30 - 34	Pounds. 21 25 7 14 14 16	$\begin{array}{c} Pounds. \\ 10, 400 \\ 3, 360 \\ 3, 040 \\ 4, 320 \\ 4, 000 \\ 2, 720 \end{array}$	Bushels. 40 51 17 23 20 9	Pounds. 9,120 4,160 4,320 6,240 4,800 5,440	Bushels. 60 71 20 40 40 46	Pounds. +1, 280 - 800 -1, 280 -1, 920 - 800 -2, 720	Bushels. -20 -20 -3 -17 -20 -37	

The only increase from manganese noted was in 1907, when there was an increase of 1,280 pounds of stover per acre. However, there was a decrease in grain. The effect of the manganese sulphate was to decrease the yield of both stover and grain in the following five years. In 1907 the decrease in grain was 20 bushels per acre. In 1908 stover was decreased 800 pounds per acre and the grain 20 bushels per acre. In 1909 the stover was decreased 1,280 pounds and the grain 3 bushels per acre. In 1910 the decrease of stover was 1,920 pounds and the grain 17 bushels. In 1911 the decrease of stover was 800 pounds and the grain 20 bushels. In 1912 the decrease of stover was 2,720 pounds and the grain 37 bushels per acre.

## EFFECT OF MANGANESE SULPHATE ON COWPEAS.

As with the corn plots, the manganese sulphate was applied to the cowpea plots beginning in the spring of 1907. Six years' results have been secured. Manganese sulphate was applied each year at the rate of 50 pounds per acre before planting.

Table XIV gives the yield of cowpea hay in pounds per square rod and pounds per acre. Columns 2 and 3 give the yield of the manganese and untreated plots in pounds per square rod; columns 4 and 5 the yield of the two plots calculated to pounds per acre. The last column gives the increase or decrease of the manganese plot in pounds per acre.

TABLE	XIVEffect	of mo	anganese	sulphate	on	cowpeas	grown	in	soil	treated	six	suc-
				cessive ye	ars							

-	Yield per s	square rod.	Calculated yield per acre.		
Year.	Manganese sulphate.	Untreated.	Manganese sulphate.	Untreated.	Increase or decrease of manganese plot.
1907	Pounds. 42 41 28 21 35 22	Pounds. 52 55 37 27 42 21	Pounds. 6,720 6,560 4,480 3,360 5,600 3,520	Pounds. 8, 320 8, 800 5, 920 4, 320 6, 720 3, 360	$\begin{array}{c} Pounds. \\ -1,600 \\ -2,240 \\ -1,440 \\ -960 \\ -1,120 \\ +160 \end{array}$

By an examination of the table it is seen that there was a decrease in the manganese-treated plots in each year except in 1912. In 1907 there was a decrease in yield of hay of 1,600 pounds per acre, in 1908 a decrease of 2,240 pounds, in 1909 a decrease of 1,440 pounds, in 1910 a decrease of 960 pounds, in 1911 a decrease of 1,120 pounds, and in 1912 an increase of 160 pounds per acre.

### EFFECT OF MANGANESE SULPHATE ON POTATOES.

The results of the six-year test of manganese sulphate on potatoes is given in Table XV. The details of the experiment and the arrangement of the table are the same as described in the test with cowpeas. In calculating from pounds of potatoes per square rod to bushels per acre the weight of a bushel of potatoes was taken as 60 pounds.

TABLE XV.—Effect of	nanganese sulphate on potatoes grown on soil treated six successive
	years.

		Yield per s	square rod. Calculated yield pe			er acre.			
	Year.		Untreated.	Manganese sulphate,	Untreated.	Increase or decrease of manganese plot.			
1908. 1909. 1910. 1911.		Pounds. 57 30 83 36 57 23	Pounds. 83 45 68 55 91 33	Bushels. 152 80 221 96 152 61	Bushels. 221 120 181 147 243 85	$\begin{array}{c} \textbf{Bushels.} \\ -69 \\ -40 \\ +40 \\ -51 \\ -91 \\ -24 \end{array}$			

There was a decrease in the yield in the manganese plot in every year except 1909. In 1909 there was an increase of 40 bushels. In 1907 there was a decrease of 69 bushels, in 1908 a decrease of 40 bushels, in 1910 a decrease of 51 bushels, in 1911 a decrease of 91 bushels, and in 1912 a decrease of 24 bushels per acre.

## ACIDITY OF THE SOIL IN THE VARIOUS PLOTS.

Acidity tests of the various plots used in this experiment were made in May, 1912, after the experiment had been in progress for five years. All of the plots, both treated and untreated for each crop, were acid. Samples were taken of each plot and lime requirement determinations made.

The sampling was done with a soil auger to a depth of 6 inches. Five borings were made in each plot and a composite sample made from the individual borings. The determinations were made on airdry soil.

The lime requirement determinations were made by means of the Veitch method.<sup>1</sup> Table XVI shows the amount of lime required according to this method for each plot to produce a neutral condition in the soil. The soil in each plot required approximately a ton of lime per acre. Where wheat was grown the manganese and the untreated plots were equally acid. In the rye, corn, and cowpea plots the manganese plots had a higher lime requirement than the untreated plots. With rye the manganese plot required 2,492 pounds of lime and the untreated 2,136 pounds per acre. With corn the manganese plot required 2,492 pounds and the untreated 1,780 pounds. With cowpeas the manganese plot required 2,492 pounds and the untreated 2,136 pounds per acre. Where potatoes were grown the untreated plot had a greater lime requirement than the manganese plot. The manganese plot required 2,451 pounds of lime per acre and the untreated plot 2,743 pounds.

TABLE XVI.—Showing the pounds of lime (CaCO<sub>3</sub>) required per acre in the various plots.

	Wheat.	Rye.	Corn.	Cowpeas.	Potat <b>oes</b> .
Manganese plot Untreated plot.	1,780	2,492	Pounds. 2,492 1,780		2,451

The results of these determinations show that the soil is an acid one and that the manganese tests were made under acid conditions. The results obtained on this soil are supported by the statements of other investigators, that the best effects of manganese can not be secured under acid conditions. After the crops were harvested in 1912, lime was added in sufficient amounts to satisfy the lime requirements for the separate plots as shown in Table XVI. Lime requirement tests will be made for each plot after the crop is harvested each year, and should any further lime be required this will be added, so as to maintain the soil, as nearly as practicable, in a neutral condition. As manganese had harmful effects on the soil when acid, it will be interesting to observe its effect when the soil is kept neutral.

## OXIDATIVE POWER OF PLOTS WITH AND WITHOUT MANGANESE.

Since Bertrand <sup>1</sup> showed that manganese played an essential part in the oxidation by the so-called oxidizing enzyme, laccase, since manganese increased the oxidizing power of a number of soils in the laboratory, and since it has been found that a number of soils of strong oxidizing power contain considerable manganese, some of which was in the highly oxidizing form of  $MnO_2$ , it became of interest to determine whether manganese had any accelerating effect on the oxidation in the soil of plots planted with wheat, rye, corn, cowpeas, and potatoes.

In 1912 composite samples from five borings to the depth of 6 inches were taken of the manganese plots and check plots: (a) early in April before the yearly application of fertilizer, when wheat and rye were 4 or 5 inches high and before the corn, cowpeas, and potatoes had been planted; (b) late in May, after the fertilizers had been added, when the corn and cowpeas had sprouted; (c) in August, after wheat and rye had been taken off, corn was in tassel, cowpeas in bloom, and potatoes were coming into bloom. The oxidation readings were made a week or two later on the air-dried samples.

When 10 or 20 grams of soil are shaken two or three times with 50-70 c. c. of a 0.125 per cent water solution of aloin, the aloin solution is changed in a few minutes from bright yellow to a cherry red. After the soil has stood for about an hour and has settled, the somewhat turbid solution is decanted and centrifuged; the supernatant liquid drawn off, and the depth of color of the different solutions compared by means of a Schreiner colorimeter, either with each other or with colored glass of a shade of red matching one of the oxidized solutions. In the present experiment the oxidation reading was made against a glass standard, which matched in tint the red color produced in the aloin solution by the sample of wheat soil collected in the spring. Ten grams of soil were employed for each test. The relative oxidation in the manganese plots and the check plots is given in the table following.

<sup>&</sup>lt;sup>1</sup> Compt. rend., **122**, 1132 (1896); **124**, 1032 (1897).

_	April.		Ju	ne.	August.		
Crop.	Check plots.	Manganese plots.	Check plots.	Manganese plots.	Check plots.	Manganese plots.	
Wheat Rye Com Cowpeas. Potatoes	$100 \\ 131 \\ 110 \\ 66 \\ 87$	$95 \\ 105 \\ 100 \\ 64 \\ 60$	110 131 130 105 91	$130 \\ 105 \\ 131 \\ 110 \\ 78$	55 78 87 53 53	64 60 75 53 55	

**TABLE XVII.**—Relative oxidation in plots treated with manganese sulphate and in the corresponding check plots growing the same crop (wheat soil in April taken as 100).

With the exception of the wheat plot, where there is shown a slight increase as an average of the three determinations, the addition of manganese sulphate has not increased the oxidative power of the soil, and in a number of instances it has lessened oxidation. The soil in general has a tendency to be acid in character and at best has not a strong oxidizing power. If the first determination, made in April, is considered (that is, the oxidative power of the plots at a time when there is little or no growth) the oxidation in the manganese plot is less in every instance than that of the check plot. This period is the best one for testing the oxidation effect of manganese unmodified by plant growth. The lessened oxidation produced by manganese sulphate agrees roughly with the lessened yields on the same plots under treatment with manganese. In 1912, for instance, the vear in which the oxidation was tested, the yield, as previously shown, of wheat, corn, and potatoes was less on the manganese plot than on the untreated plot, while rye showed a slight increase and the yield of cowpeas was practically the same.

In the second determination, made in June, the oxidation power of the manganese plot is on the average more like that of the check plot.

In the third determination, made in August, shortly after wheat and rye had been taken off, the manganese plot was on the average again less than the check plot.

As previously pointed out, the manganese plots, with the exception of the potato plot, showed a higher lime requirement than the check plots. Under acid conditions the formation of organic compounds capable of acting as oxygen carriers or as activators of inorganic oxidizing compounds such as manganese salts is much lessened or entirely inhibited. This is indicated from the results with the acid soil under investigation, for the addition of manganese did not increase the oxidizing power of the soil nor indeed of plants growing therein. This oxidizing power of the plants was tested in the case of wheat. By carefully removing the soil from the young wheat plants growing on the plots, the oxidizing power of the intact roots when placed in aloin solution was found to be no greater in the case of the

plants from the manganese plot than from the check plot. The relative oxidation, in fact, was 97 and 100, respectively.

In neutral solution the oxidation power of the plant root is increased by manganese sulphate, though manganese sulphate itself has little oxidizing action on aloin, except in the presence of hydrogen peroxide or activating organic matter. Addition of 0.5 c. c. of a 3 per cent hydrogen peroxide added to 70 c. c. of aloin solution shaken with soil greatly increased the oxidation of the soil from the plots, the manganese fertilized plot in particular. It is quite possible that the soils which normally give direct oxidation of aloin contain both organic and inorganic peroxide. It has been found, in fact, that organic matter in a state of autoxidation forms peroxide.<sup>1</sup> Alkalies and alkaline salts favor the formation of the peroxides.

As analyzed by Mr. W. O. Robinson, of the Bureau of Soils, the soil from the various parts of the experiment farm varied in manganese content, calculated as MnO, from 0.034 per cent to 0.064 per cent. The manganese-treated plot contained 0.060 per cent MnO, the check plot 0.064 per cent. Of 26 American soils analyzed by Robinson,<sup>2</sup> the average content of manganese was 0.071 instead of 0.20 per cent MnO previously given. The experiment farm has, therefore, an average manganese content.

Soils may have practically the same quantity of manganese and still vary greatly in oxidizing power, so oxidation in soils, if due to manganese, depends on the nature of the manganese as much as on the amount. In previous work<sup>3</sup> it was found that soils of strong oxidizing power, such as the Hagerstown loam and the Clarksville silt loam, contain considerable manganese, while the Takoma loam soil, the Elkton silt loam, and the Cecil sandy loam, which have very little oxidizing power, contain little manganese. When 100 parts of manganese per million in the form of the sulphate, chloride, carbonate, and dioxide were added to the three soils poor in manganese, no increase in the power to oxidize aloin was noted in the case of the chloride, sulphate, or carbonate, and the dioxide produced but slight increase. When, however, dilute organic hydroxyacids, such as citric, malic, and tartaric, 5 c. c. n/10 acids to 100 grams of soil, and corresponding salts, such as sodium citrate and sodium tartrate, were added to the soils to which the manganese had been added, there was a decided increase in the power to oxidize aloin. The greatest increase in oxidation occurred in the soils to which manganese dioxide and citric acid had been added. Addition of citric acid and sodium citrate to the soils from manganese-treated

<sup>&</sup>lt;sup>1</sup> Schönbein, J. prakt. Chem., **81**, 16 (1860). Manchot and Herzog., Liebig's Ann. Chem., **316**, 318, 331 (1901). Bach, Monit. Sci. (4), **11**, II, 479 (1897); Compt. rend., **126**, 1066, 4159 (1898).

<sup>&</sup>lt;sup>2</sup> M. X. Sullivan and W. O. Robinson, Manganese as a fertilizer. Circ. 75, Bureau of Soils, U. S. Dept. Agr. (1913).

<sup>&</sup>lt;sup>8</sup> Bul. 73, Bureau of Soils, U. S. Dept. Agr.

plots and the check plots increased their oxidizing power, the sodium citrate especially. Addition of organic matter, such as darkened pyridine, which is in a state of autoxidation, markedly increased the oxidizing power of the soils in laboratory tests.

As already stated, the oxidative power of a soil depends not so much on the amount of manganese as on the form of the manganese and the nature of the organic matter. Organic matter in a state of autoxidation may oxidize aloin directly or act as an activator of inorganic oxidizers such as manganese. Organic matter in a state of autoxidation seems to be lacking in the plots. Addition of manure to various plots on the Arlington farm has greatly increased the oxidizing power and also the crop production, thus illustrating, as previously pointed out,<sup>1</sup> that the factors that favor oxidation also favor, to some degree, soil fertility. In many soils, especially those carrying considerable organic matter and of neutral reaction, the addition of manganese increases the oxidation in soil and also the crop yield. The action of the manganese may be direct or indirect; direct in that it stimulates the plant to an increased growth, or indirect in that it increases the metabolism of microorganisms which place at the service of the plant more material, organic and inorganic, which is readily assimilated, or by furthering the oxidation of material which is injurious to crop growth. Among the injurious substances found in soils under study for low productiveness are dihydroxystearic acid,<sup>2</sup> salicylic aldehyde,<sup>3</sup> and vanillin,<sup>4</sup> all which are modified by oxidation.

As regards manganese, Bertrand has shown it to be the most active element in promoting oxidation changes. In soils we have found it capable of promoting active oxidation, especially in the presence of suitable organic matter. By its strong oxidizing power manganese would render injurious material in the soil harmless or even beneficial, and by the oxidation of inert or rather stable organic matter might cause the nitrogen and other substances contained in the organic matter to become more rapidly available to plants. According to Giglioli,<sup>5</sup> the presence of compounds which accumulate combined oxygen with a capacity of gradually giving it off, facilitates the development of the roots in the deeper strata of the soil, which otherwise they would not be able to penetrate. When a ditch was dug in a region where manganese dioxide was acting as an oxidizer, a deep system of roots was found.

In various experiments abroad, as already shown, manganese salts have been tested as fertilizers. Where the action of the manganese

<sup>&</sup>lt;sup>1</sup> Bul. 73, Bureau of Soils, U. S. Dept. Agr.

<sup>&</sup>lt;sup>2</sup> Bul. 53, Bureau of Soils, U. S. Dept. Agr.

<sup>&</sup>lt;sup>8</sup> Bul. 88, Bureau of Soils, U. S. Dept. Agr.

<sup>•</sup> Jour. Agr. Research, vol. 1, p. 359 (1914).

<sup>5</sup> Bol. quindicinale della Soc. degli Agr. Ital., 13, 974 (1908).

has been beneficial it is probably due (1) to the increased oxidation produced in the plant roots whereby the plant is stimulated to greater activity and to increased absorption of the material useful for its growth and general metabolism; (2) to the stimulation of the activity of microorganisms of the soil; (3) to an increased oxidation within the soil. In this connection it is of interest to note that Robin and Bardet<sup>1</sup> concluded that colloidal metals, especially manganese, promote oxidation in the tissues of animals and intensify metabolism.

Where manganese has been of little value or has given decreased yields, conditions were such that stimulating actions on plant and microorganisms did not come into play, or, on account of the acid reaction of the soil, the effect of the stimulation led to reduction processes being predominant. Large applications of manganese have been found injurious, undoubtedly because of excessive stimulation and excessive oxidation in microorganisms and in the plant, with a resulting change in the biochemical activities of plant and microorganisms and in the conditions of inorganic and organic soil constituents, the ultimate result of which change is injurious to the growing crop.

Soils poor in oxidative power should be improved by the addition of oxidizing substances, organic or inorganic, or, better, by treatment which favors their formation, such as the addition of lime and manure to acid soils, of manure and manganese to nonacid soils. In soils of high oxidation power much further increase in the oxidation power may indeed be harmful. Excess of manganese in soils has been found injurious, as shown by the work of Loew and Sawa<sup>2</sup> on rice, peas, and cabbage; of Salomon<sup>3</sup> on wheat; by the investigations of Kelley 4 on Hawaiian soils; and of Guthrie and Cohen<sup>5</sup> on the failure of grass on Australian soil. When manganese is added its effect will undoubtedly vary with the nature of the soil, the nature of the crop, the form of the manganese added, and the nature of the associated organic matter. In general its effect is to promote oxidation. In the presence of carbohydrates it may cause reduction of nitrates, through the reducing compounds formed in the oxidation of the carbohydrates. A review of the literature on manganese as a fertilizer shows its effect has been variable.<sup>6</sup>

What quantities of manganese should be used in a soil to obtain favorable action can be determined at present only by experimentation. In this paper it is pointed out that, on the acid soil of the experiment farm, 50 pounds of manganese sulphate to the acre decreased crop yields and gave in general a reduced rather than an

<sup>&</sup>lt;sup>1</sup> Compt. rend., 138, 783 (1904).

<sup>&</sup>lt;sup>2</sup> Bul. Col. Agr. Tokyo, 5, 161 (1902-3).

<sup>&</sup>lt;sup>1</sup> La Staz. per. agr. Ital., 38, 1015 (1905); 40, 97 (1907).

<sup>4</sup> Hawaiian Sta. Press Bul. 23; J. Ind. Eng. Chem., I, 533 (1909); Buls. 26, 28, Hawaii Agr. Sta.

<sup>&</sup>lt;sup>5</sup> Agr. Gaz. New South Wales, 21, 219 (1910).

<sup>&</sup>lt;sup>6</sup> Bul. 73 and Circular 75, Bureau of Soils, U. S. Dept. Agr.

30

increased oxidation. Addition of manure increased the oxidation power in general, but the effect of manure was not tested in conjunction with manganese.

## CATALYTIC POWER OF PLOTS WITH AND WITHOUT MANGANESE.

In previous work <sup>1</sup> it has been shown that in soil, as in plant and animal tissue, there is associated with oxidation the power to decompose hydrogen peroxide. The property of tissue to decompose hydrogen peroxide has been attributed to an enzyme, catalase, and the process is known as catalysis. This process is greater in strong vital soils and appears to be dependent not on an enzyme, but on the nature of the soil constituents, especially manganese and the organic matter.

In testing the catalytic power of soils, 5 grams of air-dried soil were placed in a large test tube having a capacity of 90 c. c., provided with a two-holed rubber stopper through which passed a small dropping funnel and a glass tube connected with a gas-measuring tube. The peroxide used was a slightly acid and rather stable solution containing approximately 3 per cent hydrogen peroxide by weight. Before using, the peroxide was made faintly alkaline to phenolphthalein by means of dilute sodium hydroxide and made up to 1.5 per cent The neutralized peroxide was dropped upon the soil by solution. means of the funnel, and the oxygen evolved was collected in the gasmeasuring tube. The criterion for the catalytic power of soils is the rate of evolution of oxygen or the time required to evolve a definite quantity, usually 50 c. c., but in soils of slight catalytic power 20, 30. 40 c. c., as the case may be. In this way many soils, productive and unproductive, surface soils and subsoils, greenhouse soils and field soils have been tested. The catalytic power is greater in strong vital soils than in weak soils, in surface soils than in subsoils, and persists for years in air-dried soils. It is weak in acid soils.

Using the method just described, the catalytic power of the soils of the plots was taken at the same time as the oxidative power— (a) in April, (b) in June, (c) in August. On account of the relatively slow catalysis, 30 c. c. was selected as the measure for comparison. The results are given in Table XVIII.

TABLE XVIII.—Catalytic	power of plots treated with	manganese and of the corresponding
5	check plots.	

	Time required to evolve 30 c. c. of oxygen.								
Crop.	April. June.		April. June.		Aug	ust.			
	Check plots.	Manganese plots.	Check plots.	Manganese plots.	Check plots.	Manganese plots.			
Wheat. Rye. Corn. Cowpeas. Potatoes.	Minutes. 36 13 11 28 24	Minutes. 16 10 10 33 29	Minutes. 14 9 5 26 16	Minutes. 13 9 7 23 20	Minutes. 15 13 6 19 16	Minutes. 11 9 8 23 20			

<sup>1</sup> Bul. 86, Bureau of Soils, U. S. Dept. Agr.

In wheat and rye plots, the catalytic power is greater in the manganese-treated soils than in the untreated soil. In the corn and cowpea plots the untreated soil is on the average slightly the better catalyzer. In the case of potatoes, the check plot is slightly the better catalyzer. The soil of the plots is not a strong catalyzer, and the differences between the plots is slight, with the exception of the wheat plots.

Catalysis has been shown<sup>1</sup> to stand in closer relation to the manganese content of the soil than oxidation, though even in the case of catalysis the nature of the associated organic matter is of great importance. Addition of manure leachings and of manure ash increased the catalytic power of the soil of the experiment plots, but their effect was not studied in connection with manganese.

In general, soils of high productiveness previously studied have had strong catalytic power, while poor soils have had, as a rule, weak catalytic power. The catalytic power, however, does not stand in as close relationship to soil fertility as the oxidation power does, though in general the presence of a strong catalytic power in a soil can be taken as a priori evidence that the many factors making for soil fertility, such as suitable organic matter, bacterial activity, oxidation, etc., would be prominent and the soil would be a productive soil. Factors which favor fertility and oxidation, such as liming and addition of manure, also favor catalysis. Though crop production is dependent on many factors, no one or two of which can be taken as an absolute criterion, it is interesting to note that the soil of the experiment plots is a poor oxidizer and catalyzer and is also of mediocre productiveness. Its poor oxidation and catalysis and likewise yields of the ordinary cultivated crops may be connected with the acid character of the soil. In a similar way the lack of favorable response in oxidation, in catalysis, or in crop growth to treatment with manganese may be connected with the acid reaction and small organic content or the nature of the latter.

### SUMMARY.

The effect of manganese on poor and good soils was studied by growing wheat in pots. Manganese chloride, sulphate, nitrate, carbonate, and dioxide had a stimulating effect in the case of an unproductive sandy loam soil. The best results were obtained when the salt was applied in amounts from 5 to 50 parts of manganese per million. Quantities higher than this gave no correspondingly larger increase and in some cases were even harmful. On a productive loam the various salts of manganese had no stimulating effect.

Further work was done by growing the crop in treated aqueous extracts of soils and studying the oxidizing power of the plants. The oxidation was tested after the plants had been growing for two weeks. The effect of manganese on the oxidizing power of the plant roots and on growth gave different results with different soils.

With poor, unproductive soils manganese salts increased oxidation and growth. This was especially true in extremely poor soils and in a soil in which were found several harmful organic compounds.

Some harmful soil constituents themselves check the oxidizing power of plant roots, and their harmfulness is overcome by fertilizers which stimulate oxidation.

Oxidation was increased in productive soils; the growth, however, was decreased. The plants showed indications of excessive oxidation. As the oxidation processes in these soils were already good, the harmful action is attributed to excessive oxidation.

The beneficial action of manganese may be due to its function of aiding and increasing the oxidation processes and other vital processes in the plant as well as in the soil, and by this means changing or destroying some noxious products detrimental to plant growth.

A 5-year field test with manganese sulphate was made, growing wheat, rye, corn, cowpeas, and potatoes. The experiments were made on a silty clay loam soil which is acid in nature.

The manganese sulphate used at the rate of 50 pounds per acre had a harmful effect on each of the crops grown.

The addition of manganese sulphate to the soil decreased rather than increased the oxidizing power of the soil, which at best does not possess strong oxidizing power.

This is in harmony with the crop yield, which was also lessened by the addition of manganese sulphate, for while crop production is not absolutely correlated with the oxidative power of a soil, yet, in general, soils of good productivity are good oxidizers, and the factors which favor oxidation favor soil productivity.

The catalytic power of the plots was slightly if at all increased by the addition of manganese sulphate.

The soil is acid in character, which condition is unfavorable to oxidation and catalysis.

The failure of manganese to increase these factors may therefore be due to the acid character of the soil.

From these tests it is concluded that manganese is not profitable as a soil treatment on soil of this nature in need of liming.

> ADDITIONAL COPIES OF THIS PUBLICATION MAY BE PROCURED FROM THE SUPPERINTENDENT OF DOCUMENTS GOVERNMENT PRINTING OFFICE WASHINGTON, D. C. AT © CENTS PER COPY V

> > WASHINGTON : GOVERNMENT PRINTING OFFICE : 1914



