### THE COPPER-MANGANESE RELATIONSHIP

## IN THE GROWTH OF OATS,

SPRING WHEAT, AND ALFALFA

BY

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#### THE COPPER-MANGANESE RELATIONSHIP

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#### INTRODUCTION

There has been considerable work done in late years on manganese and its relationship with the growth of plants. The interest in trace elements is growing and we are now attempting to find a reason or reasons why deficiencies or toxicity occurs as plants are growing.

Most of the work done with copper has been done on organic soils. Our problem, therefore, is to see if copper and manganese have a definite relationship in the mineral balance of plants.

In this investigation there were two soils used and the growth of Oats, Spring Wheat, and Alfalfa were observed after applying varying amounts of lime, manganese, and copper.

Sommer (16) suggests that the function of Copper in plant metabolism is that of chlorophyll formation. The usual method of administration is by the use of bordeaux mixture in the form of spray. The observance in this investigation was with copper sulphate administered to the soil. In this manner it is believed to serve as a catalyst.

In other investigations with manganese deficiencies it was found that these conditions were mainly overcome by the addition of manganese sulphate. With copper sulphate added to

1. Figures in parentheses refer to "Literature Cited," P. -

soils it was found that some crops were least responsive on acid soils when varying amounts of lime were added.

# REVIEW OF LITERATURE

Willis (18) reports on his work carried on in 1936 with the relationship of copper to manganese and iron., He found that copper serves as a catalyst, and it serves as a soil amendment, decreasing the availability of iron and possibly manganese. It may be favorable or not, depending on the oxidation intensity and the manganese content of the soil. Although no conclusive evidence has been found it is assumed that the maintenance of manganese in field soils is dependent on the presence of a catalyst such as calcium. Copper is most beneficial on well-aerated soils.

McHargue (10), in experimenting with acid soils which contained approximately one-tenth of one per cent of manganese, found that only small amounts of the total manganese were soluable in water. By adding manganese in the form of the sulphate to the acid soil he caused a decrease in the yields of the crops. An excess of manganese sulphate in a soil renders it sterile with respect to the growth of plants. Calcium Carbonate in the soil causes a diminution in the toxic effects produced by an excess of manganese sulphate.

Experimenting with the relation of copper on different soil types in Florida, Hill (6) found that he obtained stimulation by using copper on soils of lowest productivity. This indicated that copper has a nutritive value and may be associated with the formation of plant hormones, possibly Vitamins, or related compounds.

Arnon (1) investigated nutrition of barley plants grown at different seasons by controlling the variables of reaction, aeration, and concentration of manganese and copper. He found that the plants were affected extensively and favorably by either forced aeration of the culture solution or by the addition of manganese, copper, or certain other metals, without forced aeration.

Piper (12-13) in experimenting with manganese, found deficiency is overcome most successfully by applying manganese sulphate or by water-logging prior to seeding. He also found in an extensive investigation on copper deficiencies, that oats grown in a copper-free nutrient solution until the development of acute deficiency symptoms occurred, recovered, and completed their normal life cycle on the addition of sufficient copper to the solution. He observed that rye has a greater absorbing power than oats and can grow to maturity on a soil on which oats fail from copper deficiency.

Lipman (8), in 1931, discovered that barley plants were unable to produce seed without the presence of a small quantity of copper in the root medium. This was given another conclusion, namely, that copper is essential in every phase of plant growth. The amount needed was very minute, one-sixteenth to one-eighth of a part per million of copper

in the root medium is sufficient.

In experiments at Michigan State College, Lucas (9) found that by the addition of copper sulphate the copper content was increased as much as three times, but the recovery amounted to a small fraction of the fertilizer application. The copper sulphate did not alter the manganese content of plants growing in adequate amounts of copper. The copper was least responsive to oats around a pH of 5.5 when grown in acid muck soils receiving varying amounts of limestone.

#### EXPERIMENTAL

In this experiment two Michigan soils were used. It was the intention to obtain sandy soils as acid as possible. The soils selected were a Fox sandy loam, and a Plainfield sandy loam. The Fox had a pH of 5.4 and the Plainfield a pH of 5.2. The soils were obtained from an area of Michigan containing vast amounts of these two soil types. Care was taken to find soils that had never been limed. The soils were screened and air-dried before potting. Three-gallon jars were used for the alfalfa and one-gallon jars for oats and spring wheat respectively. A uniform application of 3-12-12 fertilizer was used in the jars and was applied in bands about three inches below the surface.

There were twelve treatments on each of two soils, and all treatments were on the basis of pounds per acre. The lime was mixed thoroughly with the soil in the jars.

The treatments were as follows:

- 1. No lime
- 2. Three tons lime
- 3. Six tons lime
- 4. Nine tons lime
- 5. No lime  $\neq$  200 # MnSO4
- 6. 3 tons lime 200# MnSO<sub>1</sub>
- 7. 6 tons lime  $\neq$  200 # MnSO<sub>4</sub>
- 8. 9 tons lime / 200# MnSO4
- 9. No lime 200# MnSO4 25# CuSO4
- 10. 3 tons lime 200# MnSO4 25# CuSO4
- 11. 6 tons lime 200# MnSO4 25# CuSO4
- 12. 9 tons lime 200# MnSO4 25# CuSO4

The seeds selected were Marion oats, Henry spring wheat, and Hardigan alfalfa. They were all planted on June 26. They were planted thickly and thinned after germination to twelve plants. On July seventh the manganese sulphate and copper sulphate treatments were added in solution. The oats and spring wheat were harvested about a week after heading, August 15. They were placed in paper sacks and weighed after allowing them to air-dry. The plants were observed during growth to see if copper and manganese affected their manner of growth. Pictures were taken to show possible differences in height and growth tendencies.

The soil was tested for the availability of manganese. Samples were obtained for these tests by mixing the contents of the jars and screening. Since there were three jars for each treatment, the soil from them was thoroughly mixed before the samples were taken. The amount of manganese in the soil was determined by the Peech method as follows: To ten grams of air-dry soil, add a quarter teaspoonfull of Darco Carbon G-60, and 40 cc. of 0.13n HCl. Shake vigorously for 1 minute and filter. Place 5 cc. of the clear filtrate in a 15 ml. centrifuge tube. To this add 0.5 ml. of concentrated  $H_2SO_4$  and mix thoroughly. Cool this mixture and add and excess of sodium bismuthate and stir. Centrifuge for five minutes and carefully pipette 3 ml. of the liquid into absorption tubes and read in a colorimeter.

The alfalfa was observed during growth in the same manner as the oats and spring wheat.

### RESULTS

### Plants During Growth

Germination was rapid and good in both soils and all crops. The growth was normal and quite uniform until after the application of manganese sulphate and copper sulphate.

Plainfield: After thirty days of growth the oats and spring wheat were slightly behind the same crops grown on Fox sandy loam. Twelve days after the addition of manganese sulphate and copper sulphate the new leaves on both crops became brown and in some cases dried up completely. The leaves on the plants which received the three-ton lime

application did not show the effects as badly as did those on the plants which received the six and nine-ton applications. The plants treated with copper sulphate had a slight difference in appearance later in growth. The grain had a shorter stem and seemed to stool more. See plate (III). After heading the grain did not fill out well. This was general on all treatments so it could have been due to the soil not being high in plant nutrients.

Fox: After thirty days of growth the oats and spring wheat reacted much in the same manner as they did on Plainfield sand. The new leaves became brown, first at the tips, then gradually over the entire leaf.

### ALFALFA

Fox: Germination was good and growth was rapid on this soil for thirty days. Within fifteen days of treatment with manganese sulphate and copper sulphate there was a difference in growth. The untreated plants with lime had a slightly greener color and were taller. In the jars treated with copper sulphate, the buds and leaves around the buds died on some stems. In some jars entire plants died.

As shown by the results in Table 1, lime alone caused an increase in alfalfa yields but decreased yields resulted from additions of manganese and/or copper. Soil analyses showed the soil treated with manganese to contain more manganese than did the untreated soil. The manganese and copper treatments decreased the height of the plants.

In observing root development, the plants without manganese sulphate or copper sulphate added, had a very good nodule development. Those with treatment had very poor nodule development and in some cases nodules were completely lacking.

Plainfield: On this soil germination and growth was also rapid during the first 30 days. The plants on this soil reacted in the same manner to treatment as the plants in the Fox sandy loam. In general the foliage was a lighter green and was somewhat yellow. This condition was found to be a nitrogen deficiency which was not experienced on the Fox sandy loam. The weights - see Table 2 in general reacted in the same manner as the Fox. The ppm of manganese in the soil had a wider margin. The nodule condition was the same.

#### DISCUSSION

In this investigation three crops were used on two acid sandy soils. It was the intention to observe the growth of these crops after varying amounts of calcium carbonate was added and see if the addition of manganese sulphate and copper sulphate materially increased or decreased plant growth. Since calcium ties up available manganese, the addition of calcium carbonate would tend to make the plants deficient in manganese. There seemed to be little success in attaining deficiency symptoms in the plants. This was perhaps due to the presence of available manganese in excess

amounts by the addition of manganese sulphate. The copper sulphate had little affect on the growth of the plants. Sommer (16) suggests that copper functions in chlorophyll formation. It takes so very little copper to satisfy the requirements of plants that some investigators say plants may receive enough from the air.

Willis (18), in his work with the relationship of copper to manganese, found copper to act as a catalyst, and it serves as a soil amendment, possibly decreasing the availability of manganese.

The oats and spring wheat seemed to show the effect of the addition of copper sulphate late in growth in the formation of grain and appearance of plants. The alfalfa during growth seemed to show the effects of treatment mainly in color. There was some difference in vegetative growth and in root formation. This may support the investigations stating the catalytic effects of copper. The root weights went down with treatment as did average heights. In the root observance it was noted that nodule formation was very lacking on the treated jars. The untreated jars had very good nodule formation. In general the foliage was a lighter green on the Plainfield soil than on the Fox soil. This was due to a nitrogen deficiency.

#### CONCLUSIONS

From observing growth and from data collected these conclusions may be drawn:

1. There seemed to be sufficient available manganese in the soil on both Plainfield

and Fox.

- 2. The copper did not materially affect the availability of manganese but slightly affected vegetative growth and root development.
- 3. Treatment with manganese sulphate and copper sulphate decreased nodule develop-ment of alfalfa on both soils.

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Table 1. The Effect of Lime, Manganese, and Copper on the Yield and Height of Alfalfa Grown on Fox Sandy Loam Soil and the Effect of Treatment on the Manganese Content of the Soil.

Treatment	pH of Soil	Average wt. in gms. Air-dry Tissue	Average wt. in gms. Root wts. Air-dry	Soil Analysis Mn PPM	Average Height of Alfalfa in inches before Harvest
1. No lime	5.0	32	28	50	11 <sup>2</sup>
2. Three tons lime	6.5	47	42	20	11
3. Six tons lime	6.9	47	45	ω	12
4. Nine tons lime	9.5	τħ	53	24	11
5. No lime -/ 200# MnSoµ	5.4	37	44	58	8 <u>1</u> 8
6. 3 tons lime / 200#MnSO4	6.6	31	33	38	σ
7. 6 tons lime / 200#WnS04	7.2	22	22	19	IO
8. 9 tons lime-/200#MnSO4	7.5	32	23	26	10
9. No 11me / 200#MnSO4 / 25#CuSO4	5.1	30	18	30	თ
10. 3 tons lime / 200#MnS04 / 25#CuS04	6.5	27	1 T t	25	01 02 03
11. 6 tons lime / 200#MnSO4 / 25#CuSO4	6.7	25	39	38	7 <u>분</u>
12. 9 tons lime / 200#MnS04 / 25#CuS04	7.9	30	30	0#	ω

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Treatment	pH of Soil	Average wt. in gms. Air-dry Tissue	Average wt. in gms. Root wts. Air-dry	Soil Analysis Mn PPM	Average Height of Alfalfa in inches before Harvest
1. No lime	5.2	33	35	ħΓ	12
2. Three tons lime	6.1	35	47	11	13
3. Six tons lime	6.7	34	33	11	12
4. Nine tons lime	7.3	31	30	OT	11
5. No lime / 200#MnSO4	5.3	30	28	10	11
6. 3 tons lime 200#MnS04	6.2	29	35	21	IO
7. 6 tons lime / 200#MnS04	6.8	32	32	29	12
8. 9 tons lime - 200#MnS04	7.2	31	30	20	IO
9. No lime / 200#MnSO4 / 25#CuSO4	5.3	24	27	63	თ
10. 3 tons lime / 200#MnSO4 / 25#CuSO4	6.2	54	59	65	10
<pre>11. 6 tons lime / 200#MnS04 / 25#CuS04</pre>	6.9	25	30	68	10
12. 9 tons lime / 200#MnSO4 / 25#CuSO4	7.3	23	24	50	σ

The Effect of Lime, Manganese, and Copper on the Yield and Height of Alfalfa Plainfield Soil and the Fffect of Thestment on the Manganese Content of the Soil Table 2.



Plate 1. The response to treatment of oats on Fox sandy loam. No. 1, copper sulphate added; No. 2, manganese added; No. 3, lime added.



Plate 2. Treatment of oats on Fox sandy loam. No. 1, 3 tons lime; No. 2, 3 tons lime / 200# MnSO4; No. 3, 3 tons lime / 200# MnSO4 / 25# CuSO4.



Plate 3. Treatment of spring wheat on Plainfield sand. No. 1, no lime - MnSO4; No. 2, six tons lime - MnSO4; No. 3, six tons lime - MnSO4 - CuSO4.



Plate 4. Treatment of alfalfa on Fox sandy loam. No. 1, no lime; No. 2, 3 tons lime; No. 3, 6 tons lime; No. 4, 9 tons lime.



Plate 5. Treatment of alfalfa on Fox sandy loam. No. 1, no lime / MnSO4; No. 2, 3 tons CaCO3 / MnSO4; No. 3, 6 tons CaCO3 / MnSO4; No. 4, 9 tons CaCO3 / MnSO4.



Plate 6. Treatment of alfalfa on Fox sandy loam. No. 1, no lime / MnSO4 / CuSO4; No. 2, 3 tons CaCO3 / MnSO4 / CuSO4; No. 3, 6 tons CaCO3 / MnSO4 / CuSO4; No. 4, 9 tons CaCo3 / MnSO4 / CuSO4.



Plate 7. Treatment of Alfalfa on Plainfield sand. No. 1, no lime; No. 2, 3 tons lime; No. 3, 6 tons lime; No. 4, 9 tons lime.



Plate 8. Treatment of alfalfa on Plainfield sand. No. 1, no lime -/ MnSO<sub>4</sub>; No. 2, 3 tons lime -/ MnSO<sub>4</sub>; No. 3, 6 tons lime -/ MnSO<sub>4</sub>; No. 4, 9 tons lime -/-MnSO<sub>4</sub>.



Plate 9. Treatment of alfalfa on Plainfield sand. No. 1, no lime / MnSO<sub>4</sub> / CuSO<sub>4</sub>; No. 2, 3 tons lime / MnSO<sub>4</sub> / CuSO<sub>4</sub>; No. 3, 6 tons lime / MnSO<sub>4</sub> / CuSO<sub>4</sub>; No. 4, 9 tons lime / MnSO<sub>4</sub> / CuSO<sub>4</sub>.