RELATIONSHIP BETWEEN SOIL ACIDITY AND COPPER DEFICIENCY IN MUCK SOILS

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE
Donald C. Ruby

1951

This is to certify that the

thesis entitled

"The Relationship Between Soil
Acidity and Copper Deficiency in Muck Soils"

presented by

Donald C. Ruby

has been accepted towards fulfillment
of the requirements for

Masters degree in Soil Science

Date March 5, 1951

O-169

V—134

Gift
4/12/51

ABSTRACT

Ruby, Donald C. Relationship between soil acidity and copper deficiency in muck soils.

The purpose of this study was two fold;

A. An investigation of the effect of the following factors on the copper content of muck soil and of Henry spring wheat grown on this muck: (1) The addition of copper sulfate as a soil amendment and as a spray. (2) The addition of copper oxide as a soil amendment. (3) The application of ashed copper deficient muck soil with and without acidification with hydrochloric acid.

B. To investigate the relationship of soil reaction on the copper content of virgin muck soils and on the leaves of poplar trees (Populus tremuloides) growing on these muck soils.

A copper deficient muck soil from the Michigan State College Muck Experimental Farm was treated in the greenhouse as follows:

A. Check - no copper added.

B. Copper sulfate ($CuSO_4 \cdot 5H_2O$) added at the rate of 100 pounds per acre.

C. Equivalent amount of copper supplied in the form of (64.8%) copper oxide as applied in Treatment B.

D. Ash obtained from burning one foot of muck surface soil, untreated.

E. Same as Treatment D except the ash was acidified with hydrochloric acid.

F. Plants sprayed with 0.186 percent solution of copper sulfate.

G. Ash obtained from burning six inches of surface muck, untreated.

H. Same as Treatment D except an attempt was made to remove the copper by suspending iron nails in a hydrochloric acid solution of the ash.

All treatments included 3-9-18 fertilizer at the rate of 3000 pounds per acre.

The copper content of both the soil and tissue was determined by the Carbamate Method.

The following data were obtained:

1. Chloride ion toxicity was believed to have caused stunted growth of Henry spring wheat when used to acidify alkaline ash material.

2. The results indicated very little relationship between pH and copper content of the soil as compared to the copper content of the wheat plant.

3. Wheat plants showing no copper deficiency symptoms were grown on both alkaline and acid muck.

4. Leaching with distilled water reduced the copper content of a muck to which ash acidified with hydrochloric acid was added.

5. Organic soil and acidified ashed muck with $MnSO_4 \cdot 5H_2O$ added at the rate of 100 pounds per acre and subsequently leached, produced plants with no copper deficiency symptoms.

Muck samples varying in degree of acidity and poplar leaves were obtained from seven areas located in Allegan, Clinton, Ingham, Jackson, Lapeer and Sanilac Counties. The pH and copper content of the muck and the copper content of the leaves were determined in the laboratory. The following results were obtained:

1. As muck becomes more acid the copper content of the soil tends to decrease.

2. From the data it appeared that pH and copper content of the soil at six of the locations had little effect on the copper content of the poplar leaves. The exception to the general trend occurred in the Baker Farm sample. In this case a possible iron - copper relationship may be present.

RELATIONSHIP BETWEEN SOIL ACIDITY AND COPPER DEFICIENCY IN MUCK SOILS

By

Donald C. Ruby

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Soil Science

1951

ACKNOWLEDGMENT

The author expresses his appreciation for the assistance, counseling and guidance given him by the following staff members:

Dr. J.F. Davis, Dr. K. Lawton and Dr. L.M. Turk, Department of Soil Science.

Dr. E.J. Benne and associates, Department of Agricultural Chemistry.

Dr. H.L. Womechel and Mr. D. Harvey, Department of Mechanical Engineering.

The writer acknowledges the many helpful suggestions and cooperation of his fellow graduate students and to Mr. R.D. Bailey of the Buildings and Utilities Division for his timely assistance in the fabrication of special ashing equipment used in the experiment.

TABLE OF CONTENTS

FIGURES

TABLES

RELATIONSHIP BETWEEN SOIL ACIDITY AND COPPER DEFICIENCY IN MUCK SOILS

INTRODUCTION

In Michigan, there is an estimated 5,000,000 acres of organic soils representing approximately one acre in eight for the state. Several different crops (8)[1] are grown on muck[2] with celery, onions and mint the most important of the special crops group. However, practically any crop may be grown on muck provided proper soil management practices and adapted varities are employed. One of the important factors encountered in the successful production of crops is the correction of copper deficiency that occurs in many of the muck areas. Results from previous work (7,8, 12,22) have indicated that copper deficiency is associated with soil reaction, and in Michigan for a number of years the soil pH has been used as a basis for making practical field recommendations. A pH of 6.5 has been recognized as the upper limit at which copper deficiency is likely to occur. However, it is also recognized (9) that a diff-

[1]-The numbers in parentheses refer to literature cited.

[2]-The term "muck" is used to include both muck and peat.

erential crop requirement exists and copper is recommended for some crops (head lettuce, spinach and wheat) even with a pH above this arbitrary value of 6.5.

In view of the fact that there is an apparent association between copper deficiency and soil reaction, this investigation was instituted to study the factors that might affect this relationship. If copper deficiency and soil reaction are closely correlated then the following hypotheses might be formulated:

1. Acid mucks deficient in copper because of the increased solubility of copper compounds in an acid medium and subsequent leaching would remove the copper from the medium.
2. The mineral soil areas surrounding the muck formation were low in copper and the resultant drainage water collecting in the muck area was low in this element and thus the resultant copper content of the plants forming the muck area was very low.
3. The availability of copper is closely correlated with soil reaction.
4. Copper deficiency in a muck soil is corrected by burning due to the resultant concentration of copper.

A consideration of some of these factors is included in this work.

REVIEW OF LITERATURE

Early work with copper in the United States was recorded in Dade County, Florida in 1927. Reprecht (18) showed that tomatoes responded to soil applications of copper sulfate.

Felix (6) found that failure of lettuce and onions on unproductive mucks in New York in later stages of growth was corrected by the addition of copper sulfate.

Results of soils investigations of Florida (2) on several species of field crops and truck crops showed a marked plant response to copper. Plots on which copper was applied produced in most cases apparently normal growth of plants in constrast with an absolute and early failure on those areas from which the treatment was withheld.

Results from Allison's (1) experiments with the application of copper sulfate on peanuts were positive.

Hunter (10) using copper treatments on several grasses revealed that an increase in both fresh weight and dry weight per acre resulted as compared to the fresh and dry weights obtained from the untreated plots.

Data from the Canal Point Breeding Station (3) of Florida showed that sugar cane responded to an application of thirty pounds of copper sulfate per acre when applied to raw sawgrass peat.

Harmer (7) found that under Michigan conditions that some species of plants responded to copper sulfate and that copper deficiency was associated with soil reaction. Results from investigations at that time indicated that fifty pounds of copper sulfate per acre was sufficient to correct copper deficiency for most crops which are copper responsive. Spinach and lettuce crops, however, required an application of one-hundred pounds per acre for complete control of the trouble. Additional application of twenty-five pounds per acre for succeeding crops gave good responses. Later he found through several observations that crop response on muck in Michigan differ (9). As a result of this a classification of crops based on the response to copper was set up.

Liming an unproductive acid peat soil did not always result in a favorable growth for corn according to the data of Willis and Piland (22). An unfavorable condition developed by liming is associated with excessive absorption of iron and lodgement of iron in the nodes of the plant. This situation was remedied by the addition of copper sulfate. Further investigation (23) by these men indicated that copper serves as a catalyst in oxidation-reduction reactions.

Orth and others (17) pointed out that copper is necessary for the formation of chlorophyll in the leaves of orange trees. It was also suggested that cattle grazing in Florida on certain pastures developed nutritional anemia or "salt sickness" and this trouble may be corrected by an application of iron or copper to the grazing area.

Harmer's (8) results suggested a direct effect of copper on the formation or function of the chlorophyll in plants.

According to Lucas (13) the increase in copper content in plants was as much as threefold, although only a very small fraction of the copper contained in a normal application of copper is recovered by the crop.

Experimental results presented by Jamison (11) suggested that since copper is largely retained in slowly soluble or slowly replaceable form, it appears that a small continuous supply in the soil may be more important than the amount of copper that is easily replaceable. An ordinary soil application of copper would doubtless be toxic were it not for its fixation.

Brown's (5) observations indicated that copper is necessary for normal metabolic activity of plant processes.

Lucas (12) showed that under Michigan conditions the copper requirement in plants was related to the copper content and pH of the soil and possibly to the nutrient balance within the plant.

A paper by Lundblad (14) reports that the ratio of copper in the soil and in vegetation does not seem to be essentially different in calcareous soils and acid soils. No relationship between pH and copper deficiency in organic soils has been reported in Sweden (15).

No significant corrlation as reported by McVickar (16) could be observed between potash, phosphorus, magnesium and calcium content or the calcium-magnesium ratio of the white oak leaves and corresponding values for the A horizon of the soil upon which the trees grew.

Vermaat and van der Bie (20) investigated certain lateritic soils and found the copper released through weathering was mainly adsorbed in the exchangeable ionic form. When the concentration became too great in these soils growing rubber trees, the copper intake was increased and the stability of the latex was adversely affected, an important factor in shipping. Soils found to have a higher amount of organic matter had a lower concentration of copper in the ionic form. It was concluded that copper was fixed in the molecule of the organic matter. Thus by increasing the organic matter by mulching ionic copper was incorporated in a molecule of circulating organic matter.

EXPERIMENTAL PROCEDURE

Greenhouse experiment

The following eight treatments replicated four times were set up in two-gallon glazed jars in the greenhouse and two crops of Henry spring wheat were grown on these treated jars.

A. Check-no copper added.

B. Copper sulfate ($CuSO_4 \cdot 5H_2O$) at the rate of 100 pounds per acre.

C. Equivalent amount of copper supplied in the form of (64.8%) copper oxide as applied in Treatment B.

D. Ash obtained from burning one foot of muck surface soil, untreated.

E. Same as Treatment D except the ash was acidified with hydrochloric acid.

F. Plants sprayed with 0.186 percent solution of copper sulfate.

G. Ash obtained from burning six inched of surface muck, untreated.

H. Same as Treatment D except an attempt was made to remove the copper by suspending iron nails in a hydrochloric acid solution of the ash.

Note- all jars contained a copper-deficient muck.

A virgin copper-deficient muck was obtained from the Michigan State College Muck Experimental Farm. This area had been recently cultivated but never fertilized. An analysis of a sample from the same general area was reported by Brown (5) as follows: Organic matter, 86.0%; total nitrogen, 3.3%; potassium, 0.21%; phosphorus, 0.12%; calcium, 2.5%; magnesium, 0.27%; iron, 1.3%; and copper, 0.0011%.

The muck was partially dried and screened through a one centimeter square mesh screen to remove root and wood fragments. A uniform application of 3000 pounds of 3-9-18 fertilizer per acre was applied to all jars. Chemically pure grades of ammonium nitrate, potassium di-phosphate and potassium chloride were used in the preparation of this fertilizer. In order to eliminate any possible induced manganese deficiency resulting from the alkaline ash addition, manganese sulfate ($MnSO_4 \cdot 5H_2O$) at the rate of 100 pounds per acre was applied to all jars in Treatments D and G. On completion of first experiment when analysis revealed that iron nails did not remove copper from the acid medium in Treatment H, manganese sulfate at the rate of 100 pounds per acre was added to this set of jars.

The required ash, fertilizer and copper materials for each jar were thoroughly mixed with 5400 grams of muck and lightly packed in the jars. The manganese sulfate was applied as a top dressing.

Twenty seeds of Henry spring wheat were planted on two different dates June 19 and August 28 in each jar and the emerging plants were later thinned to 6-10 plants per jar.

Ashing process- Muck weighing 6000 grams and of uniform moisture content (this was assumed to be equivalent to one foot of surface muck from an area of the same dimensions) was placed in a polished steel box of 11 gauge metal with the dimensions of 6"x20" and 8" high. The box was covered with an asbestos plate perforated with several holes one quarter inch in diameter. Three boxes of this type and size were prepared together with two smaller boxes 5"x12" and 3" high. The muck samples were then placed in a gas furnace located in the Forging Building and temperature held between 600-650 degrees centigrade for six hours. This furnace could accommodate three samples at one time. The covers were removed after the first three hours of the ashing process. In this process the muck was reduced to approximately one-third of its original volume. The samples were then transferred to an electric muffle furnace and held at about 650 degrees centigrade (a dull red color of the box) and the ashing process continued for another 8 to 20 hours.

The weight of the ash from the above samples varied between 300 to 350 grams.

A number of difficulties were encountered in this ashing process: 1- The steel boxes deteriorated rapidly as was evidenced by scaling and resultant slight contamination of the ash with the iron. 2- Corroded contact points on the muffle furnace. 3- One hour of manual operation of the gas furnace was necessary before it would operate automatically.

Acidifying the ash- Approximately 300 milliliters of concentrated hydrochloric acid was required to reduce the pH of the ashed muck to 6.36, the pH of the original muck sample. Increments of the acid were added over a 48 hour period.

Removal of copper from solution- One dozen iron nails were suspended in an acidified sample of the ash. This procedure was based on the electromotive series theory that copper in the solution would be replaced by the iron and the copper deposited as a coating on the nails.

Harvest- The wheat was harvested at the time the seeds were in the milk stage of maturity.

Laboratory Experiment

Determination of copper in plants- A composite sample of the straw and grain from the four replications of each treatment was dried at 65 degrees centigrade. The plant material was then ground in a Wiley Mill and this prepared plant tissue used in the determination of copper. Between 3 to 5 gram samples of plant material representing each treatment was oven-dried at 105 degrees centigrade, weighed and ashed. The ash was treated gently with concentrated hydrochloric acid and then brought to a boil for several minutes. The solution was then transferred to a 200 milliliter volumetric flask and brought up to volume for each determination. Aliquots were taken from each flask for copper analysis and the copper content determined by the Carbamate Method.

Determination of copper in muck soil- The same procedure was used for the determination of the copper content of the muck as was used for the plant material. A thoroughly mixed sample of 3 to 8 grams of muck soil was oven-dried at 105 degrees centigrade, weighed and ashed. The ash was then heated gently with concentrated hydrochloric acid and bought to a boil for several minutes. The solution was placed in a 200 milliliter volumetric flask and brought up to volume. Copper was determined in aliquots of solution from the flask.

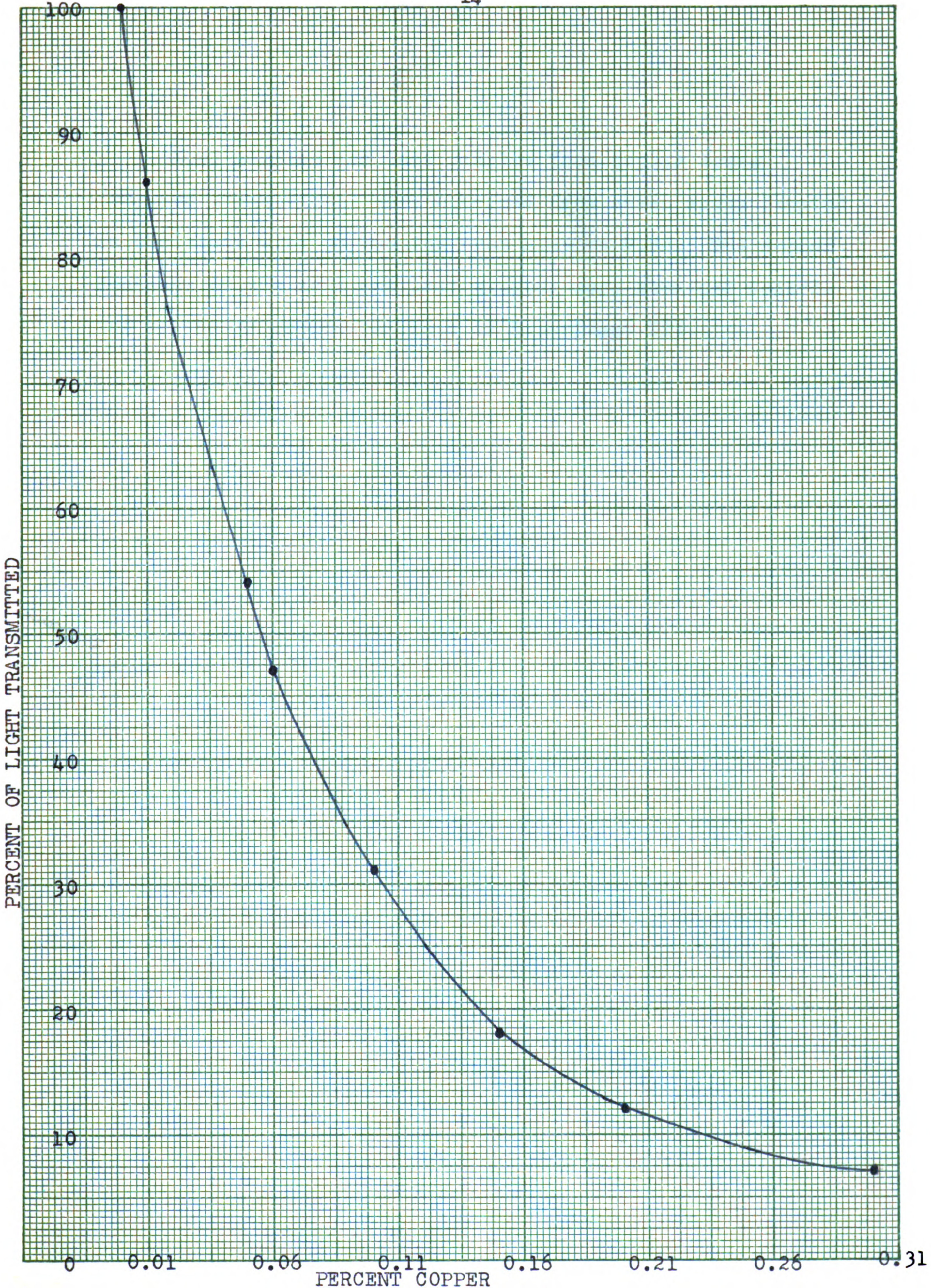
Standard Curve- In using the Carbamate Method a standard curve was set up to chart the copper concentrations. The standard copper solution was made up by dissolving 0.7587 grams of anhydrous copper sulfate (Merchs reagent quality 99.688% pure) in distilled water and diluted to one liter. One hundred milliliters of the above solution was then diluted to one liter thus resulting in a concentration of 0.03 milligram of copper per milliliter. The latter stock solution was used in the construction of the standard curve (Fig.I) based on the concentrations reported in Table 1. Copper was determined colorimetrically using a Lumetron photo-electric colorimeter model 400-A and a lantern blue glass filter of 420 mu.

Some of the difficulties encountered in the Carbamate Method of copper determination are as follows: 1- Too small amounts of copper in the sample resulted in transmission values close to the blank transmission value. Thus, the error was greatly increased in the determination of the copper content. This difficulty of high transmission readings was partially overcome by taking larger aliquots for copper analysis and (or) larger samples of material. 2- Elemental iron proved to be an interfering ion in some soils. When iron interference was realized smaller aliquots and (or) smaller samples of muck were used in the determination. 3- At first the filtering process was used to separate the residue from the liquid portion of the sample

Table 1- Dilutions of copper sulfate solution used in the construction of the standard curve.

Mg/ml copper	Ml. copper : Ml. distilled water	Lantern blue glass filter of 420 mu. percent transmission
0.030	10.0 : 0.0	7
0.020	6.7 : 3.3	12
0.015	5.0 : 5.0	18
0.010	3.3 : 6.7	31
0.006	2.0 : 8.0	47
0.005	1.7 : 8.3	54
0.001	0.3 : 9.7	86
0.000	0.0 : 10.0	100

for copper analysis. This procedure was found to be very time-consuming even when used under a vacuum. A check on the experiment using solutions with and without residue in the bottom of the volumetric flask was found to give practically the same results. The filtration process was then dispensed with.


100
90
80
70
60
50
40
30
20
10
0
PERCENT OF LIGHT TRANSMITTED
0.01
0.06
0.11
0.16
0.21
0.26
0.31
PERCENT COPPER

Muck samples and leaf samples from poplar trees (*Populus tremuloides*) were obtained from seven areas located in the state with pH ranging from 4.35 to 7.88. The copper contents of the soil and leaf samples were obtained according to the procedure outlined in Experiment III.

EXPERIMENT I

The Effect of Soil Amendments on the First Crop of Henry Spring Wheat

The experiment was set up as previously described in Experimental Procedure.

Henry spring wheat was planted June 19, 1950 at the rate of approximately 20 seeds per jar. In general all plants germinated in normal length of time except in jars of Treatments E and H. Emergence of plants was retarded approximately one week by the hydrochloric acid treatment. When the plants reached a height of 4 to 6 inches they were thinned to stand leaving 6 to 10 plants per jar.

Plants of Treatment F had two applications of copper solution sprayed on its leaves. These applications were made on July 21 and 28, 1950.

A good stand of wheat was obtained in all jars except in those of Treatments E and H. In these pots the plants remained stunted throughout the course of the experiment.

The untreated muck soil contained 0.0030 percent copper which was higher than was anticipated. Soil from a near-by area analyzed 0.0016 percent copper as shown by data obtained from experiment III. The relatively high copper

Table 2- The effect of various treatments on the copper content of a copper-deficient muck and on Henry spring wheat grown on these different treated jars under greenhouse conditions.(3)

Treatments	Percent copper plant		Percent copper soil		pH soil		Remarks
	1st crop	2nd crop	1st crop	2nd crop	1st crop	2nd crop	
Copper-deficient muck	0.0027	0.0013	0.0031	0.0030	6.36	6.36	Normal growth Normal growth
100 pounds $CuSO_4 \cdot 5H_2O$ per acre	0.0015	0.0015	0.0091	0.0091	6.36	6.36	Normal growth Normal growth
Equivalent amount of copper as CuO (64.8%)	0.0015	0.0012	0.0180	0.0180	6.36	6.36	Normal growth Normal growth
One foot ashed muck left alkaline	0.0013	0.0011	0.0066	0.0063	8.00	8.00	Normal growth Normal growth
One foot ashed muck acidified with HCl	---[4]	0.0013	0.0064	0.0046	6.36	7.64	Very small plants Small plants
Copper solution 0.186% sprayed	0.0170[5]	0.0120[5]	0.0032	0.0032	6.36	6.36	Normal growth Normal growth
Six inches ashed muck left alkaline	0.0015	0.0012	0.0044	0.0042	7.80	7.80	Normal growth Normal growth
Acidified ashed muck, attempt removal of copper with iron nails[6]	---[4]	0.0007	0.0060	0.0047	6.36	6.36	Very small plants Normal plants
Known copper-deficient muck[7]		0.0011		0.0015		5.90	Small plants

3-Samples for copper and pH determination were made at the beginning and ending of experiment.
4-Not enough plant material for copper determination.
5-Copper was not washed off plant material.
6-Nails did not remove copper and normal growth may be due to $MnSO_4 \cdot 5H_2O$ effect.
7-Treatment added with second crop to check original muck used in experiment.

Fig.II. The effect of the addition of copper sulfate and of ashed muck acidified with hydrochloric acid on the growth of Henry spring wheat in the greenhouse (first crop).

0- no copper; 1- 100 pounds copper sulfate per acre; 3- ashed muck acidified with hydrochloric acid.

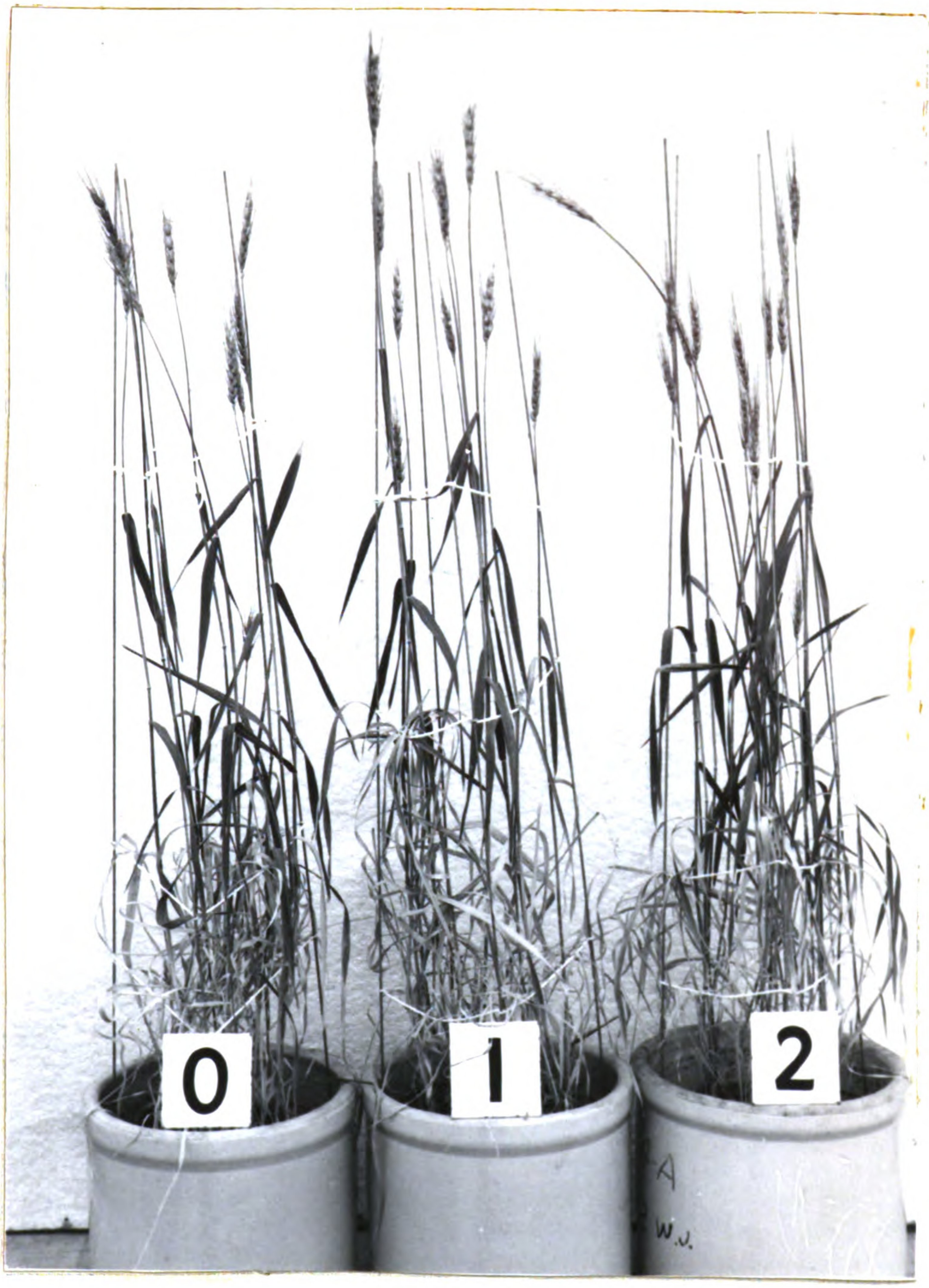


Fig. III. The effect of the addition of copper sulfate and of ashed muck (untreated) on the growth of Henry spring wheat in the greenhouse (first crop).

0- no copper; 1- 100 pounds copper sulfate per acre; 2- ashed muck (untreated).

content may explain the reason for normal growth of plants in the jars receiving no copper (Fig. II). Also, in Fig. II the apparent toxicity of the hydrochloric acid treatment may be observed.

As shown by the condition of plants in Fig. III the addition of one foot of ashed muck without hydrochloric acid treatment did not interfere with the normal growth of wheat.

Plants sprayed with 0.186 percent copper solution did not appear to be copper deficient.

In general the pH of the soil and copper content of the soil had little if any effect on the copper content of the plants. Although the plant material of the check jar indicated a high copper content this may have been due to outside contamination unknown to the writer. Wheat plants grown on these same jars under conditions of Experiment II actually showed copper deficiency symptoms.

EXPERIMENT II

The Effect of Soil Amendments on the Second Crop of Henry Spring Wheat

The purpose of the experiment was to study any possible differential effect that might occur with a second crop in view of the fact the general area from which this muck was obtained had previously been shown to be a copper-deficient muck.

After the harvest of the first crop of Henry spring wheat the muck soil was screened through a one centimeter square screen to remove most of the roots of that crop and the soil again replaced in each individual 2-gallon jar from which it had been removed. Each jar of soil was screened separately to avoid contamination. The muck from jars of Treatments E and H was transferred to 4-gallon jars and leached with 4.5 gallons of distilled water in order to remove the excess chloride ions that may have caused toxicity to the plants. This procedure required approximately one week to complete.

Fertilizer (3-9-18) was applied at the rate of 2000 pounds per acre to each 2-gallon jar. Chemically pure materials were used in preparing the fertilizer as in Experiment I.

Another Treatment, J, was added to the experiment in which a known copper-deficient muck was used as a check. The soil of these jars was fertilized with 3000 pounds per acre of 3-9-18 fertilizer.

Twenty seeds of Henry spring wheat were sown on August 28, 1950 in each jar. No apparent delay in emergence of plants in any treatment was noted. When the plants reached a height of 4 to 6 inches they were thinned to stand leaving from 6 to 10 plants per jar.

Two applications of 0.186 percent copper sulfate solution were applied to plants in Treatment F on October 20 and 27, 1950.

Plants were harvested on December 15, 1950 at the time heads were emerging from the boot.

As indicated by the data in Table 2 there is little apparent relationship between pH and percent copper in the plant or percent copper in the soil to the percent copper in the plant. Plants from Treatment H were very low in copper content as compared to plants from the other treatments. The fact that an addition of manganese sulfate to jars of Treatment H apparently corrected a condition observed in the plants growing in jars to which acidified ashed muck was added might indicate that a manganese deficiency was induced by the subsequent leaching process.

Fig. IV. The effect of the application of copper sulfate on a copper-deficient muck and ashed muck acidified with hydrochloric acid with subsequent leaching on the growth of Henry spring wheat in the greenhouse (second crop).

0- no copper; 1- 100 pounds copper sulfate per acre; 2- ashed muck acidified with hydrochloric acid and leached.

Fig. V. The effect of the application, on a copper deficient muck, of copper sulfate and ashed muck acidified with hydrochloric acid inwhich iron nails were suspended in an acidified solution of the ash to remove copper from solution, with subsequent leaching, on the growth of Henry spring wheat in the greenhouse (second crop).

0- no copper; 1- 100 pounds copper sulfate per acre; 3- ashed muck acidified with hydrochloric acid, attempt copper removal by iron nails, added manganese sulfate 100 pounds per acre and leached

Fig. VI. The effect of the application of copper sulfate and ashed muck (untreated), on a copper-deficient muck, on the growth of Henry spring wheat in the greenhouse (second crop). 0- no copper; 1- 100 pounds copper sulfate per acre; 4- ashed muck (untreated).

As shown in Fig. IV plant growth was still adversely affected. This poor growth seems to be due to manganese deficiency rather than chloride toxicity. Muck soil in jars shown in Fig. V seem to produce plants with normal growth under similar conditions as above plants except manganese sulfate was added.

The plants produced on the muck receiving no copper were copper deficient in Experiment II. A logical explanation as to the reason for the failure of the plants in the first crop of wheat produced on the same jars to develop copper deficiency symptoms is difficult to establish other than that the original sample of muck contained sufficient copper for one crop of wheat but not for the second crop.

According to the data in Table 2 leaching with distilled water reduced the copper content of the muck from 0.0064 percent to 0.0046 percent. The data also showed that copper was not removed as a result of suspending iron nails in the acidified ash solution. Plants showing copper deficiency symptoms were found only in jars from the check treatment.

The appearance of plants (Fig. VI) showed that the addition of ashed muck did not adversely affect the growth of wheat under the conditions encountered in this experiment. Manganese sulfate was applied to correct any possible induced

manganese deficiency resulting from the increased alkalinity from the ash application. It was assumed that copper deficiency did not develop because of the copper contained in the ash and not because of any soil reaction relationship.

Plants sprayed with an 0.186 percent copper solution did not develop copper deficiency symptoms. However, the relatively high copper content of plants from this treatment as reported in Table 2 were in part due to the failure to wash the excess copper remaining on the leaves from the spray application.

Copper added in the form of copper oxide was apparently as effective as an equivalent amount of copper sulfate in correcting copper deficiency in wheat plants. No logical explanation for the comparative contents of copper in muck treated with equivalent amounts of copper oxide and copper sulfate can be advanced.

An application of one-half the amount of ash was as effective in preventing copper deficiency in wheat as was double this amount.

Plants growing on the known copper deficient muck (Treatment J) showed typical copper deficiency symptoms such as die-back of the tips, loss of turgor and tissue necrosis. The symptoms developed by plants from Treatment A were similar but not as pronounced.

EXPERIMENT III

Relationship of the Soil Reaction and the Copper Content of Virgin Muck with the Copper Content of Poplar Leaves

The purpose of this experiment was to compare the copper content of some virgin mucks, the pH of these mucks and the amount of copper in a standard plant growing on these soils. Poplar trees (*Populus tremuloides*) were selected because they can be found growing over a wide range of conditions.

Samples of seven muck areas were obrained within a 150 mile radius of Michigan State College in Southern Michigna located in Ingham, Jackson, Clinton, Sanilac, Lapeer and Allegan Counties. The samples were taken at the depths of 0-6 inches and 24 inches. Approximately 300 leaves from each of two poplar trees growing on these areas were obtained at the time of the sampling of soil. The muck samples were taken between the two trees from which the leaf samples were obtained on July 25 and 28, 1950.

The pH of the muck soils was determined with a glass electrode. The leaves and soil were analyzed for copper by the Carbamate Method.

The poplar leaves were dried in an oven at 65 degrees centigrade to facilitate grinding. Then the leaves were ground in a Wiley Mill and placed in stoppered glass jars until analyzed. The ground leaf material was then thoroughly mixed and oven-dried at 105 degrees centigrade. Samples of 3 to 5 grams were weighed out and then ashed at approximately 650 degrees centigrade. The ash was taken up in concentrated hydrochloric acid and brought to a boil for several minutes then transferred to a 200 milliliter flask and brought up to volume.

The data presented in Table 3 showed that with the exception of the Baker Farm data the pH of the soil had very little relationship to the copper content of poplar tree leaves. The pH of the muck soils on the Lynn Farm were 4.27 and 4.70 for the 0-6 inch and 24 inch depths respectively and resultant values for copper content were very low. The copper content of poplar tree leaves growing on this soil was not essentially lower than the copper contents of poplar leaves on other muck areas investigated. The pH of the muck samples from the Walling Farm for the 0-6 inch and 24 inch depths was 7.83 and 7.53 respectively. This soil had three times as much copper as the Lynn Farm muck soil but the

Table 3- The effect of pH and copper content of virgin mucks on the percent of copper in poplar leaves (<u>Populus tremuloides</u>).

Location	Depth inches	pH	Percent copper		
			Soil	Leaves	
				Tree A	Tree B
Baker Farm Ingham Co.	0-6 24	7.88 7.58	0.0039 0.0022	0.0047	0.0042
Baldwin Farm Ingham Co.	0-6 24	6.15 6.52	0.0018 0.0009	0.0012	0.0010
Boysen Farm Allegan Co.	0-6 24	6.18 6.12	0.0018 0.0010	0.0018	0.0018
Lynn Farm Jackson Co.	0-6 24	4.27 4.70	0.0007 0.0005	0.0013	0.0013
MSC Muck Farm Clinton Co.	0-6 24	6.86 7.09	0.0016 0.0010	0.0009	0.0009
Schoenfeld Farm Lapeer Co.	0-6 24	4.35 4.40	0.0006 0.0007	0.0011	0.0012
Walling Farm Sanilac Co.	0-6 24	7.83 7.53	0.0021 0.0031	0.0013	0.0013

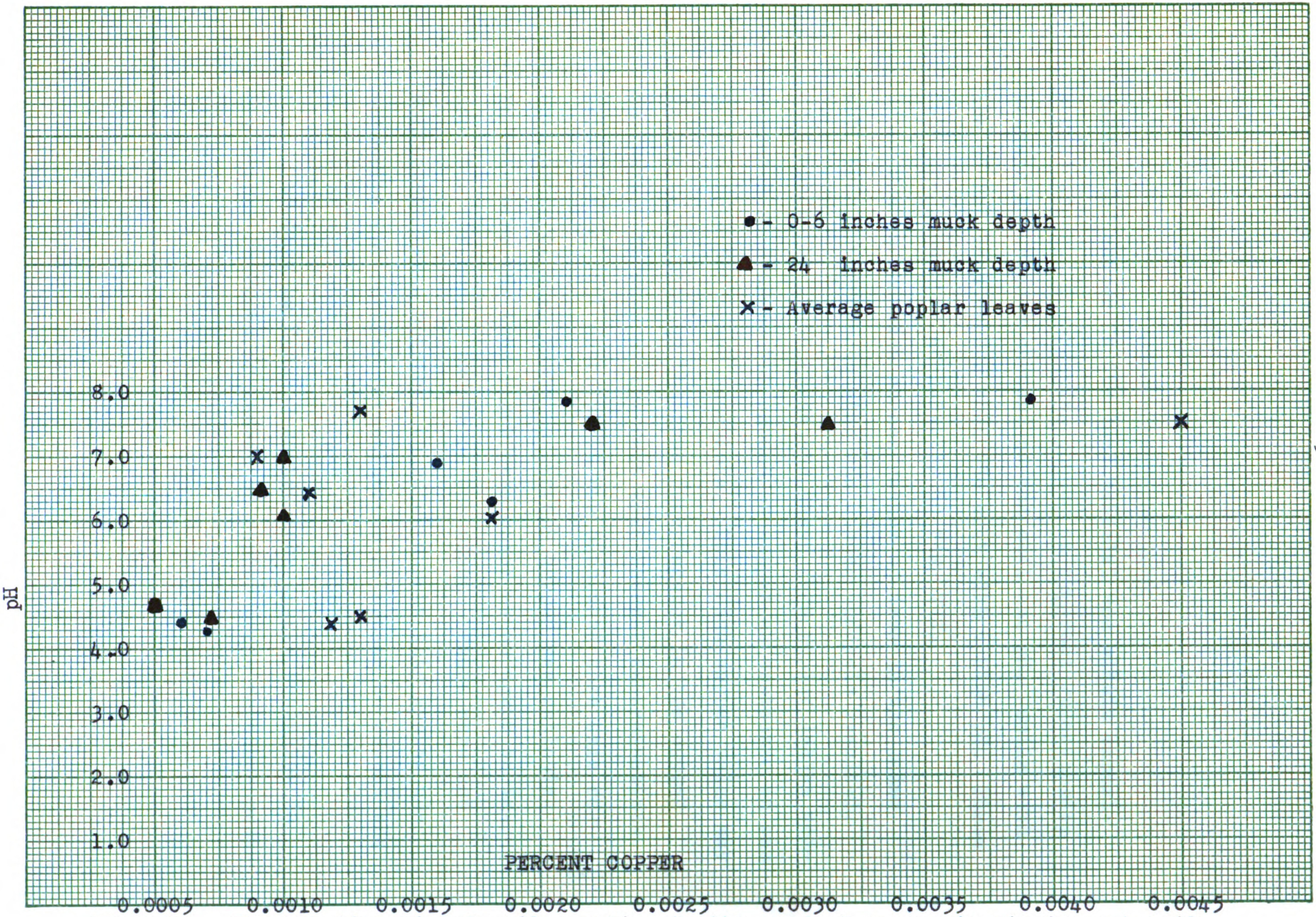


Fig. VII. The relationship of soil reaction to the percent copper in virgin muck soil and poplar leaves.

percent of copper in the leaf material was within experimental error. The results showed an apparent relationship between the copper content of the soil and pH. Soils with low pH had less copper than the muck with a high pH. These data are presented graphically in Fig. VII.

Due to the high concentration of iron in the Baker soil iron interference with the copper analysis resulted. As compared to other mucks the Baker Farm poplar leaves contained 3 to 5 times the amount of copper as contained in the leaves from the other locations. This high copper value may be due to in part to the iron interference in the copper analysis. In view of the fact that several determinations were made on this material it was concluded that this relationship of high value on percent copper was reliable. In this case the iron might have acted as an agent in increasing the copper intake of the plant. There were not sufficient data, however, to substantiate this latter observation and further investigation is needed to reveal the nature of any such iron-copper relationship.

The data in Table 3 showed very little variation in the copper contents of leaves of poplar trees in close proximity at the same location.

GENERAL DISCUSSION

It has been shown by the data of various workers (7,8, 12) that there is a relationship between soil reaction and copper deficiency symptoms of crops produced on muck soil. In general the more acid the muck soil, the more likely that plants growing on these soils will develop copper deficiency symptoms. On this basis, under Michigan conditions the pH of the soil is, in part, the determining factor in recommending the use of copper. It is also recognized that a differential crop requirement for copper exists. Crops such as wheat, spinach, lettuce and dill are examples of very copper responsive plants. In view of these two situations, it is concluded that any pH limit setup as indicative of the point that copper deficiency will occur is at best arbitrary.

In general the copper content of virgin muck soils was found to be associated with the pH of the sample. Soils of low pH were lower in copper content. On the other hand, it has been reported (14,15) that under conditions existing in Sweden that no relationship was found between pH and the occurrence of copper deficiency symptoms in plants growing on organic soils in that country.

It was assumed from the data obtained during the course of this investigation that the increase in pH due to the add-

ition of ashed muck to a copper deficient muck was not the causal agent in correcting the copper deficiency symptoms of spring wheat grown on this acid muck without any copper amendment. The actual cause was ascribed to the concentration of copper, as a result of the added ash.

An attempt was made to remove the copper from the ash, acidified with hydrochloric acid by suspending iron nails in the solution. This technique did not remove any great amount of copper, as evidenced by the comparative copper contents of the treatments in which no attempt was made to remove the copper and the treatment in which an attempt was made to reduce the copper content.

It was found that by leaching the acidified ash treated jars that a reduction in copper content resulted. This situation might support the hypothesis that copper in an acid medium could be rapidly removed by leaching. However, this observation was not supported with data showing the comparative rates of removal of copper from muck to which the acidified ash had been added.

An increase in the copper content of the muck soil did not result in an increased percentage of copper in the straw and grain of the spring wheat plants. Even though the amount of grain and straw produced on jars of the various treated mucks was in most cases small.

The addition of hydrochloric acid used for the acidification of the ash caused an apparent toxicity to the growth of spring wheat. It was believed that this situation was caused by an excess amount of chloride. The toxic effect of the added hydrochloric acid was overcome by the subsequent leaching with distilled water.

Manganese sulfate was added to jars of muck to which ash had been mixed in order to correct any possibility of induced manganese deficiency resulting from the increase in pH.

It was evident from the data obtained in the course of this work that copper oxide was as effective as copper sulfate in correcting copper deficiency symptoms in muck soil. There was no logical explanation offered, however, for the reason of the comparative copper contents of the muck treated with equivalent amounts of copper oxide and copper sulfate.

Spraying dilute solution of copper sulfate on the leaves of the wheat was effective in correcting copper deficiency symptoms. The apparent high percent of copper in the leaf tissue as a result of the spray application of copper sulfate was considered due to the fact that the excess copper was not removed from the leaves before the sample was prepared for copper analysis.

Although a plant may show symptoms of copper deficiency, it does not necessarily mean that this plant is lower in the percent of copper than a normal growing plant. However, the total amount of copper in the plant growing normally would be much higher.

From the data obtained in these experiments, very little correlation between the copper content of a soil and the copper content of poplar leaves was observed. There was, however, general agreement in that the more acid soils had the lowest copper content. One soil from the Baker Farm appeared to be an exception to the behavior of the other samples. This soil had the highest copper content of any of the samples and the poplar leaves contained from 2.5 to approximately 4 times as much copper as did leaves collected from any of the other locations. During the determinations of copper in the laboratory iron interference was troublesome in the determination of the percent of light transmitted through the solution. It was assumed that the soil was higher in iron than the other mucks. It is believed, however, that the relatively high copper content for both the soil and the leaves is actually real and not the result of any iron interference, because the samples were checked a number of times and as far as can be ascertained the difficulty from the iron interference was eliminated.

Willis and Piland (22) pointed out that raising the pH of an unproductive acid peat by liming does not always result in a favorable growth of corn. Excessive iron absorption and lodgement of the iron in the nodes of the corn plant was associated with liming. It was also found that copper sulfate added to this acid muck corrected this unfavorable condition. In view of this reported iron-copper relationship the data obtained may indicate a possible iron-copper relationship in which the iron in some way acts as an agent in increasing the copper intake of the plant. However, there is no specific data to substantiate this latter observation and further investigation is needed to reveal the nature of any such iron-copper relationship.

Attention should be called to the apparent lack of variation in the copper contents of poplar trees growing in close proximity at the same location.

GENERAL SUMMARY

In this study the following factors were investigated in the greenhouse; the addition of copper sulfate as a soil amendment and as a spray, the addition of copper oxide as a soil amendment and the application of ashed copper-deficient muck soil with and without acidification with hydrochloric acid. These factors were investigated in the greenhouse using an acid copper deficient muck soil obtained from the Michigan State College Muck Experimental Farm. Spring wheat was used as the indicator crop.

The relationship of soil reaction on the copper content of virgin muck soils and the leaves of poplar trees (Populus tremuloides) growing on these muck soils was investigated.

The following results were obtained:

1. A chloride ion toxicity was observed on plant growth when hydrochloric acid was used to lower the pH of the organic soil to its original pH 6.36.

2. The results indicated very little relationship to exist between the pH and amount of copper in a muck and the amount of copper in Henry spring wheat and poplar leaves (Populus tremuloides).

3. The occurrence of copper deficiency symptoms in spring wheat could be prevented by the addition of copper sulfate applied as a soil amendment or as a spray, by the addition of copper oxide, and by the addition of ashed copper-deficient muck.

4. The copper content of strongly acid virgin mucks was lower than the copper content of mucks with a higher pH.

5. Leaching a muck to which acidified ash had been added reduced the copper content of the soil.

6. An application of 100 pounds of manganese sulfate per acre stimulated the growth of wheat when added to muck soil containing acidified ash.

7. There was some indication that iron may facilitate copper intake of the plant but further investigation is necessary to reveal the nature of any iron-copper relationship.

BIBLIOGRAPHY

(1) Allison, R.V. Use of copper sulfate on peanuts. Fla. Agr. Exp. Sta. Annual Report, p. 112 R. 1928.

(2) _______. Soils investigations. Fla. Agr. Exp. Sta. Annual Report, p. 120 R. 1927.

(3) ________. Copper sulfate on sugar cane. Fla. Agr. Exp. Sta. Annual Report, p. 114 R. 1928.

(4) Assoc. Offical Agr. Chem. Offical and tentative methods of analysis, Carbamate Method, Wash., D.C., 6th edition, p. 123. 1945.

(5) Brown, J.C. Influence of copper compounds applied to muck soil on the yield, growth pattern and composition of certain crops. Thesis for Ph. D. Mich. State College, East Lansing, Mich. 1949.

(6) Felix, E.L. Correction of unproductive muck by the addition of copper. Phytopatyology, 17:49-50. 1927.

(7) Harmer, P.M. Crops respond to copper sulfate on acid muck. Mich. Muck Farmers Assoc., 17th Annual Convention Report, East Lansing, Mich., p. 22, 46. 1935.

(8) ______. Muck soils of Michigan. Mich. Agr. Exp. Sta. Bul. 314, p. 42-46. 1941.

(9) ______. Studies on the effect of copper sulfate applied to organic soils on yield and quality of several crops. Proc. Soil Sci. Soc. Amer., 10:284-294. 1945.

(10) Hunter, I.H. Copper fertilizer application on several grasses. Fla. Agr. Exp. Sta. Annual Report, p. 121 R. 1928.

(11) Jamison, C.V. Adsorption and fixation of copper in some sandy soils of central Florida. Soil Sci., 53:287-297. 1942.

(12) Lucas, R.E. Effects of copper applied to organic soil, alone and in association with manganese and zinc, on composition of crop and reactions in the soil. Thesis for Ph.D., Mich. State College, East Lansing, Mich. 1947.

(13) ____. The effects of the addition of copper, zinc and manganese on the absorption of the elements by the plants grown on organic soils. Proc. Soil Sci. Soc. Amer., 10:269-274. 1945.

(14) Lundblad, K. The availability and fixation of copper in Swedish soils. Plant and Soils, 1:296. 1949.

(15) ________. Private communication from Sweden to Dr. J.F. Davis, Soil Sci. Dept. Mich. State College, No relationship between pH and copper deficiency in organic soils, Sept. 1949.

(16) McVickar, J.S. Composition of white oak leaves in Illinois as influenced by soil type and soil composition. Soil Sci., 68:317-329. 1949.

(17) Orth, O.S., G.C. Wickwire and W.W. Burge. Copper in relation to chlorophyll and hemoglobin formation. Science, 79;33-34. 1934.

(18) Ruprecht, R.W. Fertilizers. Fla. Agr. Exp. Sta. Annual Report, p. 35 R. 1927.

(19) Sommers, A.L. Copper and plant growth. Soil Sci., 60;71-79. 1945.

(20) Vermaat, J.G. and G.J. vander Bie. Occurrence of copper in tropical soils. Plant and Soils, 2;257-282. 1950.

(21) Weber, G.F. Nail head rust. Fla. Agr. Exp. Sta. Annual Report, p. 73 R. 1927.

(22) Willis, L.G. and J.R. Piland. The influence of copper sulfate on iron adsorption by corn plants. Soil Sci., 37:79-83. 1936.

(23) ______ and ______. Evidences of copper-iron antagonism. Jour. Agr. Res., 52:469-476. 1936.