New York Agricultural Experiment Station.

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BULLETIN No. 41—NEW SERIES.

APRIL, 1892.

I. INFLUENCE OF COPPER COMPOUNDS IN SOILS UPON VEGETATION.

II. SPRAYING WITH FUNGICIDES FOR PREVENTION OF POTATO BLIGHT.

III ANALYSES OF MATERIALS USED IN SPRAYING PLANTS.

GENEVA, N. Y.

The Bulletins published by the Station will be sent free to any farmer applying for them.

*Connected with Fertilizer Control.

BULLETIN No. 41—NEW SERIES.

I. INFLUENCE OF COPPER COMPOUNDS IN SOILS UPON VEGETATION.

The effect of metallic poisons on the health and development of plants is a subject which in former years has been considered of economic importance because of injury to vegetation in the vicinity of chemical or metallurgical works. The question whether plants are capable of absorbing poisonous compounds by their roots, or whether small amounts of such compounds found in the ash of certain plants are derived only from deposits from the atmosphere on the surface of the plant, has been thought worthy of scientific investigation in this connection, as also has the question whether plants are injured by the presence in their systems of any amount of such compounds less than a poisonous dose; or whether, as claimed by Dr. Freytag,* "the absorption of poisonous metals causes no disturbance until a certain degree of concentration is reached, when the plant rapidly withers and dies."

New interest in the effects of metallic poisons in the soil, on the health and development of plants grown therein, has recently been developed since spraying with arsenites and copper compounds, for various insect and fungous attacks of cultivated plants, has come to be extensively practiced. It has been suggested that these remedies may prove to be worse than the diseases, and fears have been expressed lest the continued application of these insecticides and fungicides may result in such an accumulation of poisonous compounds as to cause sterility of soil more disastrous than the ravages of insect and fungous enemies.

For the purpose of investigating the relations of these metallic poisons in the soil to cultivated plants grown therein, a series of experiments have been instituted at this station.

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* Prof. Phillips in Rep. Western Pa. Engineers' Soc'y, 1882, p. 166.

Preliminary investigations were made with soil containing a large per cent. of copper, applied in the form of sulphate, to discover what injurious effects on vegetable life such amount of this salt would have, and to serve for comparison with subsequent experiments with soils containing smaller amounts of copper salts. The results of these experiments have been so marked that it has been thought desirable to publish the data thus far obtained, with the explanation that it is simply the result of preliminary work in this line, and that reports of the more thorough and extended experiments now in progress will be published in due time.

In these experiments soils were used containing the relatively enormous amounts of two per cent. and five per cent. by weight* of copper sulphate, which was dissolved in hot water and the solution thoroughly mixed with common potting soil.

In other words, in one soil mixture there were ninety-eight parts by weight of potting soil, and two parts of copper sulphate; this is referred to in this bulletin as the "two per cent. soil mixture." In the other mixture there were ninety-five parts of potting soil and five parts of copper sulphate; this is referred to as the "five per cent. soil mixture."

Seeds of plants representing widely differing natural orders were planted in these soils, and at the same time an equal number of the same kinds of seed were planted for checks in similar soil, to which no copper sulphate was added. Care was taken to select good seed, and to give both the soil mixtures and checks exactly similar conditions and treatment.

As compared with the check plants, those plants grown in the soil mixtures showed marked differences in germination, foliage, period of maturity, total height and weight of plants, yield of seed, and chemical composition.

Series 1 consisted of peas planted in soil containing five per cent. of copper sulphate; and in Series 2 an equal number of peas were planted in untreated soil for checks.

Series 3 consisted of tomatoes planted in the five per cent. soil mixture and an equal number of seeds planted in untreated soil formed Series 4 of check plants.

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* A comparison of the weight of an air-dried sample of this soil with its weight before drying showed 12 per cent. of moisture.

In Series 5 wheat was planted in the five per cent. soil mixture and check wheat plants constituted Series 6.

In each series above mentioned more seeds germinated in the copper soil than in the check soil. The difference amounted to seventeen per cent. with the peas, twenty-two per cent. with the tomatoes, and twelve per cent. with the wheat. The accompanying graphic illustration furnishes a convenient comparison of the number germinated in each series. The copper sulphate soil mixture is designated as "five per cent."

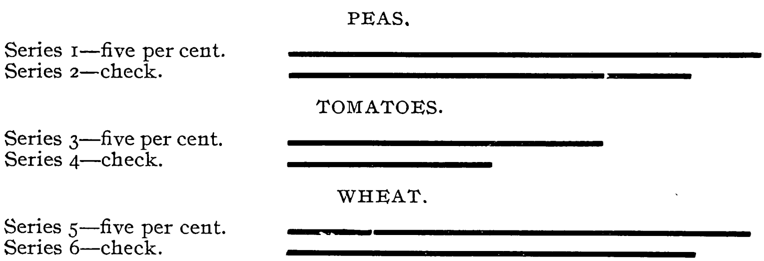

Chart I comparing the number of germinations in five per cent. soil and check soil.

While the number of seeds germinated in the five per cent. soil exceeded in each instance the number germinated in the check soil the average length of time required for germination was less in each case with the check soil than with the five per cent. soil. This difference is illustrated by the accompanying graphic chart and amounted to fifty-five per cent. with the peas, eleven per cent. with tomatoes, and fifty per cent. with the wheat.

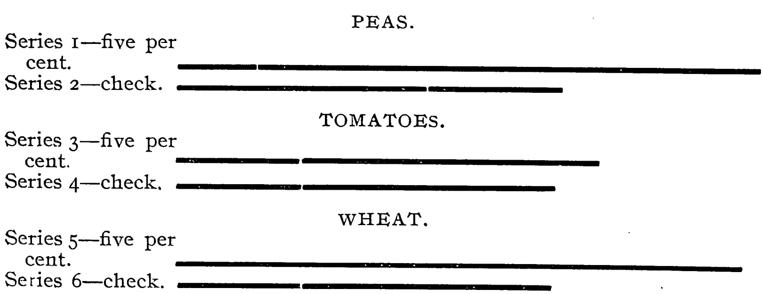

Chart II comparing the average time required for germination in five per cent. soil and check soil.

It may be well to note that in chart II it is not intended to compare the length of time required for germination of seeds of the different kinds of plants but simply to compare the germination in the five per cent. soil in each case with its check series.

The seeds used in series 3 and 4 were of a dwarf variety originated at this Station and known as the "Station" tomato. These plants, even in the check soil, did not seem to make satisfactory growth and it was decided to repeat the experiment with tomatoes, using seed of a standard sort. This experiment will be referred to as series 7 for the five per cent. soil and series 8 for its check. The same general results were shown with these series in germination as were obtained in all previous series, namely, the five per cent. soil gave the greater number of germinations and the average time required was longer than with the check soils.

Figure I from a photograph of series 7 and 8 taken about six weeks after the seeds were planted well shows the striking difference in the development of plants grown in the 5 per cent. soil as compared with those grown in the check soil. Plants transplanted from box I into common potting soil soon began to assume natural color of foliage and after two or three weeks started into vigorous growth, while those left in box I remain about the same height they were when photographed, having made little if any growth.

In series 9 peas were planted in soil mixed with two per cent. by weight of copper sulphate and series 10 was used as its check. Series 11 contained tomatoes planted in the two per cent. soil mixture, with series 12 for its check. In series 13 wheat was planted in the two per cent. soil mixture and series 14 constituted its check. Chart III compares the number of plants germinated in each series with 2 per cent. soil and the corresponding checks. With peas the 2 per cent. soil showed seventeen per cent. greater germination than the checks, with tomatoes six per cent. and with wheat the check soil gave seventeen per cent. greater germination.

FIGURE I.

No. I. Tomato plants grown in soil containing 5 per cent. Copper Sulphate. No. II. Check Plants in untreated soil.

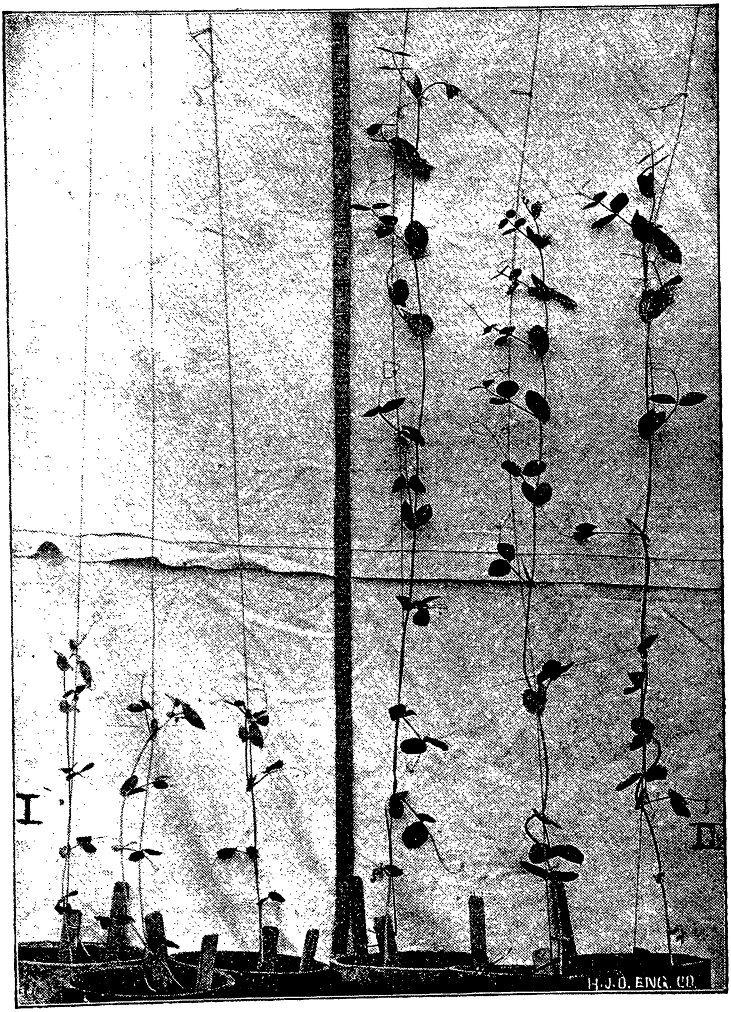

FIGURE II.

No. I. Peas grown in soil containing 5 per cent. Copper Sulphate.
No. II. Grown in check soil.

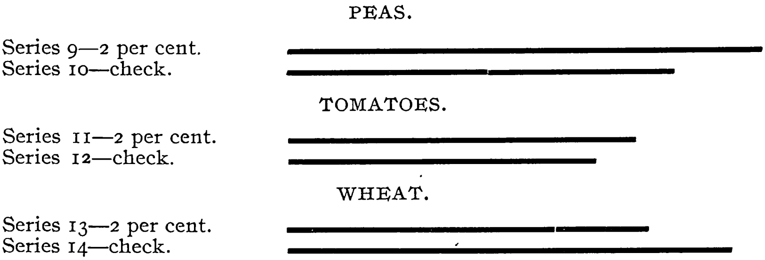

Chart III, Comparing the number of germinations in 2 per cent. soil and check soil.

Chart IV compares the average time required in germination for varieties in two per cent. soil compared with the same varieties in check soil.

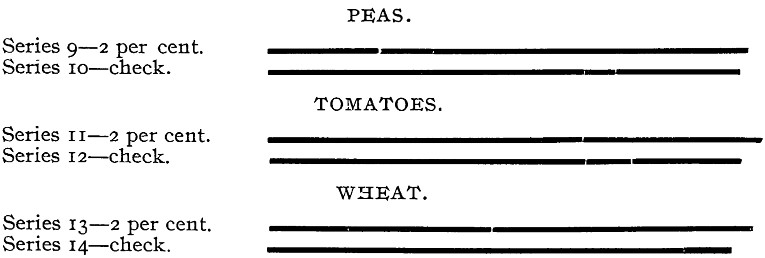

Chart IV, Comparing average time required for germination in 2 per cent. soil and check soil.

In each case the average time for germination was greater with seed planted in the two per cent. soil than with the checks, but the difference was but slight and not so marked as it was in the case of 5 per cent. soils. The peas and tomatoes, as in all preceding series noted in this bulletin, showed a decidedly greater number of seeds germinated than did the checks, but series 13 broke the record and gave the exceptional result of a greater number of germinations in the check soil than in the copper soil.

FOLIAGE.

The foliage of all plants grown in the two per cent. soil mixture was of deeper green than that of the check plants. The foliage of plants grown in the five per cent. soil mixture also showed a marked difference in color from the check plants grown in untreated soil, and had a deeper green color even than the two per cent. plants. On the average the leaves were smaller with plants grown in the copper soils than leaves of the check plants.

PERIOD OF MATURITY.

Peas grown in the two per cent. soil mixture seemed to be more vigorous for the first few weeks than the check plants grown in untreated soil; they also came to maturity earlier but finally showed a dwarfed appearance and the yield was less than with the check plants. In the five per cent. soil mixture the peas grew very slowly, did not ripen any earlier than the check peas and gave a remarkably insignificant yield both of vine and peas. Chart V compares series 1, 2, 9 and 10 as to average height to which the plants grew in each series.

PEAS.

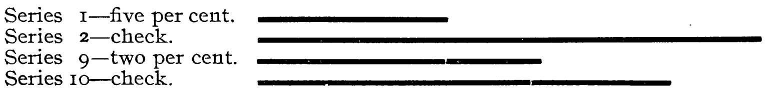

Chart V, Comparing average height of peas.

It will be noticed that the peas were dwarfed in the two per cent. soil mixture, and very much so in the five per cent. mixture. In the former instance the check plants attained 45 per cent. greater height, and in the latter instance 167 per cent. greater height.

Figure II, reproduced from a photograph of the plants at maturity, illustrates the dwarfing effect of a mixture of five per cent. of copper sulphate in the soil. The group of plants marked "I" were grown in the five per cent. soil mixture, and group "II" consists of plants grown in untreated soil for checks.

Figure III is also reproduced from a photograph in which group "I" consists of peas grown in soil mixed with two per cent. of copper sulphate, and group "II" consists of plants grown in untreated soil. When it is remembered that all these plants were from carefully selected seeds, planted at the same time and given similar treatment, the effect of the copper soils is indeed striking.

About a month after planting the peas, a few of the strongest and best plants were selected for continuing the experiment till

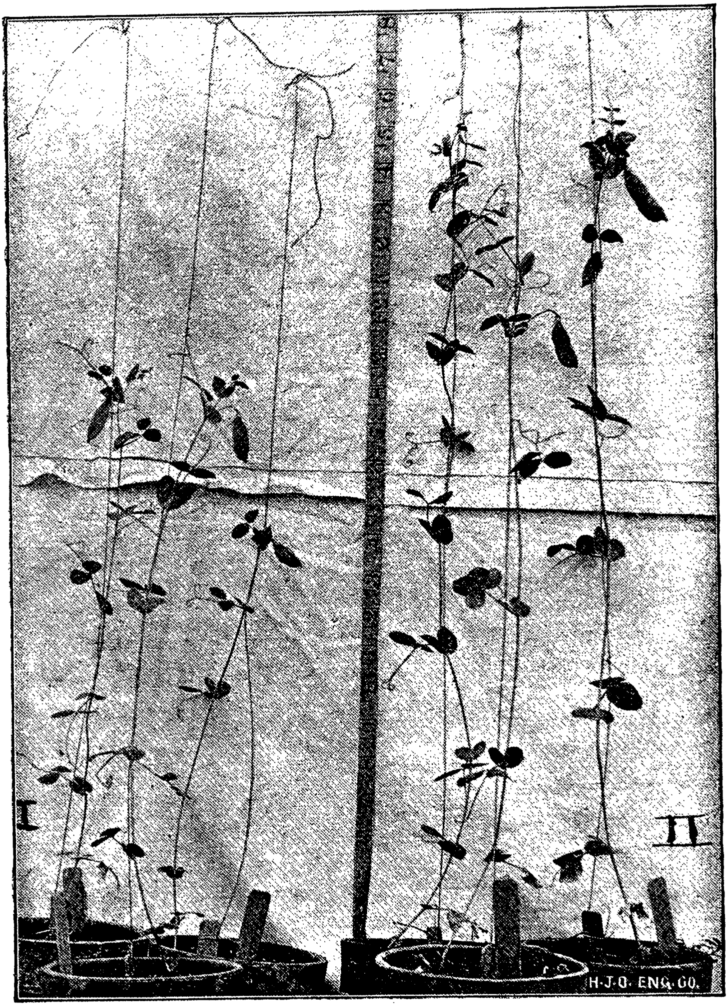

FIGURE III.

No. I. Peas grown in soil containing 2 per cent. Copper Sulphate
No. II. Grown in check soil.

the plants ripened seed, an equal number ot plants being selected for each Series. The seeds produced by the check plants exceeded the product of the same number of vines grown in five per cent. soil by three hundred fifty per cent. and in the two per cent. soil by sixty-six per cent.

PEAS.

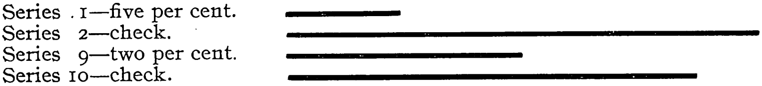

Chart VI, Comparing number of peas borne in Series 1, 2, 9 and 10.

This also furnishes a marked exhibit of the effect of the copper soils on the vital processes of the plant, but a more striking illustration is seen when the entire weight of the peas produced is compared as in Chart VII. The total weight of the seeds of the checks in series 2 exceeded the total weight of the seeds of the five per cent. plants by six hundred forty-four per cent., and check seeds in Series 10 weighed ninety per cent. more than the product of the two per cent. plants in Series 9. The difference in the weight of the vines of Series 2 was three hundred sixteen per cent. more than those of Series 1, and in Series 10 was ninety-six per cent. more than in Series 9.

PEAS.

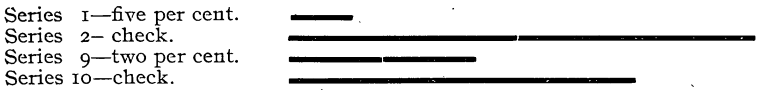

Chart VII, Comparing weight of peas produced in Series 1, 2, 9 and 10.

ROOTS.

It was noticed in these experiments that plants grown in the copper sulphate soil mixtures were remarkable for the meager development of their root systems. Indeed, in some cases they seemed to have hardly any roots, just a few short stubs. When plants grown in the copper soils were removed or thinned out, it was discovered that they had a very loose hold on the soil and were easily pulled out by the roots while the plants growing in check soils had a firm hold on the ground and frequently were broken off at the top of the ground in the effort to pull them up by the roots. Since none of the plants reported on in this bulletin were ever transplanted except as noted under Series 7 and 8, and since no other cause was discovered to which the difference in the development of the root systems could be ascribed, it is believed that the presence of large amounts of copper compounds in the soil was the only cause of the differences observed. The relation of copper compounds to the development of roots is under further investigation. It may be remarked that* Phillips has found that roots of certain plants fail to develop when transplanted into soil containing one-half per cent. carbonate of copper.

CHEMICAL COMPOSITION.

Chemical analysis of the plants removed from series 7 and 8 about seven weeks after planting the seed, was made to discover whether any of the copper applied to the soil in the form of the sulphate had been absorbed into the plant tissues. Only the tops were subjected to analysis. The roots were not analysed on account of the danger of particles of soil adhering to the roots and vitiating the results. The analysis of the tomato tops of series 7 grown in 5 per cent. soil showed in the air dried substance 0.0608 of one per cent. of copper equivalent to 0.2396 of one per cent. crystallized copper sulphate. In series 8 of check plants no copper was found. Other analyses made are reserved from publication at present, till other investigations now in progress are completed. It may be noted, however, that analysis of peas showed the presence of copper both in the vines and in the seeds. An analysis by Comboni† of grapes sprayed with copper solutions disclosed the presence of copper not only in the ash of pulp and skins but also in the wine and seeds of the berry.

Since writing the above report of these investigations the "Landwirthschaftliche Jahrbücher, Band XXI (1892) Heft 1 u. 2" has come to hand. It contains (p.p. 263–276) an article by Dr. Emil Haselhoff "On the Injurious Effects of Solutions of Copper Sulphate and Copper Nitrate on Soil and Plants" in which the following conclusions are stated as a result of the experiments therein reported.

"I. Soluble copper salts are injurious to plants. The injurious action begins when the solution (water culture) contains 10 milli-

* Rep. Engineer's Soc'y of W. Pa., 1882, p. 166.

† Biedermann's Central Blatt für Agrikulturechemie, Vol. XIX p. 129.

grams of copper oxide per liter, while at the same time, when the amount of copper oxide is not more than 5 milligrams per liter, there is no marked retarding action.

II. By spraying soil with copper sulphate or copper nitrate the nourishing elements of the soil, especially lime and potash, are dissolved and leached out, while the copper oxide is precipitated and retained in the soil. Both of these actions reduce the productiveness of the soil.

III. The injurious action of copper sulphate and copper nitrate solutions is more marked with barley and oats than with grass. Copper sulphate is more harmful to the growth of corn than to the growth of beans.

IV. Upon the addition of lime ($CaCO_3$) to the soil this action is counteracted as long as any of the lime remains not acted upon. As soon as the excess of the lime is acted upon the destructive action of the copper begins, as well as the leaching away of the potash from the soil."

As stated in the beginning of this article, it is not the purpose of the writer to draw conclusions from the preliminary experiments herein reported, but simply to call attention to the very interesting facts noted, and reserve conclusions till more thorough investigations are completed.

II. RESULTS OBTAINED BY SPRAYING WITH FUNGICIDES FOR THE PREVENTION OF POTATO BLIGHT.

On July 9th before the appearance of blight, spraying experiments were started to note the effectiveness of the two best known and popular fungicides, viz., Bordeaux mixture and ammoniacal solution, in their power to keep in check this disease. On that date an application was made of a mixture called liquid copperdine, a manufactured article sent out by one of the leading fertilizer manufacturers and claimed to be made from the U. S. Department reports for the ammoniacal solution. After using this mixture it was found by analysis that it was of but one-fourth the strength of the department formula and its further use on potatoes was discontinued and the ammoniacal solution of standard strength used in comparison with Bordeaux mixture. These remedies were applied with a Field Force Pump Co.'s knapsack sprayer, using a Vermorel nozzle, to every alternate third row of potatoes commencing at the first with Bordeaux mixture and third with ammoniacal solution and so on, thus leaving every other row as checks. This was done on a plat of White Star potatoes, measuring six-tenths of an acre, the applications being repeated at intervals of three weeks, with results as given in potato table No. 1. By the middle of August, about every vine on rows not sprayed showed the effects of blight, while those sprayed either with Bordeaux mixture or ammoniacal solution were green and vigorous. At the time of harvest, the latter part of September, each row that had received treatment could be plainly distinguished, by being very much greener and more vigorous.

On July 31st a square of thirty-six feet was staked off in the center of a quarter acre plat of late planted potatoes, and the vines within the square sprayed with Bordeaux mixture three times at intervals of two weeks. By the middle of August the entire plat surrounding this square showed signs of blight, while the sprayed square continued growing. When the main crop of potatoes were harvested, this plat was left in order to see how long the vines of the sprayed portion would resist the attack of the fungus. On October 6th the sprayed vines had turned brown and died, but probably from natural causes, as no signs of mildew could be seen. The entire plat was then harvested, and a comparison of the yield of sprayed versus unsprayed vines made in the following manner: the sprayed square contained two hundred and eighty-eight hills; seventy-two hills, or one-fourth that number, were staked off on each side immediately surrounding the sprayed square, thus obtaining the same conditions as regards the previous treatment of the soil. The results of this test will be found in potato table No. 2.

It will be seen that the sprayed portion gave a larger number of both merchantable and small tubers, but a larger per cent of merchantable than small, also that the sprayed section had less than .29 of one per cent of decayed tubers against about two per cent from the unsprayed. The average weight of merchantable tubers from the sprayed section was 6.49 ounces as against 5.74 ounces from the unsprayed, showing that the benefit of spraying lay in keeping the vines in a healthy growing condition until the tubers had obtained their normal size. While the unsprayed section shows a very low per cent. of decayed tubers, the probabilities are that had the conditions that prevailed through July, when the blight made its appearance, continued through August and September, a large part of the crop would have been decayed.

Through July, the average maximum temperature was 76.5° F., with 3.52 inches of rainfall, conditions favorable to the blight. In August the average temperature was 78.5° F., with but 3–16 inches of rain; and in September, the average temperature was 77.8° F., with but .47 inches of rainfall, creating unfavorable conditions for tubers to decay. While in 1890, when a large per cent of the potato crop of this section decayed, the conditions were entirely different, the average maximum temperature for July being 80° F., for August, 77.6° F., for September .69° F., with a rainfall for those months of 1.07 inches for July, 4.34 inches for August and 5.81 inches for September, making 4.07 inches more rain-fall for those three months in 1890 than this year with an average lower temperature. There is therefore but little doubt that the lower temperature combined with the excessive rainfall of that year was the active agent in causing the decay of the potato.

The conclusions drawn from this experiment seem to be that spraying with either Bordeaux mixture or ammoniacal solution should be practiced by potato growers. Even in a year of partial exemption from blight it would pay, as table No. 2 shows an increase of forty-eight bushels per acre on the sprayed section over the unsprayed. It may be advisable to use the Bordeaux mixture in connection with London purple or Paris green when either of the latter are used for the potato beetle as it has been discovered that dissolving either Paris green or London purple in the Bordeaux mixture prevents the damage to leaves so often caused by these arsenites: as the lime used in the Bordeaux mixture renders the arsenic insoluble.

The conclusion is also reached by the results obtained in table No. 1, and by other spraying experiments that the Bordeaux mixture has given better results this season than the ammoniacal solution.

SPRAYING POTATOES—TABLE NO. I.

Bordeaux mixture. Rows 1. 5, 9, 13, 17.		Check. Rows 2, 4, 6, 8, 10, 12, 14, 16, 18, 20.		Ammoniacal solution. Rows 3, 7, 11, 15, 19.	
Average No. of tubers. Per row.	Average weight tubers. Per rows.	Average No. of tubers. Per row.	Average weight tubers. Per row.	Average No. of tubers. Per row.	Average weight tubers. Per row.
1,038.2	318.1	989.5	286.6	1.052	309

SPRAYING POTATOES—TABLE NO. 2.

Sprayed square of 288 hills.					
Number of merchantable tubers.	Weight in pounds.	Number of small tubers.	Weight in pounds.	Decayed tubers.	Weight in pounds.
1.054	426	226	——	3	1—
Unsprayed 288 hills.					
Number of merchantable tubers.	Weight in pounds.	Number of small tubers.	Weight in pounds.	Decayed tubers.	Weight in pounds.
1.004	360	189	18	20	10—

III. ANALYSES OF MATERIALS USED IN SPRAYING PLANTS.

Most of the substances commonly used at present in spraying plants contain some compound of copper; in some instances the copper compounds and other necessary materials are purchased seperately, and the mixing is done at home, while in other cases, special preparations, containing copper compounds and other essential ingredients, mixed ready for application, which are found in the market, are used. The sale of copper compounds in the form of crude materials and of special preparations has increased enormously in the past year or two and, therefore, offers an inviting field for adulteration and imposition.

During the past year, the chemist has examined several copper compounds separately and also some of the special preparations that are being put upon the market. The investigation was undertaken with a view to finding out something in regard to the following points:

1st. Whether copper compounds are adulterated.

2d. To what extent they are adulterated, if at all.

3d. Whether the special preparations put on the market are pure; whether they are mixed in proper proportions; and whether they are offered for sale at reasonable prices.

Samples of four different kinds of materials have been examined, as follows:

1st. Copper sulphate in three different forms. (a) Crystals of copper sulphate. (b) Crystals of copper sulphate powdered. (c) Dried or anhydrous copper sulphate.

2d. Copper carbonate in two forms. (a) Precipitated copper carbonate. (b) "Hydrated" copper carbonate.

3d. A prepared mixture called "Copperdine," as put up for 1891 and for 1892. (a) Copperdine in dry form. (b) Copperdine in solution.

4th. A sample of prepared Bordeaux mixture.

PROPERTIES OF COPPER SULPHATE.

In order that some of the points connected with the analysis of the various samples of copper sulphate may be more clearly understood, a few statements are made regarding some of the properties of copper sulphate before presenting the results of analysis.

Copper sulphate, commonly called blue vitriol, blue stone or copper vitriol, may occur in three forms or conditions. In the form with which we are most familiar, it appears in crystals, varying in size, of a beautiful blue color. One hundred pounds of it contain the following amounts of different elements;

Copper,—25.4 lbs.
Sulphur,—12.8 "
Oxygen,—57.8 "
Hydrogen,—4.0 "

The four pounds of hydrogen are combined with 32 lbs. of the oxygen, forming 36 lbs. of water, which is known commonly as water of crystallization. The remaining 25.8 lbs. of oxygen are combined with the sulphur in the same manner as in sulphuric acid, and the oxygen and sulphur, combined with the copper in the proportions above given, together with the water, form crystallized copper sulphate. Stating its composition in a somewhat different form, we can say that crystallized copper sulphate contains in one hundred pounds—

Copper	25.4 lbs.
Sulphuric acid (combined)	38.6 "
Water	36.0 "

Now, if we heat one hundred pounds of copper sulphate in an oven to the temperature of boiling water, the crystals will gradually lose their color and crumble to pieces, leaving a bluish-white powder. At this temperature twenty-nine of the thirty-six pounds of water are driven off. If this powder is heated to 400° F., the remaining seven pounds of water will be driven off and we shall obtain a white powder, which is called *anhydrous* or *dehydrated copper sulphate;* that is, copper sulphate free from water. This form of copper sulphate is being put upon the market for spraying mixtures. It has the advantage of being in a finely powdered condition and in a more concentrated form, containing as it does, if pure, forty pounds of copper per hundred. It possesses the disadvantage of absorbing moisture from the air rapid ly. which renders its composition uncertain.

ANALYSES OF COPPER SULPHATE.

1. The first sample of copper sulphate was obtained by Mr. D. G. Fairchild from the Nichols Chemical Co. (Laurel Hill Chemical Works) 45-49 Cedar St., New York City. This sample contained 99.6 per cent of copper sulphate. This was practically pure. In order to make sure that this sample was not misleading, another sample was obtained from the company through Mr. Morton Minot of Brockport, and this gave the same results, on analysis, as the first sample.

2. The next sample of copper sulphate was obtained from one of the drug stores in Geneva. It contained 98.1 per cent. of copper sulphate.

3. The third sample of copper sulphate was sent to the Station for analysis by Mr. J. Burroughs, West Park, N. Y. It contained 98.6 per cent. of copper sulphate. This sample contained a considerable amount of free or uncombined sulphuric acid, which had partially destroyed or eaten the paper wrapped around it. The presence of the free sulphuric acid would not render the copper sulphate injurious, if it were intended for use in the Bordeaux mixture or for the preparation of copper carbonate, since, in either case, the free acid would be completely removed or neutralized in such a way as to form a harmless compound.

4. The fourth sample of copper sulphate examined was in powdered form ; that is, the ordinary crystallized copper sulphate reduced to a fine powder by grinding. This was obtained from W. S. Powell & Co., Baltimore, Md., and contained 98.1 per cent. of copper sulphate. This sample contained noticeable quantities of dirt, which was present probably by accident rather than by design. It is readily seen that powdered copper sulphate offers a better opportunity for adulteration than do the large crystals.

5. The next sample was crystallized copper sulphate, sent out by W. S. Powell & Co., for the season of 1892. It contained 99.6 per cent. of copper sulphate.

6. The sixth sample was powdered crystallized copper sulphate, from W. S. Powell, for the season of 1892. It had evidently lost some of its water of crystallization and was, therefore,

found to contain about one per cent. more of copper than ordinary crystalized copper sulphate. The sample contained a small amount of insoluble dirt.

7. The seventh and last sample of copper sulphate was called "Dried copper sulphate" and was sent out by W. S. Powell & Co., for the season of 1892. This sample was found to contain 90.8 per cent. as much copper sulphate as copper sulphate which has been thoroughly dried at 212° F should contain, or 81.8 per cent. as much as should be contained in copper sulphate which has been dried completely at 400° F. Copper sulphate in this form very readily absorbs moisture and the diminished per cent. was doubtless due to the fact, that, after it was dried, it absorbed some moisture. The sample contained some dirt. The main objection to be urged against buying copper sulphate in this dried form is that its composition is very apt to be uncertain, owing to its tendency to absorb moisture when it is exposed to the air.

PROPERTIES OF COPPER CARBONATE.

Copper carbonate is a somewhat complex chemical compound, and it would take us too far into chemistry to attempt to explain its composition in detail. Suffice it to say that most of the copper carbonate we have to deal with contains, if pure, in one hundred pounds —

Copper,—57.4 lbs.
Carbon,—5.4 "
Oxygen,—36.3 "
Hydrogen—0.9 "

It is known in nature in crystalline form under the name of Malachite. Copper carbonate when made by precipitation, as is the case in the common methods of artificial preparation, is a greenish powder. Unless thoroughly washed, it will contain some sulphate, when made in the ordinary way. The sulphate probably does no harm in spraying mixtures when the quantity is small.

ANALYSES OF COPPER CARBONATE.

1. The first sample of copper carbonate examined, was obtained at one of the Geneva drug-stores. It contained 88.1 per cent of copper carbonate. The sample dissolved to a clear solution in acids, except a small amount of dirt which remained in

suspension. The diminished per cent. of copper carbonate was probably due to the presence of some moisture, though this was not determined.

2. The second sample was obtained from another drug-store in Geneva. It contained 62.8 per cent. of copper carbonate. This sample contained a considerable quantity of some kind of white powder, which failed to dissolve in nitric acid. The presence of this insoluble matter, coupled with the low per cent. of copper carbonate, gave evidence of serious adulteration. With pure copper carbonate at 40 cents a pound, this sample was worth not over 25 cents a pound.

3. The third sample of copper carbonate came from W. S. Powell & Co., Baltimore, Md., and was put up for the season of 1892. It contained 89.4 per cent. of copper carbonate. It was found to be not entirely free from sulphate. It did not make a perfectly clear solution in acids.

4. The fourth sample was called "Hydrated" copper carbonate. So far as could be ascertained, this "hydrated" compound is nothing more than the ordinary copper carbonate saturated with water. Taking the mixture as it was, it contained 59.4 per cent. of copper carbonate. It was not entirely free from dirt and contained a considerable amount of sulphate. There is one advantage in having the copper carbonate saturated with water,—it dissolves more readily in ammonia. This, however, is an operation that is not beyond the ability of the average fruit-grower, who could himself well moisten the carbonate with water before treating with ammonia. The objections to putting such a form on the market are (1st,) that it is not needed, since anyone can "hydrate" his copper carbonate by mixing it with water; (2d,) the manufacturer places no guarantee upon it, and it contains less than 60 per cent. as much copper carbonate as the simple dry copper carbonate. It would be possible to overcome this latter objection.

ANALYSES OF "COPPERDINE."

1. The first sample of copperdine analyzed was in dry form, prepared for the season of 1891. It was put up in a two-pound can and claimed to be a mixture of copper carbonate and ammonium carbonate in the proportions recommended by the U. S.

Department of Agriculture. The price of the two pound can was 75 cents. The materials were not well mixed, so that in order to obtain a fair sample for analysis, over half of the contents of the can was removed and mixed thoroughly ; from this a sample was taken for analysis. The mixture, on analysis, was found to contain nearly 7 per cent. of copper, which would be equivalent to about 8¾ ounces of copper sulphate, or to about 4 ounces of copper carbonate. The two pounds of dry copperdine, therefore, contained about 4 ounces of copper carbonate and 28 ounces of ammonium carbonate. If these materials were purchased at retail at a drug-store in Geneva, they would cost as follows :

4 ounces of copper carbonate at 40 cts. per pound.........10 cts.
28 ounces ammonium carbonate at 11 cts. per pound......19 cts.

Total cost of materials in 2 pounds of dry copperdine......29 cts.

If the copper carbonate were made from copper sulphate and sal soda, the cost of four ounces would be about 4 cents instead of 10 cents, and this would reduce the cost of two pounds of copperdine to 23 cents. Allowing for the cost of mixing, which is very slight, and of the tin can, in which the material is put up, two pounds of copperdine can hardly cost the manufacturer more than 30 or 35 cents. As each two-pound can sells for 75 cents, the margin of profit is not difficult to calculate.

Another question arises in connection with the use of this mixture, and that is this,—"Is it properly prepared, so that, when used in accordance with the directions given, it will not be too weak or too strong ?" The directions on the can indicate that the two pounds of material are to be dissolved in 40 gallons of water, making an equivalent of about one ounce of copper carbonate to ten gallons of water, which is the exact strength recommended by the U. S. Department of Agriculture.

The mixture easily dissolved in water, forming a clear solution. While this preparation is properly made so far as regards strength, the fruit growers can decide whether it is the most economical form to purchase for use.

2. Another sample of dry copperdine, as prepared for the season of 1892, was examined. Its general characteristics were like those of the first sample. It was found to contain 7 35 per cent of copper, equivalent to about one-tenth of an ounce more of

copper than the first sample. It was found to contain some sulphate. When dissolved in water, the solution was turbid and dirty. This sample was sent out under the name of "Ammoniated Carbonate of Copper."

3. The "Liquid Copperdine," as put up for 1891, was found to contain 2 per cent. of copper, equivalent to about 1⅛ ounces of copper carbonate. The liquid form, therefore, contained a little more than one-fourth the copper carbonate contained in the dry form. The cost of its materials, reckoned on the same basis, would be 8½ cents. Allowing for cost of mixing and of can, the total cost of two pounds of "Liquid Copperdine" might, perhaps, approximate as high as 12 or 15 cents. Each two-pound can sold for 50 cents, giving a considerably increased rate of profit, even over the dry form.

As regards its strength, when used according to directions, the liquid form as put up for 1891 was found to dilute. The directions for using are to dilute the contents of one two-pound can in seven bucketfuls of water, which may mean anywhere from 20 to 30 gallons. Taking the lower number, we should then have an equivalent of 1⅛ ounces of copper carbonate to 20 gallons of water, while the official proportions are an equivalent of one ounce of copper carbonate in 10 gallons of water. The solution made from this "Liquid Copperdine" for 1891 was, therefore, only about half as strong as the official solution ; and, if one used 30 gallons of water for dilution, then the solution would be only one-third as strong as it should be.

4. A sample of "Liquid Copperdine," as prepared for the season of 1892, was also examined. It was found to contain 4.73 per cent. of copper, or nearly two and one-half times as much copper as the sample prepared for 1891. This mixture is, therefore, of proper concentration. It is a solution of copper carbonate in ammonia. It contained some sulphate.

ANALYSIS OF "PREPARED BORDEAUX MIXTURE."

This sample was from a lot prepared for the season of 1892. It is put up in dry form. It was found to contain 11.62 per cent of copper. The official mixture contains 15.24 per cent. of copper. Hence this "prepared" Bordeaux mixture contains only

76.2 per cent. as much copper as it should contain. This may be due to incomplete mixing of materials.

SUMMARY OF RESULTS.

1. *Copper Sulphate*, in the form of large crystals, may be relied upon as being fairly pure ; but, when it is in the form of powder, it is always safe to test its purity. The dried form of copper sulphate is objectionable on account of the uncertainty of its composition, which changes on exposure to air, and, being in a powdered form, it can readily be adulterated. The comparatively low price of copper sulphate does not offer the temptation for adulteration that the more expensive form of carbonate does.

2. *Copper Carbonate*, on account of its relatively high price and also on account of its finely divided condition, is, probably, quite liable to adulteration, and should always be tested. All the samples that were tested for sulphate showed its presence, but probably not to an injurious extent.

3. "*Copperdine*," in dry form, costs the fruit-grower twice as much as he himself could prepare it for, but contains the proper amount of copper.

"Copperdine" in liquid form, as put up in 1891, cost three or four times as much as it could be prepared for, and contained only one-half or one-third as much copper as it should. It was therefore worse than worthless because misleading to the fruit grower. However, the sample for 1892 proved to be up to the official strength. The samples of copperdine for 1892 showed the presence of sulphates.

4. The "prepared" Bordeaux mixture for 1892 does not appear to be up to the required official strength.

HOW TO DETECT IMPURITIES IN COPPER COMPOUNDS.

While the help of a chemist is needed to tell how much copper a substance contains, a few suggestions may be given which will enable anyone to test roughly samples of copper sulphate and copper carbonate as well as Paris Green, in regard to their purity.

1. *Copper Sulphate*, if pure, should dissolve completely in warm water, making a clear solution, free from sediment or suspended matter.

2. *Copper carbonate* should dissolve completely in nitric acid, commonly called aqua fortis. If it does not dissolve completely it is impure and probably adulterated. Copper carbonate, if pure, should also dissolve completely, or nearly so, in strong ammonia water, used in considerable quantity. Both the foregoing tests should be applied. Of course, copper carbonate could be adulterated by using finely powdered or dried copper sulphate, but this could easily be detected by treating with water, since copper sulphate easily dissolves in water, while copper carbonate does not.

3. *Paris Green* should, if pure, dissolve completely in strong ammonia water, used in liberal quantity.

Such simple tests as the foregoing may be applied by any one, and while they will not prove an infallible guide, they will serve as a fairly reliable indication regarding the purity of the compounds mentioned. When adulterants are added, they have generally been found to exist in the form of some finely powdered white substances, such as barium sulphate, gypsum, etc., which are insoluble or but slightly soluble in water, acids or alkalies.

IMPORTANCE OF USING PURE CHEMICALS AND MIXTURES.

Contradictory results have been obtained in using copper compounds and prepared mixtures for spraying fruit trees, grape vines, etc. It is suggested that, in many cases, the widely varying results may have been due to the use of impure copper compounds, which failed to make spraying mixtures of the required degree of strength. The use of commercially prepared mixtures of inferior strength may also account for some failures. It can readily be seen that purity and strength of chemicals and commercial preparations are absolutely necessary, if trustworthy results are to be expected.

CONCLUSIONS.

Fruit growers who have to use large quantities of copper compounds, should for the sake of economy, buy the separate ingredients of some reliable house, that can guarantee purity; they should test their compounds, to make doubly sure, and should do their own mixing. Persons who have occasion to use only small amounts of spraying mixtures may find it advantageous and economical of time to purchase prepared mixtures ready for use, provided they can be sure that the preparation is reliable in strength and not extravagantly high in price.

ANALYSES OF SPRAYED GRAPES.

In September, 1891, the New York City Board of Health seized and destroyed large quantities of grapes, on the ground that they had been sprayed with copper compounds and were poisonous. This action caused a serious loss to many grape growers. Mr. D. G. Fairchild, representing the United States Department of Agriculture, visited the Hudson River regions, where the grapes were grown which had been seized. He took pains to secure the worst sprayed bunches of grapes obtainable from those vineyards from which the condemed grapes came. These samples were given to the Chemist of this Station for analysis.

In some instances, the copper compounds could be seen upon the berries, but it could be seen to be more plentiful upon the stems. In three samples, the berries were separated from the stems and the amount of copper determined upon each. In one instance, the berries and stems were not separated.

The samples from Marlborough were taken from two different vineyards. The samples 3 and 3a were from the same vineyard; in sample 3a, the copper was estimated upon the berries and stem together, and not separately. In the table below, the copper is given as metallic copper, the number of grains found for one pound of berries and stems.

Locality where samples of grapes were obtained.	From one pound of berries and stems. Grains, estimated as metallic copper, on berries.	Grains, estimated as metallic copper, on stems.	Grains, estimated as metallic copper, on berries and stems.
(1) Milton, N. Y.	$\frac{1}{120}$	——	$\frac{1}{50}$
(1) Milton, N. Y.	——	$\frac{1}{90}$	
(2) Marlborough, N. Y.	$\frac{1}{120}$	——	$\frac{1}{40}$
(2) Marlborough, N. Y.	——	$\frac{1}{60}$	
(3) Marlborough, N. Y.	$\frac{1}{120}$	——	$\frac{1}{12}$
(3) Marlborough, N. Y.	——	$\frac{1}{14}$	
(3-a) Marlborough N. Y.	——	——	$\frac{1}{16}$
Average for all samples	$\frac{1}{120}$	$\frac{1}{30}$	$\frac{1}{20}$

The results embodied in the table above, we may summarize as follows:

1. The amount of copper, estimated as metallic copper, found on the *berries*, was very constant in the different samples, averaging 1–120th of a grain for each pound of fruit (berries and stems.)

2, The amount of copper, estimated as metallic copper, found on the *stems*, varied from 1–90th to 1–14th of a grain for each pound of fruit, berries and stems, and averaged 1–30th of a grain.

3. If the copper were on the berries in the form of sulphate of copper, each pound of berries would contain about 1–30th of a grain of copper sulphate. When copper sulphate is prescribed by physicians as a tonic or astringent, the dose is from one-fourth to two grains. Hence, if a person were to eat and swallow the grape skins as well as the pulp of the berry, it would be necessary to to eat from 7½ to 60 pounds of grapes, in order to get a tonic dose of copper sulphate. Or, if one were to eat berries and stems, it would be necessary to eat from 1¼ to 10 lbs. to get a tonic dose of copper sulphate.

To get an amount of copper that would be regarded as serious if taken at one dose, one would need to eat not less than 3000 pounds of grapes, skins included, or not less than 500 pounds, including berries and stems; and it is safe to say that if an attempt were made to get a dangerous dose of copper into the body in this way in a short time, a person would be in a dangerous condition many times from the grapes alone, before running any risk from the copper. To state the matter in another way, if one were to eat each day one pound of these worst sprayed grapes, including the skins, and if all the copper taken in this way were to accumulate in the body, it would require over eight years to accumulate an amount of copper that would, if taken at one dose, be considered dangerous, not necessarily fatal.

4. As a matter of fact, copper, when found upon sprayed grapes in New York State, exists, not in the form of a sulphate, but in the form of a carbonate or hydroxide, both of which forms are not readily soluble and which would, therefore, be even less dangerous than if present in the form of sulphate of copper. Most of the copper found was on the stems, which people do not eat; and the rest of the copper was on the outside of the skin of the berries, which most people do not eat.

5. The results obtained from estimating by chemical analysis the amount of copper on grapes, which were selected as being the worst sprayed that could be found, therefore, seem to justify the assertion that it is simply an absolute impossibility for a person to get enough copper from eating grapes to exert upon the health any injurious effect whatever.