THE TOXIC INFLUENCE OF FLUORINE

IN PHOSPHATIC FERTILIZERS ON THE GERMINATION OF CORN

By

H. Howe Morse

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INTRODUCTION

Marked reduction in the per cent of germination of seeds of cultivated plants has often resulted from the application of fertilizers in contact with or near the seed. The causes and remedy for this injury have been the subject of numerous investigations. The Committee on Fertilizer Placement of the National Fertilizer Association (7) and co-operating agricultural experiment stations have accomplished much to remedy this objectionable effect by determining safe and effective methods of fertilizer application. Some excellent work has also been done to determine some of the causes of this fertilizer injury. It was believed, however, that there was need for further knowledge concerning this matter, and therefore, the presented investigation was undertaken.

HISTORICAL

The literature is replete with observations of retardation and inhibition of germination and growth caused by fertilizers and other chemical compounds. As early as 1733 Jethro Tull (14) noted that "too much nitre corrodes a plant". That was approximately one hundred years before the first shipment of Chilean nitrate from Iquique. Late in the nineteenth century an active interest was taken in the problem by French and German investigators. These early investigations were concerned chiefly with laboratory tests using solutions of single salts.

Claudel and Crochetelle (3) investigated the effect of KCl, K_2SO_4, $(NH_4)_2SO_4$, $NaNO_3$, ammoniated superphosphate, and basic slag on the germination of seeds. All of these materials at the concentrations used in their experiment except basic slag (which is relatively insoluble), retarded germination.

Vincent (15), working with wheat seeds and several soluble fertilizer salts, concluded that the ability to germinate was decreased with increase in concentration of the salt.

Much later, in 1921, Rudolphs (9) showed that the retarding action, with some exceptions, could be attributed to an interference with absorption of water by the seed as a result of the high osmotic concentration of the salt solutions.

Numerous other workers employing solutions, pot and field tests have supported the findings of these men. Little doubt remains that high osmotic concentrations have a retarding effect on germination.

There is, however, another source of injury to germination due to toxic substances, which cannot be attributed to high osmotic concentration.

Sigmund (12), working with peas, corn, and rape seeds, found that a 0.5 per cent solution of KF entirely prevented germination.

Bokorny (2) found that a 0.1 per cent solution of NaF was very injurious to cress seedlings and that a 0.1 per cent solution of HF completely prevented the germination of cress, barley, peas, flax, and bean seeds.

It is well known that phosphate rock contains a considerable quantity of fluorine. The analyses by Jacobs and Reynolds (5) and also of Marshal and co-workers (6) show that the fluorine content of rock phosphate ranges between three and four per cent for most of the samples analyzed. Moreover, the first mentioned investigators showed that most of this fluorine is carried over into the product during the manufacture of superphosphates, and the latter workers found that some fluorine is present in the phosphoric acid used for making treble superphosphate.

Allison (1), growing corn in tumblers, found that heavy applications of 18 per cent superphosphate prevented germination.

Rost (8), in pot and field work, found that both 16 and 46 per cent superphosphates were injurious to corn at heavy rates of application.

The 46 per cent superphosphate was more toxic in equivalent amounts than the 16 per cent superphosphate. Contact with the soil for one month before planting largely overcame the toxicity of both fertilizers.

EXPERIMENTAL

Toxicity of Superphosphates to Germination of Corn

To investigate the toxicity of various fertilizer materials, a method was used similar to that used by bacteriologists in testing the efficiency of disinfectants. The organisms (corn seeds in this case) were placed for a definite number of hours in the material investigated and then placed in a suitable medium for growth. The effect of the treatment on viability was then compared with a control run parallel with the treated organisms.

Pastes were made by moistening fertilizers with distilled water. Each paste was placed in a two-pound glass butter dish having a loose glass cover. One hundred seeds of corn were embedded in each of the pastes for the time designated. Corn seeds of uniform size and high germinative power were used. Any seeds that showed indication of mechanical injury or poor quality were discarded. After remaining in the paste for a definite number of hours, the seeds were removed, well washed with distilled water, weighed and placed in "rag dolls" to germinate. For the fluid treatments the same procedure was used except that 500 cc. Ehrlenmeyer flasks were used as containers during the treatment and these were stoppered with absorbent cotton.

The "rag doll" consisted of a strip of cheese cloth eight inches wide and thirty inches long. The hundred seeds were spread uniformly on each strip and then rolled up with the cloth using a glass rod as an axis to give stiffness to the roll. Each "rag doll" was placed in a five pint jar containing one inch of distilled water so that the wick action of the cheese cloth moistened the seeds. The jars were then connected by means of rubber tubing and aerated with moist air four times daily. Germinated seeds were removed daily and the number that germinated was recorded. As the reaction of the medium for plant growth may influence germination, the pH values of the pastes and solutions were measured by means of the quinhydrone electrode. The results of the experiment are given in Table 1.

These results show that commercial ammonium sulfate and potassium chloride were injurious to germination. The toxic effect produced by the two superphosphates was especially severe. Three hours immersion in these two materials was sufficient to reduce germination seventy-five per cent and the twelve hours immersion killed practically all of the seeds. Similar toxicity was not shown by monocalcium phosphate, phosphoric acid, or sulfuric acid in the concentrations used. Neither was it shown by rock phosphate in water. However, when rock phosphate and 0.143 <u>N</u> sulfuric acid were mixed, a product was obtained that was highly toxic to germination.

Since retardation of germination due to high osmotic concentration of the medium is related to the water absorption of the seed the weight of seeds before and after immersion in the fertilizer pastes was recorded. The per cent increase in weight of the seeds is shown in Graph 1. It is at once apparent that the phosphates interfered with water absorption much less than the more soluble ammonium sulfate and potassium chloride which, in turn, were less toxic than the phosphates. The interference with water absorption, then, does not afford an explanation of this injury.

The high acidity of the phosphates evidently did not account directly for their toxicity under the conditions of the experiment, because the more acid phosphoric and sulfuric acids did not produce a similar effect. Therefore, an explanation of the injury must be sought elsewhere.

Qualitative tests showed that concentrated sulfuric acid formed hydrofluoric acid from rock phosphate. When the mixture was heated a heavy etching was produced on a glass plate. Therefore, it seemed desirable to investigate fluorine as a possible source of injury to germination.

TOXICITY OF SOME FLUORINE COMPOUNDS TO GERMINATION OF CORN

Solutions of hydrogen fluoride and sodium fluoride were made containing known concentrations of fluorine. The strengths of these solutions were checked by titration with 0.1 N thorium nitrate using alizarin as an indicator, according to the method of Willard and Winters. The pH values of the solutions were determined by means of the quinhydrone electrode.

Four hundred cubic centimeters of each solution were placed in separate five-pint jars. In each of these were placed two "rag dolls" each containing one hundred seeds of corn. One of these "rag dolls" contained Polar Dent corn (the same variety used in the previous experiment), the other contained Pickett's Yellow Dent corn. In addition to the jars containing the fluoride solutions four more were added to the series. One of these contained 400 cc. of 0.143 N H_2SO_4, the second an equal volume of 0.072 N H_2SO_4, the third 400 cc. of 0.072 N H_2SO_4 plus one gram of CaF_2 per 100 cc. of solution, while in the fourth jar solid CaF_2 was sprinkled directly on the seeds in the "rag doll" and 400 cc. of water was added. The jars were connected in series by tubing, aerated, ~~etc.~~, as in the first experiment.

It should be noted that this experiment and the subsequent ones differ from the first one in that the seeds were exposed to the reagents continuously through the wick action of the "rag doll", while in the first experiment the seeds were exposed to the reagents only for a limited space of time. The results are given in Table 2.

Several salient facts were brought out by the data of the second experiment. Hydrogen and sodium fluoride were both toxic to germination of corn and their toxicity increased with concentration. Hydrogen fluoride was more toxic than sodium fluoride. These results are in accord with the findings of Bokorny (2). He attributed the toxicity to the passage of fluorine into the seed where it united with the calcium present there to form insoluble calcium fluoride. He states: "The calcium is an integral constituent of many cell organs and probably occurs as calcium proteinate in the same." His theory is further supported by his results on the effects of potassium oxalate and oxalic acid. Both these materials proved injurious in 0.1 per cent solutions, especially the latter which killed the seeds of cress.

Sigmund, also, found that 0.5 and 0.3 per cent solutions of tartaric acid (another chemical which forms an insoluble compound with calcium) were injurious to wheat and killed pea and rape seeds. But Sigmund obtained no germination of peas, wheat, and rape when he used solid calcium or barium fluoride.

In the present investigation, however, repeated attempts to obtain injury to corn by solid calcium fluoride indicated that it had no effect on the germination of corn. Seeds of corn completely embedded in the moist salt germinated readily. When 0.072 N H_2SO_4 was added to calcium fluoride the results were entirely different. Then the material became highly toxic, allowing no germination to take place, probably due to the formation of hydrogen fluoride.

The strength of the sulphuric acid used also had an effect on germination. In the jar containing 0.143 N H_2SO_4 not only was the per cent germination reduced but the roots showed signs of severe injury, barely emerging from the seed, and the shoots were also injured but to a less extent. In some cases the shoot appeared before the root which is the reverse of the natural process. The seedlings soon became covered with mold and it was doubtful if they would have survived if left to grow. The 0.072 N H_2SO_4 treatment proved to be injurious also but the effect was relatively much less severe. Salter and McIlvaine have shown that a nutrient solution having a pH of 2.17 allowed 26 out of 30 corn seeds to germinate. The seedlings did not flourish, however, and eventually died. A solution of pH 2.96, on the other hand, allowed nearly perfect germination (29 out of 30) but growth was retarded. Hence the acidity must be taken into account as a factor affecting germination.

It should also be noted that the corn seeds showed a marked variability with respect to their susceptibility to fluorine injury. For example, in the case of Pickett's Dent in the hydrogen fluoride solutions nine per cent of the seeds were able to germinate in three hundred parts per million of fluorine whereas only seventy per cent of the seeds germinated in a solution containing one hundred parts per million of fluorine. Moreover, the Polar Dent variety appeared to be more susceptible to fluorine injury than Pickett's Dent in this experiment and also in subsequent ones.

The question arose as to whether the fluorine had a retarding effect on germination. The weighted mean (daily per cent germination times days) is very useful to express the time required for germination and is easily compared with the germination means from the other treatments. These values are found in the last column of Table 2. The solutions of one hundred parts per million of fluorine appear to have hastened germination to a slight extent but above two hundred parts per million a retarding action occurred. Similar effects may be observed in later experiments.

RELATION OF FLUORINE IN SUPERPHOSPHATE TO GERMINATION

Because fluorine in fertilizers seemed to be a source of injury to germination and it should be in a soluble form in order to be toxic, an investigation of the amount of soluble fluorine in fertilizers and its effect on germination was undertaken. Preliminary work showed that the quantity of soluble fluorine extracted from superphosphate was dependent on the quantity of water used and the length of time of shaking the fertilizer with the water. There was also a considerable difference in the amount of soluble fluorine in different superphosphates. Therefore, the following procedure was followed:

Two samples of 44 per cent superphosphate of different origin (which will hereafter be designated as A and B), and one sample of 20 per cent superphosphate were obtained from stock supplies used at this station. These samples were air dried in the laboratory and placed in suitable containers. Definite quantities of the air dry fertilizer were weighed to one milligram and added to 400 cc. of water in a 550 cc. glass bottle. These bottles were then stoppered and shaken for six hours in a shaking machine. Preliminary work had shown that two hours shaking was sufficient to attain a maximum content of soluble fluoride in the extract, but six hours was allowed for shaking in order to insure complete equilibrium. After shaking, the solutions were filtered and placed in stoppered bottles. Aliquots of the solutions were used to determine the freezing point depression by the usual Beckman thermometer method, the pH value by the quinhydrone electrode and the soluble fluorine content by the method proposed by Willard and Winters. All these determinations were made in duplicate. Jars containing "rag dolls" were set up as before and 200 cc. of solution were added to each. The germination test was run similar to and concurrently with that of the pure fluorine compounds so that conditions of temperature, etc. were the same for both experiments. Table 3 gives the results of the tests.

A glance at Table 3 is sufficient to show that superphosphate B was more toxic than the 20 per cent superphosphate which in turn was more toxic than superphosphate A. The injury to germination produced by the solutions from 20 per cent superphosphate increased with an increase in concentration of soluble fluoride. The same holds true for superphosphate A and superphosphate B. But, as might be expected, the acidity and osmotic concentration also increased with increasing amounts of fertilizer. In fact, the question might be raised whether or not the toxicity was entirely due to these last named factors. To answer this question one treatment was selected in which the values of these factors were the least. In the case of superphosphate B one gram of fertilizer per 100 cc. of water gave a freezing point depression of only .19°C which corresponds to an osmotic value of 2.28 atmospheres. Shive (11) obtained as good germination in solutions of 8.0 atmospheres as he did with the control cultures. The author found in further work with C. P. ammonium sulfate and potassium chloride solutions that corn seeds could germinate at much higher osmotic concentrations. Perfect germination was obtained in solutions of ammonium sulfate having a freezing point depression as ~~high~~ great as 1.44°C. For potassium chloride the limit was still ~~higher~~ greater, being 1.82°C.

The pH of the superphosphate solution under discussion happens to coincide with that of the solution used by Salter and McIlvaine on corn in which they obtained no reduction in germination. Also the slightly greater acidity of the four gram solution of superphosphate A did not produce such toxicity. The fluorine content of the solution from superphosphate B was 154 parts per million. The per cent germination was approximately the same as that in 100 parts per million of fluorine as hydrogen fluoride (Table 2). It must be true, therefore, that the toxicity of the fluorine in the superphosphate is modified by other factors.

A comparison of the solution of superphosphate B having two grams of fertilizer per 100 cc. with that of 20 per cent superphosphate having four grams per 100 cc. of water shows that the osmotic values and acidity are practically the same, and that toxicity to germination varies directly with the fluorine content. Each of these solutions, however, was less toxic than corresponding solutions of hydrogen fluoride. In the three mentioned cases the pH of the solution was higher than that of the corresponding hydrogen fluoride solutions. The solution of 20 per cent superphosphate containing 12 grams of fertilizer per 100 cc. contained 200 parts per million of fluorine and its acidity is practically the same as the hydrogen fluoride solution of that strength. The injury to germination in this case is slightly greater than that of the hydrogen fluoride solution. It appears, then, that the toxicity is favored by high acidity. This conclusion is further supported by the fact that hydrogen fluoride proved more toxic than sodium fluoride.

Had superphosphate A been omitted from the experiment the explanation of Table 3 and some later experiments would have been greatly simplified for its injury to germination is much less than would be expected from its soluble fluorine content. There were, however, three major differences between this fertilizer and the other two fertilizers. The acidity was less and the soluble fluorine was less for a given weight of available P_2O_5 than in the case of the other two fertilizers. Superphosphate A also contained a small amount of copper as shown by qualitative analysis of the material. No trace of copper was found in the other two fertilizers. There is need of further investigation to determine the exact cause for the lower toxicity of superphosphate A.

The time required for germination in the various solutions is given in the last column of Table 3. Increasing amounts of fertilizer caused greater retardation of germination. The degree of retardation was not wholly controlled by osmotic concentration, but was affected by other factors as well. No doubt the fluorine content played some part in retarding germination.

REDUCTION OF TOXICITY OF SUPERPHOSPHATES BY THE PARTIAL REMOVAL OF FLUORINE

Although the results of the foregoing experiments indicated that soluble fluorine was responsible for the toxicity of the investigated superphosphates to the germination of corn, an exact interpretation of the results was complicated by the influence of other factors which may have had some effect on germination. An attempt was made, therefore, to remove the soluble fluorine from the superphosphate by a method which would cause the least possible alteration of the physical and chemical properties of the superphosphate used. For this purpose the volatilization method seemed best adapted because it did not require the addition of any foreign substance except water and, fortunately, the fluorine distilled over at a low temperature (120°C) which removed only a trace of phosphoric and sulfuric acid.

Twenty-four grams of superphosphate B was accurately weighed into a 400 cc. Ehrlenmeyer flask and placed in a constant temperature oven at 135°C$\pm$ 2°. The stoppered flask was connected to a water-cooled condenser on the outside of the oven by means of glass tubing. The superphosphate was alternately wetted and dried by the addition, through a capillary tube, of approximately 10 cc. portions of distilled water followed by several hours of drying at 135°C. The distillate was received in a suitable container. During eight days of alternate wetting and drying 225 cc. of distillate was obtained. The hard cake of superphosphate formed by this procedure adhered to the flask so strongly that removal was not attempted, but the flask as well as its contents was broken up in a mortar, placed in a 550 cc. bottle, 400 cc. of distilled water added, shaken for six hours, and then filtered. The physical appearance of the fertilizer after shaking did not seem to be different than that of the original superphosphate. The filtrate and the distillate from the superphosphate were analyzed and used for germination tests as in the preceding experiment.

Table 4 shows that all of the soluble fluorine was not removed from the superphosphate by this method, but it was greatly reduced in quantity. The reduction in soluble fluorine content was accompanied by a decrease in the toxicity of the superphosphate. The distillate from the superphosphate, on the other hand, was highly toxic to germination. This toxicity, no doubt, was due to the high concentration of fluorine which must have been in combination as hydro-fluosilicic acid because of the method used for separation. The osmotic concentration of the distillate was much too small to have an appreciable effect on germination, and it has been shown in Table 2 that .072 N H_2SO_4 having a pH of 1.43 was not as toxic as this distillate which had a pH of 1.89. Hence, the toxicity must have been due chiefly to the soluble fluorine present.

EFFECT OF SOME SOILS ON TOXICITY OF FERTILIZER SOLUTIONS TO GERMINATION OF CORN

Results obtained with solution cultures are often quite different from those obtained if the solution is added to the soil. The soil usually reduces the toxicity of solutions and may completely overcome it. An experiment was run to determine if this were true with fluorine in fertilizers. If the solution had been added to the soil the possibility of determining the effect of the soil on soluble fluorine would have been eliminated due to lack of suitable methods for extracting the soil solution. Therefore an intermediate method was chosen.

Solutions of superphosphate B were made as the solutions given in Table 3 except that 50 grams of soil (oven dry basis) were added for each 100 cc. of water used. The procedure for shaking, analysis, and germination was the same as before. The germination tests ran concurrently with those of the aforementioned solutions. The results are given in Table 5.

The addition of soil to the solutions caused a marked reduction in the soluble fluorine content and in the acidity. This effect was accompanied by a great change in the toxicity of the fertilizer. More than twelve times as much superphosphate B with soil added was required to produce the same degree of toxicity obtained when one gram of superphosphate B was used without soil (Table 3). The reduction in fluorine content, no doubt, is due to the formation of insoluble calcium fluoride which according to Table 2 is not toxic to germination of corn. Brookston loam was more effective than Miami silt loam in reducing the soluble fluoride content of the solution. The osmotic value of the solutions was not greatly changed. The retarding effect of the solutions is shown in the last column of Table 5. Six grams of superphosphate B plus soil appeared to hasten germination, but the more concentrated solutions showed a retarding influence on the germination.

RELATION OF FERTILIZER PLACEMENT TO GERMINATION OF CORN IN POT EXPERIMENTS

Having determined that soil was effective in overcoming the toxicity of the superphosphates to corn, experiments were run in the greenhouse to investigate the toxicity of the fertilizers when placed in the soil with the seed. Two-gallon glazed jars were used, containing soil made up to definite moisture contents using 7000 grams of air-dry soil in the case of Brookston loam and 8000 grams in the case of Miami and Fox soils.

The rate of application of fertilizer was based upon a hill application in a circle three inches in diameter with the corn planted in check rows three and one-half feet apart. By this method only 1/250 of the total area is covered.

Hence, an application of 25 pounds per acre in the hill equals 25 times 250 or 6250 pounds per acre broadcast for the area covered.

25 lbs./acre in hill	=	6,250 lbs./acre broadcast
50 lbs./acre in hill	=	12,500 lbs./acre broadcast
100 lbs./acre in hill	=	25,000 lbs./acre broadcast
200 lbs./acre in hill	=	50,000 lbs./acre broadcast
400 lbs./acre in hill	=	100,000 lbs./acre broadcast

The fertilizer was applied with large salt shakers, covering the entire cross section of the soil at the broadcast rates noted. Fifty seeds were planted per jar at a depth of two and one-half inches. The jars were made up to weight every other day by adding water to the lower soil through a glass tube placed through the center of the soil column.

An experiment was conducted to determine what effect placing the embryo against the fertilizer would have upon germination as compared to the same treatment with the endosperm toward the fertilizer. Corn was planted on Miami silt loam at ten per cent moisture content, using 20 per cent superphosphate in contact with the seed. The placements and results are given in Table 6.

Since the water was added to the lower part of the soil column the movement of moisture in the soil was predominantly upward as it would be in the field if no rains occurred during the time for germination. Under these conditions the fertilizer below the seed was injurious to germination of corn regardless of whether the fertilizer was in contact with the embryo or the endosperm. The fertilizer above the seed produced greater injury when the embryo came in contact with the fertilizer than when the endosperm did. Plate 1 shows these jars twelve days after the seed was planted. Similar results with regard to facing of the embryo of the corn kernel toward or away from the fertilizer were obtained by Coe, using Ammo-Phos in contact with the seed. The experiment indicates that when the diffusion of the fertilizer takes place in a direction away from the seed a few millimeters separation of seed and fertilizer may make a profound difference in the per cent germination for when the fertilizer was above the seed in contact with the endosperm germination was much better than when the embryo was exposed to the fertilizer.

INFLUENCE OF SOIL MOISTURE ON TOXICITY OF FERTILIZERS TO GERMINATION OF CORN

Truog and his co-workers (13) found that the injury to germination of corn caused by a complete fertilizer varied inversely with the moisture content of the soil. An experiment was conducted to determine if the same were true for superphosphates. Jars of Miami silt loam were made up to definite moisture content. The fertilizer was applied beneath the seed in contact with the embryo. Superphosphates A and B and 20 per cent superphosphate were included in this experiment. The amount of fertilizer used in the case of the more concentrated carriers was such that an equivalent amount of available P_2O_5 was used in all three sets of pots. Watering was accomplished in the same manner as before. Daily counts were made of the number of plants emerging from the soil and from these the weighted mean for time of emergence was calculated. Table 7 contains these results.

The data show that germination was both retarded and reduced by a decrease in soil moisture content. Similar results were obtained by using Brookston loam at 20 per cent and 15 per cent soil moisture content. Due to the nature of the experiment reliable chemical analysis of the solution coming in contact with the seed was impossible but from the laboratory results certain suppositions seem justified. The lower moisture content of the soil probably resulted in a higher concentration of soluble material including fluorine at the surface of the seed. Also, no doubt, there was a slower rate of reaction between fertilizer and soil at the lower moisture content than at the higher one for diffusion in the soil was probably slower. The combination of the two conditions named should have favored a higher soluble fluorine content as well as a higher osmotic concentration in the dryer soil resulting in retardation and inhibition of growth.

EFFECT OF MIXING SUPERPHOSPHATES WITH SOILS VS. DIRECT CONTACT WITH SEED ON GERMINATION

An experiment was set up to determine the effect on germination of mixing the superphosphates with the soil as compared to the placement of the same in direct contact with the seed. The jars for the direct contact treatments were made up as before placing the fertilizer below the seed in contact with the embryo. In the jars where mixing of fertilizer with the soil was desired, one kilogram of air-dry soil was mixed with the fertilizer, brought to the desired moisture content, and placed in a layer over untreated moist soil. In this layer the corn kernels were planted. The layer of fertilized soil was approximately one inch thick and was covered by a layer of unfertilized soil. Three soils were used--Brookston loam at 20 per cent moisture content, Miami silt loam at 15 per cent moisture content, and Fox sandy loam at 12 per cent moisture content. The moisture content was approximately one-half of the moisture holding capacity. The results of the experiment are recorded in Table 8.

By mixing the fertilizer with the soil the toxicity of the fertilizer was almost completely overcome except in the case of the heaviest application of the 44 per cent superphosphates on Fox sandy loam. More than sixteen times as much fertilizer could be applied without reduction in germination by mixing with the soil than when the fertilizer was used in direct contact with the seed. When the superphosphates were in direct contact with the seed the reaction between soil and fertilizer was not complete enough to overcome its toxicity.

It was supposed that the soil type might play an important part in the ability to overcome toxicity. Except for the heaviest application on Fox sandy loam, the results are rather unconvincing. The direct contact results indicate that reaction between soil and fertilizer was not sufficient to produce significant differences whereas the reaction between the mixed soil and fertilizer was great enough to overcome toxicity in the majority of the cases.

The lower toxicity to germination of superphosphate A is again brought out in the direct contact treatments of Table 8. The difference between the toxicity of superphosphate B and 20 per cent superphosphate, however, was diminished as compared to the toxicity produced as shown in Table 3. This can be accounted for by the fact that a greater weight of dry fertilizer was used in the case of 20 per cent superphosphate which must have reduced the moisture content in the immediate vicinity of the seed.

Increased retardation of emergence of corn occurred with increasing amounts of fertilizer. The seed in soil mixed with fertilizer came up 1.3 days earlier as an average than when the same rate of application was applied in direct contact with the seed.

TOXICITY OF FERTILIZERS TO GERMINATION OF CORN IN FIELD EXPERIMENTS

The final experiment with respect to toxicity of superphosphates was conducted in the field. The fertilizer was applied in the hill in a circle three inches in diameter and the seeds planted in direct contact with the fertilizer, using amounts of the 44 per cent fertilizers equivalent in P_2O_5 content to the amounts applied in the 20 per cent superphosphate applications. For each treatment ten hills were planted with five kernels of corn per hill. Samples of soil were taken at the time of planting on which moisture content and pH were determined. Emergence counts were made at 12 and 21 days from date of planting. The final emergence is given in Table 9.

The results of the greenhouse tests are confirmed by the field tests. There was a marked difference produced by facing the embryo toward or away from the fertilizer. The low moisture content probably accounts for the lower per cent germination on Hillsdale sandy loam. Superphosphate A proved less toxic than superphosphate B or 20 per cent to germination. The per cent germination, however, was much higher in the field experiment than it was in the greenhouse experiment. This may be due, in part, to the fact that only a circular area three inches in diameter was covered with fertilizer whereas in the jars in the greenhouse the entire cross section of the jar was covered. The plants that grew showed a marked tendency to send the roots through the soil beyond the fertilizer rather than through the fertilizer. Further comparison of per cent germination between the greenhouse and field tests scarcely seems justified because different soils were used having different moisture contents and the climatic environment was entirely different.

SUMMARY

In this investigation (1) laboratory, greenhouse, and field experiments have shown that the superphosphates investigated were capable of exerting a toxic influence on the germination of corn due to their content of soluble fluorine; (2) the soils used in the experiment were effective in reducing or overcoming the toxicity provided that sufficient reaction took place between the soil and the fertilizer. These two facts furnish a satisfactory explanation of (3) the high toxicity of superphosphates when placed in direct contact with the seed and also (4) the reduction of this toxicity when the superphosphates were mixed with the soil. (5) Corn was found to be quite variable in its susceptibility to fluorine injury. (6) The facing of the embryo of the seed toward

the superphosphate resulted in greater reduction in germination of corn than when the position of the kernel was reversed, provided that the fertilizer diffused away from the seed. (7) There was considerable difference in the amount of injury produced by the three superphosphates investigated. Further research is needed to determine the effects of nitrogen and potash carriers on the soluble fluorine content and toxicity of the superphosphates in mixtures of these fertilizers.

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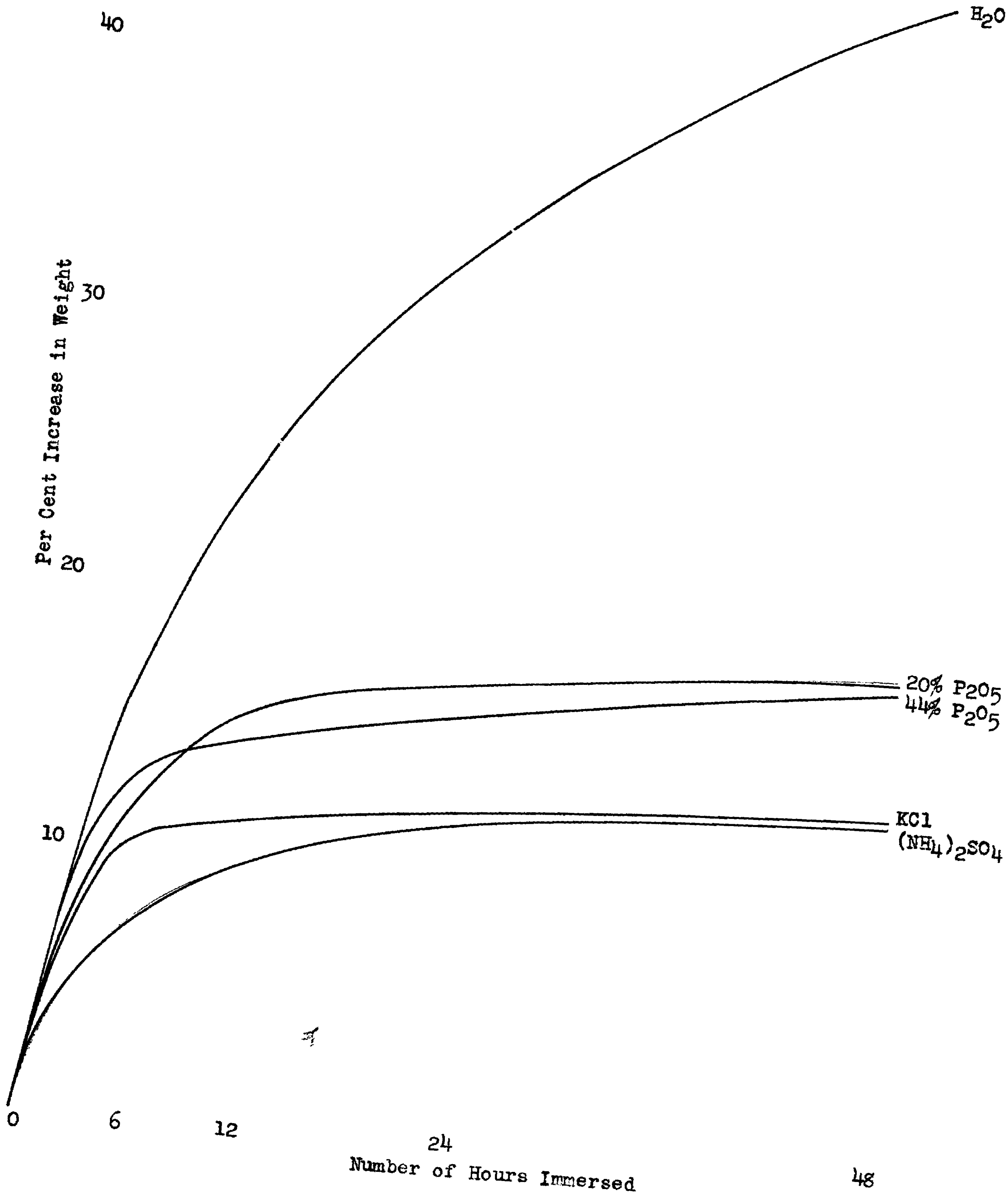
GRAPH I

PER CENT INCREASE IN WEIGHT OF CORN SEEDS PLANTED IN MOIST FERTILIZER



RELATION OF FERTILIZER PLACEMENT TO GERMINATION OF CORN

PLATE I

20% superphosphate on Miami silt loam at ten per cent moisture content. Fertilizer was placed above the seed.

C -- No fertilizer
1 -- 12,500 lbs/acre in contact with endosperm
2 -- 12,500 lbs/acre in contact with embrye
3 -- 25,000 lbs/acre in contact with endosperm
4 -- 25,000 lbs/Acre in contact with embrye

Table 1

Per Cent Germination of Corn after Immersion in Fertilizer Materials

Treatment	Substance	Concentration of Medium	pH of Medium	Number of hours immersed: 1	3	6	12	24	96
				Per Cent Germination					
1	H_2O (distilled)	——	——	—	—	—	—	98.5 (a)	—
2	$(NH_4)_2SO_4$ (com'l)	Paste	4.23	—	—	—	93	85	88
3	KCl (com'l)	"	6.90	—	—	—	84	77	65
4	Superphosphate 20% P_2O_5	"	2.48	87	27	7	1	0	0
5	Superphosphate B 44% P_2O_5	"	2.41	86	24	9	0	0	0
6	Ca $(H_2PO_4)_2$ C. P.	"	1.56	—	—	—	—	91	—
7	H_3PO_4	0.1 M	1.61	—	—	—	—	99	—
8	Rock phosphate & H_2O	5 gm./100 cc.	7.16	—	—	—	—	97	—
9	H_2SO_4	0.143 N	1.20	—	—	—	—	95	—
10	Rock phosphate & .143N H_2SO_4	5 gm./100 cc.	1.86	—	—	—	—	0	—

(a) Average of 10 determinations of 100 seeds each
Standard deviation = 1.12%

Table 2

Influence of Some Fluorine Compounds on the Germination of Corn

Substance	PPM Fluorine	pH	% Germination Polar Dent	% Germination Pickett's Dent	Days for Germination
Check	---	----	98.5 (a)	99.2 (a)	2.35
H F	100	2.88	49	70	2.25
"	200	2.66	9	22	3.00
"	300	2.49	0	9	4.00
"	400	2.40	0	0	
NaF	100	5.47	61	72	2.00
"	200	5.57	10	65	2.40
"	300	5.61	12	23	2.95
"	400	5.63	0	0	
.143 M H_2SO_4	---	1.20	15	26	3.05
.072 M H_2SO_4	---	1.43	68	67	2.10
.072 M H_2SO_4 & 1% CaF_2	---	1.44	0	0	
CaF_2 (solid)	---		98	99	2.30

(a) Average of 10 determinations of 100 seeds each.
Standard deviation 1.12 and 0.75 respectively

Table 3

Per Cent Germination of Corn in Fertilizer Solutions

Fertilizer	g. fert. / 100ccH_2O	Freezing point lowering	pH	ppm soluble fluorine	% germination Polar Dent	% germination Picketts Dent	Days for germination
Check	--	--	--	---	98.5	99.2	2.35
Superphosphate 20%	4	.30	2.93	117	57	87	2.80
	8	.53	2.75	172	35	41	3.60
	12	.74	2.65	200	7	14	3.95
	16	.91	2.59	243	1	3	5.00
	20	1.01	2.51	270	0	1	5.00
Superphosphate A 44%	4	.52	2.94	147	91	96	2.30
	8	1.00	2.81	173	74	93	3.00
	12	1.34	2.76	214	64	68	3.85
	16	1.66	2.69	256	14	30	4.80
	20	1.98	2.66	327	3	3	4.85
Superphosphate B 44%	1	.19	2.96	154	52	69	2.65
	2	.30	2.91	263	22	33	3.80
	3	.43	2.87	385	12	10	3.95
	4	.53	2.84	513	1	5	4.80
	5	.64	2.82	61[illegible]	0	5	6.80
	6	.77	2.77	670	0	0	

Table 4

Reduction of Toxicity of Superphosphates by the Partial Removal of Fluorine

Treatment	g. fert: 100cc H_2O	Freezing point depression	pH	ppm fluorine	% germination Polar Dent	% germination Picketts Dent
Check	0	—	—	—	98.5	99.2
Superphosphate B (unheated)	6	.77	2.77	670	0	0
Superphosphate B (heated)	6	.59	2.22	133	56	61
Distillate from heated fertilizer	-	.05	1.89	1015	0	0

Table 5

Effect of Soils on Toxicity of Fertilizer Solutions to Germination of Corn

Treatment	g. 44% fert / 100cc H_2O	Freezing point lowering	pH	ppm fluorine	% germination Polar Dent	% germination Picketts Dent	Days for germination
Check	—	—	—	—	98.5	99.2	2.35
44% superphosphate(B)	6	.77	2.77	670	0	0	
44% superphosphate(B)	6	.69	3.18	77	91	96	2.20
plus 50 g. Miami	8	.84	3.07	116	95	99	2.55
silt loam(pH 5.18)	12	1.23	2.97	130	79	87	3.55
per 100 cc soln.	16	1.52	2.88	177	38	35	4.70
	20	1.97	2.79	214	3	12	6.10
44% superphosphate(B)	6	.68	3.96	12	95	96	2.05
plus 50 g. Brookston	8	.85	3.69	22	96	95	2.35
loam (pH 7.13)	12	1.23	3.43	44	95	95	3.05
per 100 cc soln.	16	1.50	3.19	70	60	62	4.30
	20	1.95	3.03	116	20	39	6.35

Table 6

Relation of Fertilizer Placement to Germination of Corn in Pot Experiments

Placement of Fertilizer	% germination 12,500 lbs/A	25,000 lbs/A
No treatment	98	100
Fertilizer below seed in contact with embryo	18	0
Fertilizer below seed in contact with endosperm	14	12
Fertilizer above seed in contact with embryo	14	10
Fertilizer above seed in contact with endosperm	82	42

Table 7

Influence of Soil Moisture on Toxicity of Fertilizers to Germination of Corn

Fertilizer	Rate of application	% germination		Days for emergence	
		15% soil moisture	10% soil moisture	15% soil moisture	10% soil moisture
Check	---	98	100	5.0	5.6
Superphosphate 20%	6,250 lbs/A	80	58	7.0	9.6
	12,500	50	14	8.6	10.0
	25,000	12	0	9.7	---
Superphosphate A 44%	2,841	96	96	6.3	7.2
	5,682	84	80	8.2	8.7
	11,364	52	12	10.0	11.2
Superphosphate B 44%	2,841	86	80	5.8	7.8
	5,682	44	48	8.4	8.8
	11,364	18	0	8.8	---

Table 8

Effect of Mixing Fertilizer with Soils on the Toxicity of Fertilizers to the Germination of Corn

Fertilizer	Rate of application lbs/Acre	% germ in Brookston loam		% germ in Miami silt loam		% germ in Fox sandy loam	
		contract	mixed	contract	mixed	mixed limed	mixed not limed
Check	------	100	98	98	100	98	98
20%	6,250	90	—	80	—	—	—
	12,500	46	98	50	98	100	100
	25,000	0	98	12	98	100	100
	50,000	0	100	0	100	100	100
	100,000	—	100	—	98	98	92
44% A	2,841	98	—	96	—	—	—
	5,682	78	96	84	98	98	100
	11,364	16	100	52	100	100	98
	22,727	0	100	0	100	100	100
	45,454	—	100	—	94	8	6
44% B	2,841	74	—	86	—	—	—
	5,682	56	100	44	98	100	100
	11,364	6	98	18	96	98	98
	22,727	0	98	0	98	100	98
	45,454	—	94	—	92	2	0
pH of soil		7.13		5.18		6.48	5.10

Table 9

Toxicity of Fertilizers to Germination of Corn in Field Experiments

Obs. No.	Fertilizer	Rate of application	Placement: above seed vs endosperm	Placement: below seed vs embryo	Placement: below seed vs embryo
1	Check	—	98	92	94
2.	20%	50 lbs/A	86	58	54
3		100	68	20	14
4		200	60	8	0
5	44%A	☼ 50	96	84	88
6		" 100	98	58	26
7		" 200	86	24	24
8	44%B	☼ 50	88	46	34
9		" 100	82	14	6
10		" 200	34	6	0
Soil type			Hillsdale loam	Hillsdale loam	Hillsdale sandy loam
Soil moisture			20.3	21.3	10.4
pH			7.86	7.81	7.84