THE PRESENCE OF ALUMINUM AS A REASON FOR THE DIFFERENCE IN THE EFFECT OF SO-CALLED ACID SOIL ON BARLEY AND RYE[1]

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INTRODUCTION

It has been found by means of field experiments conducted at the Rhode Island station that under conditions where liming exerted very little influence upon the growth of rye, barley was increased two to threefold (4). These crops were selected in the present instance simply as convenient representatives of crops differently affected by acid-soil conditions.

In a previous article by us (5), the method of water culture there described being the same as in the present instance, it was shown that barley seedlings were not more susceptible than rye seedlings to injury by acidified nutrient solutions, even though so-called acid soils are much more deleterious to barley than to rye. The reason for the different effect of acid soil and acid nutrient solutions has interested the authors for a number of years. The present paper is a record of their intermittent work on the subject.

Unless otherwise stated, the solution work with seedlings was conducted in 250 cc. wide-mouthed bottles under such conditions that the transpiration could be measured during the few weeks of the experimental period. The total transpiration could be compared with the final weight of the green tops.

EFFECT OF ACID IN WATER AND SAND CULTURES

There are so many different cultures involved in the present work that a condensation of the data seems desirable. Therefore, in most cases the transpiration and weight of the green tops accompanying each bottle are not given, but the effect of a stated treatment is considered to be shown by comparing the average of both these observations derived from duplicate cultures. For example, in recording some additional data concerning the relative effect on rye and barley seedlings of sulfuric acid added to the nutrient solution, the depression in growth of the rye based upon the averages of transpiration and weight of the green tops, as just explained, is represented by 100 in each case, and the depression in the growth of barley in individual instances is ex-

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pressed as related thereto. In different experiments and under a number of different conditions the depressing effect on barley caused by the acid was, in comparison with 100 as representing the effect on rye, 124, 103, 102, 101, 95, 100, 99, 99, 96, 121, 98, 98, 96, 120, 75, 113; average, 103.

This agrees with the earlier work in showing that barley and rye seedlings are affected practically alike by acid added to a nutrient solution containing the usual essential elements.

Realizing that conditions attending the growth of seedlings in water culture are quite different from those in the field, a nearer approach to field conditions was made by growing the seedlings in sand and nutrients with and without the addition of acid, usually sulfuric. Sometimes sea-beach sand and again quite pure quartz sand was used without any special treatment. In other experiments the sand was digested in hot acid, washed, and ignited previous to its use. If the depression in the growth of rye is expressed in each case by 10, the relative depression in the growth of barley becomes 18, 8, 23, 11, 22, 9, 13, 6, 9, 10, 10, 13, 10, 13, 14, 4, 12, 17, 25, 18, 26, 10, 12, 15, 21, 27, 16, 8, 17, 10, 10, 23, 12, 6, 13, 4, 12, 13, 14, 13, 10, 15, 13, 11, 16; average, 14.

It may be seen that on the average the sulfuric acid depressed the growth of barley more than it did that of rye. In many instances, however, the difference was slight, as was nearly always the case in water cultures, and the authors were inclined to the opinion at the time that the exceptions were accountable mainly to abnormal differences in the relative vigor of the two kinds of seedlings. For the purpose of determining the difference in the effect of acid on various strains and varieties of barley and rye, a number of samples of these grains were kindly furnished upon request, by the agricultural experiment stations of the states of Utah, Minnesota, Iowa and Pennsylvania, and of the province of Ontario.

It was found by carrying on water cultures with these seeds that when the various strains were grown under the same conditions, either in neutral or acid cultures, there were some marked differences in the relative results. Therefore, in order to ascertain whether the relative effect of acid on the two kinds of seedlings was really dependent on the method of culture, water cultures and prepared sand cultures were carried on at the same time and with the same lot of seeds in each of a number of tests. The results are given in table 1, where it may be seen that the relative depression was about the same with the two kinds of seedlings, both in the water and sand cultures.

These results show that acidity present in connection with the ordinary plant nutrients has a relative effect on the two kinds of seedlings very different from that of so-called acidity in connection with the soil; for, as has been shown in the field repeatedly at this station, barley is much more sensitive than rye to acid-soil conditions.

TABLE 1

The relative effect of acidity on the weight (in grams) of the green tops of barley (B) and rye (R) seedlings when grown in sand and water cultures

	August 1911		September 1911		March 1913		March 1913		March 1913		Relative average weight	
	B	R	B	R	B	R	B	R	B	R	B	R
Sand culture												
Nutrients	4.5	3.6	3.9	2.6	4.2	1.9	4.4	2.2	3.7	2.2	100	100
	4.3	3.6	4.2	2.5	4.0	1.9	4.5	2.2	3.8	2.1		
Nutrients plus least amount of acid	3.7	2.8	3.5	2.2	2.9	1.5	3.4	1.8	3.3	1.6	82	81
	3.4	2.8	4.0	2.3	3.0	1.5	3.7	1.9	3.1	1.2		
Nutrients plus largest amount of acid	1.4	2.2	3.1	1.5	1.0	0.8	2.2	1.1	1.6	1.1	47	59
	1.3	1.8	2.7	2.0	1.1	1.0	2.8	1.3	2.3	1.5		
Water cultures												
Nutrients	5.3	5.6	8.1	4.5	8.4	6.2	8.2	5.6	8.8	6.7		
	5.1	5.8	7.9	4.0	8.8	6.2	8.2	4.9	8.9	5.9	100	100
	5.2	6.2	8.3	4.3								
Nutrients plus least amount of acid	3.3	4.7	7.1	4.2	8.3	4.3	7.4	4.1	7.7	5.6		
	3.6	5.5	7.8	4.3	8.1	4.3	7.6	4.1	7.9	5.2	88	84
	4.2	5.7	7.4	3.5								
Nutrients plus largest amount of acid	2.1	3.7										
	2.5	3.5			7.1	2.9	6.4	3.1	6.5	4.1	54	60
		3.5			6.9	2.7	5.7	2.9	6.0	3.6		

INFLUENCE OF THE EXTRACT OF AN ACID SOIL

That the special characteristics of an acid soil are transmitted to its extract is shown by the effect of an alkaline material, sometimes the hydroxide of sodium and again of calcium, either on the aqueous extract of soil from permanent plat 23 or on the same extract after adding nutrients. For a number of years this unlimed soil had received sulfate of ammonia, as the source of nitrogen in fertilizer chemicals. It was therefore very acid and imparted sufficient of its characteristics to the extract so that barley seedlings grew much less normally than rye seedlings, unless alkaline materials especially were added to the extract. The following numbers represent the percentage loss in weight of rye and barley seedlings caused by withholding alkaline materials from, in comparison with adding them to, the extracts of this soil:

Rye.................... −2, 2, 22, 7, −10, 30, 49, 16, 36, 1; Average, 15
Barley.................. 41, 36, 44, 39, 10, 61, 57, 52, 64, 49; Average, 45

When it had been shown that rye was much less affected than barley by acid soil and its aqueous extract, whereas acidity produced artificially in sand and water cultures affected both seedlings about alike, the question arose as to whether the soil and extract contained some factor which protected the rye from the usual deleterious effect of acidity as exhibited in artificial cultures. Any treatment which would destroy such a possible agency for protecting the rye seedlings would be expected to exert a relatively greater detrimental influence on the rye than on the barley which appears not to be protected. To throw light on this point possibly, seedlings were grown in beakers and the effects noted of certain soil treatments which will now be mentioned.

Under like manurial conditions barley and rye seedlings were grown (a) in unheated soil from the unlimed sulfate of ammonia plat, (b) in the same soil after sterilization in an autoclave at about 125°C. under 15 pounds pressure for one hour, and (c) in similarly sterilized soil to which an infusion from the original soil was added subsequently. The two experiments which were

TABLE 2

The effect on the growth of barley and rye seedlings of heating an acid soil at different temperatures

	EXPERIMENT I RELATIVE WEIGHT OF GREEN TOPS		EXPERIMENT II RELATIVE WEIGHT OF GREEN TOPS	
	Barley	Rye	Barley	Rye
Unheated soil	100	100	100	100
Soil heated at 100°C	82	94		
Soil heated at 260°C	36	36	53	45
Soil heated at 360°C	113	94	116	90
Soil heated at 420°C			121	100

conducted did not furnish evidence that the hypothetical agent for protecting the rye consisted of some organism, for the soil infusion was not more beneficial to the rye than to the barley. The barley especially, however, made a very unsatisfactory growth due to the acid-soil conditions. From a similar viewpoint the soil was treated with toluol instead of being sterilized by heat, but the results do not warrant any statement of interest in connection with the idea that the rye was influenced by the association of some lower form of life which enabled it to withstand the acid conditions. Coville (2) claims that the blueberry, another acid-soil plant, has a mycorrhizal fungus associated with it "which is able to assimilate nitrogen from the surrounding organic matter, and perhaps from the atmosphere also, and to convey it into the plant without taking along with it a large amount of the poisonous soil moisture."

Soil taken from the unlimed ammonium sulfate plat in the fall of 1913 was heated at various temperatures prior to growing rye and barley seedlings in it with optimum nutrients (table 2). By the calcium-acetate method, the amount of calcium oxide required to neutralize two million pounds of soil was 7200 pounds for the unheated soil, and for soil heated several hours at 100°, 260° and 360°C., it was 5760, 5400 and 3240 pounds, respectively. When heated for 10 hours at not less than 420°C. the amount of calcium oxide required was reduced to 2200 pounds.

Although heating the soil decreased the acidity, there was a decided increase in toxicity when the temperature of heating was around 260°C., which, however, affected the two kinds of seedlings about alike. Heating at the higher temperatures developed no toxicity, but seemed to be beneficial for barley; indicating that some substance toxic especially to barley may have had its effect reduced by the heating. In view of evidence to be presented that aluminum is such a substance, the thought arises that its availability might have been decreased by dehydration effected by the heat.

ADDITION OF SUBSTANCES TO ASCERTAIN IF THEY HAVE AN UNLIKE EFFECT ON THE TWO KINDS OF SEEDLINGS

Inasmuch as rye and barley are affected differently by acid soils, it was evident that some factor besides acidity must be potent. It seemed desirable, therefore, to make next the following tentative tests to ascertain whether treatment with other materials than those of an alkaline nature would have a specific effect on either kind of seedlings.

The acidity of hydrogen peroxide was nearly neutralized with sodium hydroxide; and, after the nutrients had been supplied, two amounts, 3 and 5 cc., were added to 250 cc. of soil extract of plat 23. The smaller addition of hydrogen peroxide increased the transpiration, but otherwise the barley seedlings were more abnormal with both amounts of hydrogen peroxide than when it was not added to the soil extract.

One of the poisonous organic substances which have been isolated from soil by the United States Bureau of Soils is dihydroxystearic acid. The Bureau kindly furnished a small amount of this material so that it might be ascertained whether its relative effect on barley and rye seedlings was similar to that exerted by acid soil. One hundred parts of the dihydroxystearic acid per million parts of a nutrient solution depressed the transpiration of barley 77 per cent and of rye 85 per cent; likewise, the weight of green barley tops was reduced 40 per cent and of rye tops 54 per cent. Fifty parts per million depressed the transpiration of barley and rye, 47 and 49 per cent, respectively, and the weight of green tops, 30 and 24 per cent, respectively. In this last experiment an amount of sulfuric acid equivalent to the dihydroxystearic acid depressed the transpiration of the barley 48 per cent and the weight of its green tops, 12 per cent. In another similar comparison with barley, the dihydroxystearic acid depressed the transpiration 47 per cent and the weight 28 per cent, whereas the sulfuric acid depressed the transpiration 29 per cent and the weight 13 per cent.

It appears from the foregoing data that dihydroxystearic acid does not account for the fact that barley is more injured than rye by acid-soil conditions, since it was fully as deleterious to rye as to barley. It likewise appears probable that the toxicity of dihydroxystearic acid is largely attributable to its acidity.

The relative effect of manure extract when added to an acidulated nutrient solution was tested. The manure extract was acidulated, boiled, and then neutralized before using. The development of both kinds of seedlings was depressed 56 per cent by the addition of acid to the nutrient solution and only about 42 per cent when the manure extract was also added. The barley and rye seedlings were again affected alike, however, and no evidence was obtained, therefore, that the manure extract contained any organic compound which served to account for the difference in the effect of acid soils on the two kinds of seedlings.

A SEARCH FOR SOME DIFFERENTIATING FACTOR IN THE SOIL EXTRACT

Half of a soil aqueous extract, with 0.0015/N acidity, was distilled from a glass retort, with the result that the distillate proved to be neutral, and the acidity of the solution remaining in the retort was double that of the original. Barley seedlings were grown with optimum nutrients dissolved in the various liquids mentioned below and the following relative averages of the transpiration and weight of the green tops secured, namely: carbon-treated distilled water, 100; soil extract, 37; distillate from the soil extract, 108; and the soil extract from which a half had been distilled, 27. The transpiration in the last instance was only a half of what it was in the original soil extract, showing that the deleterious substance simply had been concentrated in the retort and not distilled off.

The toxic factors in the extract of the soil from the unlimed sulfate of ammonia plat were not segregated by dialysis, for after a strongly toxic extract had been placed in a dialyzer for one week, the diffusate and dialyzate were shown to be equally toxic to barley seedlings. This indicated that the toxicity was of a crystalloidal nature.

Upon failure to get evidence that the toxicity was probably due mainly to organic material, it was decided to continue the investigation more especially with inorganic substances in mind.

Since nitrification would not be expected to take place normally in the unlimed plat to which sulfate of ammonia is applied as a source of nitrogen, experiments were conducted with seedlings in solution to see if rye makes relatively better use than barley of sulfate of ammonia as a source of nitrogen. If such were the case, the ability of rye to grow better than barley on the plat might be explained. It may be seen from table 3, however, that the growth of the two seedlings was depressed about alike when calcium nitrate was replaced by ammonium sulfate on the basis of equal nitrogen, that is, an average depression of 63 per cent. This depression was doubtless due to the development of acidity where ammonium sulfate was used, rather than to this particular nitrogen combination; for, as may be seen in the table, it was necessary only to have present with the ammonium sulfate some calcium carbonate or sodium hydroxide in order to obtain practically normal growth. It would hardly be expected that under the experimental conditions there would be nitrification, and it is true that at least in some of the solutions, ammonium salts were left as such after the removal of the seedlings. The residual solutions when made up to the original volume had an average alkalinity in case calcium nitrate was used of 0.0002/N with phenolphthalein, and of 0.014/N with methyl orange as indicators; whereas when ammonium sulfate was used, instead of alkalinity there was an average acidity of 0.019/N with phenolphthalein and 0.0008/N with methyl orange. Carbon dioxide was eliminated from the solutions before using phenolphthalein as an indicator.

TABLE 3

Relative effect of equivalent amounts of calcium nitrate and ammonium sulfate in nutrient solutions on the average of the relative transpiration and weight of green barley and rye seedlings

	EXPERIMENT							
	I	II	III		IV		V	
	Rye	Rye	Barley	Rye	Barley	Rye	Barley	Rye
$Ca(NO_3)_2$	100	100	100	100	100	100	100	100
$Ca(NO_3)_2$ plus $CaCO_3$							97	95
$(NH_4)_2SO_4$	44	38	31	43	32	35	35	35
$(NH_4)_2SO_4$ plus $CaCO_3$							91	87
$(NH_4)_2SO_4$ plus NaOH (varying amounts)		54			60	55	88	78

The acidity of the solutions when sulfate of ammonia was unaccompanied by a base was sufficient to account for the depression in the growth of the seedlings.

In order to ascertain whether the ash constituents of the soil extract were in any way responsible for its different effects on rye and barley, an aqueous extract was made, and evaporated to dryness. The residue was ignited, and then dissolved in hydrochloric acid. Most of the acid was evaporated, and the remainder neutralized with sodium hydroxide. Nitrogen was supplied in the solution in such a proportion of ammonium and calcium nitrates as was necessary to control the reaction of the solution. To a portion of the soil extract, which was not evaporated, the same amounts of nitrogen and of sodium chloride were added as were present in the other solution.

Barley and rye seedlings were grown under neutral and acid conditions, not only in the above solutions, but in a regular nutrient solution. The results may be found in table 4. The results are so arranged that the development in the neutral solutions in each of the three cases is represented by 100 so that the relative effect of the acid cultures may be seen readily by referring to the table.

Rye exhibits its usual tendency, though less than has been sometimes the case, to withstand better than barley, the toxic effect of the soil extract in its original condition. It is of importance to notice that the same tendency also exists in connection with the acid nutrient solution containing the ash constituents only of the soil extract. That is, the growth of the rye was depressed much less than that of the barley. When the acid was added to the ordinary nutrient solution, however, the growth of the rye was, in general, depressed fully as much as that of the barley; an observation which is in accord with what has usually been noticed heretofore.

TABLE 4

The relative effect on barley and rye seedlings of an extract of an acid soil, of the ash in the same, and of an acid nutrient solution

	EXPERIMENT I				EXPERIMENT II			
	Relative weight of green tops		Relative transpiration		Relative weight of green tops		Relative transpiration	
	Barley	Rye	Barley	Rye	Barley	Rye	Barley	Rye
Soil extract of plat 23 neutralized with NaOH	100	100	100	100	100	100	100	100
Soil extract of plat 23 unneutralized	75	74	61	66	78	92	43	67
Solution of the soil-extract ash	100	100	100	100	100	100	100	100
Solution of the soil-extract ash plus H_2SO_4	82	107	75	94	74	86	43	54
Nutrient solution	100	100	100	100	100	100	100	100
Nutrient solution plus the H_2SO_4	74	79	56	58	59	50	40	25

Evidence having been secured that some inorganic element or elements were responsible for the different effects produced by the acid-soil extract, determinations were made in the fall of 1913 of certain ingredients in an aqueous extract prepared as follows from soil of the unlimed ammonium sulfate plat. Various 2-pound portions of the soil were each mixed with 2.5 liters of distilled water, and allowed to stand about an hour, after which the liquid parts were poured off to furnish 20 liters of extract, which was then passed through a Chamberland filter. This solution contained the following in parts per million: N, 15.9; SiO_2, 0.7; SO_3, 65.2, and Al_2O_3, 27.8. The last two were present in about equivalent amounts.

The two kinds of seedlings were next grown in the presence of certain of the elements not generally considered as exerting any nutrient influence on plant growth.

The effect of even chromium was determined, because a positive qualitative test for this element was reported upon examining the aqueous extract. Potassium chromium sulfate in an acid nutrient solution failed, however, to give indications that it inhibited the growth of rye seedlings any less than that of barley seedlings.

Although manganese was absent from the soil extract, recent work at the Alabama station (3) makes it of especial interest to record that in connection with three trials of potassium permanganate as an oxidizer, the results given in table 5 had been obtained, which showed that the effect of manganese on the two seedlings was not essentially different. The basal solution contained optimum nutrients.

A trace of iron was present in the soil extract but the authors had already failed to find that this element in acid solutions affected the two seedlings differently (6).

TABLE 5

Relative average transpiration and weights of green tops showing effect of potassium permanganate

	EXPERIMENT I		EXPERIMENT II		EXPERIMENT III		AVERAGE	
	Barley	Rye	Barley	Rye	Barley	Rye	Barley	Rye
No $K_2Mn_2O_8$	100	100	100	100	100	100	100	100
2 parts per million $K_2Mn_2O_8$	91	86	84	95			87	91
4 parts per million $K_2Mn_2O_8$	87	78	89	97	90	88	89	88
8 parts per million $K_2Mn_2O_8$	84	71			81	73	82	72

ALUMINUM AS THE CAUSE OF THE UNLIKE EFFECT OF ACID SOIL ON RYE AND BARLEY SEEDLINGS

The relative percentage depression in the average of the transpiration and weight of green rye and barley seedlings caused by adding to a nutrient solution sufficient aluminum, usually in sulfate, to produce in most cases about the same concentration of aluminum as was present in the soil extract, is shown below by different comparative tests:

Rye..........31, 30, 30, 26, 18, 18, 17, 30, 21, 34, 37, 22, 15, 19; Average, 25
Barley.......67, 66, 62, 47, 47, 68, 62, 57, 44, 57, 46, 56, 48, 42; Average, 55

It may be seen from the preceding values that the aluminum and accompanying acidity are much less deleterious to rye than to barley; whereas it has been shown previously that the two seedlings are affected alike by acidity when unaccompanied by aluminum. In most instances the two sets of conditions, with and without aluminum, existed in the same experiment so that the differences could not be attributable to other varying conditions. Similar results were obtained also in sand cultures.

It having been shown that there exists a specific difference in the effect of aluminum on rye and barley, it seemed probable that the element either tends to protect rye more than barley from the deleterious effect of acidity, or else it is less toxic to rye than to barley. In either case the growth of the barley would be depressed more than that of the rye.

The possibility was recognized that the association of aluminum with chromium or with silicon, two other non-nutrient ingredients of the aqueous extract, might be even more effective than the aluminum itself. A number of water cultures containing in the nutrient solution different proportions of these elements were conducted, but it was found that chromium and silicon, either with or without aluminum, exerted no unlike effect upon the two seedlings.

To decide between the two hypotheses regarding the manner in which aluminum affects rye and barley differently, it was necessary to know the comparative acidity of the nutrient solution when, to one aliquot, aluminum sulfate was added, and to another, an equivalent amount of free sulfuric acid. Under these two conditions the barley was depressed equally and the rye very unequally.

If the hydrolysis of the aluminum sulfate was insufficient to produce a degree of acidity about like that of the free sulfuric acid, then the depression in the growth of the barley must be attributable in part to the toxicity of the aluminum. Miyake (7) found that the hydrogen-ion concentration of a solution of aluminum chloride was about one-third as great as in an equivalent solution of hydrochloric acid. This led him to think that aluminum itself in some form might have been toxic, since the above-mentioned solutions with which he worked proved to be about equally injurious to rice seedlings.

In our work the nutrient solution containing aluminum sulfate was found to have about one-fourth the hydrogen-ion concentration which existed when an equivalent amount of sulfuric acid was added. This led the authors to believe that aluminum exerted its different effect because of its more pronounced toxicity to barley rather than because of an exclusive protective influence on rye.

It was recognized that extreme care was necessary in working with nutrient solutions containing such elements as phosphorus, iron and aluminum to be sure that the effect of the aluminum was not prevented by precipitation. Had this occurred in the rye cultures more than in the barley cultures, for instance, the conclusion that aluminum was less toxic to rye than to barley would have been erroneous. Owing to the difficulty of differentiating with certainty in culture solutions between a slight chemical precipitation, and turbidity naturally arising from other suspended material, certain precautions are necessary in work of this kind. Furthermore, without special precautions precipitation might take place on the roots.

When the phosphorus was reduced to only the very small amount necessary for nutrient purposes, and such proportion of ammonium nitrate and calcium nitrate used as would maintain or increase the acidity, it was felt that if a solution remained perfectly clear from standing prior to the introduction of the seedlings, it was not probable that any subsequent precipitation could have taken place.

Some attempt was made to ascertain whether aluminum is toxic in neutral or alkaline solutions, using citric acid and tartaric acids or their sodium salts for the purpose of holding the aluminum in solution, even if in complex ions. Under these conditions, however, the two seedlings seemed to be affected more nearly alike, and the difficulties of knowing positively whether the aluminum had been maintained in true solution led to the abandonment of this line of work at least temporarily. It would be very desirable to know the range of circumstances in which aluminum is toxic.

TABLE 6

The relative effect of aluminum sulfate, and its equivalent and twice this amount of sulfuric acid, on the weight of the green tops per ten barley and ten rye seedlings

SPECIAL ADDITIONS TO THE NUTRIENT SOLUTION	WEIGHT OF GREEN TOPS			RELATIVE WEIGHT OF GREEN TOPS		
	Barley (2-rowed)	Barley (6-rowed)	Rye	Barley (2-rowed)	Barley (6-rowed)	Rye
	grams	*grams*	*grams*			
None	3.88 3.80	4.63 4.63	2.78 3.09	100	100	100
8 cc. 0.1/N sulfuric acid	2.12 2.26	3.05 2.26	1.73 1.60	58	59	59
4 cc. 0.1/N sulfuric acid	3.29 2.86	3.73 3.23	2.11 2.60	82	76	83
Aluminum sulfate (added sometime previously)		3.32 2.85	2.43 2.54		67	86
Aluminum sulfate (just previously added)	2.59 2.51	2.91 3.04	2.09 2.72	68	65	83

An experiment typical of the many which have been conducted with aluminum salts will now be described somewhat in detail. It was conducted in the greenhouse between January 8 and 29, 1918. The results may be found in table 6. In the series where the aluminum sulfate is there mentioned as having been "added sometime previously," it was mixed with the nutrient solution a few weeks before the experiment was begun, to afford full opportunity for the aluminum to be precipitated if any of the ingredients could throw it out of solution. In the other series the aluminum sulfate was not added to the nutrient solution until just before it was supplied to the seedlings. There was no significant difference, however, in the two series.

Even if the aluminum remained in solution prior to the introduction of the seedlings, it was recognized that the nutrient solution must not become physiologically alkaline as a result of the growth of the seedlings for fear that the aluminum would be precipitated as a consequence and the purpose of the experiment be thwarted. Previous tests had taught us that the reaction of the nutrient solution may be controlled conveniently by varying the ratio of calcium nitrate to ammonium nitrate, and in the present experiment a sufficient proportion of ammonium nitrate was added so that the acidity of the solutions would at least not be reduced in the presence of the growing seedlings.

A liter of the basal nutrient solution contained 15 cc. 0.2/N $Ca(NO_3)_2 . 4 H_2O$, 10 cc. 0.1/N NH_4NO_3, 8 cc. 0.1/N KCl, 8 cc. 0.2/N $MgSO_4 . 7 H_2O$, 1 cc. of a solution containing 8.3 gm. of $CaH_4(PO_4)_2 . H_2O$ per liter, and 10 cc. of a dilute $Fe_2(NO_3)_3$ solution. In the series receiving the larger addition of sulfuric acid 8 cc. of a 0.1/N solution was also added in the liter. The aluminum sulfate was made equivalent to this larger application of acid, and it may be seen that the aluminum depressed the growth of barley much more than it did that of rye, although again both seedlings were depressed alike by either concentration of acid.

TABLE 7

Percentage depression caused by sulfuric acid and by aluminum sulfate

TRANSPIRATION				WEIGHT OF GREEN TOPS			
Barley		Rye		Barley		Rye	
H_2SO_4	$Al_2(SO_4)_3$	H_2SO_4	$Al_2(SO_4)_3$	H_2SO_4	$Al_2(SO_4)_3$	H_2SO_4	$Al_2(SO_4)_3$
65	71	64	31	40	43	42	28
61	54	59	18	38	33	41	24
58	58	62	31	48	56	49	37
62	49	53	34	59	42	47	40
Average 62	58	60	29	46	44	45	32

Although it is obvious that the growth of barley is depressed much more than that of rye by aluminum, it is of interest to consider whether the rye is actually affected by the aluminum itself. The results given in table 7 will assist in consideration of this point. As there arranged, the percentage depression is given on both the transpiration and weight of the green tops caused in four typical experiments by the addition singly of sulfuric acid and aluminum sulfate in equivalent amounts to an optimum nutrient solution.

It may be seen that barley was affected about alike by equivalent amounts of sulfuric acid and aluminum sulfate, but that rye was depressed about twice as much by the acid as by the aluminum salt. If the latter is hydrolyzed about one-fourth as extensively as the acid, which seems to be the case, judging from the hydrogen-ion determinations referred to previously, then not more than half the depressing effect exerted on the rye would seem to be attributable to acidity, leaving a portion of the effect to be chargeable directly to the aluminum even in case of the rye. From this point of view aluminum would seem to be some three times as toxic to barley as to rye. Only an approximate quantitative consideration, however, is warranted until more work has been done on the actual acidity of the nutrient solution as influenced by the addition of the sulfuric acid and aluminum sulfate, both before and after the growth of the barley and rye seedlings. Judging from the appearance of the roots of the seedlings, there was very little effect of the aluminum on the rye but a very marked effect on the barley (fig. 2, plate 1).

Such experiments seem to warrant the idea that aluminum itself in solution in certain acid soils may be a factor differentiating their effect on plant genera, whereas acidity from whatever source may affect the plant genera alike. Ruprecht and Morse (8) at the Massachusetts station did not discriminate as to which component of the aluminum salts was responsible for toxicity.

Investigators at the Indiana station state in connection with their work (1, p. 368) as follows:

> The facts that aluminum nitrate and soil extract of the same normality with respect to aluminum are of approximately equal toxicity, and that aluminum nitrate and nitric acid of the same normality are of approximately equal toxicity, point to the acid as the toxic agent.

If in our search for a cause of the different effect of acid-soil conditions on different kinds of plants we had not rigidly excluded every toxic factor which affected alike the two kinds of plants, which were selected because of the unlike effect of acid soils upon them, it is doubtful if a probable cause would have been discovered.

One could find readily enough, many factors toxic to plants in general. An investigator is liable to fix his attention on one of these, and because of circumstantial evidence which he accumulates, conclude that he has found the cause which is responsible for the deleterious effect of acid soils.

If, however, the very genera which are affected decidedly differently by a particular set of acid-soil conditions are grown in circumstances where a specific factor is the only variant, it will be found that many of the assumed causes are only contributory to the principal reason for the effects observed in the field.

It may be found eventually that the principal disturbing factor is different under one set of acid-soil conditions than under another set, and even that the same factor may not account for the different effects in case of all genera.

EFFECT OF MANURIAL TREATMENTS OF THE SOIL ON THE AMOUNT OF ACTIVE ALUMINUM

Inasmuch as aluminum is toxic, in connection with acid, to barley and probably other crop plants, it may be true that the improvement of certain soils by liming or phosphating is due in part to a reduction in the amount of active aluminum. To gain indications regarding this point, in the spring of 1914 samples of soil from certain permanent field plats were taken, dried, and sifted through a 1-mm. sieve. With frequent shaking for a period of three days, the soil was treated with water through which carbon dioxide was conducted in such a way as to maintain a saturated solution and atmosphere.

The following determinations were made:

PLAT NUMBER	SPECIAL FIELD TREATMENT	Fe_2O_3, Al_2O_3, P_2O_5	Fe_2O_3	Al_2O_3, P_2O_5
		per cent	*per cent*	*per cent*
23	Sulfate of ammonia, unlimed	0.063	0.007	0.056
25	Sulfate of ammonia, limed	0.040	0.010	0.030
27	Nitrate of soda, unlimed	0.044	0.010	0.034
29	Nitrate of soda, limed	0.036	0.010	0.026
54	Dissolved bone, unlimed	0.059	0.007	0.052
66	Roasted aluminum phosphate, unlimed	0.047	0.007	0.040
68	No phosphate, unlimed	0.080	0.008	0.072
67	No phosphate, limed	0.048	0.014	0.034

The amount of aluminum and phosphorus oxides, which was determined by difference, proved to be too small for separation of the two. The first four plats received an equal liberal amount of acid phosphate annually. However, experiments at this station have shown that liming tends to increase the availability of phosphorus; consequently, if the differences are attributed to aluminum there will be at least no exaggeration. In no case had the liming been sufficient to maintain even a neutral soil reaction. Nevertheless, the results show that there was probably more active aluminum in the more acid soils, especially the very acid soil from plat 23. The four remaining plats are a part of the "phosphate experiment." The results suggest that both the phosphating and the liming may have reduced the active aluminum, even though here again the soil has never been fully neutralized. The data are recorded mainly for their suggestiveness, with a full realization of their incompleteness.

To ascertain the influence of uncombined phosphoric oxide in reducing the amount of active aluminum in soil from the unlimed sulfate of ammonia plat, 250-gm. lots of the soil were mixed intimately with water and different amounts of a solution, 25 cc. of which contained 2.5 gm. of P_2O_5, and allowed to stand for about a month, when the following was found to be soluble in 20 per cent acetic acid by digesting for 24 hours at 50 to 60°C. with occasional shaking:

	P_2O_5	Al_2O_3*
	per cent	*per cent*
Check soil receiving no P_2O_5	0.013	0.566
Soil receiving 1.3 gm. P_2O_5	0.015	0.524
Soil receiving 1.9 gm. P_2O_5	0.046	0.260
Soil receiving 3.0 gm. P_2O_5	0.077	0.101

* The following percentages of certain ingredients sometimes claimed to be in a deleterious form have been found from time to time in the dry fine soil of the same general nature, which is a granitic glacial drift, namely: Al_2O_3 4.64, Fe_2O_3 3.46, Mn_3O_4 trace, soluble in a hot, strong solution of hydrochloric acid; Al_2O_3 and Fe_2O_3 1.46, soluble in 0.20/N HNO_3 in 5 hours at 40°C.; Al_2O_3 and Fe_2O_3 0.50 ,soluble in 0.04/N HNO_3; and Al_2O_3 0.20, soluble in 0.013/N HNO_3. Not enough iron was dissolved in the latter solvent to impart a yellow tint to the aluminum hydroxide precipitate, showing how relatively soluble the aluminum was in very dilute acid. Not more than a tenth as much calcium and magnesium oxides as aluminum and iron oxides is dissolved by the various solvents.

Indications were likewise obtained as to the effect of acid phosphate upon both the reaction and the aluminum of an acid soil, by using a sample which was taken from the unlimed sulfate of ammonia plat early in the spring of 1914. Three lots of soil of 2,000 gm. each were mixed respectively with 95, 190 and 380 gm. of acid phosphate. They were then kept moist and stirred frequently for about three weeks, when it was found by the calcium-acetate method that the calcium oxide requirement in pounds per two million pounds of soil was as follows: check soil, 4608; smallest application of phosphorus, 5472; medium, 7272; and largest, 11,880. The same soil treated in a similar manner, except that the lots stood for six months instead of three weeks, exhibited by the ammonia method[2] a similar increase in lime requirements with the increasing phosphate applications: namely, 7194, 9184, 11,463 and 14,783 pounds. Then the different lots of soil were placed in beakers, and nutrients were added, including a small application of mono-calcium phosphate to the soil untreated with the acid phosphate. Calcium carbonate was also added in certain beakers. Barley and rye seedlings were then grown with the average results shown in table 8, which as usual are the averages of duplicate cultures.

As usual the rye grew much better than the barley on the untreated acid soil, but not after the liming. Even the smaller amount of acid phosphate represented an application of nearly 50 tons per acre; that is, it was much larger than is made in farm practice. It is important to notice that in spite of the large amount of acidity represented by this application, the growth of the barley was markedly increased and the amount of active aluminum decreased. This reduction in active aluminum was not accompanied by an

[2] Submitted by the late L. P. Howard of the Rhode Island station to the 1916 Convention of the Association of Official Agricultural Chemists for publication in its journal, but not yet printed.

increased growth of rye, thus furnishing further evidence that aluminum is much less toxic to rye than to barley.

The progressive toxicity of aluminum sulfate was demonstrated by adding to 250 gm. of an unlimed fertilized soil in different beakers, 4, 8, 12, 16 and 24 cc. of a solution containing 13.665 gm. of hydrated aluminum sulfate per liter, and then growing barley. Without the aluminum, 1.90 gm. of the green tops were produced, and with the successive aluminum applications, 1.88, 1.30, 1.30, 1.15 and 0.85 gm., respectively.

Characteristic growth responses by barley and rye were observed by planting their seeds with basal nutrients in an unlimed soil from permanent plat 84, which for years had received no manurial treatment in the field. Without special treatment barley, as usual on acid soil, made a poor growth, 39 gm. of dry tops per 8-inch pot; while rye produced 60 gm., or the same as the barley after the soil was limed. The addition of 4.5 gm. of hydrated aluminum sulfate to the unlimed soil depressed the growth of barley 32 per cent and that of rye 11 per cent. An equivalent amount of sulfuric acid depressed

TABLE 8

Results showing effect of acid phosphate on the amount of active aluminum in the soil

SPECIAL SOIL TREATMENT	WEIGHT OF GREEN TOPS		Al_2O_3 SOLUBLE IN DILUTED ACETIC ACID
	Barley	Rye	
	gm.	*gm.*	*per cent*
None	1.05	2.02	0.105
Calcium carbonate	2.33	1.94	
Smaller amount of acid phosphate	1.80	1.74	0.039
Calcium carbonate and larger amount of acid phosphate	1.95	1.95	0.005

the barley 40 per cent and the rye 11 per cent. Again the aluminum depressed the barley more than the rye. Probably the added sulfuric acid associated itself with sufficient aluminum in the soil so that its action was similar to that of the aluminum sulfate, for by itself the acid has been shown repeatedly to depress both kinds of plants alike.

To obtain on a larger scale the effect of thorough phosphating on plants which usually respond favorably to liming, cultures were carried on in 8-inch Wagner pots, using soil from the unlimed sulfate of ammonia plat. Four different experiments were conducted using the ordinary nutrients, including phosphorus for nutrient purposes, in each pot. When this was the only treatment both table beets and cos lettuce made practically no growth and the less sensitive barley only a small one. In the first experiment with beets, the maximum yield of roots, brought about by liming was 350 gm. per pot, obtained with about 3800 pounds of calcium oxide per acre in finely divided hydrate. In spite of treatment with probably too large an amount of acid phosphate for beets, even for the purpose at hand, at the rate of about 50 tons per acre, there was a production of 167 gm. per pot, although the acid reaction to litmus paper has been much intensified. In the second similar experiment with beets it was possible to produce only 200 gm. by optimum liming; while phosphating alone, with 14 tons of acid phosphate per acre, led to the production of 107 gm. In the third experiment 200 gm. of green lettuce leaves were produced with the optimum application of lime and 73 gm. where 14 tons of acid phosphate per acre was used. A phosphating with twice this amount, however, resulted in 272 gm., or much more than was produced by any other of a large number of treatments which were made for another purpose in the same experiment (fig. 1, plate 1). The results of the fourth experiment, with barley, are shown best by the yields of the dry, mature crop given in table 9.

The striking fact is that acid phosphate in abnormal applications, which increased the acidity of acid soils, should promote normal growth where practically no growth of very sensitive crops was possible before its application.

TABLE 9

Results showing the effect of acid phosphate on the yield of barley

	DRY BARLEY STRAW AND GRAIN PER POT	
	Grams	Relative weight
No special addition	36	100
Precipitated $CaCO_3$, 2.75 tons per acre	64	178
Acid phosphate 25 tons per acre	92	256
Acid phosphate 25 tons, and $CaCO_3$ 2.75 tons per acre	105	292
Acid phosphate 50 tons per acre	126	350
Acid phosphate 50 tons, and $CaCO_3$ 2.75 tons per acre	134	372

The practical advantages of phosphating and liming may often prove to be due to the precipitation of aluminum quite as much as to supplying phosphorus as a nutrient and lime as a reducer of acidity.

SUMMARY

In the present study of the cause of the unlike effect of acid soils on different kinds of plants, rye was chosen as a plant which will grow well on such soils, and barley as one which is quite deleteriously affected by the same conditions.

Seedlings of these two plants were, however, affected about alike by a given amount of acidity in connection with nutrient culture both in water and in sand.

Sterilization of the soil, either by heat or toluol, did not cause any change which with certainty influenced differently the two kinds of seedlings.

Substances which affected rye and barley about alike, and therefore did not suggest the real differentiating factor, were as follows: Hydrogen peroxide, dihydroxystearic acid, manure extract, ammonium sulfate, potassium permanganate, chromium and silicon.

The aqueous extract of an acid soil affected barley and rye the same as the acid soil itself. By distillation, the toxic principle of the extract was concentrated in the residue, the distillate being nontoxic. The dialyzate and diffusate arising from dialysis of the extract both had the same effect upon the two seedlings.

The search was made among the inorganic constituents for the active factor, largely because the ash of the soil extract when brought into solution had the same effect as the acid soil.

Aluminum proved to be the element which was responsible for the different influence on the plants.

Equivalent amounts of aluminum sulfate and of sulfuric acid, when added to an optimum nutrient solution, produced about the same depression on the growth of barley. Although the sulfuric acid caused a similar depression of the rye, the aluminum salt caused very little depression, and scarcely affected the rye roots. The nutrient solution when it contained the acid was found to have about four times the concentration of hydrogen-ions as when it contained aluminum sulfate. Therefore, the toxic effect of the latter on the barley is attributable largely to the aluminum.

Treatment of an acid soil with either phosphoric oxide or acid phosphate reduced the amount of active aluminum in the soil. Unusually large additions of acid phosphate caused remarkable growths of plants so sensitive to an untreated acid soil that previously no growth was possible, and this was in spite of the fact that the acidity of the soil was very much increased by the acid phosphate. The active aluminum, however, was much decreased by the treatment.

The results indicate that the practical advantage of phosphating and liming may often prove to be due to the precipitation of active aluminum quite as much as to supplying phosphorus as a nutrient and lime as a reducer of acidity.

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PLATE 1.

Fig. 1 (see p. 275). Cos lettuce, showing that an unusually large amount of acid phosphate was more beneficial than lime in case of an acid soil upon which lettuce could not grow. All pots received the same basal optimum nutrients.

	green lettuce gm.
1. (At left.) No special addition	0
2. 1500 lbs. per acre of CaO in hydrated lime	70
3. 2000 lbs. per acre of CaO in hydrated lime	145
4. 3000 lbs. per acre of CaO in hydrated lime	179
5. 4000 lbs. per acre of CaO in hydrated lime	201
6. 28 tons per acre of acid phosphate	277

Fig. 2 (see p. 271). Showing the like effect of acid and the unlike effect of an equivalent amount of aluminum sulfate on barley and rye. All bottles received the same basal optimum nutrients.

	Relative transpiration	Relative weight of green tops
1. (At left.) Barley with no special addition	100	100
2. Barley with sulfuric acid	31	55
3. Barley with aluminum sulfate	24	45
4. Rye with no special addition	100	100
5. Rye with sulfuric acid	35	54
6. Rye with aluminum sulfate	65	75

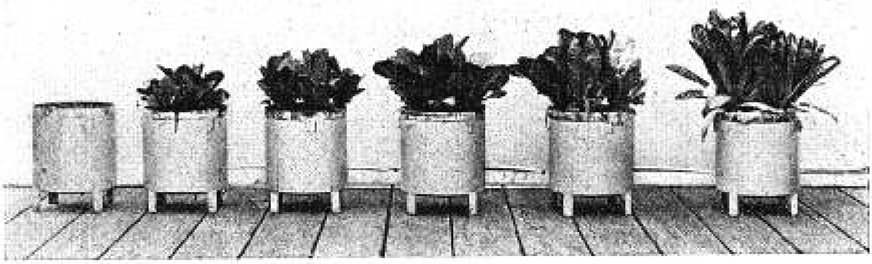

FIG. 1

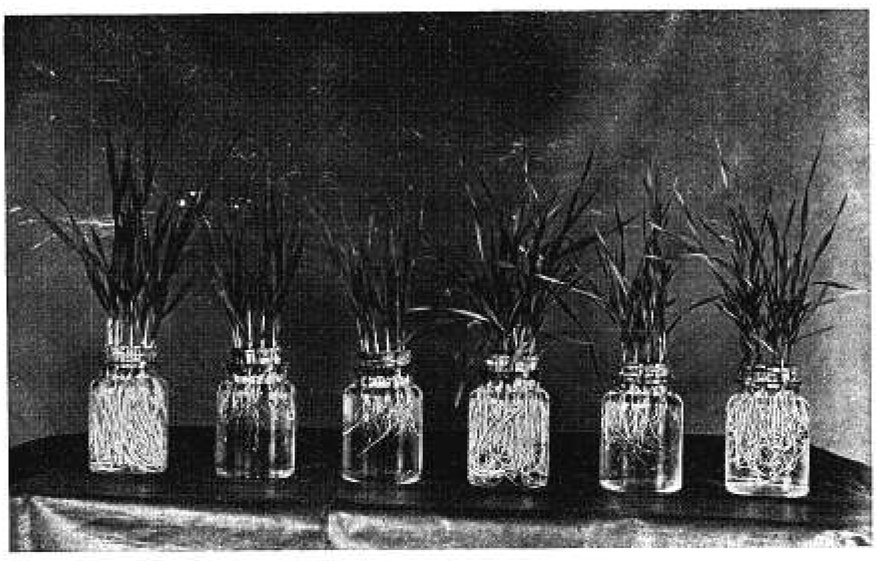

FIG. 2