ALUMINUM SALTS AND ACIDS AT VARYING HYDROGEN-ION CONCENTRATIONS, IN RELATION TO PLANT GROWTH IN WATER CULTURES

S. D. CONNER AND O. H. SEARS

Purdue University Agricultural Experiment Station[1]

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INTRODUCTION

While there is a rather extensive literature upon the subject of the injurious effect of various acids and of aluminum salts upon plants in water cultures, there are so many variables which may affect plant growth that it is difficult to correlate the results obtained by different investigators. One of the factors which may cause a great variation in growth is the kind of nutrient solution and the method of using it. Without doubt this factor is one of the most important. There are very many combinations of various salts, proportions, and strengths which have been used, as well as sizes of containers and periods of frequency of changing the nutrient—all of which may vary the results obtained. The purity of the distilled water as well as that of the salts varies greatly. The kind of plant grown, the uniformity of the seed, and its freedom from, or affection by, disease may often cause variation in results.

Abbott, Conner and Smally (1) found in 1913 that solutions of aluminum nitrate and nitric acid were toxic to corn seedlings in dilute nutrient solutions. The toxicity of the aluminum nitrate was found to be approximately equal to that of nitric acid of the same normality. They suggested that the acid radical might be the toxic agent. Miyake (6) in 1916, in a study of the effect of aluminum chloride and hydrochloric acid on the rice plant in distilled water, found that the toxicity of aluminum chloride was equal to that of hydrochloric acid of the same normality. He determined the hydrogen-ion concentration of the solutions and found that the aluminum salt was more toxic than the acid at the same hydrogen-ion concentration and concluded that aluminum itself in some way was toxic. Hartwell and Pember (3) in 1918, after considerable work to find a suitable nutrient, found that, while aluminum sulfate was of equal toxicity toward rye as was sulfuric acid, barley was much more affected by aluminum salts than by an acid of the same hydrogen-ion concentration. They concluded that the toxicity of aluminum salts on barley is attributable largely to the aluminum.

[1] Professor Sears is now with the University of Illinois, Urbana, Ill.

EXPERIMENTAL

With the object in view of investigating the relative toxicity of hydrogen ions and aluminum ions in a series of water cultures with aluminum salts and their corresponding acids, under controlled conditions, with seedlings of several cereals, experiments were started in 1919. In a first series of tests the grain was germinated in white moist silica sand, then washed and transferred to wide-mouth bottles of 480 cc. capacity. Paraffined cork stoppers were grooved on the sides and three seedlings held in place by rubber bands. In some preliminary tests the barley seedlings were partially affected by *helminthosporium* and *fusarium* enough to confuse the results. Rye and corn also were more or less affected by *fusarium* and other fungus diseases. In later tests the rye and corn were sterilized in dilute silver nitrate, then washed in water, in sodium chloride solution, and again rinsed. This almost entirely prevented any infection. The barley used in later tests through the courtesy of the Wisconsin Experiment Station, was given a hot-air treatment of 24 to 30 hours. This almost entirely prevented infection by *helminthosporium* and at the same time caused no injury to germination. With the later tests 2100 cc. wide-mouth jars were used and the seedlings were supported by cotton in ¼-inch holes cut with a cork borer in the edge of the wide, flat, paraffined corks. Germination was made in large jars of tap-water over which was stretched paraffined mosquito netting.

The first series of tests on rye, pop corn, and barley were grown in duplicate in Tottingham's (8) sub-optimiun solution, 480-cc. bottles were used and the nutrient changed weekly. The results of these tests are shown in table 1.

Both top and root weights are the relative total dry weights of the duplicate sets of six plants. A study of these results show that for barley as well as rye, the aluminum salts have given higher average yields than the acids. With pop corn there was a tendency for the aluminum salts to reduce the yield more than the acids did. These results are not believed to be significant, because the nutrient used was later shown not to be suited to show this point and equivalent pH values were not held in acids and aluminum salts.

If the results are averaged according to acid groups, there is little difference among the strong acids. The plants grown with sulfuric acid show slightly the lowest weights, then hydrochloric acid, nitric acid, phosphoric acid and tartaric acid follow in order. Tartaric acid tended to average higher than any of the mineral acids or their aluminum salts. A correlation of the pH values before and after growth, shows that in every case where there was a good growth of barley the hydrogen-ion concentration was markedly lowered. This change in pH value occurred in the N/4800 concentrations of the strong acids and their aluminum salts only. It occurred with the N/2400 as well as the N/4800 phosphoric acid solutions, and with all solutions of tartaric acid or aluminum tartrate. This is in accord with the results reported by Hoagland (4).

TABLE 1

Growth of rye, barley and pop corn in Tottingham's nutrient solution, May, 1919

NUMBER	TREATMENT	pH VALUE OF SOLUTION		WEIGHT OF PLANTS RELATIVE TO CHECK		
		Beginning	End	Rye	Barley	Corn
				per cent	*per cent*	*per cent*
1	Check	6.4	6.5	100	100	100
2	HNO_3 N/600	2.9	2.9	29	17	77
3	HNO_3 N/1200	3.1	3.1	41	24	53
4	HNO_3 N/2400	3.4	3.5	71	34	105
5	HNO_3 N/4800	3.6	6.3	73	65	186
6	$Al(NO_3)_3$ N/600	3.9	3.7	52	33	51
7	$Al(NO_3)_3$ N/1200	3.9	3.8	65	33	39
8	$Al(NO_3)_3$ N/2400	4.0	3.9	70	42	63
9	$Al(NO_3)_3$ N/4800	4.1	6.4	69	65	103
10	H_2SO_4 N/600	2.9	2.9	28	19	48
11	H_2SO_4 N/1200	3.1	3.1	32	25	61
12	H_2SO_4 N/2400	3.4	3.5	57	34	144
13	H_2SO_4 N/4800	3.7	6.3	97	53	136
14	$Al_2(SO_4)_3$ N/600	3.9	3.9	56	28	38
15	$Al_2(SO_4)_3$ N/1200	3.9	4.0	53	34	58
16	$Al_2(SO_4)_3$ N/2400	4.0	4.0	63	31	77
17	$Al_2(SO_4)_3$ N/4800	4.1	6.3	56	45	126
18	HCl N/600	2.9	2.9	20	21	41
19	HCl N/1200	3.1	3.1	29	23	70
20	HCl N/2400	3.4	3.5	61	35	85
21	HCl N/4800	3.7	6.4	78	63	93
22	$AlCL_3$ N/600	3.8	3.8	54	34	49
23	$AlCL_3$ N/1200	3.9	3.9	84	37	55
24	$AlCL_3$ N/2400	3.9	4.0	81	42	49
25	$AlCL_3$ N/4800	4.0	6.7	57	69	79
26	Tartaric Acid N/600	3.1	5.9	29	29	42
27	Tartaric Acid N/1200	3.4	6.4	61	42	60
28	Tartaric Acid N/2400	3.5	6.4	101	77	77
29	Tartaric Acid N/4800	3.8	6.5	132	87	115
30	Aluminum Tartrate N/600	3.9	6.5	96	43	110
31	Aluminum Tartrate N/1200	4.1	6.8	91	75	107
32	Aluminum Tartrate N/2400	4.1	6.5	74	92	239
33	Aluminum Tartrate N/4800	4.2	6.5	72	89	92
34	$Al_2(SO_4)_3$ N/600 + H_3PO_4 N/600	3.0	4.1	32	24	44
35	$Al_2(SO_4)_3$ N/600 + $CaH_4(PO_4)_2$ N/600	3.3	3.4	48	27	54
36	$Al_2(SO_4)_3$ N/600 + $Ca_2H_2(PO_4)_2$ N/600	3.6	3.6	53	33	86
37	$Al_2(SO_4)_3$ N/600 + $Ca_3(PO_4)_2$ N/600	4.0	5.3	56	56	119

TABLE 1—*Concluded*

NUMBER	TREATMENT	pH VALUE OF SOLUTION		WEIGHT OF PLANTS RELATIVE TO CHECK		
		Beginning	End	Rye	Barley	Corn
				per cent	*per cent*	*per cent*
38	$Al_2(SO_4)_3$ N/600 + H_2SiO_3 N/600	3.8	3.8	77	26	52
39	$Al_2(SO_4)_3$ N/600 + $CaSiO_3$ N/600	3.9	4.2	72	33	75
40	$Al_2(SO_4)_3$ N/600 + $CaCO_3$ N/600	4.3	7.0	50	55	63
41	$Al_2(SO_4)_3$ N/600 + $MgCO_3$ N/600	4.0	4.3	61	39	47
42	$Al_2(SO_4)_3$ N/600 + Dextrose 0.1 gm	3.9	4.0	58	died	died
43	$Al_2(SO_4)_3$ N/600 + Mannit 0.1 gm	4.0	4.1	53	died	34
44	$Al_2(SO_4)_3$ N/600 + Glycerine 0.1 gm	4.1	4.2	52	died	40
45	$Al_2(SO_4)_3$ N/600 + Carbon Black 0.1 gm	3.8	4.0	82	36	43
46	H_3PO_4 N/600	3.2	3.5	56	35	45
47	H_3PO_4 N/1200	3.6	4.1	45	42	98
48	H_3PO_4 N/2400	3.9	6.3	44	79	136
49	H_3PO_4 N/4800	4.2	6.4	69	86	76
50	H_2SO_4 N/600 + $CaCO_3$ N/600	3.6	6.9	none	99	200

Total dry weights of roots and tops on checks:
6 rye plants, 3 weeks old .... 0.531 gm.
6 barley plants, 3 weeks old .... 0.896 gm.
4 pop corn plants, 4 weeks old .... 0.254 gm.
Hydrogen-ion concentration was taken by colorimetric method at beginning and end of test on barley.

The only supplementary treatments which caused good growth in barley were those that decreased the hydrogen-ion concentration. It should be noted, however, that calcium carbonate was of much greater benefit in reducing the toxicity of sulfuric acid than it was in correcting the aluminum sulfate injury, although it corrected the acidity in both solutions. In some of the results on corn shown in table 1, as well as in some preliminary work with barley, the nutrient checks did not show as good growth as the treatments of weaker acids and aluminum salts. This was thought to be due at least partly to lack of available iron. For the same reason the N/4800 aluminum-salt rye cultures were inferior to those containing more aluminum. In the later tests, citrate of iron was substituted for phosphate of iron with satisfactory results. These results are in accord with the work of Jones and Shive (5) and others who have found that iron is a more important ingredient in nutrient solutions than earlier investigators thought.

Plate 1 shows the relative growth of rye, pop corn, and barley with sulfuric acid and aluminum sulphate of equivalent normality. The rye roots show a greater tolerance toward aluminum salts than either pop corn or barley. The difference in top growth is not so apparent.

It was thought, from the first year's work, that it would be necessary to devise some method of holding the hydrogen-ion concentration constant, before definite conclusions could be reached. A constant flow of nutrient was tried in a tentative test without success. The flow of nutrient was regulated by Hofmann pinchcocks. This test was a failure on account of inability to secure an equal flow in all bottles. To regulate this condition 2100-cc. bottles were used and the nutrient changed daily instead of weekly.

Barley was grown in Shive's (7) R_4C_5 sub-optimum nutrient solution in the next test. Glass bottles of 2100 cc. capacity were used and the nutrient changed daily except at the end of the test when the changes in pH values of the solutions were noted. Nutrients of 0.025, 0.1, and 0.4 atmospheres osmotic pressure and sulfuric acid of four strengths were used. Table 2 shows the growth of barley nutrients of different strength and corresponding variable hydrogen-ion concentrations. Because of the buffer action of the stronger nutrients, it was necessary to use more acid to keep the pH values constant.

TABLE 2

Growth of barley in three concentrations of Shive's R_4C_5 solution, February, 1920

Number	Treatment	pH	0.025 Atmosphere			0.1 Atmosphere			0.4 Atmosphere		
			Normality equivalent	Total weight of 4 plants	Relative growth	Normality equivalent	Total weight of 4 plants	Relative growth	Normality equivalent	Total weight of 4 plants	Relative growth
				gm.	per cent		gm.	per cent		gm.	per cent
1	Check...	5.8	0	0.8667	100.0	0	1.6615	100.0	0	2.7854	100.0
2	H_2SO_4...	3.4	N/2600	0.3997	46.1	N/2400	0.7814	47.0	N/1600	1.1999	43.1
3	H_2SO_4...	3.8	N/6200	0.5335	61.6	N/4800	0.8527	51.3	N/3300	1.1659	42.0
4	H_2SO_4...	4.0	N/9000	0.5332	61.5	N/7200	1.0371	62.4	N/4100	1.4744	52.9
5	H_2SO_4...	4.2	N/12000	0.6022	69.5	N/9600	1.0118	60.9	N/4700	1.8917	67.1

The normality equivalent given in the table is the normality of a solution made with pure water and the given amount of acid. Table 2 shows that the stronger the nutrient, the greater was the growth; but that there is a somewhat closely corresponding depression in growth of treated plants as conpared with check plants. The amounts given are the total weights of four barley plants. Figure 1 shows graphically the pH values of the different nutrient solutions after 3 weeks' growth of barley. These values were determined by the colorimetric method in duplicate solutions. The two checked quite closely in all readings and the values used are the average of both determinations. The change in values took place in proportion to the size of the plants. The richer the nutrient, the greater was the pH change; also, the weaker the acidity, the greater the change.

In May and June, 1920, new series of water cultures were conducted with rye, barley and corn. Shive's R_4C_5 nutrient of 0.2 atmospheres pressure was used. Lime water was added to bring it to a pH value of 6.3. Sulfuric acid

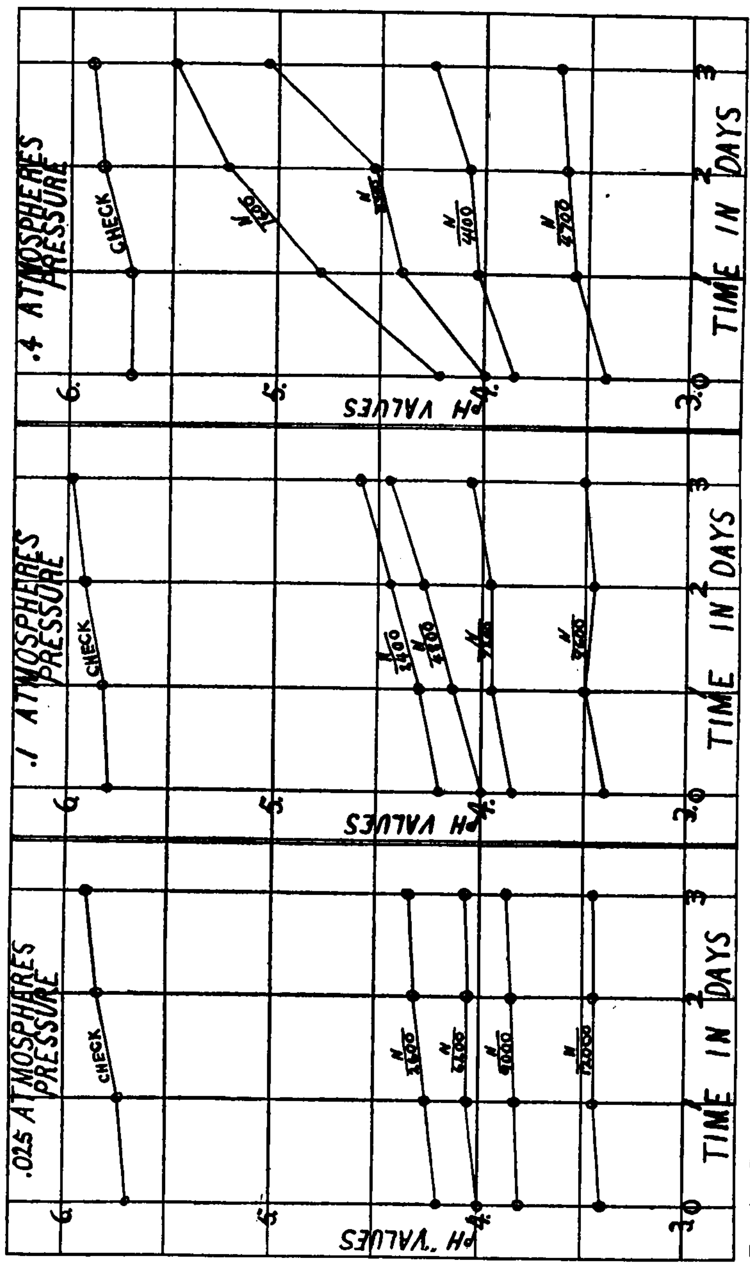

Fig. 1. Change in Hydrogen-Ion Concentration of Shive's R_4C_5 Nutrient Solution of Varying Strength and Acidity, Due to Growth of Barley in it

and aluminum sulfate were added to vary the pH from 3.6 to 5.7 on the acid and from 3.9 to 5.7 for the aluminum sulfate. The value pH 3.9 was taken as the strongest concentration for aluminum sulfate because it would take an excessively large quantity of aluminum sulfate to increase the concentration beyond pH 3.9. Table 3 shows the treatment, hydrogen-ion concentration of nutrient used, and the relative weights of rye, barley and yellow dent corn grown n water cultures. These results confirmed those of the previous tests, that aluminum salts on an average were less toxic than the same hydrogen-ion concentration of acid, even when the pH value was maintained by frequent changing of nutrient in large containers. The weights given are for the air-dry total roots and tops of four plants grown in duplicate jars. Shive's nutrient has a fairly large amount of phosphate in it, thus allowing for the possibility of aluminum precipitation. Plate 2 shows the growth of barley grown

TABLE 3

Growth of rye, barley and corn with constant hydrogen-ion concentration in Shive's R_4C_6 solution

NUMBER	TREATMENT	NORMALITY EQUIVALENT	pH	4 DRY RYE PLANTS, 3 WEEKS		4 DRY BARLEY PLANTS, 3 WEEKS		4 DRY CORN PLANTS, 10 DAYS	
				Total weight	Per cent of check	Total weight	Per cent of check	Total weight	Per cent of check
				gm.		*gm.*		*gm.*	
1	H_2SO_4.......	N/1800	3.6	0.5591	43	0.8647	31	1.45	78
2	H_2SO_4.......	N/3000	4.3	0.4033	31	1.6750	59	1.66	90
3	H_2SO_4.......	N/4000	5.0	0.9269	72	1.5277	54	2.29	124
4	H_2SO_4.......	N/4800	5.7	1.3241	103	2.6647	94	2.06	111
5	$Al_2(SO_4)_3$.....	N/1000	3.9	0.5416	43	0.9597	34	1.59	86
6	$Al_2(SO_4)_3$.....	N/1750	4.3	0.9155	71	1.8081	64	1.63	88
7	$Al_2(SO_4)_3$.....	N/2500	5.0	0.9671	75	2.6494	93	1.85	100
8	$Al_2(SO_4)_3$.....	N/3500	5.7	1.0857	84	2.7252	96	2.18	118
9	Check.......	0	6.3	1.2872	100	2.8363	100	1.85	100

in Shive's nutrient at the end of 3 weeks. Both roots and tops show a gradual increase in size when the hydrogen-ion concentration is lowered either in the presence of sulfuric acid or aluminum sulfate. Some difference in habit of root growth may be noted when comparing the acid with the aluminum salt.

Plate 3 shows the growth of dent corn with the treatments given in table 3. Although the nutrient was changed daily and the pH value kept constant, the corn shows an astonishingly healthy appearance at pH 3.6 in the sulfuric acid solution. It is doubtful if any natural soils ever have a pH value as low as 3.6. The results given in table 3 as well as those in table 1 show that corn has done better with a pH value around 5 than it has at 6.3 and 6.4.

In trying to correlate these results with those of Miyake (6) and Hartwell and Pember (3) it should be noted that Miyake did his work with distilled water containing no nutrients. Hartwell and Pember used a nutrient low in phosphate, also one which they said "must not become physiologically alkaline as a result of the growth of the seedlings, for fear that the aluminum would be precipitated." To do this, they replaced part of the nitrate with an ammonium salt. A preliminary test with Hartwell and Pember's nutrient showed that there was a tendency for their nutrient not only not to become alkaline, but it actually became more acid as the plants removed ammonium ions.

Table 4 shows the relative elementary composition of the nutrient solutions used in the various tests. The ideal nutrient for such studies remains to be worked out. Hartwell and Pember's nutrient allows for very good growth in control bottles but the ammonium ion should be reduced in proportion to the nitrate ion in order more nearly to hold the nutrient at a fixed hydrogen-ion concentration. If nutrients are changed daily or oftener and the plants grown in large containers this is not so important a factor. While Tottingham's nutrient which we used, contained approximately the same amount of phosphorus as Hartwell and Pember's nutrient, it was very much more dilute

TABLE 4

Relative composition of different nutrients

ELEMENT	TOTTINGHAM'S	SHIVE'S	HARTWELL AND PEMBER'S
	gm. per liter	*gm. per liter*	*gm. per liter*
P	0.002	0.055	0.002
N	0.008	0.042	0.070
K	0.010	0.067	0.030
Ca	0.007	0.060	0.053
Mg	0.009	0.013	0.020
S	0.012	0.018	0.026

so far as the other elements were concerned, and did not allow good growth in the check solutions.

As a further check on the question, barley and rye were grown in Hartwell and Pember's nutrient. Table 5 gives the treatment, pH values and relative whole plant weights of the barley and rye at the end of 2 weeks. The pH values were held fairly constant by daily changes of nutrient in 2100-cc. bottles. In a separate test in the small 480-cc. bottles the same nutrient with barley growing in it changed from pH 6.0 to pH 4.3 in three days. The nutrient solutions above pH 4.2 all tend to approach an equilibrium at about pH 4.2 whether containing sulfuric acid or aluminum sulfate or no added treatment. Table 5 shows that aluminum sulfate is much more toxic to barley than sulfuric acid, except at a hydrogen-ion concentration of 5.0 or above. Similar results were obtained in small bottles. Rye is more tolerant than barley toward aluminum but even rye did better with the acid than it did with the aluminum sulfate. There was no sign of aluminum precipitation with Hartwell and Pember's nutrient as there was with Shive's, yet the nutrient seemed to contain enough phosphate for normal growth. Plate 4 shows the relative growth of barley and rye at different hydrogen-ion concentrations with sulfuric acid and aluminum sulfate in Hartwell and Pember's nutrient. Both roots and tops of barley were stunted by the aluminum salts. These last results seem to show fairly conclusively that aluminum is in itself toxic. Everything seems to indicate that phosphorus will help prevent aluminum toxicity.

Both pot and field tests at the Indiana Agricultural Experiment Station (2) bear out the contention that aluminum is in itself toxic and that with many soils and crops the presence of soluble salts of aluminum is a more important factor than is the mere hydrogen-ion concentration of the soil.

It must be granted, however, that everything else being equal, the higher the hydrogen-ion concentration, the more chance there is for aluminum to

TABLE 5

Growth of barley and rye in Hartwell and Pember's nutrient

NUMBER	TREATMENT		pH	RELATIVE WEIGHTS	
				Barley	Rye
		cc.		*per cent*	*per cent*
1	0.2*N* H_2SO_4	2.00	3.9	73	65
2	0.2*N* H_2SO_4	1.00	4.2	93	95
3	0.2*N* H_2SO_4	0.50	5.0	90	90
4	0.2*N* H_2SO_4	0.25	5.7	101	95
5	0.2*N* $Al_2(SO_4)_3$	5.00	3.9	47	55
6	0.2*N* $Al_2(SO_4)_3$	1.30	4.2	68	65
7	0.2*N* $Al_2(SO_4)_3$	0.75	5.0	91	80
8	0.2*N* $Al_2(SO_4)_3$	0.50	5.7	121	90
9	(Check)		6.3	100	100

be present in soluble form. Thus for two reasons a determination of hydrogen-ion concentration in the soil is of value in determining its productivity.

The methods involving the use of salts of strong acids, such as the Hopkins potassium nitrate method, are very valuable from a practical as well as a theoretical standpoint. They show the amount of soluble aluminum present in the soil better than other types of soil acidity methods, such as the lime-water methods, which in adition measure the less toxic acid, organic compounds in the soil.

SUMMARY

1. Water cultures of barley, rye and pop corn in Tottingham's sub-optimum nutrient solution showed approximately the same degree of toxicity with acids and aluminum salts, of equal normality.

Wherever good growth was made the hydrogen-ion concentration of the solution was decreased.

About the same toxicity was obtained with acids and aluminum salts of nitric, sulfuric and hydrochloric acids. Phosphoric acid showed less, and tartaric acid the least, toxicity.

2. With Shive's R_4C_5 nutrient at 0.025, 0.1 and 0.4 atmospheres osmotic pressure, and with varying hydrogen-ion concentration, greater growth was obtained with the stronger solutions. The ratio of growth of treated plants at the varying pH values to that of the check was approximately the same with the nutrient at all strengths.

Wherever growth was made a lowering of the hydrogen-ion concentration was noted. This was in proportion to the size of the plants.

3. Three series of cultures were made with barley, rye and dent corn in Shive's nutrient, with four corresponding degrees of hydrogen-ion concentration for sulfuric acid and for aluminum sulfate. It was found that sulfuric acid was more toxic at the same pH value than aluminum sulfate with this nutrient. More or less precipitate was noticed in the bottles containing aluminum salts.

In this test 2100-cc. containers were used and the nutrient changed daily to prevent variation in pH value.

4. Hartwell and Pember's nutrient, which contains very much less phosphorate in proportion to the other elements, was used in cultures with barley and rye at the same pH value of sulfuric acid and aluminum sulfate.

In this nutrient aluminum sulphate proved to be much more toxic to barley than did the same hydrogen-ion of sulfuric acid. Rye was slightly more injured by the aluminum salts than by the acid.

Hartwell and Pember's nutrient tends to become more acid as the plants grow.

5. It is concluded that the toxicity of aluminum salts is due to the aluminum ion more than it is to the hydrogen ion on such plants as barley and that this toxicity is reduced when much phosphate is used in the nutrient.

These results confirm the conclusions of Hartwell and Pember and Miyake.

6. Acid soils are toxic to many plants largely because they contain easily soluble aluminum salts.

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PLATE 1

Illustrations of Water Cultures with Varying Strengths of Sulfuric Acid and Aluminum Sulfate; Tottingham's Nutrient.

Fig. 1. Rye.
Fig. 2. Barley.
Fig. 3. Pop Corn.

FIG. 1

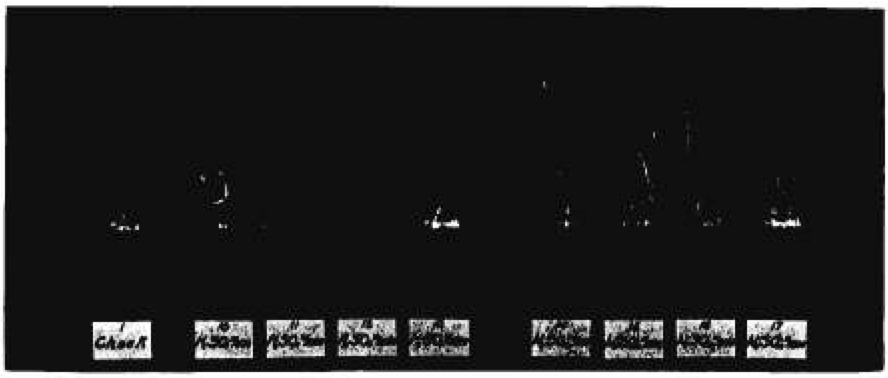


FIG. 2

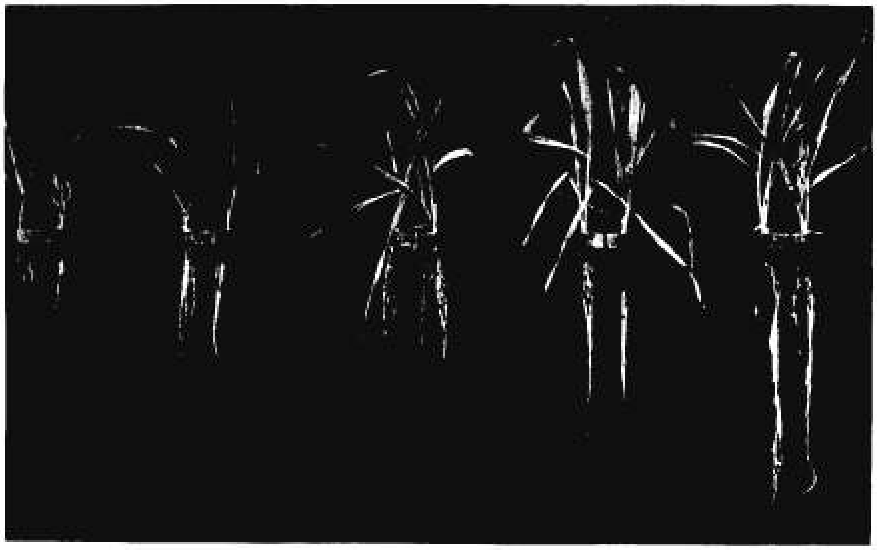
FIG. 3

PLATE 2

Illustrations of water cultures with barley in Shive's nutrient. See table 3 for treatments.

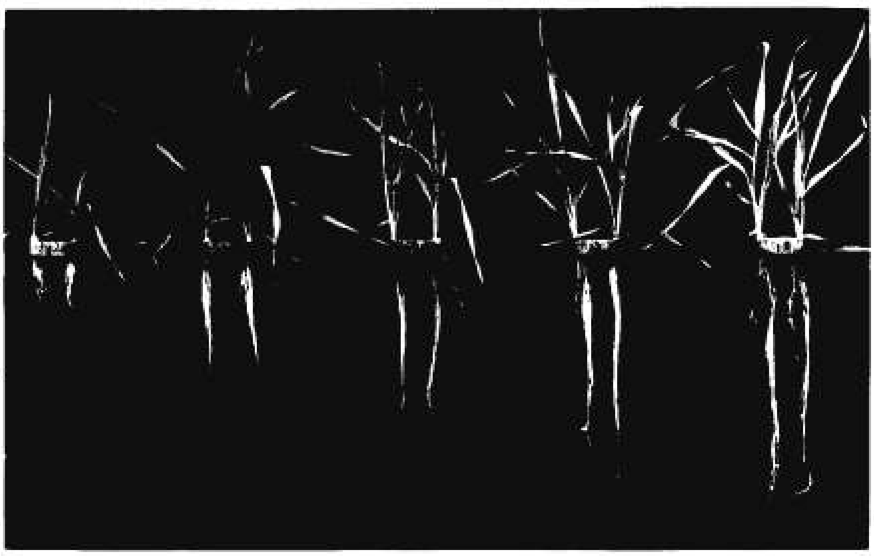
Fig. 1. Growth of barley with varying pH values of sulfuric acid. Check plants at right.

Fig. 2. Growth of barley with varying pH values of aluminum sulfate. Check plants at right.



pH 3.6 H_2SO_4 | pH 4.3 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 6.3 Check

FIG. 1



pH 3.8 $Al_2(SO_4)_3$ | pH 4.3 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$ | pH 6.3 Check

FIG. 2

PLATE 3

Illustration of Water Cultures with Dent Corn in Shive's Nutrient at Varying pH with H_2SO_4 and $Al_2(SO_4)_3$. See Table 3 for Treatments, Check at Right.

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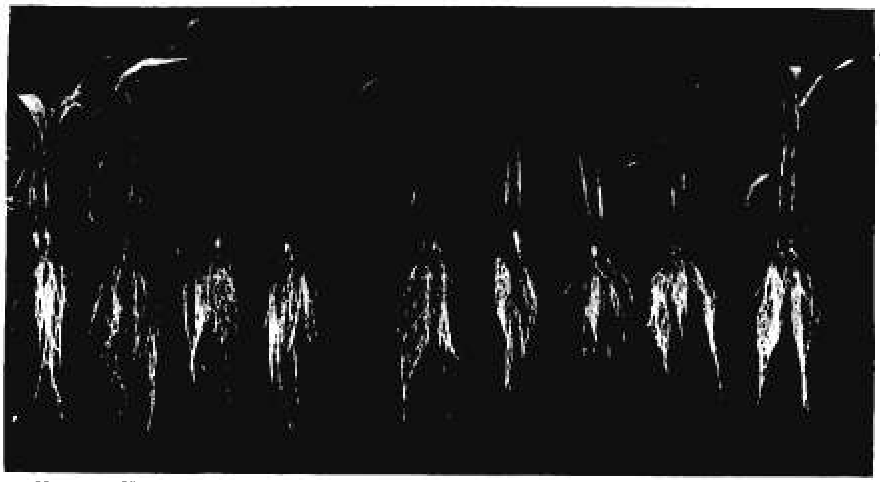
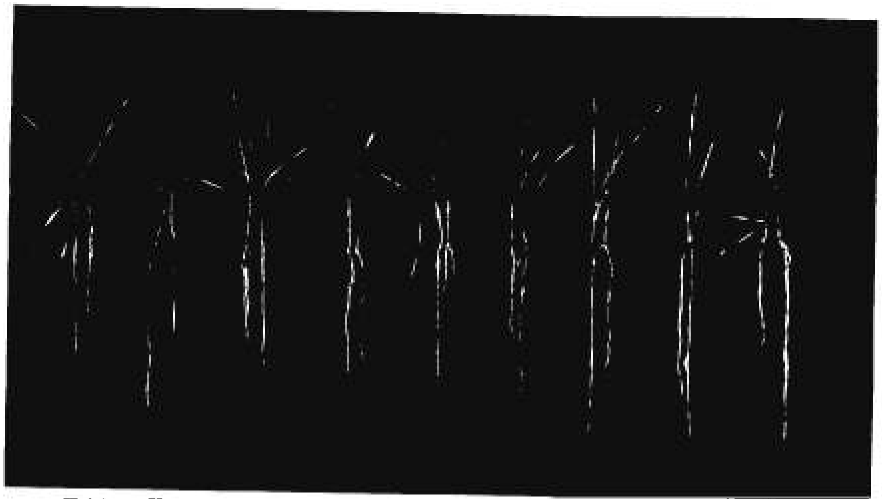


pH 3.6	pH 4.3	pH 5.0	pH 5.7	pH 3.8	pH 4.3	pH 5.0	pH 5.7	pH 6.3
H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	Check

PLATE 4

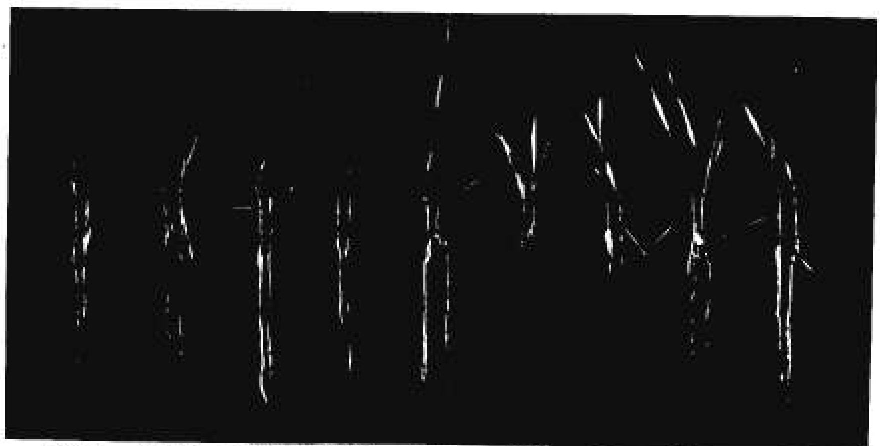
Illustrations of Water Cultures in Hartwell and Pember's Nutrient. See Table 5 for Treatments, Check at Left; Otherwise Numbered from Left to Right.

Fig. 1. Rye.
Fig. 2. Barley.



pH 6.3 check | pH 3.9 H_2SO_4 | pH 4.2 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 3.9 $Al_2(SO_4)_3$ | pH 4.2 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$

FIG. 1



pH 6.3 Check | pH 3.9 H_2SO_4 | pH 4.2 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 3.9 $Al_2(SO_4)_3$ | pH 4.2 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$

FIG. 2