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TOXICITY OF ALUMINUM ON SEEDLINGS AND ACTION OF CERTAIN IONS IN THE ELIMINATION OF THE TOXIC EFFECTS¹

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(WITH FOUR FIGURES)

Introduction

The physiological action of aluminum ions in a nutrient medium has been studied in humid areas for approximately 25 years. The relative abundance in the earth of this element would suggest frequent solution of portions, but the solution tension of aluminum compounds in nature prevents appreciable quantities from reaching the ionic stage. It has been found, however, that aluminum occurs in nearly all seed plants, which would indicate that the hydrogen ion concentration in the immediate area of roots is not the same as its concentration in the soil mass.

The toxicity of aluminum is not so easily determined as is the toxicity of the salts of the alkali and alkali earth elements. This is due to the fact that the salts of aluminum which are appreciably soluble are those of the strong acids, and these salts in turn are strongly hydrolyzed in aqueous solution, resulting in secondary formation of an acid. This in turn gives rise to hydrogen ions. The trials made may result in part from the measurement of the sum total of hydrogen and aluminum ion toxicity. This may occur in water or in soil media.

McLEAN and GILBERT (16) found that the organic compound, aluminum citrate, would in part pass through a pyroxylin membrane, and that the non-diffusible colloid portion could induce toxicity.

In general the object of these experiments was to attempt to ascertain the action of aluminum on plants. It was hoped to determine: (1) the toxicity of aluminum salts of organic acids (these salts do not precipitate aluminum hydroxide when the alkalinity is raised); (2) the counter-active

¹ Contribution of the Massachusetts Agricultural Experiment Station no. 175.

effects of aluminum toxicity by the presence of a certain anion $(OH)^-$, and cations Ca^{++} and K^+ .

Review of literature

The trials to determine the action of aluminum on plants in nutrient solutions and in soil have been numerous. The harmful effects of the aluminum ion in water are not difficult to demonstrate, but when attempts are made with a three phase and heterogeneous medium such as soil, where the varied hydrogen ion concentration, adsorptive properties, varied quantities if water, and diverse activity of microorganisms enter the picture, the matter is largely one of circumstantial evidence with respect to evaluating the deleterious effects of aluminum.

The reaction of plants to aluminum is in a measure dependent upon their degree of adaptation to their habitat. Thus plants which are closely related to those of the prehistoric past subsist on less potassium, calcium, and magnesium and have in their ash abundant quantities of aluminum, iron, and silica. STOKLASA (27) has found that xerophytes and mesophytes are sensitive to aluminum while hydrophytes are to a greater degree resistant to the element. One of the lycopods contains slightly more than 35 per cent. of aluminum oxide in its ash, while a plant like the common pea may contain but 20 p.p.m. in the ash (2). Mesophytes that by chance grow in a medium of moist or marshy ground contain more aluminum than those adapted to cultivated soil.

The harmful effects of aluminum as suggested by STOKLASA (29) are contractions of the protoplasm, and stronger solutions may soften or even dissolve this substance. He found that when strong harmful concentrations were used there was less aluminum absorbed by the plant than when more dilute solutions were used, and from this concludes that the process is not one of simple absorption but one of alteration of permeability and disturbance of the cell colloids. This eventually leads to outward passage of calcium, potassium, and magnesium. The aluminum in turn prevents entrance of excess iron into the tissues. SKEEN (25) has found that calcium ions have an antagonistic effect upon the aluminum which causes the toxicity. Also MCLEAN and GILBERT (15) have demonstrated that aluminum poisoning was accompanied by reduced absorption of dyes, of nitrates, and of water. The aluminum was found for the most part in the cortex and concentrated in the nucleus of the protoplasm.

RUPRECHT (23) states that the first layer or two of cells in the growing part seem to be principally affected. The harm was probably due finally to lack of nourishment rather than to poisoning itself. Szücs (31) concludes that aluminum, like yttrium and lanthanum, has the capacity to retard plasmolysis instead of increasing permeability as was formerly thought. This effect is to retard the relative capacity to take up other nutrients. It solidifies protoplasm. DENISON (7) found that aluminum salts stimulate ammonifying organisms but act adversely upon nitrifying bacteria. Mc-GEORGE (13) finds that sugar cane grown in acid soils containing soluble iron and aluminum is characterized by abnormal accumulations of these elements in the nuclei surrounding the xylem cells at the nodal point of the stalk. MAGISTAD (17) states that water cultures of aluminum were found to prevent the formation of lateral rootlets on barley, but not on rye.

INCREASED GROWTH RESPONSE DUE TO ALUMINUM.—ROTHERT (22), one of the first investigators of aluminum toxicity, reported that definite limited amounts of aluminum salts may stimulate plant development. McLEAN and GILBERT (16) found that concentrations of aluminum in solutions of low concentration, such as 3–13 p.p.m., stimulate growth. SOMMER (26), by careful purification of salts, found that millet showed a markedly increased growth rate due to the presence of aluminum in the solution. The effect was especially marked with respect to the quality of the seeds. MAZÉ (18), also by using extreme care in purification of salts, found aluminum essential for adequate development of corn. STOKLASA (28), by using a low concentration (0.0002 atomic weight of aluminum per liter) obtained increased growth of plants as compared with those solutions containing no aluminum.

In the plant world there is obviously an extreme variance of tolerance and requirement as concerns elements; and a generalization or incompatible comparison is always misleading. The indirect effects of aluminum may not be due to the aluminum but to the acidity produced by the salt. This is especially true for the aluminum salts of strong acids.

COVILLE (6), in order to attain a high acidity for acid loving plants, Rhododendron, Vaccinium, Franklina, and Hydrangea, added aluminum sulphate and obtained remarkable results in soils that had become too alkaline.

CONDITIONS CONDUCIVE TO ACTIVE ALUMINUM.—Active aluminum is found more abundantly (1) in acid soils, (2) in soils low in organic matter, (3) in humid areas when the seasonal water supplies are low, and (4) in arid regions when the alkalinity becomes high. STOKLASA (30) states, "the richer the soil in decomposed organic matter the stronger the combination of aluminum sulphate and aluminum chloride which can be used without injury to plant life." GILBERT and PEMBER (9) found the dry weight yields of barley plants grown in samples of acid soils from several soil types, widely separated geographically, very closely correlated with active aluminum. This corresponds with the findings of PIERRE, POHLMAN, GORDON, and MCILVAINE (21). TURNER (34) found that aluminum is invariably actively present only in soils with pH values less than 5.1. The amount of replaceable aluminum, however, is not regular with respect to hydrogen ion con-

centration. MIYAKE (20) reports that the toxicity of aluminum chloride for rice seems to be approximately equal to that of hydrochloric acid of the same normality, but that the concentration of hydrogen ions found formed by the hydrolysis of aluminum chloride is less than that formed by dissociation of hydrochloric acid of the same normality.

It is stated by MAGISTAD (17) that data relating to the solubility of aluminum in water and soil solutions show that at pH 5 there are 1-2 p.p.m. of aluminum oxide equivalent in solution. As the acidity decreases to the neutral point the solubility decreases almost to zero. When the acidity becomes greater than pH 5 the solubility increases until pH 4.5 is reached, at which point the solubility increases rapidly. Strongly alkaline soils were found to contain much aluminum. One, at pH 9.01, contained 31 p.p.m. These data are analogous to those of LIGON and PIERRE (11).

McGEORGE (13) states that acidity *per se* or hydrogen ion concentration of the intensity present in our most acid soils has absolutely no influence upon growth of sugar cane. It is, he states, the aluminum salts which are present in such soil types that retard plant growth. McGEORGE, BREAZEALE, and BURGESS (14), in their work on electrometric titration measurements of the solubility of aluminum compounds at different hydrogen ion concentrations, conclude that from pH 5 to 7.5 aluminum is almost completely insoluble, while at pH 8 the aluminate forms. Black alkali soils contain appreciable amounts of water soluble aluminates.

TOLERANCE OF DIFFERENT PLANTS.—MCLEAN and GILBERT (15) found considerable variance in plant tolerance. Most sensitive are lettuce, beets, timothy, and barley; medium sensitive are sorghum, cabbage, oats, and rye; resistant are corn, turnips, and red top (the last is especially resistant). SKEEN (25) found the white lupine to be about three times as resistant to aluminum as is the kidney bean.

REMEDIAL MEASURES FOR ALUMINUM TOXICITY.—The suggestions that have been made for alleviating the toxicity of aluminum have been the application of neutralizing agents and buffers. Also the calcium ion has been demonstrated to overcome it (25). It has been found that lime, phosphate, and organic matter remedy the bad effects of aluminum. In reclamation of alkaline lands summer leaching has been suggested for elimination of soluble aluminum compounds.

Other workers have made valuable suggestions as to active aluminum occurrence and agencies for its elimination (5, 10, 19, 7, 20, 3, 4, 1, 24).

OPPONENTS OF THEORY OF ALUMINUM TOXICITY IN SOILS.—Owing to the apparent action of aluminum in acid solutions and soils, the question has been raised as to which ion, the H⁺ or Al⁺⁺⁺, is the one that is destructive to plant tissue. Thus after years of experimentation, adversaries of the aluminum toxicity theory maintain that inaccurate observations account for the appraisal of this element in toxicity. STOKLASA (30) says: "The statement that aluminum compounds in the soil have an injurious effect on plant growth is based on no exact experimental foundation." LINE (12) states regarding the toxic aluminum theory of soils that "old evidence and fresh experimental work seem to show that this theory is no longer tenable," that most of the aluminum in the water is in the form of colloidal hydroxide.

Methods

Aluminum citrate and aluminum tartrate were the salts used. Seedling stages of the soy bean (variety Manchu), corn (variety Sweepstakes), and Japanese buckwheat were the plants employed in the growth trials.

The seeds were germinated in a dish in the dark, and when the sprouts were about 10 mm. long they were transferred to the growth medium. The sprouts of the buckwheat were about 8 mm. long. The roots dipped into the solution.

CRITERIA OF GROWTH.—Three criteria of growth were used: (1) root elongation, (2) length of top, and (3) total dry weight. There is greater simplicity with respect to behavior in the seedling stage than in the later periods of growth. In the early stages of growth the plant is well supplied by ions, and the organic matter of the seed is sufficient to afford protection from starvation of plants grown in distilled water. The protoplasm seems to be reactive to the toxic constituents of the solution.

The investigation involved the toxicity of aluminum citrate for corn; aluminum citrate and tartrate for soy beans; and aluminum tartrate for buckwheat. The concentration of each salt ranged from 0.00012 to 0.006 M, or 2, 5, 15, 30, 50, 70, 85, 95, 98, and 100 per cent. of 0.006 M. Tests were also made to show the effects upon growth of mixtures of the aluminum salt and calcium nitrate, calcium hydroxide (freshly prepared), and potassium hydroxide. In the case of the mixtures eleven sets of percentage molecular proportions were used: 0+100, 2+98, 5+95, 15+85, 30+70, 50+50, 70+30, 85+15, 95+5, 98+2, and 100+0.

The methods relating to roots were essentially the same as those described by TRELEASE and TRELEASE (32) and by EISENMENGER (8). For each culture two pyrex beakers (tall form without lip) were used. The smaller beaker was of 300-cc. capacity, the larger of 600-cc. capacity. Over the top of the small beaker was stretched a piece of paraffined mosquito netting which was secured below the rim by a ligature of paraffined thread. The smaller beaker was placed inside the larger one, and the culture solution was poured in until the liquid levels inside and outside the smaller beaker were even at its top.

When the seedlings from the germinating dish were of the required length they were placed on the mosquito netting so that the roots dipped

into the culture solution. Duplicate cultures of 25 plants were used for each experimental solution, a total of 50 plants for each concentration. The cultures were placed in a dark room and the seedlings were allowed to grow until the primary roots of the control culture had acquired an average length of about 95 mm., or until these roots had elongated 85 and 87 mm. (95-10 or 95-8).

The length of the primary root, the maximum length of top, and the total dry weight of each individual plant were then recorded and the average computed. From the average of root length was deducted the average length of the roots at the time the seedlings were taken from the germinating dish. The difference constituted the average root elongation value for the The growth data here presented are relative values. Each relaculture. tive growth value was obtained by dividing the average elongation of root, top, and total dry weight of a given culture by the average elongation of root, top, and total dry weight of the control culture and multiplying this quotient by 100. With each group were four beakers containing 25 plants each in a complete nutrient medium. These 200 plants were designated as controls. For corn the control was Knop's solution. For soy beans and buckwheat the control contained: CaHPO₄, 0.0011 M; MgSO₄, 0.0057 M; CaSO₄, 0.0013 M; KCl, 0.0037 M; and KNO₃, 0.007 M. There was little difference in the controls with respect to reactivity toward plants, but for soy beans the latter was slightly more favorable than was Knop's.

The temperature during the growth period of the seedlings varied from 21° to 22° C. The time required for the roots of the control solution to acquire an additional length of 85 or 87 mm. varied from 95 hours for buckwheat to 116 hours for corn. When a series of single salt solutions was used, two additional cultures of 25 plants each grown in distilled water were used. The distilled water was obtained from a Barnstead still.

Discussion

Corn

Roots.—As previously stated, corn has been regarded as one of the plants more resistant to aluminum toxicity. In the present experiment, however, 15 per cent. of 0.006 M aluminum citrate exerted a decidedly retarding effect on the growth of corn roots. This amount is approximately equal to 22 p.p.m. of aluminum (fig. 1 B). Amounts higher than this exerted only a slightly increased toxicity on roots compared with that at 15 per cent. of 0.006 M. The plants thus affected showed lesions of the primary root principally. The end of this root eventually assumed the nature of an open wound. The lateral roots showed no such effects except those branching from near the injury. (See table I for comparative data.)

Roots	Tops	Dry weight	PERCENTAGE 0.006 M ALUMINUM CITRATE	REACTION
%	%	%	%	pH
66.3	53.8	68.4	0	5.82
83.5	62.1	88.0	2	4.75
48.6	51.1	76.6	5	4.50
24.8	50.9	67.7	15	4.50
18.7	32.5	52.1	30	4.50
12.6	32.2	47.1	50	4.05
16.8	29.4	47.5	70	3.64
11.4	29.4	39.0	85	3.55
11.9	22.4	39.5	95	3.55
13.3	24.9	42.5	98	3.50
7.2	13.4	34.9	100	3.43

TABLE I

GROWTH OF CORN SEEDLINGS IN SOLUTIONS OF ALUMINUM CITRATE

Roots are by far the most injured by the toxic solution; their variation due to variable concentration causes more marked breaks in the growth curve than is the case with curves of the relative length of tops and curves of the total dry weight. Thus the relative length of tops and relative total dry weight (fig. 1 B, C) indicate that the greatest deviation occurs between concentrations of 15 and 30 per cent. of 0.006 M, while the greatest deviation in relative root length occurs between 5 and 15 per cent. of 0.006 M.

TOPS AND TOTAL DRY WEIGHT.—The relative diminution due to aluminum citrate is greater for the tops than for total dry weight. In view of the fact that the diminution of relative length of roots is most pronounced,

Roots	Tops	Dry weight	PERCENTAGE 0.006 M CALCIUM HYDROXIDE	REACTION
%	%	%	%	pH
66.4	53.9	68.8	0	6.61
93.1	55.2	75.2	2	7.85
117.1	68.4	87.5	5	7.85
121.6	74.3	97.9	15	9.0
111.7	80.2	82.6	30	9.6
80.5	63.6	88.0	50	9.6
57.7	53.9	79.5	70	9.6
32.0	28.9	62.3	· 85	9.6
25.0	30.6	71.1	95	9.6
26.1	37.6	69.5	98	Λ^*
26.9	44.9	71.2	100	Λ^*

TABLE II GROWTH OF CORN SEEDLINGS IN SOLUTIONS OF CALCIUM HYDROXIDE

* Λ indicates values greater than preceding figure.

ROOTS	Tops	DRY WEIGHT	Percentage 0.006 M aluminum citrate	PERCENTAGE 0.006 M CALCIUM HYDROXIDE	REACTION
%	%	%	%	%	pH
27.0	44.9	71.2	0	100	V*
23.0	50.0	77.0	2	98	9.0
16.8	46.6	82.0	5	95	9.0
41.7	66.5	113.4	15	85	8.8
84.5	69.2	100.7	30	70	8.37
126.7	78.3	110.6	50	50	5.60
94.5	57.2	78.9	70	30	4.18
42.2	36.1	62.5	85	15	3.70
14.0	20.6	49.1	95	5	3.40
12.4	11.3	42.5	98	2	3.40
7.2	13.4	34.6	100	0	3.43

TABLE III

GROWTH OF CORN SEEDLINGS IN SOLUTIONS OF ALUMINUM CITRATE + CALCIUM HYDROXIDE

* V indicates values above pH 9.0.

it is probable that the plants affected contained less water or had more thickened anatomical parts than the normal plants, as is the case in some pathological conditions. The corn grown in the higher aluminum concentrations probably was competing more for water than were normal plants.

MIXTURES OF ALUMINUM CITRATE AND CALCIUM HYDROXIDE.—In growing plants in mixtures of the salts of the more electro-positive elements, the relative effects are more easily shown, for the growth effects are for the most part those produced by the cations. When mixtures containing aluminum salts are concerned a more complex relationship is introduced, owing to the secondary products of hydrolysis. Thus in the solutions of all aluminum salts

Roots	Tops	DRY WEIGHT	Percentage 0.006 M calcium nitrate	REACTION
%	%	%	%	pH
66.4	53.8	68.8	0	$\bar{6.61}$
96.1	82.1	89.5	2	6.67
94.1	82.1	95.9	5	6.37
99.9	97.0	97.8	15	6.30
92.3	97.8	97.4	30	6.25
78.9	85.8	76.7	50	6.25
83.0	90.7	83.3	70	6.14
87.8	93.1	91.9	. 85	5.95
81.1	84.3	88.6	95	5.95
78.0	93.4	83.6	98	5.95
75.5	78.1	77.0	100	5.51

TABLE IV

GROWTH OF CORN SEEDLINGS IN SOLUTIONS OF CALCIUM NITRATE

TABLE V

GROWTH OF CORN SEEDLINGS IN SOLUTIONS OF ALUMINUM CITRATE + CALCIUM NITRATE

Roots	Tops	DRY WEIGHT	PERCENTAGE 0.006 M ALUMINUM CITRATE	Percentage 0.006 M calcium nitrate	Reaction
%	%	%	%	%	pH
75.5	78.1	77.0	0	100	5.07
88.7	48.2	· 71.3	2	98	4.33
77.1	76.1	70.8	5	95	4.05
55.7	65.7	62.8	15	85	3.85
62.4	63.9	70.5	30	70	3.68
45.9	46.6	54.0	50	50	3.66
32.2	41.6	57.9	70	30	3.50
20.2	35.2	57.5	85	15	3.50
10.3	17.7	40.8	95	5	3.50
3.6	12.4	30.3	98	2	3.50
7.2	13.4	34.9	100	0	3.51

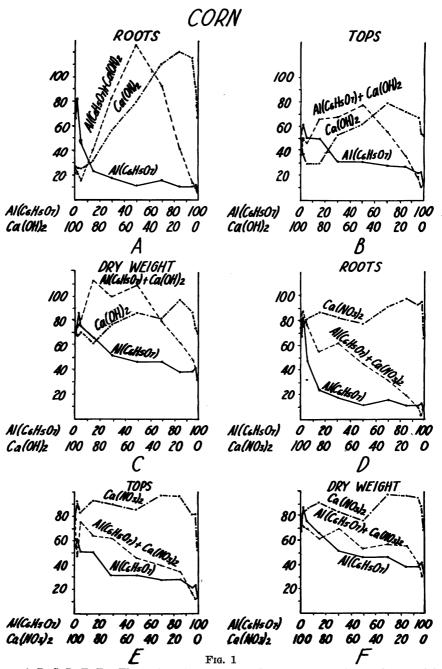
the cation gives rise to hydrogen ions in measurable quantities. We are not dealing with two elements, which are cations, but in addition the cation hydrogen ions in excess of hydroxyl anions. The influence of the additional ions renders interpretation of relative growth data more difficult. In this investigation growth data were compared when corn seedlings were grown in aluminum citrate alone, in calcium hydroxide, and in mixtures of the two compounds. The total molecular concentration was not changed, 0.006 M of calcium hydroxide and aluminum citrate.

In order to express more adequately the effects of these compounds when

Roots	Tops	DRY WEIGHT	PERCENTAGE 0.006 M ALUMINUM CITRATE	PERCENTAGE 0.006 M POTASSIUM HYDROXIDE	REACTION
%	%	%	%	%	pH
13.6	52.9	79.8	0	100	9.8
31.7	52.3	77.8	2	98	9.7
16.7	36.1	65.8	5	95	9.7
18.5	38.4	74.5	15	85	9.6
25.2	49.0	79.1	30	70	9.0
73.8	69.6	94.3	50	50	8.36
32.0	43.5	68.0	70	30	6.00
14.3	36.5	70.4	85	15	4.15
11.9	29.2	67.1	95	5	3.84
12.1	25.6	64.1	98	2	3.45
7.2	13.4	34.9	100	0	3.43

TABLE VI

Growth of corn seedlings in solutions of aluminum citrate + potassium hydroxide



A, B, C, D, E, F: Elongation of corn roots and tops together with total dry weight in simple solutions and mixtures of aluminum citrate and calcium hydroxide, also in simple solutions and mixtures of aluminum citrate and calcium nitrate. Ordinates represent percentages of elongation and total dry weight; abscissas represent percentage molecular proportions of 0.006 M.

in mixture, it is essential to know what is the effect of calcium hydroxide when used singly (see table II). The molarity was based on 0.006 M calcium hydroxide. The curve (fig. 1 A) would indicate that low concentrations of calcium hydroxide are stimulating to growth but that at higher concentrations the relative growth curve rapidly falls for the relative root length, and to a lesser degree for tops and total dry weight. The deleterious effect is not to a great extent due to the calcium ion, but rather to the hydroxyl ion. For all cases the range of toxicity is greater for the aluminum salt than for the calcium base (fig. 1 A, B, C).

One of the most outstanding characteristics of growth relationships is the abnormal stimulation to growth of roots in the seedling stage when the plants are grown in mixtures of aluminum citrate and calcium hydroxide (table III). In part this is due to the neutralization of the acidic properties of the aluminum compounds. The neutralization is not the cause of the increased growth, however, for roots and total dry weight are greater than the growth results with either the aluminum salt or the calcium base. This reaction does not confine itself to single groups, but applies to all plants used in the experiment, which represent the mean of thousands of plants. It would seem that a neutral salt would indicate the effect of calcium ion without the accompanying neutralization of the hydroxyl ion.

It may be stated that the combined action of the hydroxyl ion and the calcium ion results in a marked effect in overcoming the toxicity of the aluminum and the hydrogen ions in growth trials.

GROWTH RESULTS OF MIXTURES OF CALCIUM NITRATE AND ALUMINUM CITRATE.—In single salt solutions one of the salts least toxic to seedlings is calcium nitrate in dilute solutions (8). The low toxicity makes it difficult to secure consistent growth results (table IV). The growth of corn seedlings in varying percentage proportions of 0.006 M was not greatly reduced from that of the controls. It does not modify to any degree the hydrogen ion concentration of a medium in which it is placed. When various molecular proportions of calcium nitrate and aluminum citrate are mixed, the results indicate that the aluminum ions and hydrogen ions increase the toxicity of the solution as compared with the results obtained from the calcium nitrate salt used singly, but that the calcium salt ameliorates the toxic effects of the aluminum ion. It can definitely be stated that the calcium ion exerts an antagonistic action on the aluminum ion as concerns growth promotion. As is shown by the relative growth promoted by the addition of calcium and hydroxyl ion formed, however, the nearly neutral salt in no instance has the extreme action that is seen when calcium oxide is used instead of the nitrate (fig. 1 D, F and table V).

ALUMINUM CITRATE AND POTASSIUM HYDROXIDE.—Potassium hydroxide was used in mixtures with aluminum citrate to determine to what extent it

TABLE VII

GROWTH OF CORN SEEDLINGS IN SOLUTIONS OF CITRIC ACID EQUIVALENT IN ACIDITY TO CORRESPONDING ALUMINUM SALT

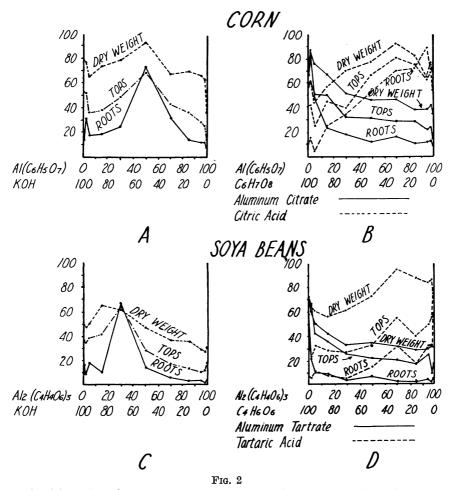
Roots	Tops	Dry weight	EQUIVALENT IN PH OF ALUMINUM CITRATE PERCENTAGE 0.006 M	REACTION
%	%	%	pH	pH
66.4	53.9	68.8	0	5.82
72.3	68.6	77.8	2	4.75
89.0	62.4	65.4	5	4.50
72.2	75.6	83.3	15	4.50
70.1	81.6	93.1	30	4.50
51.4	66.5	78.0	50	4.05
34.1	39.9	70.7	70	3.64
25.0	45.5	57.3	85	3.55
4.5	25.2	45.4	95	3.55
15.7	42.2	60.9	98	3.50
10.2	41.7	54.8	100	3.43

would resemble calcium hydroxide in growth promoting properties when mixed with the same aluminum salt. In no instance did it cause the abnormally large growth which occurred with the calcium base. There was low toxicity over a wide range of concentration of the mixture as shown by total dry weight. For roots and tops a point was attained where marked improvement occurred, 50 per cent. of 0.006 M of each component. On one side of this point the hydrogen and aluminum ions were apparently too

TABLE VIII

Growth of soy bean seedlings in solutions of aluminum tartrate + potassium hydroxide

Roots	Tops	DRY WEIGHT	PERCENTAGE 0.006 M ALUMINUM CITRATE	PERCENTAGE 0.006 M POTASSIUM HYDROXIDE	REACTION
%	%	%	%	%	pH
16.9	38.1	49.4	0	100	9.8
8.6	34.7	47.8	2	98	9.4
18.2	38.5	50.8	5	95	9.2
10.1	41.4	65.8	15	85	9 .0
67.8	64.4	62.4	30	70	9.0
14.2	28.9	47.2	50	50	7.66
6.0	17.8	36.9	70	30	5.30
3.0	13.9	36.4	85	15	4.15
4.3	11.0	29.3	95	5	3.85
1.4	11.8	26.2	98	2	3.56
4.8	18.0	31.4	100	0	3.45



A: Elongation of corn roots and tops together with total dry weight of corn seedlings grown in simple and mixed solutions of aluminum citrate and potassium hydroxide.

B: Elongation of corn roots and tops in addition to total dry weight of seedlings grown in aluminum citrate, and in citric acid, the latter of sufficient concentration to make the acid solution of pH equal to the corresponding aluminum salt solutions.

C: Elongation of soy bean roots and tops in addition to dry weight of seedlings grown in simple and mixed solutions of aluminum tartrate and potassium hydroxide.

D: Elongation of soy bean roots and tops in addition to total dry weight of seedlings grown in aluminum tartrate and tartaric acid. Concentration of the acid was sufficient to make it of pH equal to the corresponding salt solutions.

active, with little antagonism of the potassium ion toward the aluminum; and on the other side the alkalinity was too pronounced. The general outline of the curve would suggest a point of neutralization for best relative growth with meager action of potassium in retarding the influence of aluminum (fig. 2 A and table VI).

COMPARATIVE EFFECT OF ALUMINUM CITRATE AND CORRESPONDING CITRIC ACID.—Some controversy has arisen regarding the extent to which the hydrogen ion causes the deleterious effects in aluminum toxicity experiments. In order to make an approximate comparison, corn seedlings were grown in water solutions that were made acid with citric acid to the same extent as were the corresponding aluminum citrate solutions. This was done by comparing indicator reactions. In the extremes of low concentration the growth was not very different. As the concentration of the salt and the acid increased there was a gradual fall in the relative growth. The fall in the growth curve (fig. 2B) is more rapid for the aluminum salt than for the corresponding acid. Thus at 50 per cent. of 0.006 M, the relative growth value of corn roots for aluminum salt is approximately 12 as compared with 51 for the acid (see table VII). At 30 per cent. of the same total concentration for the total aluminum salt concentration on corn roots the value is about 18, and for the acid, 70. This would suggest that the toxicity of aluminum is always augmented by hydrogen ions, but the relative effects are not nearly of equal value. It may be stated that much of the actual toxicity of aluminum salts is due to the aluminum ion.

SOY BEANS

Soy beans were grown during the seedling stage in various percentage proportions of 0.006 M aluminum tartrate and citrate. Aluminum tartrate contains proportionately twice as much aluminum as does the same molarity of aluminum citrate. Tartaric acid is a dibasic acid, while the citrate is a salt of a tribasic acid.

Roots.—At a concentration of 5 per cent. of 0.006 M aluminum tartrate, the toxicity toward the root system is nearly equal to the maximum, equivalent to about 16 p.p.m. of aluminum.

TOPS AND TOTAL DRY WEIGHT.—The maximum toxicity as indicated by tops and total dry weight is not attained until the plants are grown in a concentration equal to 30 per cent. of 0.006 M. This is only slightly less than 100 p.p.m. (fig. 3 A, B, C). At this concentration and higher the roots seemingly did not grow at all.

As with corn, the soy beans were grown in solutions containing fractional parts of the total molecular concentration, 0.006 M calcium hydroxide. At moderately low concentrations there is a marked stimulation to growth in the seedling stage. This increase is measurably greater than that of the control. Although soy beans have been classified as of low lime requirement (33), concentrations of calcium hydroxide equivalent to 0.0018 M of calcium appear to augment growth above the control for roots of the beans.

Roots	Tops	Dry weight	TARTARIC ACID EQUIVA- LENT TO PH OF CORRE- SPONDING PERCENTAGE OF ALUMINUM SALT	REACTION
%	%	%	%	pH
59.6	73.3	76.8	0	6.61
32.8	55.5	87.4	2	4.45
32.4	49.4	84.5	5	4.44
17.8	40.1	88.9	15	4.25
32.1	55.7	95.8	30	3.80
15.5	33.0	73.2	50	3.62
5.9	27.5	61.4	70	3.54
8.3	29.7	56.2	85	3.54
11.9	33.6	61.3	95	3.45
6.9	24.6	65.8	98	3.49
7.5	38.8	66.8	100	3.45

TABLE IX GROWTH OF SOY BEAN SEEDLINGS IN SOLUTIONS OF TARTABLE ACID

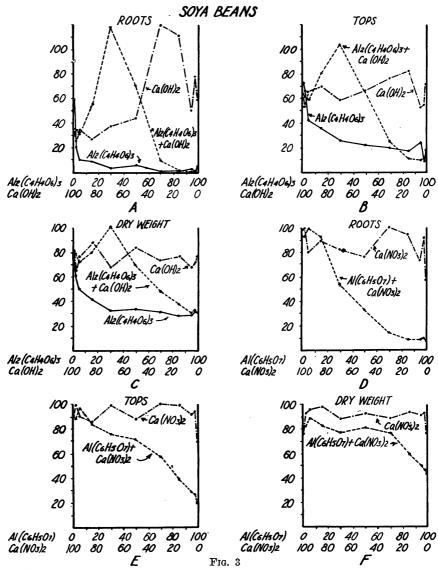
Above this concentration the growth of roots falls rapidly. The various concentrations of calcium oxide do not materially affect the relative growth of tops and total dry weight. The lowest concentration is not appreciably different in affecting growth promotion from that of the highest concentration.

MIXTURES OF ALUMINUM TARTRATE AND CALCIUM HYDROXIDE.—When the aluminum salt and the calcium base are mixed in various proportions the growth stimulation properties are changed. The marked relative growth is indicative when the proportions of 0.006 M are 30 per cent. of the aluminum salt and 70 per cent. of the base. The pH of the solution promoting maximum

Roots	Tops	Dry weight	PERCENTAGE 0.006 M ALUMINUM TARTRATE	REACTION
%	%	%	%	pH
59.7	73.3	76.8	0	6.61
21.4	66.7	61.6	2	4.75
10.9	42.5	50.9	5	4.44
9.8	36.8	52.9	15	4.25
4.5	26.9	33.2	30	3.80
6.6	22.5	34.8	50	3.62
0.4	20.9	32.2	70	3.54
0.5	17.5	29.0	85	3.54
3.0	25.0	29.5	95	3.45
0.5	9.9	31.9	98	3.45
4.8	18.0	31.4	100	3.45

TABLE X

GROWTH OF SOY BEAN SEEDLINGS IN SOLUTIONS OF ALUMINUM TARTRATE



A, B: Elongation of roots and tops of soy beans grown in simple and mixed solutions of aluminum tartrate and calcium hydroxide. Ordinates represent percentages of elongation for standard solution; abscissas represent percentage molecular proportions of 0.006 M.

C: Dry weight of soy beans grown in simple solutions and mixture of aluminum tartrate and calcium hydroxide.

D: Elongation of roots of soy beans grown in simple salt solution and mixtures of aluminum citrate and calcium nitrate.

E: Elongation of tops of soy beans grown in single salt solutions and in mixtures of aluminum tartrate and calcium nitrate.

F: Dry weight of soy beans grown in single salt solutions and mixtures of aluminum tartrate and calcium nitrate. Ordinates represent percentages of elongation and total dry weight; abscissas represent percentage molecular proportions of 0.006 M.

Roots	Tops	Dry weight	PERCENTAGE 0.006 M CALCIUM HYDROXIDE	REACTION
%	%	%	%	pH
59.7	73.3	76.8	0	6.61
78.7	55.5	73.0	2	7.85
50.6	53.2	67.6	5	7.85
111.2	83.0	77.3	15	8.10
120.0	76.9	74.6	30	9.7
44.2	66.8	84.3	50	9.7
38.3	59.1	67.5	70	9.7
27.6	70.1	88.7	85	9.8
35.1	66.4	76.8	95	9.8
24.2	53.5	64.6	98	Λ
36.5	64.7	82.5	100	Λ

TABLE XI GROWTH OF SOY BEAN SEEDLINGS IN SOLUTIONS OF CALCIUM HYDROXIDE

growth in single calcium hydroxide solutions was slightly above 9 (table XI). The pH of the mixture solution yielding best relative growth was about 6.5 (table XII). The beneficial effects of the mixture were in part due to calcium ion with an accompanying optimum pH for this particular concentration. The abrupt drop in growth curve suggests neutralization. It might be added that calcium hydroxide and aluminum salts are the only mixtures used that yield results in which the stimulation to growth in some instances is higher than that of the controls. The writer has not a positive explanation as of behavior. The comparison is made with mixtures of aluminum salt and cal-

TABLE XII Growth of soy bean seedlings in solutions of aluminum tartrate + calcium hydroxide

Roots	Tops	DRY WEIGHT	Percentage 0.006 M aluminum tartrate	Percentage 0.006 M calcium hydroxide	REACTION
%	%	%	%	%	pH
36.6	64.7	82.5	0	100	
35.3	62.2	79.9	2	98	
31.4	59.4	72.8	5	95	
54.1	81.1	80.1	15	85	7.65
118.1	104.3	100.8	30	70	6.50
71.5	65.4	70.3	50	50	5.66
10.3	25.4	48.9	70	30	4.18
1.2	11.8	38.6	85	15	3.70
0.0	10.0	31.0	95	5	3.60
1.3	12.0	33.5	98	2	3.60
4.8	18.0	31.3	100	0	3.45

Roots	Tops	Dry weight	PERCENTAGE 0.006 M CALCIUM NITRATE	REACTION
%	%	%	%	pH
59.7	73.3	76.8	0	6.61
92.5	94.8	92.8	2	6.65
74.0	92.5	91.0	5	6.37
95.0	99.8	93.4	15	6.30
100.2	100.7	89.0	30	6.25
76.7	88.4	92.7	· 50	6.14
82.8	99.4	88.3	70	5.95
89.4	85.3	97.0	85	5.95
80.1	90.1	95.9	95	5.95
99.3	99.5	92.9	98	5.95
98.6	90.7	76.0	100	5.51

TABLE XIII

GROWTH OF SOY BEAN SEEDLINGS IN SOLUTIONS OF CALCIUM NITRATE

cium nitrate, and mixtures of aluminum salt and potassium hydroxide. This would suggest that an expression of pH is more significant when stated in relationship to other elements than as an entity itself.

MIXTURES OF ALUMINUM CITRATE AND CALCIUM NITRATE.—The toxicity of calcium nitrate toward soy bean seedlings is only slight, approximately like that of the same salt toward corn (table XIII).

Mixtures of calcium nitrate and aluminum citrate are more indicative of an approximate mean of the toxicity of calcium nitrate and aluminum citrate each used singly. Another trial of a series of concentrations with

TABLE XIV

GROWTH OF SOY BEAN SEEDLINGS IN SOLUTIONS OF ALUMINUM CITRATE + CALCIUM NITRATE

ROOTS	Tops	DRY WEIGHT	PERCENTAGE 0.006 M ALUMINUM CITRATE	PERCENTAGE 0.006 M CALCIUM NITRATE	REACTION
%	%	%	%	%	pH
93.0	90.7	81.2	0	100	5.07
92.8	87.9	81.9	2	98	4.33
99.6	96.4	88.8	5	95	4.05
92.3	84.0	82.6	15	85	3.85
54.0	75.8	77.3	30	70	3.68
33.2	71.9	81.0	50	50	3.66
14.8	57.8	76.7	70	30	3.50
8.7	39.3	59.5	85	15	3.50
8.6	28.6	50.1	95	5	3.50
9.1	26.9	46.8	98	2	3.50
8.1	19.7	43.8	100	0	3.51

Roots	Tops	Dry weight	PERCENTAGE 0.006 M ALUMINUM TARTRATE	REACTION
%	%	%	%	pH
5.7	13.5	29.7	0	6.61
9.0	13.5	25.1	2	4.75
3.7	11.3	29.9	5	4.44
3.1	10.1	33.7	15	4.25
15.1	15.2	56.3	30	3.80
13.4	12.0	61.3	50	3.62
14.8	14.3	53.7	70	3.54
12.1	10.4	52.3	85	3.54
14.3	10.7	31.6	95	3.45
5.3	9.4	39.4	98	3.49
11.5	8.1	20.0	100	3.45

TABLE XV Growth of buckwheat seedlings in solutions of aluminum tartrate

aluminum citrate used singly would have lent itself to a fuller explanation of this action. The two growth curves, however, that of calcium nitrate and that of aluminum citrate and calcium nitrate, are not greatly different from those when corn was used; it thus seems a reasonable conclusion that the growth curve of the single aluminum salt would not be greatly different from that for corn (table XIV).

The calcium ion effect on total dry weight suggests a definite detoxifying effect. As in corn, this is more pronounced for relative total dry weight and relative length of top than for roots (fig. 3 D, E, F).

TABLE XVI Growth of buckwheat seedlings in solutions of aluminum tartrate + calcium hydroxide

Roots	Tops	DRY WEIGHT	PERCENTAGE 0.006 M ALUMINUM TARTRATE	PERCENTAGE 0.006 M CALCIUM HYDROXIDE	REACTION
%	%	%	%	%	pH
127.9	70.9	93.7	0	100	v
177.5	73.6	94.0	2	98	9.0
194.7	66.6	86.6	5	95	8.0
168.3	66.4	77.4	15	85	7.65
81.0	52.8	90.1	30	70	6.50
21.9	17.9	43.2	50	50	5.60
22.2	10.2	24.3	70	30	4.18
16.7	11.4	21.1	85	15	3.70
17.7	8.1	16.1	95	5	3.40
16.2	7.4	20.5	98	2	3.40
11.5	8.1	20.0	100	0	3.40

MIXTURES OF ALUMINUM TARTRATE AND POTASSIUM HYDROXIDE.—To determine the effect of the different hydrogen ion concentrations, bean plants were grown in mixtures of the two compounds aluminum tartrate and potassium hydroxide. As with corn, there seemed to be a rather definite point for favorable growth promotion. The potassium ion here as before did not seem to overcome the toxicity to any great extent; but at one concentration, 30 per cent. aluminum tartrate, 0.006 M, and 70 per cent. potassium hydroxide, 0.006 M, there was a fair medium for growth promotion. It is the writer's opinion that it is more of an index of favorable hydrogen ion concentration than a favorable mixture of the other cations, aluminum and potassium. The pH for the best growth in this trial was between 8 and 9 (table VIII). This was approximately the same as for corn in the aluminum citrate and potassium hydroxide mixture.

TABLE XVII

Growth of buckwheat seedlings in solutions of aluminum tartrate + potassium hydroxide.

Roots	Tops	Dry weight	PERCENTAGE 0.006 M ALUMINUM TARTRATE	Percentage 0.006 M Potassium Hydroxide	REACTION
%	%	%	%	%	pH
1.6	9.2	24.9	0	100	9.6
2.8	9.4	28.4	2	98	9.4
3.1	10.3	26.7	5	95	9.2
16.4	13.8	31.2	15	85	9.0
87.6	78.7	71.5	30	70	9.0
13.7	37.2	44.4	. 50	50	7.66
4.3	13.7	24.6	70	30	5.30
4.0	10.1	23.5	85	15	4.15
3.1	6.5	12.0	95	5	3.84
3.5	6.5	10.7	98	2	3.56
11.7	8.1	20.0	100	0	3.45

It is worthy of note that the seemingly optimum pH of solutions for the seedling stage is not like that of most soils for yielding crops. The optima are higher for solutions. For permanent growth in soils at high pH much of the common vegetation of a humid region would not thrive so well as at a lower pH. This may be due to precipitation and complete isolation of some required element of the field, or it may be possible that the hydroxyl ion only slowly permeates the protoplasm of the seed and does not disturb the equilibrium during the short time the seedling gets its nutrients from the seed.

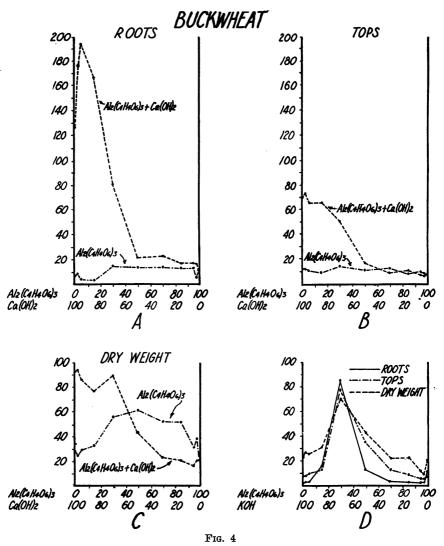
COMPARISON OF TOXICITY OF ALUMINUM TARTRATE AND TARTARIC ACID.— Water solutions were made acid with tartaric acid, comparable to the acidity of the corresponding aluminum salt, aluminum tartrate, at different concentrations and soy bean seedlings were grown in the solution. This was a similar procedure to that adopted for corn. The results are as with corn in citric acid. The aluminum salt solutions with hydrogen ion concentrations the same as those of the corresponding acid caused lower relative growth rates than did the acid. This was the case for roots, tops, and total dry weight (fig. 2 D and tables IX and X).

BUCKWHEAT

Corn and soy beans bore considerable resemblance in their reaction to aluminum salts. Buckwheat in certain respects demonstrates a different behavior. This plant in the seedling stage is seemingly more sensitive to distilled water-low osmotic pressures. This was indicated by the results of several trials, each trial including 50 seedlings. Also for single salt cultures of aluminum tartrate there is little difference between the comparative lengths of tops and roots (table XV). The plant seems to be more sensitive to low concentrations than it is to moderate concentrations of aluminum tartrate. At 0.0018–0.003 M the relative growth is better for roots, tops, and total dry weight than it is at lower and higher concentrations of the same salt. In other experiments the relative growth. In the case of buckwheat the relative top length is almost equally affected. The total dry weight is higher, suggesting low water content or thickening and branching of stems and roots.

MIXTURES OF ALUMINUM TARTRATE AND CALCIUM HYDROXIDE.—Relative growth of buckwheat is promoted by the higher concentrations of lime rather than by the lower concentrations. The root system is most markedly affected by high proportions of calcium hydroxide (approximately 95 per cent. 0.006 M calcium oxide and 5 per cent. 0.006 M aluminum tartrate). This effect diminishes rapidly with lower lime nutrients, until at the point at which the proportions are 50 per cent. of 0.006 M lime and 50 per cent. of 0.006 M aluminum tartrate the results are almost the same with respect to relative growth as if no lime were added at all (table XVI). The same behavior applies, only to a more limited degree, to the case of relative length of tops. With respect to total dry weight the mixture finally indicates over a range a condition of apparent additive effect with respect to toxicity, the mixture promoting a smaller relative growth than the single toxic salt (fig. 4 A, B, C).

MIXTURES OF ALUMINUM TARTRATE AND POTASSIUM HYDROXIDE.—When potassium hydroxide is mixed with aluminum citrate in different proportions the growth is retarded markedly except in one proportion. This proportion is approximately 30 per cent. of 0.006 M aluminum tartrate and 70



A: Elongation of roots of buckwheat seedlings grown in single salt solutions of aluminum tartrate, and in mixed solution of aluminum tartrate and calcium hydroxide.

B: Elongation of tops of buckwheat seedlings grown in single salt solutions of aluminum tartrate, and in mixed solution of aluminum tartrate and calcium hydroxide.
C: Total dry weight of buckwheat seedlings grown in single salt solutions of

aluminum tartrate and in mixed solutions of aluminum tartrate and calcium hydroxide.

D: Elongation of roots and tops in addition to total dry weight of buckwheat seedlings grown in mixtures of aluminum tartrate and potassium hydroxide. Ordinates represent percentages of elongation and total dry weight; abscissas represent percentage molecular proportions of 0.006 M. per cent. 0.006 M potassium hydroxide. In all others the growth falls off markedly. For seedlings growing in water solutions this probably indicates an optimum pH. The potassium evidently does not have much effect in alleviating the toxicity of aluminum, and at the higher pH the condition is too alkaline for the plants to thrive. The optimum pH is almost 9 (table XVII). This optimum does not nearly approach the optimum for mixtures of the aluminum salt and lime with respect to the degree of relative growth (fig. 4 D). Mixtures of lime and aluminum salts for all plants investigated have wide and high limits of growth, while potassium mixtures at nearly the same pH have narrower and lower limits of relative growth.

Summary

1. Organic aluminum compounds exert a distinct toxic effect on the plants of corn, soy beans, and buckwheat. The toxicity increases with increased concentration.

2. The toxicity for the three plants could be most effectively overcome by calcium hydroxide. Calcium nitrate could be used as an antagonist of aluminum, but not as effectively as the calcium base.

3. Potassium hydroxide was less effective in counteracting the toxicity of aluminum than was calcium hydroxide. It apparently served to neutralize the acidity of the aluminum salt.

4. The favorable hydrogen ion concentration is not the same for all solutions. The optimum pH varies with the components and their proportions present in the solution.

5. Comparing the hydrogen ion concentration of the organic acids with similar hydrogen ion concentrations of the corresponding aluminum salts of these acids, it is shown that at appreciable concentrations the aluminum salt suppresses growth to a markedly greater extent than does the acid.

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