6-1-1929

The Use of Certain Crop Plants in the Determination of "Active" Aluminum in the Soil as Compared with Extraction by Dilute Acetic Acid

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THE USE OF CERTAIN CROP PLANTS

IN THE DETERMINATION OF "ACTIVE" ALUMINUM IN THE

SOIL AS COMPARED WITH EXTRACTION BY DILUTE ACETIC ACID

A thesis submitted to the Faculty of the Rhode Island State College in partial fulfillment of the requirements for the degree of Master of Science

by

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June 1, 1929.

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THE USE OF CERTAIN CROP PLANTS IN THE DETERMINATION OF "ACTIVE" ALUMINUM IN THE SOIL AS COMPARED WITH EXTRACTION BY DILUTE ACETIC ACID.

INTRODUCTION AND STATEMENT OF PROBLEM

For more than twenty years much attention and study has been given by agronomists, plant physiologists, and soil chemists to the element aluminum, its compounds, and their effects upon plant growth.

Many attempts have been made to determine "active" aluminum in the soil as related to its effect on plant growth. To date however little agreement has been obtained with the various chemical methods between the amounts of "active" aluminum found and actual depression of growth. In this problem an attempt was made to determine if the removal of aluminum by crops correlates better with aluminum toxicity than does pH or weak acid extraction, toxicity having been demonstrated agronomically.

LITERATURE

Among earlier workers there was much difference of opinion concerning the relation between acid soils and aluminum toxicity as to whether the acidity *per se*, or the aluminum made soluble by the acidity was the cause of the depression in the growth of plants.

The first to call attention to the possible toxic effects of salts of aluminum were Abbott, Connor and Smalley (1)[1] who, working with marshy situations, found soils which were unproductive, although fairly well supplied with plant food. They conclude that the nitrate in the soil was, in part, combined with aluminum and inferred that aluminum nitrate was responsible for the unproductiveness of the soil in question.

[1] Reference is made by number to "Literature Cited."

In contrast to the opinion of those workers, are the conclusions of Hartwell and Pember (12) (13) who, working with solution cultures, sand cultures, and soils from the experimental plats of the Rhode Island Agricultural Experiment Station, decided that the aluminum ion, rather than any single aluminum salt, was responsible for the effects noted in the growth of rye and barley.

Numerous other workers have demonstrated the toxicity of aluminum and its salts upon plant growth. Ruprecht (27) claims that aluminum sulphate, when present in culture solutions in concentrations of more than 40 p. p. m., has a very toxic action on clover seedlings. Mirasol (24),working with sweet clover, finds that in the absence of calcium, aluminum is toxic when applied in amounts chemically equivalent to the acidity of the soil and fatal when applied in amounts chemically equivalent to five times the acidity of the soil. Myaké (25) considers aluminum chloride toxic to rice seedlings in concentrations greater than N/7500. Hoffer (14) shows a definite connection between the presence of aluminum and iron salts in the soil and root-rot in corn. Hardy (11), and Connor and Sears (7) confirm the conclusions of Hartwell and Pember that the aluminum ion is responsible for the toxic effects.

In contrast to the above opinions is the contention of Line (17) who claims that the toxic aluminum theory of acid soils is not tenable and that the depression of plant growth in culture solutions is due to the precipitation of phosphorus as aluminum phosphate or to increased acidity.

Gile (10) states that from investigations which have been conducted thus far it does not appear to have been established that aluminum salts are toxic to plants in the same sense as are mercury or copper.

Covel (6) finds aluminum sulphate to be beneficial to rhododendrons, blueberries, and hydrangia when used in acid soils.

The quantities of aluminum and its compounds which are toxic to plants appear to vary with different plants. The medium used, whether sand, solution cultures, or different soils, is also important.

McLean and Gilbert (22) (23) found a wide variation in the sensitiveness of plants when grown in solution cultures. Lettuce, beets, and radishes were the most sensitive, sorghum and barley were placed in a medium class, and turnips and redtop were the least sensitive. These same authors found that very small amounts of aluminum (3-13 p.p.m.) were stimulating but that higher concentrations were toxic. They also noted that, by using the haematoxylin test, the aluminum absorbed by the plants accumulated only in the cortex, mainly in the protoplasm, and also appeared to be concentrated in the nuclei.

Stoklasa (30) finds that small quantities of aluminum are stimulating to the plant, and that aluminum chloride and aluminum sulphate in soils do not have the same toxic effect as in solution. The richer the soil in organic matter, the stronger the concentration of aluminum salts the plant can tolerate.

Magistad (20) claims that at acidities less than pH 5.0 alfalfa, red clover, rye, and oats suffered little or no aluminum injury while corn and beans were injuriously affected. Since most of the acid soils found under field conditions fall within the range of pH 5.0 to 7.0, the beneficial effects due to lime result from a decrease in acidity and not from a decrease in the soluble aluminum present.

Yoshii (32) recently reports that Aspergillius niger withstands concentrations of aluminum sulphate up to 0.005M or 4.16 p. p. m. of aluminum, Elodea cannadensis is damaged by 0.001M or 0.83 p. p. m. of aluminum, while in more dilute solutions new sprouts and roots are formed. Experiments with many higher plants show an 0.002M solution or 1.66 p. p. m. of aluminum to be toxic but that more dilute solutions are stimulating.

Dennison (9) claims that soluble aluminum salts stimulate ammonification but affect nitrification adversely, especially with increased concentrations of the salt. Sommer (29) found that all plants in their natural state absorb aluminum. Additions of this to culture solutions in which peas were growing, gave only small increases in dry weight but slightly greater increases in seed. With millet, aluminum gave marked increase in growth and great increase in the quantity of seed. Sommer concludes that aluminum is essentail to the normal development of the plant.

Kratzman (16) using a microchemical method based upon the formation of a double sulphate of caesium and aluminum, examined several hundred plants, representing many botanical families, and found aluminum to be present quite extensively, certain species being much richer in this substance than others.

McCollum (21) and his associates, using a spectographic method, declare that aluminum is not a constituent of either plant or animal matter. In direct contradiction to this is the recently published work of Kahlenberg and Class (15). These men, using a Hilger quartz prism spectograph, as did McCollum, found aluminum to be present in eggs, carrots, potatoes, lean beef, beef tendons, and various other materials.

As the natural result of the observed injurious effects of aluminum and its salts, various remedies have been proposed and tried. Hartwell and Pember (12), by use of lime on acid soils, reduced toxicity. They consider that the advantage of phosphorus and lime may often be due as much to the inactivation of the aluminum as to the effect of the calcium in reducing acidity. Burgess and Pember (5) by use of large quantities of superphosphate, reduced the solubility of aluminum in weak acids.

Dennison (9) claims that calcium carbonate is the most effective material for reducing the toxic action of aluminum salts on nitrification

Ruprecht (27) believes that the toxic effect of iron and aluminum can, in a large measure, be overcome by calcium carbonate. Mirasol (24) advances the idea that calcium carbonate corrects toxicity by precipitating the aluminum as calcium aluminate and that superphosphate at the rate of 400 pounds per acre reduces toxicity by forming an insoluble phosphate of aluminum. Burgess and Pember (5) report that both greenhouse and field observations indicate that large amounts of decaying organic matter (compost, manure or green manure) are efficient in counteracting the deleterious effects of "active" aluminum upon sensitive crops such as lettuce, spinach, and beets.

PROCEDURE

Methods for the Determination of Aluminum

Somewhat more than four years ago the writer had occasion to make a series of aluminum determinations upon soils, and in connection with that work various methods for the determination of aluminum were studied. Iron usually occurs with aluminum and is a disturbing factor because of the difficulty of obtaining a complete separation of the two elements. Phosphorus is another source of trouble in working with crops and soils.

Scott (28) gives various methods for the gravimetric determination of aluminum. Blum (3) has also published a gravimetric method. Both of these methods are satisfactory for the determination of aluminum alone or when large amounts are present, but are useless when quantities as small as 30 p. p. m. or less are to be determined.

Lundell and Knowles (19) and Patten (26) recommend the precipitation of iron and aluminum together as phosphates. This procedure requires the addition of 20 cc. of a 10 per cent ammonium hydrogen phosphate solution, followed by dilute ammonium hydroxide until the color of the solution just changes from blue to yellow, using thymol blue as an indicator. Twenty-five cc. of 25 per cent ammonium acetate are added and the solution boiled, filtered, and washed with a hot 5 per cent solution of ammonium nitrate. It is then ignited.

The iron is determined in a separate portion of the material and the amount deducted from the weight of combined iron and aluminum phosphates, thus obtaining the aluminum by difference.

Magistad (20) also precipitated iron and aluminum together as phosphates at pH 5.0 and determined the iron in a separate portion and calculated the aluminum by difference. These methods are not satisfactory for the reason that the iron must be determined separately and deducted from the combined phosphates. When small quantities of aluminum are present any error in the amount of iron would also effect the aluminum.

With the above method it very often happened that on ignition the precipitate, instead of being pure white ferric phosphate was colored more or less red, indicating that some iron had been precipitated as ferric hydroxide, thus introducing an error for the weight of combined phosphates.

Atack (2) has published a colorimetric method which depends upon the formation of an aluminum lake with Alizarin S. This method in our hands was most unsatisfactory in the presence of iron and phosphorus, although Lipman (18) considers the Alizarin method dependable.

The method adopted at that time was that of Patten (26). The soil extract or ashed plant material was heated with aqua regia, evaporated to dryness, taken up with HCl (1-1) and again evaporated, heated for one hour at 110°C. to dehydrate silica, again taken up with HCl (1-5) filtered and washed free from chlorine and the solution made up to a volume of 100 cc. Aluminum and iron were precipitated together as phosphate by the addition of 20 cc. of 10 per cent solution of sodium acid phosphate, neutralizing with dilute ammonium hydroxide just to the appearance of a yellow color , using thymol blue as an indicator; adding

25 cc. of a 25 per cent solution of ammonium acetate, heating to 70-80° C. for twenty minutes, allowing to stand, filtering, washing with hot 5 per cent ammonium nitrate solution, igniting and weighing as combined phosphates of iron and aluminum. Iron was determined in a separate portion using the Jones reductor and titrating with potassium permanganate solution. The amount of iron phosphate subtracted from the combined phosphates give the aluminum phosphate which was calculated to aluminum oxide and so reported. The same criticism applies to this method as to that of Magistad regarding the precipitation of basic aluminum hydroxide.

Using the above method, numerous determinations were made on soils and plant materials. The method was reasonably satisfactory when appreciable amounts of aluminum were present but with large quantities of iron and small amounts of aluminum its accuracy was questioned.

Since the accuracy of the above method was questionable under certain conditions the recently published method of Yoe and Hill (31) proved of interest. This method is intended for the colorimetric determination of aluminum in water using aluminon (The Ammonium Salt of Aurin Tricarboxylic Acid). The writer had the opportunity to collaborate with the department of chemistry of the Michigan Agricultural Experiment Station in adapting this method to the determination of small amounts of aluminum in soil extracts and in plant materials. Many determinations were made on synthetic solutions containing known quantities of aluminum, iron, phosphorus, calcium, and magnesia until it was possible to obtain agreement within a 10 per cent error between the quantities of aluminum added and those found.

This method is as follows for plant material. Two to twenty-five grams of dry tissue are charred over a flame; the char extracted with hot water and filtered through ashless paper. The paper and residue are ignited in an electric muffle, kept below redness, and washed into the beaker used to contain the hot water extract, with HCl (1-3). Five cc.

of concentrated HNO_3 are added and the solution evaporated to dryness. It is taken up with HCl(1-1), again evaporated to dryness, heated at 110° C. for one hour, taken up with HCl (1-5), filtered and washed free from chlorides. The final volume is made to 25, 50, or 100 cc. depending on the amount of dry material taken and its expected aluminum content. A soil solution or extract is treated in the same manner after the HCl and HNO_3 are added.

Iron and aluminum are separated in the following manner. Five or 10 cc. of solution are placed in a centrifuge tube having graduations at 10 and 20 cc.; water is added to make a volume of 10 cc. and 0.1 gram ammonium hydrogen phosphate and a few drops of thymol blue are added. Neutralize with dilute ammonium hydroxide until the solution just turns blue, then add 1 cc. of saturated ammonium acetate solution. Let stand 30 minutes at room temperature.

Centrifuge, decant, and wash the precipitate with 3 cc. of 5 per cent ammonium nitrate solution. The mixture is again centrifuged and decanted. Dissolve the iron and aluminum phosphates in the centrifuge tube, adding 0.5 cc. of 6N HCl, dilute to 5 cc. with water, add 2.5 cc. 6N NaOH, 1 cc. acetic acid (1-2), heat on a steam bath for 20 minutes, and dilute to a volume of 10 cc. and centrifuge. The precipitate contains the iron and the supernatant liquid the aluminum. Transfer 5 cc. of the liquid to a 50 cc. volumetric flask. Add 15 cc. water and the dilute HCl until litmus paper on the flask just turns red, and make up to volume.

Determine the aluminum in the following manner. Transfer an aliquot of 5 to 20 cc. (which should be only slightly acid) to a 50 cc. volumetric flask, add water to make volume of 20 cc. Add 5 cc. of 5N ammonium acetate solution, 5 cc. of 1.5N HCl and 2 cc. of a 0.1 per cent solution of aluminon. Allow to stand 20 minutes for the color to develop, add 5 cc. of 5N ammonium chloride solution, then add sufficient 3.2N ammonium carbonate solution to make the pH 7.0 to 7.1. Make up to volume and allow to stand for one-half hour. Then compare in a colorimeter with a water solution containing a known quantity of aluminum which has had the color developed in the same manner.

Blanks should be run on all reagents used and the quantity of aluminum found, if any, deducted from the amount found in the unknown.

Soils

Description of Soils

The soils selected for this work were taken from various plats on the Rhode Island experimental field, their previous fertilizer treatment being a matter of record. The soils selected were chosen for the following reasons:

1. They had received different fertilizer treatment.

2. They were of various pH values, from strongly acid to markedly alkaline.

3. By using these soils it was thought possible to compare two or more factors. Soils from plats 25 and 29 had received lime in the form of carbonate but had received nitrogen from different sources; soil 25 from ammonium sulphate and soil 29 from nitrate of soda. Soils 55N and 56N had been treated alike except for the amounts of lime applied. The same is true of soils from plats 65N and 66N but these had received three times the quantities of phosphoric acid that had been applied to the former soils. With these two soils the effects of different quantities of lime and phosphoric acid as well as the effect of the two fertilizer elements in the presence of each other could be compared.

Soils 74S and 82N should show the effects of fertilizer with and without lime. Soils from the market garden area show the effects of manure and peat.

4. Another important reason for selecting these particular soils was that crops of spinach (a crop very sensitive to toxic aluminum) had shown marked differences in yields on these different soils.

The soils used, fertilizer treatments, pH values, lime requirement, and yields of spinach in bushels per acre are shown in table 1.

Acid Extraction of Soils

Extractions of the chosen soils were made with 0.5N, 0.1N and 0.02N acetic acid. The extractions with 0.5N acid as used by Burgess (6) had not shown the small differences in active aluminum which were reflected in yields of spinach. Especially was this true with soils from the market-garden area where differences in "active" aluminum had never been as great as in some other soils, although differences in yields of spinach had been noted. It was hoped that extraction with 0.02N acid would show differences more closely correlated with yields. The quantities of "active" aluminum extracted from the soils by the various strengths of acid are shown in table 2.

Discussion of Results on Soils

Referring to the tables mentioned above it appears that with soils 25 and 29 extractions with 0.1N acid show results for "active" aluminum such as might be expected from the pH and lime requirement. The same relation is noted when the yields of spinach and "active" aluminum are compared. "Active" aluminum content as shown by extractions with other strengths are exactly reversed from what would be expected from pH value and yields of spinach.

Comparing soils 55N and 56N, the results for "active" aluminum with all extractions are in accord with what might be expected from the pH and are in accord with results seen for yields of spinach. With soils 65N and 66N, only the results from extraction with 0.5N acid are such as would be expected from the pH value. The yields of spinach are in accord with the aluminum results obtained with 0.5N acid extraction.

A comparison of results on the above four soils indicates the value of phosphoric acid in reducing the quantities of "active" aluminum and this fact is further shown by the spinach yields (table 1). The amounts of "active" aluminum obtained by extraction with 0.02N acid bear a closer relation to the yields of spinach than do the others.

The beneficial effects of lime when used with fertilizer are shown by the results on soils 74S and 82N. All results are in agreement with the yields for spinach, that crop being a failure on soil 82N and not markedly different on 74S from the yield on soil 55N. Even though the aluminum content does not agree especially well with the results on the above plats the agreement with the 0.02N acid extraction is closer between soil 55N and 74S than with any of the others.

Results from the market garden area with all extractions are in accord with what would be expected from the pH values but are exactly opposite from what is indicated by the yields of spinach on the two soils. No aluminum determinations made previously have shown the aluminum content of the peat soil to exceed that in the manured soil. This fact makes it evident that "active" aluminum is not responsible for the poorer growth of spinach on the peat soil. It may be noted, however, that the active aluminum content of the soils and the yields of spinach are in accord; the amounts as extracted with 0.02N acid showing the smallest differences and thus agreeing with the differences in the soils as indicated by the yields of spinach. The quantities of "active" aluminum extracted by 0.5N acid are larger than the amounts found by Burgess and Pember (5). This might be explained by the fact that the soils used in these determinations had all passed a 2 mm. sieve, while those used by Burgess were not so fine and the acid extracts aluminum from the fine material to a greater extent than from the coarse.

Crops

Crops Grown in Solution Cultures

The crops selected were buckwheat, oats, and Japanese millet. These were chosen for the reason that it has been shown by the work of McLean on solution cultures, analysis by the writer (table 3), that these plants when grown in water cultures containing various amounts of aluminum were able to make considerable growth, and also to extract from the solution appreciable amounts of aluminum.

Glasshouse Culture

The crops were grown in the greenhouse using Wagner pots filled with the selected soils. At the time the pots were filled one gram $NaNO_3$ was thoroughly mixed with the soil in each pot and one-half gram more was added in solution to each pot on February 2, 1929. To correct for a lime induced chlorosis, manganese sulphate at the rate of 25 pounds per acre was added on January 29, 1929, to pots 19 and 20 containing millet growing on soil 55N; to pots 29, 30, 154, and 156 containing oats growing on soils 55N and 74S. Pots 35 and 36 containing the same crop growing on soil 65N received the same treatment on January 30, 1929.

Discussion of Results with Plants

Buckwheat

This crop was harvested February 25, 1929, 91 days after planting. The plants had practically completed vegetative growth and ripened a few seeds. Many green seeds and a few late blossoms were present. The plants were dried, ground, and the aluminum determined according to the method given above. The green- and dry-matter weights, the aluminum content of the plants, together with the quantities of aluminum removed per pot are shown in table 4.

From this table it may be seen that there is, in most cases, a very close agreement in the dry-matter weights from duplicate pots, the greatest variation being 2.6 grams and the average 1.9 grams.

Considering yields, the largest was on soil from the market garden area fertilized with manure and treated with lime and manganese. This soil showed next to the smallest content of "active" aluminum when extracted with 0.5N and 0.02N acid. (Table 2).

The smallest yield was from soil 56N. This soil showed the second largest content of "active" aluminum by all extractions. These results are in accord with the pH values and figures for the lime requirement (table 1). Yields from soil 82N which has the highest "active" aluminum content, is the exact average for the entire series thus showing that large amounts of "active" aluminum in the soil do not seriously depress the growth of buckwheat plants.

Soils from Plat 90 of the market garden area had the lowest "active" aluminum content, and this is reflected in the quantity of aluminum in the crop, but for some reason the weight of crop was not as large as on several other soils. Yields of crops on this plat have been persistently low.

No evidence is shown of material benefits from large applications of phosphoric acid or lime.

Regarding the quantities of aluminum removed per pot it is seen that there is a close relation between amounts removed and the "active" aluminum content of the soil in the following cases:

1. Extractions with 0.5N acid, soils 29, 55N, 74S, 82N, 90, and 118.

2. Extraction s with 0.1N acid, soils, 25, 29, 65N, 74S, 82N, and 90.

3. Extractions with 0.02N acid show fair agreement for soils 56N, 65N, and 82N.

Considering the quantities of aluminum removed from soils 65N and 66N there is some indication that phosphorus inhibits the taking up of aluminum by the plant. There is no evidence of a similar effect in the case of lime.

Results on buckwheat are in accord with those obtained by McLean (table 3) who found that large quantities of aluminum did not depress growth and that increased amounts of this element in the culture solution were reflected in the aluminum content of the plant.

Judging from the above results it would appear that the aluminum content of buckwheat is a good indicator of the amount of "active" aluminum in the soil as shown by extraction with 0.1N acid.

Millet

On March 18, 1929 when this crop was harvested, 111 days after planting, it had made good growth. All plants had formed heads containing more or less grain. The green and dry-matter weights, the aluminum content of the plants, and the quantities of aluminum removed per pot are shown in table 5.

From the above table it will be seen that the agreement in weight between duplicate pots is not as close as with buckwheat.

Millet made its best growth on soils 25, 29, 90, and 118. The first two are soils from the lime experiment with pH values well up toward alkaline conditions. The two latter soils have pH values within the alkaline range. The yield on soil 118 is the highest of the millet series.

Comparing the yields on the four soils 55N, 56N, 65N, and 66N we find those on the two latter soils materially larger than on the former. This is marked indication of the beneficial effects of phosphoric acid on millet.

Plants on soil 74S were so affected by chlorosis as to make little growth and are not further considered.

On soil 82N which is the most acid, the plants made slightly better growth than on soil 66N. This result cannot be due either to lime or to increased amounts of phosphoric acid. With millet as with buckwheat on the market garden area, the yield on soil 118 is superior to that on soil 90, again showing the characteristic depressing effect of the peat soil.

The aluminum removal of the millet both in the content of the plant and the quantities removed from the soil per pot are very much smaller than was found with buckwheat. This again is in accord with the results obtained by McLean (table 3). The great difference in aluminum content between the two crops is especially noticeable in the results on soil 82N. Millet grown on this soil contained the largest quantity of aluminum, but because of the dry weight of crop, it did not show as large a removal of aluminum from the soil as did the plants grown on soil 118.

Practically no difference exists between the results obtained on soils 55N and 56N either in the aluminum content of the plants or the quantity removed from the soil. With soils 65N and 66N there is only a very small difference in the aluminum content of the plants, but because of the difference in the dry matter there is much variation in the quantity of aluminum removed from the soil. Comparisons of the four soils give but slight indications that larger applications of phosphoric acid decrease the aluminum content of the plant. As was the case with buckwheat, millet plants from soil 82N contained the largest quantity of aluminum.

Plants grown on soil 90 and 118 have an aluminum content which is about the average for the series. With this crop, in only a few cases is there shown any relative agreement between the "active" aluminum of the soil and the amount of that element in the plants. The amount removed from soil 25 shows some agreement with the "active" aluminum as determined from extraction with 0.1N acid (table 2).

As was true with buckwheat the high "active" aluminum in soil 82N is reflected in the high aluminum content of the millet plants grown on this soil.

Oats

These were harvested April 5, 1929, 115 days after planting. The plants had made excellent growth and some plants had started to head. In a few cases smut was seen. The green- and dry-matter weights, the aluminum content of the plants, and the quantities of aluminum removed per pot are shown in table 6.

Considering this table it is seen that plants grown on soils 55N and 90 give very poor agreement in yields from duplicate pots. Results from pot 29 are discarded as obviously defective. Also there is, in case of 138 and 139, soil 29, a wide variation in the aluminum content of the plants. The same is true for pots 41 and 42.

Oats made the best growth on soils 25, 29, and 90 respectively. Comparing the first two soils, there is a slightly larger yield on soil 25. This soil received its nitrogen from sulphate of ammonia.

Comparing the harvest weights from soils 55N and 56N, it appears that the best growth was made on soil which had received the lesser amounts of lime, and the same relation is true with soils 65N and 66N. These results are not in keeping with those found with buckwheat and millet. Contrasting the yields on the above four soils, the beneficial effects of increased phosphoric acid appear; this fact has been true with both the other crops grown.

Weights of the oat crop grown on soil 74S were less than those produced on soil 82N. This has also proved true with both buckwheat and millet. The need of soil 74S for more manganese may explain this fact. Yields of oats from the market garden soils indicate the superiority of manure over peat.

Considering the aluminum content of the plants, it is again shown that plants grown on the soil containing the largest quantity of "active" aluminum contain the most aluminum. Results from soils 55N, 56N, 65N, and 66N show that in the absence of large amounts of lime the aluminum content of the plant increases; also that large quantities of phosphoric acid are correlated with better growth and with increased aluminum in the plant.

As was found with the two other crops, plants from soil 82N contained the most aluminum, while the plants grown on soil 74S had a somewhat smaller aluminum content. The beneficial effects of lime and manure in increasing the weight of the crop are found to be the same in decreasing the aluminum content of the plants.

Although the quantities of aluminum removed by duplicate pots do not agree in several cases, yet the relation between the average removal from the two pots is, with one exception, the same as was found for the other crops. The exception was on soils 90 and 118 where there was the same removal from each soil.

GENERAL DISCUSSION

It may be possible to obtain general comparisons of value if an aluminum sensitive crop is used as an index. Reference is therefore made henceforward to yields of spinach as shown in table 1.

The beneficial effects of lime upon yields of spinach are very noticeable between soils 55N and 56N. The same holds true for buckwheat and millet but is not true for oats. With soils 65N and 66N the advantageous effects of lime when used with larger applications of phosphoric acid are very marked. This relation is not found with any of the three crops grown.

Comparing yields of spinach from soils 55N and 65N, the desirable results from incréased amounts of phosphoric acid are very noticeable. The same effect is seen with buckwheat, millet, and oats; being more prominant with millet than with the other two crops.

The great differences observed with spinach on soils 74S and 82N are in no way reflected in the yields of the three crops grown, which are in no measure as sensitive to aluminum as is spinach. Soils from the market garden area, 90 and 118, give variations in the yield of spinach which are concordant with those noted with buckwheat, millet, and oats, the differences with these being greater than with spinach. The value of lime as a corrector of the injurious effects of aluminum is shown much better with a sensitive crop like spinach than with the particular crops used in this work.

In view of the sensitivity of spinach to aluminum, it would be expected that the "active" aluminum in soil 29 would be less than that in soil 25. This proved to be true with the quantities obtained with 0.1N acid extraction (table 2) although the differences shown with 0.02N acid extraction are very small.

Soil 56N is much more acid than 55N and would be expected to contain more "active" aluminum. This was found to be true with all strengths of acid used for extraction and the difference is reflected in the yields of spinach.

Yields of spinach and pH values would indicate that soil 66N contains more "active" aluminum than 65N. This is found to be true with 0.5N acid extraction. The failure of this relation to appear by extractions with other strengths of acid might be explained by the fact that with the amounts of phosphoric acid used the aluminum was precipitated and not taken out by the more dilute concentrations of the acids.

Soil 82N, the most acid of the group, failed to produce a crop of spinach. From this we should expect this soil to have a high "active" aluminum content and this proved true with all strengths of acid. This soil contained the largest quantity of "active" aluminum of the series.

The good yield of spinach on soil 74S, which may be due to the application of manganese, was but little smaller than that on soil 55N. This would indicate a slightly higher content of "active" aluminum in this soil. This proved true only with extractions with 0.1N acid. To judge from the pH of the two soils we would expect soil 55N to have the greater "active" aluminum content. This was true with the extractions with 0.5N and 0.02N acid.

Using yields of spinach as an indicator we would expect soil 55N to contain less "active" aluminum than either 56N or 66N and more than 65N. This proved to be true with the extraction with 0.5N acid. The pH values of the four soils would indicate that soil 56N should contain the most "active" aluminum. This was found to occur with all strengths of acid used.

Considering the spinach crop on the two soils one would expect only small differences in "active" aluminum in the two soils from the market garden area. Extraction with 0.02N acid agree with the above difference. Also we should expect soil 90 to have the larger "active" aluminum content. This was not found to occur. On the contrary the results for this element were what might be expected from pH values, thus showing that "active" aluminum may not be the cause of the effects noted upon spinach grown on this soil.

The relations between the "active" aluminum content of the soils and the quantities of this element found in the plants is shown in Figure 1. In this the largest quantity of aluminum has the value of 100. From this figure it is seen that in only one case (soil 82N) is the relation between the aluminum content of the plant and the quantities of aluminum found in the soil by all extractions the same. With extractions with 0.5N acid we find agreements in the aluminum content of plant and soil as follows:

Buckwheat - Soils 25, 65N, 90, and 118
Millet - Soils 25 and 65N
Oats - Soil 90

With 0.1N acid agreements occur as follows:

Buckwheat - Soil 66N and 90
Millet - Soils 56N and 65N
Oats - Soils 66N and 90

Extractions with 0.02N acid show the following cases of agreement,

Buckwheat - Soils 29 and 118
Millet - Soils 29 and 66N
Oats - Soils 25, 65N, and 118

The above tabulation indicates that extractions with 0.02N acid gives the best agreement between the aluminum content of the plant and the "active" aluminum in the soil.

Lime with smaller quantities of phosphoric acid as compared with phosphoric acid alone apparently lowers the quantity of aluminum in the plant. Larger quantities of phosphoric acid lower the aluminum content of the plant in the case of millet and oats. In this connection it would be interesting if the quantities of aluminum in the spinach plants could be known to see if the above facts were true with a sensitive crop.

It was found by McLean (table 3) that in solution cultures the largest yield was with oats. Buckwheat and millet ranked second and third. It was also found by the same worker that crops grown in the solution containing the most aluminum showed the greatest aluminum content per plant. This last is wholly in accord with the findings in this work.

The quantity of aluminum removed from the soil per pot is dependent both upon the growth and the aluminum content of the plant. Buckwheat, although it did not have as large a growth as millet or oats because of the high aluminum content of the plant, removed materially more than the other crops. Millet, because of the smaller quantity of aluminum in the plants, removed much less aluminum from the soil. Oats with the largest harvest weight of the three crops grown removed but comparatively little more aluminum from the soil than millet, and very much less than buckwheat.

Braezeale (4) has advanced the theory that the tolerance of plants to alkali is the result of environment and adaptation to this substance through many generations. Possibly the same reasoning might explain the large aluminum content of buckwheat with no depression in growth. Buckwheat is a member of the family Polygonaceae, which family is able to make satisfactory growth in poor and acid soils and it may be that through centuries of existence under such conditions this plant has acquired the ability to store up large quantities of aluminum without serious growth depression. Buckwheat would, without question, be considered in that group of plants which Kratzman (16) has called "aluminum storing plants."

SUMMARY

In the preceding pages are stated certain observations made during the course of the work on methods for the determination of aluminum; the analysis of soils for this element; growth, and analysis for aluminum of the crops used. These observations may be summarized as follows.

The literature relating to aluminum in soil, plants, and animal substance; and to the toxicity of this element and its salts to plant growth is reviewed. Various methods for the determination of aluminum in soil and plant materials are discussed. A colorimetric method for the determination of small amounts of aluminum in soil and plant material is described.

The past fertilizer treatment of the ten soils from the Rhode Island Agricultural Experiment Station plats, pH values of these soils and their content of "active" aluminum as shown by extraction with 0.5N, 0.1N and 0.02N acetic acid are shown.

The yields in bushels per acre of spinach grown on these soils are given.

The relation between soil acidity and yields of spinach are discussed.

The reasons for choosing certain soils and crops for this work are stated.

The yields per pot of the chosen crops on the designated soils are given.

The quantities of aluminum in the plants grown on the various soils, also the relation between "active" aluminum in the soils and the quantity of that element in the plant is shown graphically.

The effect of lime and phosphoric acid on the "active" aluminum of the soil, also the effect of these two substances on the aluminum content of the plant is discussed.

CONCLUSIONS

As a result of this work the following conclusions appear justified.

The described colorimetric method for the determination of small amounts of aluminum is superior to all previous ones because of the fact that small quantities of phosphorus as found in soils and plant material are not troublesome, and that iron is no longer a source of error.

With no one of the crops used is there complete agreement between the aluminum in the plant and the "active" aluminum of the soil as shown by extraction with the three strengths of acid used.

Differences in "active" aluminum in the soil as indicated by yields of spinach are in fair agreement with the amounts of "active" aluminum extracted by 0.02N acetic acid.

The quantities of "active" aluminum extracted by 0.5N acid and the aluminum content of buckwheat are so large as to be useless in indicating small differences of "active" aluminum in the soil. For a crop sensitive to aluminum toxicity the quantities of "active" aluminum as shown by extractions with 0.02N acetic acid are of value.

Large quantities of "active" aluminum in the soil are correlated with large aluminum content of the plant. This fact, together with the different quantities taken up by buckwheat, millet, and oats are in agreement with results obtained in culture solutions.

Results on a soil supplied with peat and limed to neutrality indicate that "active" aluminum is not responsible for the effects noted in the growth of crops on this soil. This is in agreement with results which have been obtained several times previously.

The beneficial effects of lime and phosphoric acid on plants in the presence of considerable quantities of aluminum are in agreement with results noted by several previous workers.

Considering the results obtained with buckwheat, millet, and oats there are no indications that the use of these plants as indicators for the "active" aluminum content of the soil is superior to extractions with 0.1<u>N</u> or 0.02<u>N</u> acetic acid, especially when the length of time necessary to complete the two determinations is considered.

The writer desires to express his thanks to Dr. B. E. Gilbert and to Mr. J. B. Smith for their kindly advice and constructive criticism and also to acknowledge the assistance of Mr. F. R. Pember under whose direction the crops used in this study were grown.

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TABLE 1

[redacted] of soils, fertilizer treatment, pH, lime requirement and yields of spinach on soils used

[redacted]	Fertilizer Treatment	pH	1928 Lime requirement CaO per acre Pounds	Yields of spinach per acre[a] Bushels	Year
Experiment					
Plat 25	$(NH_4)_2 SO_4 + Ca CO_3$[b]	6.02	2,016	2,112	1925
" 29	$NaNO_3 + Ca CO_3$[b]	6.07	1,881	2,432	1925
osphate Experiment	Pounds N, Pounds P_2O_5, Pounds K_2O				
Plat 55N	80 50 150 More lime	6.44	1,080	1,118	1928
" 56N	80 50 150 Less lime	4.94	2,565	Failure	1928
" 65N	80 150 150 More lime	5.93	1,323	1,625	1928
" 66N	80 150 150 Less lime	5.01	2,376	122	1928
oject I					
Plat 74S	Complete fert. + $CaCO_3$ + Mn	7.88	216	1,011	1925
" 82N	" " no $CaCO_3$, no Mn	4.64	3,708	Failure	1925
rket Garden Area					
Plat 90	Peat + Mn	7.64	252	1,475	1927
" 118	Manure + Mn	7.37	459	1,548	1927

ight of bushel = 12 pounds.

lso adequate P_2O_5 and K_2O.

TABLE 2

[redacted]nd relative "active" aluminum content of soils as shown by extraction with three strengths of acetic acid

[redacted]	P. p. m. "active" aluminum extracted by[a]			Relative amounts of "active"[b] aluminum extracted by		
	0.5N acetic acid	0.1N acetic acid	0.02N acetic acid	0.5N acetic acid	0.1N acetic acid	0.02N acetic acid
e Experiment						
Plat 25	427.0	64.0	7.0	38	60	23
" 29	501.0	49.0	8.0	45	45	26
sphate [redacted]periment						
Plat 55N	537.0	23.0	5.5	48	21	18
" 56N	856.0	76.0	12.0	76	71	40
" 65N	503.0	58.0	3.8	44	54	13
" 66N	713.0	17.0	1.6	63	16	5
oject I						
Plat 74S	412.0	41.0	3.3	36	38	11
" 82N	1118.0	107.0	30.0	100	100	100
rket Garden Area						
Plat 90	164.0	17.0	1.1	15	16	3
" 118	235.0	75.0	2.7	21	70	9

xtracted from dry soil that passed a 2 mm. sieve, calculated to a basis of dry soil.
ased on Plat 82N as 100.

TABLE 3

[redacted] crops grown in solution cultures by McLean with analysis by Adams

[redacted]	Aluminum added P. p. m.	Dry matter weight of crop Grams	Al_2O_3 in crop (Dry matter basis) Per cent	Mg. of Al_2O_3 Recovered (Dry matter basis)
rnip	1.80	4.97	0.0252	125
"	7.20	4.16	0.0508	212
"	14.40	3.15	0.0398	125
bbage	7.20	9.35	0.0641	599
"	14.40	4.68	0.1090	510
"	28.80	4.00	0.1590	637
rghum	1.80	7.70	0.0375	288
"	14.40	7.47	0.0040	30
ats	1.80	9.78	0.0299	292
"	3.60	12.37	0.0241	298
"	7.20	11.41	0.0353	402
"	14.40	12.53	0.0365	457
ckwheat	1.80	2.99	0.0223	68
"	3.60	3.99	0.5640	249
"	7.20	4.58	0.0857	413
"	14.40	4.12	0.2530	1045
llet	1.80	1.62	0.0129	21
"	3.60	2.28	0.0329	75
"	7.20	3.22	0.0040	13
"	14.40	4.04	0.1430	577
e	1.80	9.74	0.1375	1248
"	14.40	17.90	0.0311	557
dtop	1.80	7.48	0.0965	732
"	3.60	5.71	0.0559	335
"	7.20	5.71	0.1080	616
"	28.80	2.01	0.0249	50
"	57.60	3.35	0.0973	326
dtop[a]	1.80	2.08	0.0301	63
"	3.60	0.87	0.4520	614
"	7.20	1.84	0.0522	96
"	14.40	0.44	0.0192	35
othy	1.80	7.57	0.0194	147
"	3.60	9.03	0.0854	751
"	7.20	8.22	0.0672	552
othy[a]	1.80	0.67	0.2380	159
"	3.60	9.50	0.0413	392
"	7.20	0.78	0.1720	134

rted at a later date than first samples.

TABLE 4

[redacted] buckwheat, aluminum content, and milligrams aluminum removed by crop

Soi[redacted]	Pot	Weight of plants: Green weight Grams	Weight of plants: Dry matter Grams	Al_2O_3 removed by crop: Mg. per 100 gms. dry matter	Average mg. per 100 grams dry matter for two pots	Milligrams removed: Per pot	Milligrams removed: Average
25	60	89.0	20.2	45.5	43.9	917.0	894.0
	61	92.0	21.0	41.9		881.0	
29	136	93.0	20.8	37.6	32.9	763.0	726.0
	174	98.0	22.1	31.0		689.0	
55N	21	44.0	lost	---	---		
	153	49.0	9.5	76.4	76.4	720.0	720.0
56N	81	43.0	9.1	89.7	89.7	816.0	816.0
	82	43.0	lost				
65N	33	54.0	12.0	20.8	28.8	258.0	300.0
	34	52.0	10.0	34.2		342.0	
66N	46	51.0	10.6	29.3	27.8	310.0	328.0
	47	58.0	12.9	26.9		346.0	
74S	151	50.0	7.1	112.5	107.7	800.0	812.0
	152	53.0	8.0	102.9		823.0	
82N	159	72.0	17.4	101.7	109.1	1764.0	1744.0
	160	69.0	14.8	116.5		1724.0	
90 M.G.	175	72.0	11.5	18.4	18.7	209.0	217.0
	74	73.0	12.4	18.5		224.0	
118 M.G.	39	105.0	19.8	17.1	17.4	338.0	380.0
		119.0	24.2	17.1		422.0	

TABLE 5

[redacted] of millet, aluminum content, and milligrams aluminum removed by crop

Soil	Pot	Weight of plants		Al_2O_3 removed by crop			
		Green weight Grams	Dry weight Grams	Mg. per 100 gms. dry matter	Average mg. per 100 grams dry matter for two pots	Milligrams removed Per pot	Milligrams removed Average
25	50	133.5	27.30	4.05	3.77	110.0	98.0
	51	129.0	26.40	3.38		87.0	
29	134	126.0	26.40	2.65	3.15	84.0	90.0
	135	141.5	31.50	3.65		96.0	
55N	19	25.0	4.30	5.70	5.16	26.0	20.0
	20	22.0	3.00	4.60		14.0	
56N	79	15.0	2.84	4.13	7.06	15.0	22.0
	80	19.0	3.80	10.00		29.0	
65N	31	48.0	6.80	4.97	4.90	38.0	34.0
	32	48.0	7.60	4.84		33.0	
66N	43	68.5	14.10	5.20	5.38	73.0	75.0
	45	66.0	13.70	5.40		76.0	
74S	141	5.0	Sample too small for use				
	142	6.0					
82N	151	65.0	12.30	11.85	11.12	14.6	14.2
	156	71.0	12.90	10.40		13.8	
90 M.G.	67	67.0	17.30	5.15	5.27	5.4	7.3
	68	105.0	10.70	5.40		9.3	
116 M.G.	37	222.0	47.40	4.00	3.45	18.90	15.0
	38	207.5	38.20	2.90		11.10	

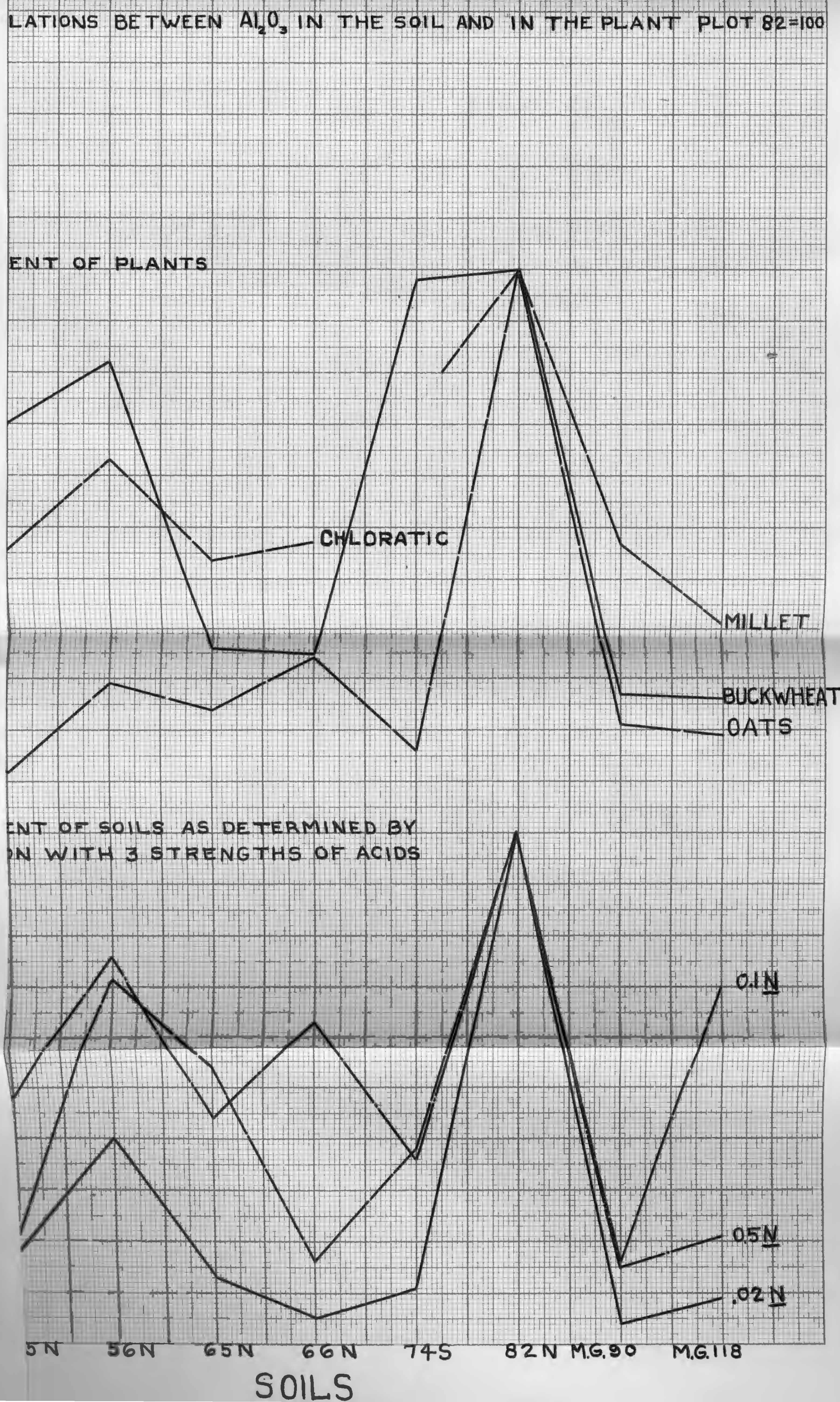
TABLE 6

[redacted] oats, aluminum content, and milligrams aluminum removed by crop

[redacted]	Pot	Weight of plants: Green weight Grams	Weight of plants: Dry weight Grams	Al_2O_3 removed by crop: Mg. per 100 gms. dry matter	Average mg. per 100 grams dry matter for two pots	Milligrams removed: Per pot	Milligrams removed: Average
25	64	301.0	47.4	5.86	5.42	278.0	263.0
	65	288.0	50.0	4.98		249.0	
29	138	269.0	44.2	6.21	4.32	142.0	126.0
	139	268.0	44.9	2.44		109.2	
55N	29	76.0	9.5	[a]0.98			
	30	143.0	20.6	5.40	5.40	110.0	110.0
56N	132	173.0	25.4	6.64	6.48	169.0	162.0
	133	152.0	24.4	6.31		154.0	
65N	35	147.0	25.3	4.62	4.92	117.0	116.0
	36	144.0	22.3	5.21		116.0	
66N	48	174.0	30.0	7.64	8.18	231.0	247.0
	49	180.0	30.3	8.71		263.0	
74S	154	101.0	10.5	1.94	2.15	20.0	25.0
	156	119.0	12.9	2.35		30.0	
82N	161	198.0	32.3	32.00	33.60	1035.0	1077.0
	162	189.0	31.4	35.10		1118.0	
90 M.G.	75	251.0	40.0	3.50	3.62	142.0	98.0
	76	150.0	14.5	3.75		54.0	
15 M.G.	41	243.0	30.4	2.40	3.20	73.0	98.0
	42	248.0	30.5	4.00		122.0	

[a]Results on this pot discarded.

FIGURE-I


LATIONS BETWEEN Al_2O_3 IN THE SOIL AND IN THE PLANT PLOT 82=100
ENT OF PLANTS
CHLORATIC
MILLET
BUCKWHEAT
OATS
ENT OF SOILS AS DETERMINED BY
ON WITH 3 STRENGTHS OF ACIDS
0.1 N
0.5 N
.02 N
5N
56N
65N
66N
74S
82N
M.G.90
M.G.118
SOILS