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ALUMINUM SORPTION BY PLANTS AS INFLUENCED BY CALCIUM AND POTASSIUM.

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ALUMINUM SORPTION BY PLANTS
AS INFLUENCED BY CALCIUM AND POTASSIUM

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SOIL SCIENCE
June, 1967

By
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ABSTRACT

The uptake of K, Ca and Al by plants was studied in three steps: first, adsorption; second, absorption by excised roots; third, uptake by the intact plants.

Cation exchange capacities of the plant roots were as follows: *Ananas comosa* (pineapple) 7.0, *Saccharum officinarum* (sugarcane) 9.5, *Zea mays* (corn) 13.6, and *Desmodium canum* (kaimi clover) 20.0 m.e. per 100 g. dry roots. Cation adsorption on root surface was observed to be a function of plant species, cation involved and cation concentrations in equilibrating media. The adsorption of Ca and Al on roots of all species increased with increasing cation exchange capacities. However, the adsorption of K was preferential on corn roots. The amount of cations adsorbed increased with their increasing concentrations in equilibrating media. The effects of one cation upon the adsorption of another cation were reciprocal. At equivalent cation concentration in the saturating solution, cation adsorption by all roots decreased with increasing cation valency. The Al adsorption was influenced by the complementary cation, being higher with Ca than with K.

In pineapple and kaimi clover roots, aluminum depressed the sorption of Ca, but stimulated that of K at low concentration. A highly significant correlation was observed between adsorption and absorption of individual cations within each plant species. It is suggested that absorption of a cation is related to its adsorption.
and amount of appropriate metabolically produced carrier by roots.

Pot experiment was conducted to investigate the effect of 5, 20 or 60 percent Ca and 1 or 10 percent K saturations on the dry matter yield and mineral composition of corn and kaimi clover. When the soil pH was allowed to vary from 5.2 to 7.0 depending upon K and Ca applications as hydroxides, K added in excess of 1 percent saturation decreased the yield of both plant species at all levels of Ca. At pH 4.9, corn yield increased by increasing K saturation at 20 or more percentage Ca, but markedly depressed at 5 percent Ca saturation. However, regardless of Ca levels, the yield of kaimi clover decreased with higher K saturation.

The amount of cations distribution from the root to the top was shown to depend considerably on the individual ions. More than 80 percent K and Ca absorbed were in the plant top, but most of Al remained in the roots. Apparently plants differ in their capacity to transfer Al into their aerial portions. The net translocation of Al in kaimi clover was twice than that in corn.
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INTRODUCTION

Ion absorption processes are intimately tied up with every aspect of plant nutrition and toxicity, hence, these processes play significant roles in practical agriculture. The process frequently involves the accumulation of elements in cells against a gradient in chemical potential; thus the phenomenon of ion absorption is of considerable theoretical interest.

The ion absorption process involves exchange processes. Cations may be absorbed in exchange for $H^+$ ions of the plant which are released to the culture medium. As a result of the exchange character of the process, anions and cations enter the plant root individually. Also cations are not absorbed at equal rates. In general, $K^+$, $NH_4^+$, $Rb^+$, and $Cs^+$ are readily accumulated, while $Ca^{++}$, $Mg^{++}$, and $Ba^{++}$ are taken up slowly.

Ion uptake by plants from a soil system may be divided into four steps: first, release of the ion from the solid phase into the soil solution; second, movement of the ion from any point in the soil solution to the vicinity of the root; third, movement of the ion from the vicinity of the root into the root; and fourth, movement of the ion to the top of the plant (Fried and Shapiro, 1961).

Aluminum sorption by plants depends mainly on plant species, pH and other nutrients present in the culture medium. Some plants clearly accumulate Al while others seem to absorb little
regardless of the status of the substrate.

The reactions of Al in solution are particularly important. When pH is very low, Al is present almost entirely as trivalent ions. As the pH rises it is gradually precipitated out as hydroxide depending on the concentration, but Al appears again in solution as aluminate in alkaline conditions.

Marked influences of ions upon the absorption of other ions have been observed. For ions of the same charge, this influence is usually competitive in nature. On the other hand, the presence of ions such as Ca++, Sr++, Ba++, Al+++ and Fe+++ has been observed to exert a stimulating effect on the absorption of K⁺, Rb⁺, and Br⁻ under some conditions.

Aluminum sorption by plants is important; first, because Al is toxic to many plants even if it is present in small amounts in nutrient media, and second, Al may influence nutrient absorption and conduction in plants. This may be particularly significant in tropical soils which are aluminous and acidic.

Cation exchange reactions involving plant roots have been adequately demonstrated. Although cation-exchange capacity of roots may not be directly involved in nutrient absorption, there is abundant evidence that this property is indirectly involved in nutrient mobilization and uptake. Some evidences indicate that exchange reactions at root surfaces are important. These evidences are:
1. Mobilization of phosphorus from relatively insoluble phosphates such as rock phosphate is more readily affected by roots with high cation-exchange capacity.

2. Roots with high cation-exchange capacity compete well for polyvalent cation.

3. Movement of cations to root surfaces seem to involve cation-exchange reactions.

4. Finally, it seems self evident that any factor which modifies the ionic composition of the root environment will have bearing on nutrient uptake.

These considerations prompted this investigation with the following objectives:

1. Determine cation-exchange capacity of the roots of various plant species.

2. Measure the adsorption of Al, Ca, and K on roots from mono-, bi- and tri-cationic solutions (pH 4.0) and bi-cationic soil suspensions.

3. Measure the amount of Al, Ca, and K adsorbed and absorbed by roots from bi-cationic solutions (pH 4.0) and soil suspensions.

4. Evaluate the effect of Al, plant species, soil materials, and pH on the adsorption and absorption of cations by roots.

5. Investigate the influence of percentage saturation of Ca and K in Kapaa soil on the yield and mineral content of plants in greenhouse experiment.
Aluminum in the soil solution and its role in soil acidity

The three major factors affecting the amount of Al present in soil are the amount and kind of aluminum compounds and pH. Acids present in low pH soil react with aluminum compounds producing soluble salts. In general Al solubility increases with increasing acidity. The simplest form of Al occurring in solution is the trivalent Al ion. According to Rorison (1958), trivalent Al is unlikely to be in the soil solution if the pH is above 4.5. Schofield (1949) stated that the trivalent aluminum ion in an aqueous solution has its six coordination positions filled with water molecules, which may be represented as Al(H_2O)_6. Lunin (1949) reported that this form occurs at relatively high hydrogen-ion concentrations. But as the pH of the solution increases, the water molecules are replaced by hydroxyl ions. Al(OH)_3·3H_2O, an insoluble hydroxide, is formed as the pH nears neutrality. Jones (1961) stated that at a pH above 7.5 aluminum becomes soluble and exists as the aluminate anion. Magistad (1925) has also postulated the presence of aluminate anions at pH values above neutrality. When anions such as chloride, sulphate, and phosphate are present in soil solution, they may be held in the coordination positions instead of water molecules. Therefore, when hydroxide is precipitated from a solution of aluminum salt,
the precipitate will contain the anion of that salt in small amounts. The amount depends upon the coordination affinity of the anion towards Al.

Aluminum salt solutions are acid because Al ions in water solution hydrolyze to give hydrogen ions and aluminum hydroxide. Although this hydrolysis occurs between pH 4 and 5, the combination of ion exchange and hydrolysis continues to take place until a higher pH is reached. Veitch (1904) found Al ions when acid soils were extracted with NaCl solution. He suggested that Al was brought into solution by base exchange. Page (1926) thought that this Al was the result of a secondary reaction of the H\(^+\) ions which dissolved aluminum from alumino-silicate. In 1946, Chernov published a monograph on soil acidity and asserted that the acidity of the mineral fraction of Podzolic soils and red earths is due to Al.

Coleman et al. (1959) reported that Al was the predominant exchange cation in well-developed upland soils. Harward and Coleman (1954) compared heat of neutralization and titration curves of H- and Al-resins with "columinated" and electrodialyzed clays. Electrodialyzed clays behave like weak acids and "columinated" clays like strong acids. Jackson (1963) reported that aluminum bonding is central to soil acidity, through not only the acidic alumino hexahydronium monomeric cations, but also through the weakly acid Al-OH\(_2\)---OH pair at edges of polymerized
("precipitated") hydroxy aluminum structures. Yarusev (1948) listed several possibilities which may explain the nature of soil acidity.

1. The source of exchange acidity of mineral soils is exchangeable Al.

2. The cause of exchange acidity of mineral soils is exchangeable hydrogen.

3. Both exchangeable hydrogen and exchangeable Al participate in soil exchange acidity.

Paver and Marshall (1934) suggested that acid clays are actually hydrogen-aluminum clays. Jenny (1961) reported that acid soils contain hydrogen and Al ions and both contribute to soil acidity. Heddleson et al. (1960) concluded from their findings that extractable soil Al generates soil acidity. Aluminum is released from the soil mineral complex by weathering.

Aluminum content in plants

Aluminum is present in small amounts in most plants. Johnson (1913) reported small amounts of Al in agricultural plants, but was not sure whether it was a constituent of plants or due to particles of clay adhering to plants. Some plants accumulate Al as demonstrated by Pfeffer (1899) who found that in Lycopodium alpinum Al made up from 22 to 27% of its ash, while only traces were found in other species of Lycopodium. In most plants the percentages of Al₂O₃ is approximately equal to that of Fe₂O₃.
and is considerably less than that of phosphorus. Liebig et al. (1942) reported that when 0.1 ppm Al was added in the nutrient solution, Al content of the root bark and finer roots increased greatly, but this treatment had little influence on Al in root wood and stems. Leaves of this treatment contained even less Al than the control. Moomaw et al. (1959) studied the Al concentration of 23 plant species growing on bauxite soils of Hawaii. They reported that 13 of them were Al accumulators, with more than one thousand parts per million of Al on a dry weight basis.

Humphreys and Truman (1964) reported that many forest soils in eastern Australia are very acid having Al+++ as the major exchangeable cation. *Pinus* spp. grown under these conditions have high foliar aluminum (mean value 745-1298 ppm). *Eucalyptus* spp. growing on the same or similar sites as those of *Pinus* spp. generally contain less than 200 ppm Al.

**Aluminum and plant growth**

The literature contains many suggestions of aluminum toxicity and of aluminum accumulation by a variety of plants. Magistad (1925), McGeorge (1925), and Hutchinson (1943) have reviewed the early work relating to the effect of Al on plant growth.

McLean and Gilbert (1928) reported that low concentrations of Al, 3 to 13 ppm, were stimulating to plants while concentrations above 13 ppm were toxic. They also demonstrated that plants vary in their susceptibility to aluminum toxicity. Lettuce,
beets, and some other plants are very sensitive, while corn is more tolerant. Nortenstine and Fiskell (1961) reported that root and top yields of sunflower were little affected by 2 to 4 ppm Al, but were depressed by 6 to 16 ppm Al.

Gilbert et al. (1935) reported that yields of 10 plant species differed widely with varying concentration of Al. The plants were arranged in three groups. Group one showed a 20% depression of growth with 2-8 ppm Al, group two required 16-32 ppm of Al and group three required 32-80 ppm Al for the same degree of depression. Vlamis (1953) concluded that acid soil is infertile to barley and lettuce, apparently due to Al toxicity.

Hawkins et al. (1951) reported low productivity due to Al and Mn toxicity. They also mentioned that toxicity was reduced by heavy application of superphosphate. Kliewer (1961) found that the presence of 1 to 2 ppm of aluminum in solution completely inhibited root growth of alfalfa. Uhlen (1959) recognized that the ratio of aluminum to other cations present in solution has a great effect on the degree of aluminum toxicity.

Action of aluminum on plants

The exact mechanism of aluminum toxicity to plants is not clearly understood. According to Szues (1912), soluble Al is toxic to plant growth because it "gels" the plant protoplasm. Fluri (1908) noticed that when aluminum was added to a nutrient solution, the rate of starch formation was decreased. Ouellette
and Dessureaux (1958), who made detailed observations of visual symptoms of numerous plants grown in sand cultures with different levels of aluminum, iron, and manganese, showed that the most striking characteristics of aluminum toxicity was stunted growth with brown discolorations and thickened root tips.

**Effect of aluminum on the uptake of calcium and phosphorus**

Several investigators reported that liming reduces the "active Al content in the soil" and thus reduces the aluminum toxicity to the plant. Chernov and Belyneva (1948) reported that calcium uptake from acid soils was completely suppressed by AlCl₃ at a pH range of 4-5. Likewise, Schmehl *et al.* (1952) suggested a possible antagonism between Al and Ca uptake by alfalfa since the absorption of Ca was depressed to one-tenth of the normal rate by the addition of 10 ppm Al to the nutrient solution. Ragland and Coleman (1959) found that 5 m.e. of Al per liter of nutrient solution not only prevented absorption of Ca by excised roots of snap beans, but also caused a loss of Ca from the roots to the solution.

It is a well-recognized fact that the addition of large amounts of calcium phosphate to acid soils will temporarily reduce the detrimental effects of these soils on plant growth. Burges and Pember (1923) applied various levels of phosphate and lime to soils in pots and made periodic measurements of pH and active aluminum. Lime alone decreased active Al but did not increase
yields. Calcium phosphate alone resulted in increased yields without reducing active Al to the same levels produced by lime treatments. Clements (1960, 1962) found that heavy application of lime as powdered coral stone increased phosphorus concentration in the plant and reduced soluble Al in the soils studied. Munns (1965) reported increased accumulation of phosphate in the roots of plants growing in media of high Al concentration, which in turn retarded growth by making Lucerne shoot phosphate deficient.

**Soil pH and calcium nutrition of plants**

Early investigators believed that the major benefit obtained by liming was due to the neutralization of soil acidity. Later, the beneficial response from liming was shown to be due to a complex function of many contributing physical, chemical, and physiological factors.

Arnon *et al.* (1942) reported that increased H$^+$ ion concentration in nutrient solution decreased the uptake of Ca$^{++}$ ions by tomato and lettuce plants. Horner (1936) studied the ecological factors associated with soil acidity by growing soybeans in clay-sand cultures. He concluded that the principal beneficial effect from liming results from increased Ca as a nutrient for plants.

Although the function of calcium in plants is well documented there are conflicting opinions in the literature as to whether Ca
is one of the factors limiting growth on acid soils. One school claims that beneficial effects of lime applications are largely due to an increased Ca$^{++}$ ion concentration, and another school claims that benefits are due to factors related to pH. Moser (1942) found that at low pH values, Ca was a more important growth factor than pH. Schmehl et al. (1952), however, working with an acid Mardin soil found that increasing the calcium concentration in the soil by adding gypsum did not increase yields of alfalfa, but in most cases, caused a significant decrease in yields. Under the experimental conditions, they found that calcium was not limiting the growth of alfalfa, because yields did not increase with increased uptake of calcium.

**Cation-exchange capacity of roots and factors affecting it**

Several workers have emphasized the importance of cation-exchange properties of plant roots. Jenny and Overstreet (1939) believed that the exchangeable properties of the root enable the plant to absorb nutrient from soil colloids through contact exchange. McLean (1956) reported that the cation-exchange capacity of roots was correlated with the relative ability of various species to absorb cations. Fox and Kacar (1964) reported that the ability of various plants to extract phosphorus from the soil was related to the exchange capacity of their root system. Alfalfa (cation-exchange capacity 50 m.e./100 g. roots) apparently mobilized more phosphorus than oat (cation-exchange capacity 24 m.e./100
In a recent investigation, Mouat (1962) obtained evidence for genetically controlled variation in root cation-exchange capacity with wheat variety "Atoea". Heintze (1961) found that cation-exchange capacity varied with age of plant, type of growth media and nutrient levels. Grasses exhibited a greater constancy of cation-exchange capacity than other plants examined.

Crooke et al. (1960) measured cation-exchange capacity, pectin, respiration and nitrogen content in successive segments of leek roots over a distance of 140 mm. from the root tip. All measurement decreased with increasing distance from the root tip.

Cation-exchange capacity determinations have been made by numerous methods. In spite of this, workers have generally concluded that dicot roots have higher cation-exchange capacity than monocot roots.

**Adsorption of cations on root and soil colloids in relation to mineral contents of plants**

The tenacity or energy with which a cation is attracted to clay colloids is determined by type of colloids, percent base saturation, and nature of the complementary cations present.

Albrecht (1940) reported that Ca availability to plants increased with increased percentage Ca saturation of Putman (beidellite) clay. Allaway (1945) determined the availability of Ca from several colloids to plants. Kaolinite, 40 percent Ca
saturated, supplied more Ca to soybeans than did Mississippi bentonite which was 80 percent Ca saturated. Mehlich and Cowell (1943) reported that for each of several levels of Ca saturation, soybeans and cotton obtained more Ca from kaolinite than from montmorillonite.

McLean and Marshall (1948) demonstrated the importance of complementary cations on the availability of a specific cation. Cation activity was measured with the clay-membrane electrode. The addition of calcium greatly increased K activity in a K, H-montmorillonite clay system. In contrast, calcium activity was halved by the addition of 10 percent K to a montmorillonite system which was 80 percent Ca and 20 percent H saturated.

Elgabaly and Wiklander (1949) went one step further and emphasized that both the root colloids and the soil colloids compete for ions. Cation uptake by plants depends upon the relative exchange capacities of root and soil colloids. Franklin (1966) found a significant linear correlation between Ca and K uptake by excised roots and exchangeable Ca and K on the excised roots.

Aluminum nutrition of plants is very complex. Plant species differ greatly in Al uptake and sensitivity. In many instances there is little relation between Al uptake and soil pH. This may be related to differences in root colloids and the way in which root interact with cations, including Al, in the growth media. Little work has been done on this subject.
MATERIALS AND METHODS

Methods of plant culture

Pineapple (*Ananas comosa*; Var. Cayenne), sugarcane (*Saccharum officinarum*; Var. H-50-7209), corn (*Zea mays*; Var. Texas 28), and kaimi clover (*Desmodium canum*; Var. H.5335) were grown in 1/4 strength Hoagland solution. Corn and kaimi clover seeds were germinated between wet filter paper in petri dishes. After a few days, seedlings were transferred to holes in wooden supports. The seedlings were supported by cotton plugs. Cuttings of sugarcane were germinated in cinders after being treated with dilute (1:800) phenol mercuric acetate (P.M.A.) solution and later transferred to 1/4 Hoagland solution which was aerated continuously. The plants were held on wooden supports above black plastic containers of nutrient solution. Pineapple crowns were grown in black mason jars containing 1/4 strength Hoagland nutrient solution but were not aerated. The nutrient solution was changed weekly. Water was added daily to keep the solution up to 2 cm. from the top of the container.

After approximately six weeks, roots were excised, thoroughly washed with distilled water and used for the following investigations.

**Determination of cation-exchange capacity of plant roots**

A slightly modified method of Crooke (1958) was used to
measure cation-exchange capacity (C.E.C.) of roots. After cutting away the aerial parts of the plants, the fine roots were separated from the coarse roots and were washed in a series of three containers of distilled water.

Ten grams of fresh, fine roots were then placed in a nylon-net basket or a plastic fly-screen made to fit into a 400 ml. beaker. The basket containing the roots was transferred through a series of three beakers, each containing 300 ml. of 0.01 N HCl. Entrained acid solution in root mats was removed by hand slinging. Roots were washed for a total period of 10 seconds in two beakers, each containing 100 ml. distilled water. Entrained water was removed by slinging. The roots were then placed in 200 ml. of 0.2 N KCl (pH 7.0), and within a period of 5 minutes, were titrated to pH 7.0 with 0.01 N KOH. Roots were washed free of KCl, dried overnight at 70°C and weighed. The C.E.C. was calculated as m.e. per 100 g. dry roots.

**Determination of adsorbed cations on plant roots**

The method for determining adsorbed cations on roots was standardized in this lab as given in the section "standardization of a method for determining the cation adsorption on plant roots". The method adopted for determining cation adsorption by roots was as follows.

Clean, fresh roots were washed for a total period of 30 seconds in a series of three beakers, each containing 300 ml. of
0.01 N HCl. Entrained acid was removed by hand slinging, and roots were equilibrated for 2 minutes with cationic saturating solutions or soil suspensions. Saturating cations were supplied in excess of the root C.E.C. but because of very low concentrations of some saturating solutions there is doubt about completeness of saturation of roots in the most dilute Al and K mono-cationic systems. Entrained solutions or suspensions were removed by hand slinging and washed for a total period of 10 seconds in two beakers, each containing 100 ml. distilled water. When soil suspension was used as saturating media, roots, still in a nylon-net basket, were washed for an additional 30 seconds by dipping in a Waring blender, running at high speed, containing 400 ml. distilled water. It was necessary to use this additional root washing to remove soil particles from root surfaces. Evidently, positively charged soil colloids were attracted to negatively charged root surfaces. These soil colloids could not be removed by the usual washing procedures but were displaced by acid desaturating solution. The turbulent action in the Waring blender was sufficient to dislodge the soil colloids so that the subsequent acid desorption solutions were essentially colloid free. Roots were desaturated in a series of three beakers, each containing 100 ml. N HCl. Root contact time with the desaturating solution in beakers 1 to 3 were 10, 50, and 60 seconds, respectively. Solutions from the three beakers were composited for chemical determinations.
Cations were then reported as adsorbed cations in m.e. per 100 g. dry roots.

**Soils studied**

Soil suspensions were prepared from surface soils representing three great soil groups. The following is a series description for each of these three soils:

**Akaka series.** Soils of the Akaka series are yellowish-red Hydrol Humic Latosols. They occur at altitudes of 800 to 6000 feet on the windward sides of the islands of Hawaii and Maui. Rainfall ranges from 120 to 300 inches per year, but the average is somewhere near 150 inches. They are the most highly leached and the most acid soils of the Hydrol Humic Latosol group. The pH varies from 4 to 4.6.

These soils possess an unusually low bulk density and a very high water holding capacity. Soil dries irreversibly, and dehydrated soil cannot be remoistened to its original form. Tamura et al. (1953) found little or no kaolin in these soils. The clays are largely oxides.

Most Akaka surface soils range in organic matter content from 15 to 20 percent (Ayres, 1943). Buffering capacity of these soils is very high (Matsusaka and Sherman, 1950). Kanehiro and Sherman (1956) reported drastic changes in the characteristics of Akaka soil on drying and showed that the cation-exchange capacity is dropped from 125.8 m.e./100 g. to 37.6
m.e./100 g. after 100 days of dehydration in the sun.

**Molokai series.** Soils of the Molokai series belong to the Low Humic Latosol great soil group. Molokai soil is found at an elevation of sea level to 2100 feet. The annual precipitation ranges from 10 to 30 inches. Soils of this series have developed on basaltic material in a semiarid to subhumid climate of subtropical regions having a pronounced dry period (Sherman and Alexander, 1959).

The soil colloids are mainly kaolinitic (1:1) calys. Iron oxides have become concentrated throughout the solum, mainly through the loss of silica and bases. The organic matter content in the uppermost horizon is commonly higher than 2 or 3 percent. The cation-exchange capacity is between 15 and 30 m.e./100 g. The pH of the virgin soils is generally near 6, but some of the members in less arid regions may have pH as low as 5.0.

**Kapaa series.** The Kapaa soil series is a very deep, well-drained Aluminous Ferruginous Latosol developed in saprolitic ferruginous bauxite on gently-sloping uplands on the island of Kauai. The soils occur on lower mountain slopes between elevations of about 200 and 1000 feet where the mean annual rainfall ranges from 60 to 100 inches. Soils of this series have high concentrations of gibbsite (X-ray analysis), the tri-hydrate oxide of aluminum. The bulk density of these soils is very high and pH varies from 4.2 to 5.0. Cation-exchange capacity is
moderate as shown by Fox et al. (1962) who reported that C.E.C. of Kapaa soil is 29 m.e./100 g.

Preparation of Al-saturated soil materials. The soils were passed through a screen (4 mesh per inch) to remove large roots and then mixed several times. Samples of soil (150 g. O.D.) and 1500 ml. distilled water were placed in 2 liter bottles and shaken for 24 hours. The suspensions were allowed to settle for 5 minutes and the supernatant liquid was decanted. This process was repeated two times to separate the fine silt and clay sized particles from the sand and coarse silt materials. The decanted materials were transferred to a buchner funnel and washed with 0.05 N HCl until leachate was free of calcium. Acid washing was necessary to obtain a pH of 3.5 to 4.2 which was required for Al solubility. The excess acid was removed by further washing with distilled water.

The acid washed materials were equilibrated in 2 liter bottles with 100 ml. AlCl₃ over a period of 24 hours. The amount of AlCl₃ added was in the ratio of 10:1 for m.e. of Al added to m.e. of C.E.C. in the soil. The soil materials were then filtered and washed with an additional 100 ml. of AlCl₃. Chlorides were removed by washing with distilled water. The soil materials obtained were assumed to be aluminum saturated and were stored moist in plastic bags for future use.
Determination of cation-exchange capacity of Al-saturated soil materials. For the purpose of this investigation, cation-exchange capacity is considered to be the total amount of Ca(OH)$_2$ required to bring soil materials to pH 7.0. Ten samples (5 g. O.D. soil) were placed in 150 ml. beakers with increments of Ca(OH)$_2$ ranging from 0 to 40 ml. Volumes were adjusted to 50 ml. with distilled water and the beakers were occasionally stirred during the period of 48 hours. After the equilibrium was established, the pH of the soil suspensions was measured with a pH meter. The pH values were plotted against milliequivalents of Ca(OH)$_2$ per 100 g. soil. The C.E.C. of soil materials was read directly from the curve.

Adsorption and absorption of cations by excised roots

Excised roots were cut into 1-2 cm. pieces, rinsed in distilled water, and centrifuged for 5 minutes at 65 x g to remove entrained water. Three grams of roots were placed in three liters of salt solution or soil suspension. This wide ratio of root:solution (1:1000) was chosen so that the composition of solutions or suspensions remained relatively constant with time. The roots were in contact with the continuously aerated solutions or suspensions for a period of 24 hours. All experiments were performed at 24°C.

At the end of the sorption period, roots were collected on a nylon net and washed for a total period of 10 seconds in two
beakers, each containing 100 ml. of distilled water. When soil suspension was used as the saturating media, roots still in the nylon-net basket were washed for an additional 30 seconds by dipping in a Waring blender containing 400 ml. distilled water. Exchangeable cations (adsorbed cations) on the roots were determined before and after the sorption period by desaturating roots in a series of three beakers, each containing 100 ml. N HCl. The times of root contact with desaturating solutions in beakers 1 to 3 were 10, 50, and 60 seconds, respectively. The cations adsorbed on the roots at the end of the sorption period were called final adsorbed cations. After desaturation in acid, roots were washed with distilled water, dried at 70°C, and analyzed for Al, Ca, and K before and after the sorption period. The difference in initial and final determinations was reported as net absorption of cations in m.e./100 g. dry roots.

Nutrient uptake by intact plants

Soil preparation and fertilization. Bulk samples of the Kapaa soil were collected from the "Bauxite Project" Kauai and stored in plastic bags to reduce evaporation and to prevent drying. The soil was passed through a screen (4 mesh per inch) to remove large roots, and then the soil was thoroughly mixed. Cation-exchange capacity of soil was measured by using normal ammonium acetate (pH 7.0) as described by Piper (1944). The leachate in this determination was analyzed for exchangeable Ca and K.
Calcium and potassium were determined by E.D.T.A. titration and with the flame photometer methods, respectively, as described under analytical methods.

Soils (2.4 Kg. per pot) were potted in gallon cans which were lined with polyethylene bags. Two series of treatments were initiated, one referred to as sulphate and the other as the hydroxide series. A blanket application of nutrients was added in each pot as follows: 100 ppm N as urea, 20 ppm Zn as ZnSO₄, 50 ppm Mg as MgSO₄, 1.6 ppm B as boric acid, and 500 ppm P as H₃PO₄. Treatments were as follows: three levels of Ca (5, 20 and 60 percent of the total C.E.C. of the soil) and two levels of K (1 and 10 percent of the total C.E.C. of the soil) saturations. All possible factorial combinations of these treatments were used in both series of treatments. In the hydroxide series, Ca and K were used as hydroxide to bring the soil to the required Ca and K saturations. The pH varied from treatment to treatment, and no attempt was made to adjust the pH of the soil. In the sulphate series of treatments, pH was adjusted to 4.9, which was the original pH of the soil, by adding required Ca as either CaSO₄ alone or in combination with Ca(OH)₂. Potassium was added as potassium sulphate.

Plant culture. Kaimi clover and corn crops were used as test crops. Kaimi clover seeds were scarified for 5 minutes in conc. H₂SO₄ and then washed with distilled water to remove
acid from the seeds. Fifteen seeds of kaimi clover and six seeds of corn were planted on 16 Aug. and 7 Oct., 1966, respectively, and, after 1 week of germination, they were thinned to eight kaimi clover and three corn plants. Distilled water was added to each pot as needed and once a day, each pot was weighed and brought to field capacity to ensure proper moisture control.

Kaimi clover (38 days old) and corn (26 days old) were cut near the surface of the soil. Roots were removed from the soil and washed with tapwater. Plant tops and tapwater washed roots were washed in dilute dreft detergent solution (0.01%) and then rinsed three times in distilled water. The samples were dried at 70°C and weighed. Samples were ground in an intermediate Wiley mill using a 20-mesh screen.

Analytical methods

Digestion of plant samples. Ground material was digested by leaving overnight in a micro-Kjeldahl flask with 15 ml. of 2:1 nitric-perchloric acid mixture. Then samples were heated until 1-2 ml. of liquid was left and only dense white fumes were visible. Digested samples were diluted, transferred completely into volumetric flasks, and brought to volume with distilled water. Blank samples were also processed in the same way.

Aluminum. The colorimetric method for Al described by Chapman and Pratt (1961) was followed. One to twenty ml. of aliquot of plant digest was transferred to 50 ml. volumetric flasks.
Two ml. of 1:100 thioglycollic acid were added in order to prevent interference of Fe in the formation of the Al complex. Ten ml. of aluminon reagent were added, then the pH was adjusted to 4.2 with NH₄OH or HCl. The volume was made to about 40 ml. and the volumetric flasks were put into a wire basket and immersed in boiling water for exactly 16 minutes. The water bath was covered during this period. The flasks were removed from the water bath, cooled for one and one-half hours, made up to volume, and mixed thoroughly. The intensity of color development was read on a Coleman junior colorimeter at 537.5 m\(\mu\). A curve factor, which was calculated from the standard curve, was multiplied by the readings for the samples to obtain the concentration (ppm) of aluminum in the aliquot.

**Calcium.** Calcium was usually determined by the E.D.T.A. method, but whenever the concentration was less than 1 ppm, the atomic absorption spectrophotometer was used.

In the E.D.T.A. method as described by Chapman and Pratt (1961), a 5 to 25 ml. aliquot containing no more than 0.1 m.e. of Ca were pipetted into a 3-inch diameter porcelain dish. Volume was made to 25 ml. with distilled water. Approximately 5 drops of 4N NaOH and 50 mg. of purpurate indicator were added. This mixed solution was titrated with 0.0107N E.D.T.A. using a 10 ml. micro-burette. The color change was from orange red to lavender or purple. The volume (ml.) of
EDTA used multiplied by its normality gave the amount of Ca as m.e. present in aliquot.

In the atomic absorption method, the sample was vaporized by a flame in the Perkin-Elmer atomic absorption spectrophotometer (Model 303). The sample values were compared with those of a standard curve and the concentration of Ca in the sample was calculated.

**Potassium.** Potassium was determined with the Beckman DU flame spectrophotometer. The solution containing the K ions was atomized into a flame and the reading was recorded. The K concentration was determined from a graph obtained by the use of appropriate standards.

**Phosphorus.** The method for P determination was similar to that described by Chapman and Pratt (1961). A 2 ml. aliquot was placed in a 50 ml. volumetric flask, diluted to 20 ml. and then 2 ml. of Barton's solution was added. The volume was made to 50 ml. with distilled water, then solution was mixed well and read on the Coleman Junior Colorimeter at 430 μ after standing for 30 minutes. The concentration of P was calculated with reference to a standard curve.

**Standardization of method for determining cation adsorption on plant roots**

Adsorption of cations on roots is affected by pretreatment of roots, concentration of saturating and desaturating solutions, and
times for root contact with saturating and desaturating solutions.

Pretreatment of roots. Barlett (1964) reported that electrodialysis or prewashing of roots in acid affected the measured exchange capacities of the roots. Acid washing of the fresh roots appeared to offer a rapid and simple method for producing hydrogen roots for subsequent experiments, provided the strength of the acid used did not injure roots. In theory, cation exchange of the root surface is almost instantaneous, so that the washing time should be kept to a minimum to reduce the chance for diffusion of cations from the interior of roots.

This experiment was conducted to study the effect of pretreatment with 0.01 N HCl on Al adsorption by plant roots. Unless otherwise stated, sugarcane was grown in cinders and pineapple was grown in distilled water for standardization of the method. Nutrients were supplied once a day for crops grown in cinders. The roots were separated from the aerial parts of the plant and were freed from the rooting medium by washing in distilled water.

One sample of pineapple roots was washed for a total period of 30 seconds in 0.01 N HCl (900 ml. acid in three beakers), and another sample was treated in an equal volume of distilled water for an equal period of time. Entrained solution on roots was removed by hand slinging. After pretreatment of roots, they were equilibrated for 20 seconds in a saturating solution (32 ppm
Al) at pH 4.0 then washed for a total period of 10 seconds with distilled water in two beakers, each containing 100 ml. distilled water. Entrained water on root surface was removed by hand slinging, and then roots were desaturated for 10 seconds in 100 ml. N BaCl₂ (pH 4.0) solution. Roots were then washed in distilled water and dried at 70°C. Results are reported in m.e. per 100 g. dry roots.

Washing roots in 0.01 N HCl improved Al adsorption capacity and helped to obtain reproducible results (Table 1). These results seem to agree with the earlier findings of other workers (Barlett, 1964; Drake et al., 1951). It was decided to pretreat roots for a total period of 30 seconds in 900 ml. of 0.01 N HCl in a series of three beakers before equilibrating in saturating solution.

Desorption solution. Since barium ions interfere in K determination by the flame photometer, some other desaturating solutions were compared. The procedure used was similar to that described under "Pretreatment of roots", except that 600 ml. of 35 ppm Ca was used as the saturating solution and 100 ml. of HCl, H₂SO₄ or N ammonium acetate (pH 4.0) were used as desaturating solutions.

Data in Table 2 clearly indicate that N HCl was the best desorption solution. It appears that exchange of adsorbed cations for H⁺ ions on the root surface became more complete as the
Table 1. Effect of Pretreatment of Roots on Al Adsorption by Pineapple Roots

<table>
<thead>
<tr>
<th>Washing of Roots in</th>
<th>Adsorbed Al in m.e. per 100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A*</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>3.9</td>
</tr>
<tr>
<td>0.01 N HCl</td>
<td>6.6</td>
</tr>
</tbody>
</table>

*A, B and C are replications.

Table 2. Influence of Various Desorption Solutions on the Amount of Ca Adsorbed on Kaimi Clover Roots

<table>
<thead>
<tr>
<th>Desorption Solution</th>
<th>Ca in m.e. per 100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td>N HCl</td>
<td>11.0</td>
</tr>
<tr>
<td>0.5 N HCl</td>
<td>9.2</td>
</tr>
<tr>
<td>0.1 N HCl</td>
<td>1.9</td>
</tr>
<tr>
<td>0.01 N HCl</td>
<td>1.0</td>
</tr>
<tr>
<td>N H$_2$SO$_4$</td>
<td>8.3</td>
</tr>
<tr>
<td>0.5 N H$_2$SO$_4$</td>
<td>7.3</td>
</tr>
<tr>
<td>0.1 N H$_2$SO$_4$</td>
<td>1.2</td>
</tr>
<tr>
<td>0.01 N H$_2$SO$_4$</td>
<td>0.67</td>
</tr>
<tr>
<td>N Ammonium Acetate (pH 4.0)</td>
<td>3.6</td>
</tr>
</tbody>
</table>
concentration of acid used was increased. Therefore, N HCl was selected as the desaturating solution for future use.

**Saturating solution- and desaturating solution-root contact times.** The method used was similar to that described under "Pretreatment of roots", except that roots were saturated in a series of four beakers, each containing 100 ml. of 0.1 N AlCl₃ or CaCl₂ or KCl for different periods of time and were desaturated with five successive washings of N HCl for 10, 50, 60, 90 and 90 seconds, with NHCl. Results are shown graphically in Figures 1 to 6.

The amounts of desorbed cations increased rapidly with time of root contact with desaturating solution up to 2 minutes, after which time slopes of the curves decreased. For pineapple the curves were almost flat between 2 and 5 minutes but for sugar-cane cations desorbed continued to increase slowly with time. Nevertheless, 2 minutes was selected as a standard desorption procedure for testing other aspects of cation-exchange by roots. The effects of variable adsorption times are plotted in Figures 7 and 8 for sugarcane and pineapple roots. Exchange reactions with roots are relatively rapid. This conclusion was also reached by Williams and Coleman (1950). A large portion of cations were adsorbed in the first 2 minutes. Therefore, 2 minutes of root contact with the saturating solution and 2 minutes desaturating time were selected. Two minutes time was selected for adsorption
Figure 1. Effect of Root Contact Time With Desaturating Solution on Al Adsorption by Sugarcane Roots
Figure 2. Effect of Root Contact Time With Desaturating Solution on Ca Adsorption by Sugarcane Roots
Figure 3. Effect of Root Contact Time With Desaturating Solution on K Adsorption by Sugarcane Roots
Figure 4. Effect of Root Contact Time With Desaturating Solution on Al Adsorption by Pineapple Roots
Figure 5. Effect of Root Contact Time With Desaturating Solution on Ca Adsorption by Pineapple Roots
Figure 6. Effect of Root Contact Time With Desaturating Solution on K Adsorption by Pineapple Roots
Figure 7. Effect of Sugarcane Root Contact Time With Saturating Solution on the Amount of Cations Desorbed in 2 Minutes
Figure 8. Effect of Pineapple Root Contact Time With Saturating Solution on the Amount of Cations Desorbed in 2 Minutes
and desorption as a precaution against diffusion of ions in and out of roots.

Although details of this methodology differ from other investigations, data can still be compared with work reported in the literature. Drake et al. (1951) and many other workers have used 5 minutes for titrating H ions in root C.E.C. determination. If saturating or desaturating times are shorter than 2 minutes, a slight variation in time will introduce a large difference in results. Later, results indicated that Al, Ca, and K were not released from the interior of roots by using these selected times (Appendix Tables 3, 4 and 5).

There is always a chance of losing adsorbed cations along with occluded cations from roots during the washing process. To examine this point, roots were pretreated by the standard procedure, washed with distilled water to remove excess acid and then equilibrated in mono-cationic solution (three beakers, each containing 500 ml. of saturating solution) for a total period of 2 minutes. An aliquot of the supernatant solution was taken from each beaker and composited for analysis. Differences between the composition of the composited, supernatant solution and its original concentration multiplied by the total solution volume was taken as the amount of cations adsorbed by the roots. This method is referred to as the "adsorption procedure" for determining cations adsorbed. The same roots were used to compare
associated cations with the standard "desorption method" as described under the section, "Determination of adsorbed cations by plant roots".

It is also possible that cations may be chelated on root surfaces and are not removed. To test this point, after cations were removed by standard desorption procedure, the roots were washed with four washes of distilled water and the adsorption-desorption procedure was repeated.

The results of these tests are reported in Appendix Table 3. These data clearly indicate that cations are neither chelated nor significantly lost when roots are washed with distilled water.
RESULTS AND DISCUSSION

Cation-exchange capacity of plant roots

Cation exchange properties of root systems have been studied by many workers. They also suggested reactive groups which may be responsible for cation adsorption (Teorell, 1935; Osterhout, 1936; Brooks, 1937; Lundegardh, 1945). But whatever may be the nature of the reactive groups on the root surface, it was found that H⁺ ions produced by metabolic processes were present on root surfaces. These H⁺ ions are readily exchanged by metallic cations such as Ca⁺⁺, K⁺ - as shown by Williams and Coleman (1950). These H⁺ ions lend themselves to quantitative determinations.

A study was made of the C.E.C. of four plant species of economic importance in Hawaii. The results are reported in Table 3.

Table 3. Cation-Exchange Capacity of Plant Roots

<table>
<thead>
<tr>
<th>Replication</th>
<th>m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pineapple</td>
</tr>
<tr>
<td>A</td>
<td>6.9</td>
</tr>
<tr>
<td>B</td>
<td>7.2</td>
</tr>
<tr>
<td>Mean</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The results indicated that the method used for determining C.E.C. of plant roots is reproducible. The C.E.C. of kaimi
clover roots was 1.5 times more than corn, 2.1 times more than sugarcane, and 2.9 times more than pineapple roots. There was a wide range in C.E.C. for the monocots. The C.E.C. of corn roots was 1.4 times greater than sugarcane and 1.8 times greater than pineapple roots. These findings are in accordance with the results reported by Drake et al. (1951). They found that C.E.C. of roots of the dicotyledonous investigated were roughly double the value for monocotyledonous. They also reported a wide range of C.E.C. of monocots. In general, the C.E.C. values of dicotyledonous as well as monocotyledonous roots were lower than the values reported by Drake et al. (1951). For example, they reported C.E.C. values of 35 and 48 m.e. per 100 g. dry roots for tomato and alfalfa, respectively, and 12 and 26 m.e. per 100 g. dry roots for barley and corn, respectively.

**Adsorption of cations from mono-cationic salt solutions**

The primary objective of this experiment was to determine the amount of Ca, K, and Al adsorption by plant roots at different concentrations in saturating solutions. The results obtained for these cations are plotted against their concentrations in the saturating solutions (Figs. 9 to 11). In these figures, the curves for pineapple and sugarcane and for corn and kaimi clover tend to pair up. This is as expected because the C.E.C. for kaimi clover and corn roots exceeded pineapple and sugarcane roots.
Figure 9. Calcium Adsorption by Roots from Saturating Solutions Which Varied in Ca Concentration
Figure 10. Potassium Adsorption by Roots from Saturating Solutions Which Varied in K Concentration
Figure 11. Aluminum Adsorption by Roots from Saturating Solutions Which Varied in Al Concentration
The curves in Fig. 9 indicated that Ca adsorption on kaimi clover roots was more than on other plant roots. If the C.E.C. of roots was high, then the amount of Ca adsorption was also high. In the order of increasing amount of Ca adsorbed, the plant species can be arranged as follows: pineapple < sugarcane < corn < kaimi clover.

When the Ca concentration in the saturating solution was increased from 0.1 to 100.0 m.e. per liter, the amount of adsorbed Ca increased more for pineapple and corn roots than for sugarcane and kaimi clover roots. In other words, Ca ions replaced relatively more H ions on pineapple and corn than on sugarcane and kaimi clover.

The amount of K adsorbed on kaimi clover roots was greater than on sugarcane and pineapple roots, but was lower than on corn roots (Fig. 10). In the C.E.C. determinations, H\(^+\) ions on roots were replaced by K\(^+\) ions, and the C.E.C. was determined by measuring the amount of H\(^+\) ions replaced from roots; but, in this procedure, the case was the reverse. The order of increasing amount of K adsorption on the plant species is: pineapple < sugarcane < kaimi clover < corn.

When the K concentration in the saturating solution was increased from 0.01 to 10.0 m.e. per liter, then the amount of adsorbed K increased more for kaimi clover roots than for other plant roots.
The amount of Al adsorbed was more on kaimi clover roots than on pineapple, sugarcane, or corn roots. The various plant species can be arranged according to the amount of Al on the roots as follows: pineapple < sugarcane < corn < kaimi clover. The order is the same for C.E.C. and Ca-exchange capacities of roots.

When the Al concentration was increased from 0.01 to 1.0 m.e. per liter, the Al adsorption increased more for pineapple and sugarcane roots than for corn and kaimi clover. In other words, Al ions replaced relatively more H ions on pineapple and sugarcane than on corn and kaimi clover.

Exchange reactions are known to be stoichiometric and governed by the laws of mass action and chemical equilibrium. Therefore, increased concentrations of saturating cations causes greater adsorption of cations. It was observed that the Ca, K, and Al adsorption increased with increase in their concentrations in saturating solutions. Helmy and Elgabaly (1958) also reported that the amount of $H^+$ replaced by $K^+$ or $Ba^{++}$ ions increased with increased concentrations of replacing cations.

More K was adsorbed than Ca or Al by all plant species. Overstreet et al. (1952) found that the metabolically active excised roots absorbed 8 to 10 times more K than Ca.

The percentage saturation of roots with cations was higher for pineapple than for other plant species. Almost 90 percent of
the exchange sites on pineapple roots were saturated K, as compared to about 45 percent of exchange sites saturated on kaimi clover roots (Table 4). It is difficult to understand why K should be held proportionally in greater amounts by pineapple roots than by other plant roots. Perhaps the molecular configuration of organic compounds in root surface membranes may be such that K can be easily and preferentially adsorbed by pineapple roots.

Adsorption of cations from bi-cationic salt solutions

The amount of Al and Ca or Al and K adsorbed on plant roots from bi-cationic solutions were investigated using solutions adjusted to pH 4.0 with HCl. At this pH, Al is soluble at the concentrations used. The results are reported in Tables 5 and 6.

Table 5 reveals that the amount of Al and Ca adsorbed on roots was greatly influenced by the concentrations of these cations in saturating solutions. At any particular Ca level, the amount of adsorbed Al increased with increasing Al concentration in the saturating solution. Similarly, at any level of Al the amount of adsorbed Ca increased with increasing concentration in the saturating solution.

If two ions, A and B, can be adsorbed on the same exchange sites, then each would be expected to interfere with the adsorption of the other. An example of this type of competition can be seen in Table 5. If Ca concentration was kept constant, the amount of
Table 4. Cations Adsorbed as a Fraction of the C.E.C. of Plant Roots

<table>
<thead>
<tr>
<th>Cation</th>
<th>Treatment Added m.e./l.</th>
<th>Pineapple</th>
<th>Sugarcane</th>
<th>Corn</th>
<th>Kaimi Clover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.1</td>
<td>0.44</td>
<td>0.43</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.56</td>
<td>0.49</td>
<td>0.55</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.67</td>
<td>0.54</td>
<td>0.64</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>0.91</td>
<td>0.72</td>
<td>0.77</td>
<td>0.57</td>
</tr>
<tr>
<td>K</td>
<td>0.01</td>
<td>0.77</td>
<td>0.59</td>
<td>0.56</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.88</td>
<td>0.69</td>
<td>0.63</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.91</td>
<td>0.76</td>
<td>0.78</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>0.97</td>
<td>0.88</td>
<td>0.93</td>
<td>0.54</td>
</tr>
<tr>
<td>Al</td>
<td>0.01</td>
<td>0.15</td>
<td>0.13</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.28</td>
<td>0.23</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.56</td>
<td>0.42</td>
<td>0.34</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Table 5. Adsorption of Al and Ca on Plant Roots from Bi-Cationic Solution of Al and Ca (pH 4.0)

<table>
<thead>
<tr>
<th>Treatment m.e./l.</th>
<th>Exchangeable Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pineapple Al</td>
</tr>
<tr>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>1.0</td>
<td>0.31</td>
</tr>
<tr>
<td>10.0</td>
<td>0.28</td>
</tr>
<tr>
<td>100.0</td>
<td>0.22</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1.0</td>
<td>0.79</td>
</tr>
<tr>
<td>10.0</td>
<td>0.51</td>
</tr>
<tr>
<td>100.0</td>
<td>0.49</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>1.0</td>
<td>2.70</td>
</tr>
<tr>
<td>10.0</td>
<td>2.62</td>
</tr>
<tr>
<td>100.0</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Table 6. Adsorption of Al and K on Plant Roots from Bi-Cationic Solution of Al and K (pH 4.0)

<table>
<thead>
<tr>
<th>Treatment m.e./l.</th>
<th>Exchangeable Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pineapple Al</td>
</tr>
<tr>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
</tr>
<tr>
<td>10.0</td>
<td>1.00</td>
</tr>
<tr>
<td>100.0</td>
<td>10.00</td>
</tr>
<tr>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
</tr>
<tr>
<td>10.0</td>
<td>1.00</td>
</tr>
<tr>
<td>100.0</td>
<td>10.00</td>
</tr>
<tr>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>1.0</td>
<td>1.00</td>
</tr>
<tr>
<td>10.0</td>
<td>1.00</td>
</tr>
<tr>
<td>100.0</td>
<td>1.00</td>
</tr>
</tbody>
</table>
adsorbed Ca decreased as the Al concentration in the saturating solution was increased. For example, when Al concentration was increased from 0.01 to 1.0 m.e. per liter, Ca adsorption from the 10.0 m.e. per liter solution decreased from 4.61 to 2.04 m.e. per 100 g. sugarcane dry roots. This trend was observed in all plant species. Likewise, if Ca concentration in the saturating solution at any level of Al was increased, the amount of Al adsorbed decreased. However, the effects of cations on one another are not equivalent. At equivalent concentrations Ca decreased Al adsorption by pineapple roots more than Al decreased Ca, but the case was reversed for other plant species.

Table 6 shows that K adsorption increased as the concentration of this cation was increased from 0.01 to 10 m.e. per liter in the saturating solution. This was true at all levels of Al. Kaimi clover roots adsorbed more K than pineapple or sugarcane but less than corn roots (Table 6). This trend is in agreement with results for the experiment using mono-cationic solutions.

The adsorption of K on roots decreased with increasing Al concentration in saturating solutions. For example, K adsorption from the 10.0 m.e. K per liter solution decreased from 6.41 to 4.88 m.e. per 100 g. dry roots by increasing Al from 0.01 to 1.0 m.e. per liter saturating solution. The effects of cations on one another were reciprocal, but Al decreased K adsorption
more than K decreased Al adsorption.

The Al adsorption was influenced by the complementary cations, being higher with Ca than with K. For instance, sugar-cane roots adsorbed 32 percent more Al from the solution containing 0.1 m.e. per liter of Al and Ca each, than from the solution containing 0.1 m.e. per liter of Al and K. This trend was observed for roots of all plants. This may be associated with the fact that percentage K saturation was higher than percentage Ca saturation on plant roots. Therefore, fewer exchange sites on roots were left for Al adsorption when K was the complementary cation. Mehlich (1953) suggested that the ratio of K to Ca adsorbed by roots is related to the concentration and proportion of RH to RCOOH of roots. If this is true, these roots, especially pineapple, are relatively high in RH groups.

The ion exchange reaction can be considered as an adsorption system either obeying the Langmuir isotherm or Freundlich isotherm, or as a reaction obeying the law of mass action. All these theories agree in that the amount of an ion adsorbed by the root increases with the concentration of that ion in the solution. The empirical equation for the Langmuir isotherm is:

\[
\frac{c}{x/m} = \frac{1}{ab} + \frac{c}{a}
\]  

(1)

where \(x/m\) is the amount of solute adsorbed by unit weight of adsorbent, \(c\) is the concentration of solution at equilibrium and \(a\)
and b are constants. An attempt was made to fit the experimental data to the above equation. The data did not follow the Langmuir adsorption isotherm. The equation for the Freundlich adsorption equation is:

$$\frac{x}{m} = k c^{1/n} \tag{2}$$

where k and n are constants. This relationship was obtained empirically by Freundlich. Taking logarithms of equation (2), we have:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \tag{3}$$

so that if \( \log n \) is plotted against \( \log c \), a straight line should be obtained. When the experimental data were plotted, points were scattered and did not fit the Freundlich adsorption isotherm.

Apparent ion-exchange equilibrium constants (Kc) involving Al and Ca or K were calculated. The results of the equilibrium measurements have been put into the form of stoichiometric equilibrium quotients for the reactions:

For bi-cationic solutions (Al + Ca)

$$\frac{3/Al}{x} + \frac{1}{Ca} = \frac{1}{Ca_x} + \frac{3/Al}{x} \tag{4}$$

where x stands for ions adsorbed on roots.

$$Kc = \frac{\frac{1}{Ca_x}}{\frac{1}{Ca}} \cdot \frac{3/Al}{3/Al_x} \tag{5}$$
For bi-cationic solutions (Al + K)

\[ \frac{3}{\text{Al}_x} + \text{K} = \text{K}_x + \frac{3}{\text{Al}} \]  \hspace{1cm} (6)

\[ K_c = \frac{\text{K}_x}{\text{K}} \cdot \frac{\frac{3}{\text{Al}}}{\frac{3}{\text{Al}_x}} \]  \hspace{1cm} (7)

Apparent exchange constants were calculated from known concentrations of Al and Ca or K and reported in Tables 7 and 8. In this model, concentrations were employed instead of activity of ions, because concentrations were low in all cases. The $K_c$ values varied widely depending upon the concentrations of Al and Ca or K present, suggesting that plant species differ markedly in their preferences for Al, Ca or K. High $K_c$ values indicate selective or preferential adsorption of Ca or K over Al by roots (Tables 7 and 8). Relatively greater affinity of roots for Ca or K occurred when Ca or K concentrations were low in bi-cationic solutions. The affinity for Ca or K decreased with increasing Ca or K concentrations in solutions at all levels of Al concentration. Aluminum in the solution also had marked effect on root affinity for Ca or K adsorption. The $K_c$ values for Ca or K increased with increasing Al concentration in solution except for pineapple roots having the lowest concentration of K in the solution.

**Adsorption of cations from tri-cationic salt solutions**

An investigation was conducted to study competition among
Table 7. Apparent Exchange Equilibrium Constants (Kc) for Ca-Al Ion Pair

<table>
<thead>
<tr>
<th>Ratio of Al to Ca Added in the Solution</th>
<th>Pineapple Ratio of Al to Ca in the Equilibrium Solution</th>
<th>Kc</th>
<th>Kaimi Clover Ratio of Al to Ca in the Equilibrium Solution</th>
<th>Kc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>1:13.23</td>
<td>0.49</td>
<td>1:16.22</td>
<td>0.37</td>
</tr>
<tr>
<td>1:100</td>
<td>1:116.09</td>
<td>0.24</td>
<td>1:185.90</td>
<td>0.11</td>
</tr>
<tr>
<td>1:1000</td>
<td>1:1160.01</td>
<td>0.086</td>
<td>1:1609.97</td>
<td>0.035</td>
</tr>
<tr>
<td>1:10000</td>
<td>1:11233.03</td>
<td>0.033</td>
<td>1:15621.87</td>
<td>0.017</td>
</tr>
<tr>
<td>1:1</td>
<td>1:0.99</td>
<td>0.82</td>
<td>1:0.89</td>
<td>1.01</td>
</tr>
<tr>
<td>1:10</td>
<td>1:10.61</td>
<td>0.36</td>
<td>1:11.08</td>
<td>0.33</td>
</tr>
<tr>
<td>1:100</td>
<td>1:105.02</td>
<td>0.19</td>
<td>1:108.82</td>
<td>0.12</td>
</tr>
<tr>
<td>1:1000</td>
<td>1:1051.00</td>
<td>0.054</td>
<td>1:1231.03</td>
<td>0.028</td>
</tr>
<tr>
<td>1:0.1</td>
<td>1:0.085</td>
<td>1.42</td>
<td>1:0.086</td>
<td>1.55</td>
</tr>
<tr>
<td>1:1</td>
<td>1:1.01</td>
<td>0.46</td>
<td>1:1.00</td>
<td>0.51</td>
</tr>
<tr>
<td>1:10</td>
<td>1:10.25</td>
<td>0.20</td>
<td>1:10.17</td>
<td>0.18</td>
</tr>
<tr>
<td>1:100</td>
<td>1:102.64</td>
<td>0.051</td>
<td>1:101.68</td>
<td>0.022</td>
</tr>
<tr>
<td>Ratio of Al to K Added in the Solution</td>
<td>Ratio of Al to K in the Equilibrium Solution</td>
<td>Pineapple Kc</td>
<td>Kaimi Clover Kc</td>
<td>Clover Kc</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>---------------------------------------------</td>
<td>-------------</td>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td>1:1</td>
<td>1:0.34</td>
<td>4.70</td>
<td>1:0.20</td>
<td>2.77</td>
</tr>
<tr>
<td>1:10</td>
<td>1:10.01</td>
<td>0.56</td>
<td>1:14.54</td>
<td>0.18</td>
</tr>
<tr>
<td>1:100</td>
<td>1:130.94</td>
<td>0.044</td>
<td>1:158.32</td>
<td>0.022</td>
</tr>
<tr>
<td>1:1000</td>
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<td>0.0048</td>
<td>1:1386.06</td>
<td>0.0028</td>
</tr>
<tr>
<td>1:0.1</td>
<td>1:0.047</td>
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<td>1:0.035</td>
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</tr>
<tr>
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<td>1:0.56</td>
<td>2.10</td>
<td>1:0.86</td>
<td>0.61</td>
</tr>
<tr>
<td>1:10</td>
<td>1:10.17</td>
<td>0.13</td>
<td>1:10.56</td>
<td>0.066</td>
</tr>
<tr>
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<td>1:107.84</td>
<td>0.0081</td>
</tr>
<tr>
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<td>1:0.016</td>
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<td>1:0.0036</td>
<td>9.74</td>
</tr>
<tr>
<td>1:0.1</td>
<td>1:0.069</td>
<td>1.82</td>
<td>1:0.082</td>
<td>0.88</td>
</tr>
<tr>
<td>1:1</td>
<td>1:0.97</td>
<td>0.18</td>
<td>1:0.99</td>
<td>0.080</td>
</tr>
<tr>
<td>1:10</td>
<td>1:10.27</td>
<td>0.021</td>
<td>1:10.10</td>
<td>0.010</td>
</tr>
</tbody>
</table>
AI, Ca and K for adsorption on plant roots. The experiment was set up factorially with three levels each of AI, Ca and K. The amount of cations adsorbed on plant roots are reported in Tables 9 and 10.

The amounts of cations adsorbed on roots of various plant species as a function of concentration is previously reported in mono-cationic solution. When the concentration of one cation in solution was increased, the adsorption of all other cations decreased. For example, when pineapple roots were equilibrated with solutions containing 0.01 m.e. Al and 0.1 m.e. Ca but increasing amounts of K, Al adsorption decreased from 1.13 to 0.72 m.e. and Ca adsorption decreased from 2.15 to 1.75 m.e. - a decrease of 36 percent for Al but only 19 percent for Ca. Similar values for kaimi clover are 16 percent decrease for Al and 48 percent decrease for Ca. The relative effects of increasing K may best be shown by roots as follows:

<table>
<thead>
<tr>
<th>Ca decrease</th>
<th>Pineapple</th>
<th>Sugarcane</th>
<th>Corn</th>
<th>Kaimi Clover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al decrease</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td>0.97</td>
<td>0.72</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Clearly there are important differences between species in the way cations are held by roots. These data suggest that increasing the K supply in an aluminum soil may interfere with Ca nutrition of kaimi clover more than for pineapple, corn and sugarcane.
Table 9. Adsorption of Al, Ca, and K on Plant Roots from Tri-Cationic Solution (pH 4.0)

<table>
<thead>
<tr>
<th>Cations treatment m.e./l</th>
<th>Cations in m.e./100 g Dry Roots</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pineapple</td>
<td>Sugarcane</td>
</tr>
<tr>
<td></td>
<td>Al     Ca     K     Total</td>
<td>Al     Ca     K     Total</td>
</tr>
<tr>
<td>0.01 0.1 0.01</td>
<td>1.13   2.15   1.93   5.21</td>
<td>1.40   2.80   2.07   6.27</td>
</tr>
<tr>
<td>0.10</td>
<td>0.98   1.91   2.15   5.04</td>
<td>1.21   2.32   2.62   6.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.72   1.75   2.82   5.29</td>
<td>0.98   1.98   3.96   6.92</td>
</tr>
<tr>
<td>0.01 5</td>
<td>0.92   2.62   1.65   5.19</td>
<td>1.10   3.20   1.90   6.20</td>
</tr>
<tr>
<td>0.10</td>
<td>0.81   2.37   1.79   4.97</td>
<td>0.86   2.89   1.98   5.73</td>
</tr>
<tr>
<td>1.00</td>
<td>0.62   1.90   1.99   4.51</td>
<td>0.76   2.04   2.70   5.50</td>
</tr>
<tr>
<td>0.01 25</td>
<td>0.64   2.89   1.23   4.76</td>
<td>0.90   3.67   1.61   6.18</td>
</tr>
<tr>
<td>0.10</td>
<td>0.42   2.66   1.36   4.44</td>
<td>0.81   3.09   1.79   5.69</td>
</tr>
<tr>
<td>1.00</td>
<td>0.31   2.17   1.86   4.34</td>
<td>0.63   2.89   2.05   5.57</td>
</tr>
<tr>
<td>0.1 0.1 0.01</td>
<td>1.27   2.16   1.78   5.26</td>
<td>2.00   1.92   1.94   5.86</td>
</tr>
<tr>
<td>0.10</td>
<td>1.32   2.39   1.89   4.60</td>
<td>1.87   1.80   2.21   5.88</td>
</tr>
<tr>
<td>1.00</td>
<td>0.98   1.32   2.17   4.47</td>
<td>1.60   1.61   1.68   4.89</td>
</tr>
<tr>
<td>0.1 5</td>
<td>0.39   2.12   1.39   4.90</td>
<td>1.82   2.24   1.80   5.86</td>
</tr>
<tr>
<td>0.10</td>
<td>1.17   1.88   1.68   4.73</td>
<td>1.61   2.10   1.98   5.69</td>
</tr>
<tr>
<td>1.00</td>
<td>0.86   1.59   1.77   4.22</td>
<td>1.31   1.87   2.04   5.22</td>
</tr>
<tr>
<td>0.1 25</td>
<td>0.12   2.61   1.17   4.90</td>
<td>1.32   2.98   1.41   5.71</td>
</tr>
<tr>
<td>0.10</td>
<td>0.96   2.44   1.29   4.69</td>
<td>1.17   2.69   1.47   5.33</td>
</tr>
<tr>
<td>1.00</td>
<td>0.64   2.07   1.66   4.37</td>
<td>0.99   2.47   1.78   5.24</td>
</tr>
<tr>
<td>1.0 0.1 0.01</td>
<td>2.00   1.59   1.60   5.19</td>
<td>2.37   1.86   1.87   6.10</td>
</tr>
<tr>
<td>0.10</td>
<td>1.61   1.17   1.48   4.26</td>
<td>2.00   1.70   1.77   5.47</td>
</tr>
<tr>
<td>1.00</td>
<td>1.39   0.98   1.63   4.00</td>
<td>1.86   1.53   1.95   5.34</td>
</tr>
<tr>
<td>1.0 5</td>
<td>0.12   1.86   1.19   4.87</td>
<td>2.04   2.11   1.37   5.52</td>
</tr>
<tr>
<td>0.10</td>
<td>1.45   1.65   1.28   4.38</td>
<td>1.82   1.93   1.52   5.27</td>
</tr>
<tr>
<td>1.00</td>
<td>1.17   1.23   1.39   3.79</td>
<td>1.61   1.62   1.67   4.90</td>
</tr>
<tr>
<td>1.0 25</td>
<td>0.12   2.38   0.98   4.68</td>
<td>1.67   2.65   1.12   5.44</td>
</tr>
<tr>
<td>0.10</td>
<td>1.10   2.22   1.09   4.41</td>
<td>1.32   2.31   1.31   4.94</td>
</tr>
<tr>
<td>1.00</td>
<td>0.96   1.65   1.35   3.96</td>
<td>1.07   1.92   1.49   4.48</td>
</tr>
</tbody>
</table>
Table 10. Adsorption of Al, Ca, and K on Plant Roots
from Tri-Cationic Solution (pH 4.0)

<table>
<thead>
<tr>
<th>Cations treatment m.e./l.</th>
<th>Cations in m.e./100 g. Dry Roots</th>
<th>Corn</th>
<th>Kaimi</th>
<th>Clover</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Ca</td>
<td>K</td>
<td>Total</td>
</tr>
<tr>
<td>0.01 0.1 0.01</td>
<td>1.76</td>
<td>3.11</td>
<td>4.71</td>
<td>9.58</td>
</tr>
<tr>
<td>0.10</td>
<td>0.99</td>
<td>2.21</td>
<td>5.22</td>
<td>8.42</td>
</tr>
<tr>
<td>1.00</td>
<td>0.81</td>
<td>1.90</td>
<td>5.95</td>
<td>8.66</td>
</tr>
<tr>
<td>0.01 5 0.01</td>
<td>1.31</td>
<td>3.94</td>
<td>4.04</td>
<td>9.29</td>
</tr>
<tr>
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<td>3.15</td>
<td>4.95</td>
<td>8.96</td>
</tr>
<tr>
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<td>0.71</td>
<td>3.02</td>
<td>5.32</td>
<td>9.05</td>
</tr>
<tr>
<td>0.01 25 0.01</td>
<td>1.17</td>
<td>4.10</td>
<td>3.98</td>
<td>9.25</td>
</tr>
<tr>
<td>0.10</td>
<td>0.77</td>
<td>3.81</td>
<td>4.09</td>
<td>8.67</td>
</tr>
<tr>
<td>1.00</td>
<td>0.66</td>
<td>3.25</td>
<td>4.27</td>
<td>8.18</td>
</tr>
<tr>
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<td>2.37</td>
<td>2.82</td>
<td>4.41</td>
<td>9.60</td>
</tr>
<tr>
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<td>2.11</td>
<td>2.09</td>
<td>4.92</td>
<td>9.12</td>
</tr>
<tr>
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<td>1.92</td>
<td>1.61</td>
<td>5.02</td>
<td>8.55</td>
</tr>
<tr>
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<td>2.07</td>
<td>3.32</td>
<td>3.98</td>
<td>9.37</td>
</tr>
<tr>
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<td>1.93</td>
<td>3.17</td>
<td>4.69</td>
<td>9.79</td>
</tr>
<tr>
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<td>1.54</td>
<td>2.98</td>
<td>4.82</td>
<td>9.34</td>
</tr>
<tr>
<td>0.1 25 0.01</td>
<td>1.87</td>
<td>3.72</td>
<td>3.69</td>
<td>9.28</td>
</tr>
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<td>3.40</td>
<td>3.89</td>
<td>8.91</td>
</tr>
<tr>
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<td>3.06</td>
<td>4.11</td>
<td>8.24</td>
</tr>
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<td>1.98</td>
<td>4.16</td>
<td>8.76</td>
</tr>
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<td>1.62</td>
<td>4.66</td>
<td>8.47</td>
</tr>
<tr>
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<td>1.96</td>
<td>1.52</td>
<td>4.72</td>
<td>8.20</td>
</tr>
<tr>
<td>1.0 5 0.01</td>
<td>2.19</td>
<td>2.87</td>
<td>3.81</td>
<td>8.87</td>
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<td>2.67</td>
<td>3.99</td>
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<td>1.90</td>
<td>2.31</td>
<td>4.75</td>
<td>8.96</td>
</tr>
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<td>1.0 25 0.01</td>
<td>1.99</td>
<td>3.09</td>
<td>3.17</td>
<td>8.25</td>
</tr>
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<td>1.76</td>
<td>2.98</td>
<td>3.32</td>
<td>8.06</td>
</tr>
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<td>1.62</td>
<td>2.82</td>
<td>3.62</td>
<td>8.06</td>
</tr>
</tbody>
</table>
If Al, Ca, and K were at equivalent concentration in tricationic saturating solutions, then K adsorption by plant roots was always the highest. This agrees with results from mono-cationic and bi-cationic solutions. Even when the concentration of Ca was ten times higher than K (0.1 m.e. Ca and 0.01 m.e. K), K adsorption at the low level of Al (0.01 m.e.) was still more than Ca on kaimi clover and corn roots. But, Drake et al. (1951) suggested that grass roots hold relatively more K than Ca and that legumes hold relatively more Ca than K.

From the data in Tables 9 and 10, the Ca/Al ratios were calculated for pineapple and kaimi clover roots. These ratios are plotted against K concentration (Figs. 12 to 14). At low and medium levels of Al and all levels of Ca (0.1, 5, and 25 m.e.), as the K concentration was increased from 0.01 to 1.0 m.e. per liter solution, the Ca/Al ratio increased on pineapple roots but decreased on kaimi clover roots. This trend was not observed at high levels of Al. This may be because K competes better with Ca than Al on kaimi clover roots, while the reverse is true for pineapple roots at low and medium levels of Al.

**Adsorption of cations from soil suspensions at variable pH**

The adsorption of cations from salt solutions by the plant roots as already discussed is oversimplified. In the natural environment both root and soil colloids compete for the sorption of cations. This study was an attempt to measure the influence of
Figure 12. Influence of K on Ca:Al Adsorbed on Plant Roots
Figure 13. Influence of K on Ca:Al Adsorbed on Plant Roots
HIGH AI

Ca (m.e./l)

- = .1
* = 5
* = 25

-- PINEAPPLE

-- KAIMI CLOVER

Figure 14. Influence of K on Ca:Al Adsorbed on Plant Roots
Al, Ca, or K associated with soil suspensions on the cation status of the supernatant solutions and on the cation adsorption by plant roots.

Colloidal size particles play a highly important role in determining the physical and physico-chemical properties of soils. Not only do colloids determine the C.E.C. of the soil but also the activity of ions in the soil solution.

**Adsorption of Al and Ca.** Akaka, Kapaa, and Molokai soil materials (silt and clay) were used in this investigation. The cation-exchange capacities of these soil materials were: Akaka, 80.1; Kapaa, 27.2; and Molokai, 22.7 m.e. per 100 g. soil. For the purpose of this investigation, Al saturated soil materials were prepared as described in the "Materials and Methods" section. Four rates of Ca (as hydroxide) equivalent to 0, 10, 20, and 60 percent saturation were added to the one percent soil suspensions. Suspensions were equilibrated for sufficient time by occasional shaking. The supernatant solutions were separated from the bulk of the soil by centrifugation and were analyzed for Al and Ca. These data are reported in Table 11.

The pH of the soil suspensions increased as increments of Ca(OH)$_2$ were added. As the pH increased, Al in the supernatant solutions decreased while Ca in the supernatant solutions increased. Calcium concentrations were greatest in the supernatant solutions from the Akaka soil suspensions at all percentages.
Table 11. Influence of the Ca(OH)$_2$ Application in 1 Percent Soil Suspension on Al and Ca Remaining in the Supernatant Solution and pH of the Soil Suspension

<table>
<thead>
<tr>
<th>Percentage Ca Saturation*</th>
<th>pH of the Soil Suspension</th>
<th>Cations in m.e./liter Supernatant Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Akaka</td>
<td>Kapaa</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>4.4</td>
<td>4.8</td>
</tr>
<tr>
<td>20</td>
<td>5.6</td>
<td>5.3</td>
</tr>
<tr>
<td>60</td>
<td>6.6</td>
<td>6.0</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca added, but not necessarily adsorbed on the soil colloids.
of Ca saturation. This was not because of low Ca retention by the Akaka soil but was related to the larger amount of Ca(OH)$_2$ added.

Although Ca(OH)$_2$ equivalent to 10, 20, and 60 percent saturation was added, the actual percentage Ca saturation was 8, 10, and 32 for the Akaka, 6, 7, and 22 for the Kapaa, and 5, 8, and 22 for the Molokai soil suspensions. The amount of Ca remaining in the Kapaa supernatant solution was slightly greater than that in the Molokai supernatant solution, even though the actual percentage of Ca saturation was similar for both soils. Thus, it appears that the bonding energy for Ca by Kapaa soil materials may be lower than by Molokai soil materials.

Aluminum and calcium adsorption by plant roots equilibrated with these soil suspensions were studied. The same levels of Ca(OH)$_2$ reported earlier were added to 1 percent soil suspensions for this investigation. The results are reported in Table 12.

Aluminum adsorption by plant roots decreased with the increasing Ca(OH)$_2$ additions to soil suspensions. For example, when Ca equivalent to 60% saturation was added, Al adsorption on pineapple roots decreased by 39 percent for the Akaka, 50 percent for the Kapaa and 33 percent for the Molokai soil suspensions. The same trend was found for sugarcane, corn and kaimi clover. The decrease in Al adsorption by roots in response
Table 12. Influence of Percentage Ca Saturation Added as Ca(OH)$_2$ in 1 Percent Soil Suspension on the Adsorption of Al and Ca by Plant Roots

<table>
<thead>
<tr>
<th>Percentage Ca Saturation*</th>
<th>pH</th>
<th>Pineapple</th>
<th>Sugarcane</th>
<th>Corn</th>
<th>Kaimi</th>
<th>Clover</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
<td>Al</td>
<td>Ca</td>
<td>Al</td>
</tr>
<tr>
<td>Akaka Soil Materials</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>4.0</td>
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<td>0.00</td>
<td>2.54</td>
<td>0.00</td>
<td>2.68</td>
</tr>
<tr>
<td>10</td>
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<td>2.00</td>
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<td>2.14</td>
<td>0.57</td>
<td>2.25</td>
</tr>
<tr>
<td>20</td>
<td>5.6</td>
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<td>0.68</td>
<td>1.92</td>
<td>0.83</td>
<td>1.98</td>
</tr>
<tr>
<td>60</td>
<td>6.6</td>
<td>1.52</td>
<td>0.82</td>
<td>1.63</td>
<td>0.94</td>
<td>1.76</td>
</tr>
<tr>
<td>Kapaa Soil Materials</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.3</td>
<td>2.94</td>
<td>0.00</td>
<td>2.98</td>
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<tr>
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<tr>
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<td>0.68</td>
<td>1.54</td>
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<td>Molokai Soil Materials</td>
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</tr>
<tr>
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<td>2.80</td>
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</tr>
<tr>
<td>10</td>
<td>4.9</td>
<td>2.17</td>
<td>0.28</td>
<td>2.41</td>
<td>0.42</td>
<td>2.35</td>
</tr>
<tr>
<td>20</td>
<td>5.5</td>
<td>1.93</td>
<td>0.35</td>
<td>2.14</td>
<td>0.50</td>
<td>2.20</td>
</tr>
<tr>
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<td>6.2</td>
<td>1.75</td>
<td>0.43</td>
<td>1.76</td>
<td>0.75</td>
<td>1.88</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca added, but not necessarily adsorbed on the root colloids.
to Ca(OH)$_2$ additions was most pronounced for the Kapaa soil suspensions. This is probably related to the fact that Ca(OH)$_2$ applications depressed Al solubility most in the Kapaa soil suspensions (Table 11). Aluminum adsorption by plant roots was more from the Molokai soil suspensions than from the Akaka or Kapaa soil suspensions whenever Ca was added, regardless of saturation percentage.

Calcium adsorption by plant roots increased with increasing Ca(OH)$_2$ additions to the soil suspensions. Plant roots adsorbed Ca in greater quantity from the Akaka than from the Kapaa or Molokai soil suspensions.

Thus, it appears that if the supernatant solution of a particular soil suspension contains high concentrations of a cation, then, accordingly, adsorption of that cation by roots should also be high. But, it is interesting to note that this did not apply when the Al adsorption by roots was compared with the Ca adsorption by roots. Aluminum adsorption was higher than Ca, even though Al concentration was lower than Ca in the supernatant solution.

The ionic environment in which a plant root exists in soil is determined by the ions dissociated from the soil colloids. The dissociation of the cations is related to the cations adsorbed on the clay mineral. This has been taken as a basis for comparing cation adsorption values from salt solution and soil suspension. The amount of Al and Ca adsorbed from the salt solution and soil
suspension at various concentrations are reported in Table 13. The adsorption values for the salt solutions were interpreted at the same concentrations as that in the supernatant solutions of the soil suspensions. These interpretations were made from three-dimensional diagrams which were drawn from the data in Table 5, except for the Al adsorption values at zero Ca which were read from Fig. 11. Three-dimensional diagrams for cations adsorbed on pineapple roots are presented in Figs. 15 and 16.

The results in Table 13 indicate that the adsorption of Al and Ca was greater from the salt solutions as compared to soil suspensions, except at the two lowest levels of Al where the adsorption of Al on pineapple roots was greater from the soil suspensions than salt solutions. For instance, at the same concentrations of Al and Ca in both types of solutions, kaimi clover roots adsorbed 4.3- to 5.0-fold higher Ca and 1.1- to 1.8-fold higher Al from the salt solutions as compared to the Kapaa soil suspensions. These large differences may be due to the presence of Fe ions in the soil suspensions which may also compete with Al and Ca for exchange sites.

If Ca concentration in the salt solution was greater as compared to Al concentration, then accordingly Ca adsorption by roots was greater than Al adsorption. But, roots adsorbed more Al from the soil suspension, even though Ca concentration was 50-fold greater than Al in the supernatant solution of that soil
Figure 15. Aluminum Adsorption by Pineapple Roots from Bi-Cationic Solutions (Al+Ca)
Figure 16. Calcium Adsorption by Pineapple Roots from Bi-Cationic Solutions (Al+Ca)
Table 13. Calculated Values of Al and Ca from the Salt Solution and Actual Values Adsorbed from Soil Suspension

<table>
<thead>
<tr>
<th>Cations in Solution m.e./l.</th>
<th>Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Salt Solution*</td>
</tr>
<tr>
<td></td>
<td>Pineapple Kaimi Clover</td>
</tr>
<tr>
<td>Al  Ca</td>
<td>Al  Ca  Al  Ca</td>
</tr>
<tr>
<td>0.60 0.00</td>
<td>3.10 0.00 5.80 0.00</td>
</tr>
<tr>
<td>0.54 0.20</td>
<td>2.38 1.90 4.30 4.68</td>
</tr>
<tr>
<td>0.18 0.80</td>
<td>1.48 2.04 3.22 6.50</td>
</tr>
<tr>
<td>0.06 2.24</td>
<td>0.56 2.98 2.06 7.26</td>
</tr>
</tbody>
</table>

Akaka Soil Suspensions

| Al  Ca                     | 3.32 0.00 5.92 0.00                  | 2.94 0.00 3.20 0.00              |
| 0.72 0.00                  | 2.32 1.84 4.00 4.60                  | 2.12 0.40 2.61 0.92              |
| 0.45 0.12                  | 1.68 2.00 3.62 6.06                  | 1.80 0.53 2.18 1.30              |
| 0.12 0.34                  | 0.36 2.20 1.98 6.90                  | 1.46 0.68 1.80 1.59              |
| 0.02 1.02                  | 0.56 2.98 2.06 7.26                  | 1.52 0.82 1.82 1.94              |

Kapaa Soil Suspensions

| Al  Ca                     | 3.50 0.00 6.04 0.00                  | 2.62 0.00 2.98 0.00              |
| 0.80 0.00                  | 2.74 1.48 4.68 4.32                  | 2.17 0.28 2.48 0.88              |
| 0.63 0.09                  | 1.82 1.80 3.88 5.84                  | 1.93 0.35 2.31 1.15              |
| 0.22 0.29                  | 0.65 1.98 2.85 6.70                  | 1.75 0.43 2.05 1.40              |
| 0.08 0.92                  | 0.56 2.98 2.06 7.26                  | 1.52 0.82 1.82 1.94              |

Molokai Soil Suspensions

*Values for salt solution are calculated from Table 5 and Fig. 11.

**Cations adsorbed from soil suspensions containing given amount of cations in supernatant solution.
suspension. For example, kaimi clover roots adsorbed 1.8 m.e. Al and 1.6 m.e. Ca per 100 g. dry roots from the Kapaa soil suspension, which had a supernatant solution containing 0.02 m.e. Al and 1.02 m.e. Ca per liter. Perhaps some Al was adsorbed on roots by contact exchange between soil and root colloids.

**Adsorption of Al and K.** Five rates of K, equivalent to 0, 0.1, 1.0, 10.0, and 20.0 percent saturation as hydroxide, were added to 1 percent soil suspensions. After KOH additions, these soil suspensions were allowed to equilibrate and were then separated from the bulk of the soil by centrifugation and analyzed for Al and K. The results are reported in Table 14.

The pH range was from 4.0 to 5.7 for the Akaka, 4.3 to 6.1 for the Kapaa, and 4.5 to 6.1 for the Molokai soil suspensions. The amount of K remaining in the supernatant solution was greater in the Akaka than Kapaa or Molokai suspensions at any percentage K saturation. The KOH additions decreased Al concentration by 5-, 7-, and 13-fold in the Akaka, Kapaa, and Molokai supernatant solution, respectively. The relative concentrations of Al in the Kapaa supernatant solutions were markedly affected by the associated cations in the soil suspensions. For example, if the results in Tables 11 and 14 for the Kapaa supernatant solutions are compared with the results for the Molokai or Akaka supernatant solutions, it is seen that when Ca is the associated cation, Al concentrations were lowest but when K is the
Table 14. Influence of the KOH Application in 1 Percent Soil Suspension on Al and K Remaining in the Supernatant Solution and pH of the Soil Suspension

<table>
<thead>
<tr>
<th>Percentage K Saturation*</th>
<th>pH of the Soil Suspension</th>
<th>Cations in m.e./liter Supernatant Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Akaka</td>
<td>Kapaa</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>4.3</td>
</tr>
<tr>
<td>0.1</td>
<td>4.1</td>
<td>4.5</td>
</tr>
<tr>
<td>1.0</td>
<td>4.3</td>
<td>4.7</td>
</tr>
<tr>
<td>10.0</td>
<td>4.7</td>
<td>5.1</td>
</tr>
<tr>
<td>20.0</td>
<td>5.7</td>
<td>6.1</td>
</tr>
</tbody>
</table>

*These are the amounts of K added, but not necessarily adsorbed on the soil colloids.
associated cation, Al concentrations were the highest in the Kapaa supernatant solutions.

When the results in Tables 11 and 14 were compared at equivalent levels of Ca and K, Al concentration in solution was more for soil suspensions containing Al and Ca (Table 11) than for soil suspensions containing Al and K (Table 14). A greater amount of K than Ca remained in the supernatant solution. This may reveal that Ca has greater replacing power than K for Al on the soil colloids.

Aluminum and potassium adsorption by plant roots equilibrated with these soil suspensions were also studied. The results are reported in Table 15.

The amount of Al and K adsorbed on roots from the soil suspensions were greatly influenced by the concentration of these cations in solution. Roots of all species adsorbed the greatest amounts of K from the Akaka soil suspensions (Table 15). The supernatant solutions of these suspensions had the highest concentration of K. In general, roots adsorbed more K than Al at 10 or 20 percent K saturation which agrees with the data in Table 14 which shows that at these K saturation levels, K concentration in the supernatant solution was greater than Al concentration.

The adsorption of Al on roots decreased with increasing KOH added to the soil suspensions. For instance, the Al adsorption on pineapple roots decreased by 56 percent for the Akaka,
Table 15. Influence of Percentage K Saturation Added as KOH in 1 Percent Soil Suspension on the Adsorption of Al and K by Plant Roots

<table>
<thead>
<tr>
<th>Percentage K Saturation</th>
<th>pH</th>
<th>Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pineapple</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>2.50</td>
</tr>
<tr>
<td>0.1</td>
<td>4.1</td>
<td>1.95</td>
</tr>
<tr>
<td>1.0</td>
<td>4.3</td>
<td>1.78</td>
</tr>
<tr>
<td>10.0</td>
<td>4.7</td>
<td>1.45</td>
</tr>
<tr>
<td>20.0</td>
<td>5.7</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Akaka Soil Materials

|                        | 4.3| 2.94      | 0.00      | 2.98 | 0.00         | 3.00 | 0.00         | 3.20 | 0.00         |
| 0.1                    | 4.5| 2.15      | 0.90      | 2.48 | 1.10         | 2.75 | 1.28         | 2.88 | 1.20         |
| 1.0                    | 4.7| 1.94      | 1.13      | 2.16 | 1.34         | 2.25 | 1.80         | 2.54 | 1.69         |
| 10.0                   | 5.1| 1.57      | 1.62      | 1.75 | 1.69         | 1.92 | 2.45         | 1.98 | 2.30         |
| 20.0                   | 6.1| 1.15      | 1.76      | 1.36 | 1.88         | 1.50 | 2.79         | 1.70 | 2.62         |

Kapaa Soil Materials

|                        | 4.5| 2.62      | 0.00      | 2.80 | 0.00         | 2.73 | 0.00         | 2.98 | 0.00         |
| 0.1                    | 4.8| 2.17      | 0.82      | 2.21 | 0.88         | 2.40 | 1.04         | 2.57 | 0.98         |
| 1.0                    | 5.3| 1.82      | 0.95      | 1.74 | 1.10         | 1.95 | 1.32         | 2.13 | 1.21         |
| 10.0                   | 5.6| 1.43      | 1.12      | 1.59 | 1.37         | 1.71 | 1.79         | 1.85 | 1.59         |
| 20.0                   | 6.1| 1.19      | 1.26      | 1.28 | 1.46         | 1.39 | 2.20         | 1.58 | 1.98         |

Molokai Soil Materials

*These are the amounts of K added, but not necessarily adsorbed on the soil colloids.*
61 percent for the Kapaa, and 55 percent for the Molokai soil suspensions. Plant roots adsorbed the greatest amount of Al from the Kapaa soil suspension at any given percentage K saturation. This agrees with the Al concentration in the supernatant solution of the Kapaa soil suspension following centrifugation.

Roots adsorbed more Al from soil suspensions in which Ca, rather than K, was the complementary cation. For instance, pineapple roots adsorbed 28 percent more Al from the Akaka soil suspension containing Ca equivalent to 10 percent saturation than from the Akaka soil suspension containing K equivalent to 10 percent K saturation. This agrees with Al concentration in the supernatant solution obtained from these soil suspensions (Tables 11 and 14). The release of exchangeable Al ions to the solution increased with increasing bonding strength of the complementary cation. Apparently, Ca is held by soil colloids with a stronger bonding energy than K, therefore making Al more available for adsorption by roots.

In order to compare the adsorption of cations from salt solutions and soil suspensions, the amounts of Al and K adsorbed by pineapple and kaimi clover roots from salt solutions were interpolated from three-dimensional diagrams, which were drawn from the data in Table 6. This was done so that the Al and K concentrations in the salt solutions were adjusted to those of the supernatant solutions of the soil suspensions and adsorption of
cations from salt solutions at those concentrations could be determined. Three-dimensional diagrams for cations adsorbed on kaimi clover roots are presented in Figs. 17 and 18. At zero K in the solution, the amount of Al adsorbed was obtained from Fig. 11. The results are presented in Table 16. The values for Al and K adsorbed by roots from soil suspensions containing the same concentrations of Al and K in their supernatant solution are also presented in this table.

Kaimi clover and pineapple roots adsorbed higher amounts of K from salt solutions than from soil suspensions (Table 16). The same was true for Ca (Table 13). At this point it would be proper to make clear that cations were added as chlorides in the bi-cationic solutions, and pH was adjusted initially to 4.0. But cations were added as hydroxides in the soil suspension and pH was not adjusted. Several workers have reported that anions exert a marked influence on the adsorption of cations by roots. In these results it is not clear how the anion influenced the adsorption of cation on roots, if it influenced it at all.

Kaimi clover roots adsorbed greater amounts of Al from the salt solutions than from the soil suspensions at all levels of K. However, pineapple roots adsorbed lower amounts of Al from the salt solutions than from the soil suspensions except at the two lowest levels of K. This may be caused by the fact that the degree of K saturation on pineapple roots was higher from salt
Figure 17. Aluminum Adsorption by Kaimi Clover Roots from Bi-Cationic Solutions (Al+K)
Figure 18. Potassium Adsorption by Kaimi Clover Roots from Bi-Cationic Solutions (Al+K)
Table 16. Calculated Values of Al and K from Salt Solution and Actual Values Adsorbed from Soil Suspension

<table>
<thead>
<tr>
<th>Cations in Solution m.e./l.</th>
<th>Cations in m.e./100 g. Dry Roots</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Salt Solution*</td>
<td>Soil Suspension**</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pineapple</td>
<td>Kaimi</td>
<td>Clover</td>
<td>Pineapple</td>
</tr>
<tr>
<td></td>
<td>Al K</td>
<td>Al K</td>
<td>Al K</td>
<td>Al K</td>
</tr>
<tr>
<td>0.60 0.00</td>
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<td>5.80 0.00</td>
<td>2.50 0.00</td>
<td>2.80 0.00</td>
</tr>
<tr>
<td>0.24 0.058</td>
<td>1.08 4.08</td>
<td>3.74 5.22</td>
<td>1.78 1.73</td>
<td>2.21 3.18</td>
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<tr>
<td>0.10 0.42</td>
<td>0.72 4.92</td>
<td>3.00 6.34</td>
<td>1.45 2.05</td>
<td>1.98 3.87</td>
</tr>
<tr>
<td>0.04 0.70</td>
<td>0.64 5.84</td>
<td>2.20 7.58</td>
<td>1.09 2.32</td>
<td>1.60 4.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Akaka Soil Suspension</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.94 0.00</td>
<td>3.20 0.00</td>
<td>Kapaa Soil Suspension</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.94 1.13</td>
<td>2.54 1.69</td>
<td>1.94 1.13</td>
<td>2.54 1.69</td>
</tr>
<tr>
<td></td>
<td>1.57 1.62</td>
<td>1.98 2.30</td>
<td>1.94 1.13</td>
<td>2.54 1.69</td>
</tr>
<tr>
<td></td>
<td>1.15 1.76</td>
<td>1.70 2.62</td>
<td>1.94 1.13</td>
<td>2.54 1.69</td>
</tr>
<tr>
<td>0.80 0.00</td>
<td>3.50 0.00</td>
<td>6.04 0.00</td>
<td>2.62 0.00</td>
<td>2.98 0.00</td>
</tr>
<tr>
<td>0.21 0.018</td>
<td>0.88 3.30</td>
<td>3.60 4.34</td>
<td>1.82 0.95</td>
<td>2.13 1.21</td>
</tr>
<tr>
<td>0.14 0.16</td>
<td>0.80 4.14</td>
<td>3.10 5.36</td>
<td>1.43 1.12</td>
<td>1.85 1.59</td>
</tr>
<tr>
<td>0.06 0.36</td>
<td>0.70 5.18</td>
<td>2.70 6.64</td>
<td>1.19 1.26</td>
<td>1.58 1.98</td>
</tr>
</tbody>
</table>

*Values for salt solution are calculated from Table 6 and Fig. 11.
**Cations adsorbed from soil suspensions containing given amount of cations in supernatant solution.
solutions than from soil suspensions which left fewer exchange sites available for Al adsorption from salt solutions. This was particularly evident at the two highest K levels in the salt solutions. For example, pineapple roots had 42 to 83 percent of the exchange sites occupied by K when the roots were equilibrated in salt solutions, but only 14 to 33 percent occupied by K when the roots were equilibrated in soil suspensions.

**Adsorption of cations from soil suspensions adjusted to initial pH**

It is well known that the solubility of Al decreases with the increasing pH. The present study was undertaken to obtain information on the amount of cations, particularly Al, adsorbed on roots as influenced by the pH of the soil suspension.

When the values for Ca or K adsorbed by roots from the soil suspensions at variable pH (Tables 12 and 15) and at initial pH (Tables 17 and 18) were compared, it was noted that roots adsorbed slightly lower amounts of Ca or K from the soil suspensions at initial pH than from the soil suspensions at variable pH. The representative data are presented below in tabular form.

<table>
<thead>
<tr>
<th>Cations Added Equivalent to % Saturation</th>
<th>Cations Adsorbed in m.e./100 g. Pineapple Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Variable pH</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>10%</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Table 17. Influence of Percentage Ca Saturation Added as Ca(OH)$_2$ in 1 Percent Soil Suspensions Adjusted to Initial pH on the Adsorption of Al and Ca by Plant Roots.

<table>
<thead>
<tr>
<th>Percentage Ca Saturation*</th>
<th>pH</th>
<th>Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pineapple</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sugarcane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corn</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kaimi Clover</td>
</tr>
<tr>
<td>Akaka Soil Materials</td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
<td>2.50</td>
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<tr>
<td>10</td>
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<tr>
<td>60</td>
<td>4.0</td>
<td>1.92</td>
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<td>Kapaa Soil Materials</td>
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<td>Al</td>
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<tr>
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<td>4.3</td>
<td>2.94</td>
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<td>2.35</td>
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<td>2.18</td>
</tr>
<tr>
<td>60</td>
<td>4.3</td>
<td>1.96</td>
</tr>
<tr>
<td>Molokai Soil Materials</td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>0</td>
<td>4.5</td>
<td>2.62</td>
</tr>
<tr>
<td>10</td>
<td>4.5</td>
<td>2.55</td>
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<tr>
<td>20</td>
<td>4.5</td>
<td>2.42</td>
</tr>
<tr>
<td>60</td>
<td>4.5</td>
<td>2.16</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca added, but not necessarily adsorbed on the soil colloids.
Table 18. Influence of Percentage K Saturation Added as KOH in 1 Percent Soil Suspensions Adjusted to Initial pH on the Adsorption of Al and K by Plant Roots

<table>
<thead>
<tr>
<th>Percentage K Saturation*</th>
<th>pH</th>
<th>Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pineapple</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al</td>
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<td>2.50</td>
</tr>
<tr>
<td>0.1</td>
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<td>2.21</td>
</tr>
<tr>
<td>1.0</td>
<td>4.0</td>
<td>1.98</td>
</tr>
<tr>
<td>10.0</td>
<td>4.0</td>
<td>1.75</td>
</tr>
<tr>
<td>20.0</td>
<td>4.0</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Akaka Soil Materials

| 0                       | 4.3| 2.94      | 0.00      | 2.98 | 0.00  | 3.00  | 0.00  |
| 0.1                     | 4.3| 2.65      | 0.82      | 2.60 | 0.95  | 2.81  | 1.09  |
| 1.0                     | 4.3| 2.32      | 1.06      | 2.51 | 1.18  | 2.60  | 1.55  |
| 10.0                    | 4.3| 2.00      | 1.31      | 2.18 | 1.52  | 2.32  | 1.92  |
| 20.0                    | 4.3| 1.78      | 1.48      | 1.85 | 1.70  | 2.07  | 2.20  |

Kapaa Soil Materials

| 0                       | 4.5| 2.62      | 0.00      | 2.80 | 0.00  | 2.73  | 0.00  |
| 0.1                     | 4.5| 2.35      | 0.77      | 2.32 | 0.80  | 2.45  | 1.00  |
| 1.0                     | 4.5| 2.20      | 0.86      | 2.10 | 0.94  | 2.20  | 1.24  |
| 10.0                    | 4.5| 2.18      | 1.00      | 1.87 | 1.21  | 2.06  | 1.58  |
| 20.0                    | 4.5| 1.96      | 1.19      | 1.56 | 1.39  | 1.88  | 1.90  |

Molokai Soil Materials

| 0                       | 4.5| 2.62      | 0.00      | 2.80 | 0.00  | 2.73  | 0.00  |
| 0.1                     | 4.5| 2.35      | 0.77      | 2.32 | 0.80  | 2.45  | 1.00  |
| 1.0                     | 4.5| 2.20      | 0.86      | 2.10 | 0.94  | 2.20  | 1.24  |
| 10.0                    | 4.5| 2.18      | 1.00      | 1.87 | 1.21  | 2.06  | 1.58  |
| 20.0                    | 4.5| 1.96      | 1.19      | 1.56 | 1.39  | 1.88  | 1.90  |

*These are the amounts of K added, but not necessarily adsorbed on the soil colloids.
By lowering the pH of the soil suspension, Ca adsorption by pineapple roots decreased more than K adsorption.

Although Al adsorbed decreased in both cases with increasing Ca or K added in soil suspensions, there was a smaller decrease in the case of soil suspensions adjusted to initial pH. This is attributed to the favorable pH for Al solubility in soil suspensions adjusted to initial pH.

The effects of plant species, cation concentration, and complementary cation on cation adsorption by roots were similar to those reported in salt solutions and soil suspensions (variable pH).

**Relationship in adsorption and absorption of cations by plant roots**

Drake *et al.* (1951) have explained differential cation uptake by plant species on the basis of variable root cation-exchange capacities. Elgabaly and Wiklander (1949) emphasized that both root colloids and soil colloids compete for ions. Cation uptake by plants depends on the relative cation-exchange capacities of root and soil colloids. But no one has yet explained how cation exchange of roots plays a direct role in differential uptake of cations by plants. In this study, an attempt was made to establish relationships between cations adsorbed and absorbed by roots.

Cation adsorption and absorption from salt solutions and soil suspensions were determined using excised roots. Samples of fresh pineapple and kaimi clover roots were weighed and placed
in sorption media. The usual system was 3 g. of roots in 3 liter of salt solution or soil suspension. Since volumes of solutions or suspensions were large in comparison with the quantity of roots used, cation concentrations in solutions or suspensions remained essentially constant during the sorption period. All solutions or suspensions were aerated and maintained at 24°C. The sorption period was 24 hours. Cation adsorption and absorption were measured by determining the adsorbed and absorbed cations of root materials before and after the sorption period. Values were expressed as m.e. per 100 g. roots. Detailed results are given in Appendix Tables 10 to 17. Cations adsorbed by roots were measured after the 24-hour sorption period. The values obtained are called final adsorption. Amounts of cations initially in the roots were subtracted from amounts obtained after the 24-hour sorption period. The values obtained are called net absorption.

The previous history of tissues is important in these types of investigations. What a plant may do at any time, under a particular set of circumstances, is preconditioned by the physiological history of the species. Physiological preconditioning includes whether plants were grown in low-salt solutions or high-salt solutions. If excised roots are low in salt, further solute may migrate inward very rapidly during a sorption experiment. With low-salt tissues, the rate of salt absorption for excised roots may
be as rapid as for intact plants. On the other hand, high-salt roots are nearer to dynamic equilibrium with respect to inorganic salt concentrations. Plants used for this investigation were grown in 1/8 Hoagland solution which was not renewed for 15 days prior to harvest. Under these conditions plant showed nutrient stress.

**Adsorption and absorption of cations by excised roots from bi-cationic solutions (pH 4.0).** Two series of bi-cationic solutions were prepared. One series contained three levels each of Al and Ca, and the other series consisted of three levels each of Al and K, making 9 treatments for each series. The cations were added as chloride in these solutions. Suitable pH values for Al solubility are between 4.0 and 4.8. Therefore all solutions were brought to pH 4.0 with HCl. Nielson and Overstreet (1955) have reported that pH 4.0 did not injure plant roots. Final adsorption and net absorption of Al and Ca or K by pineapple and kaimi clover roots and cation concentrations in solutions are reported in Tables 19 and 20.

The amounts of cations (Al and Ca or K) adsorbed by roots were lower than root cation-exchange capacities. Apparently, some of the exchange sites on roots were occupied by H ions. Graham and Baker (1951) found that plants had measurable amounts of H on their root surface. The percentage hydrogen saturation on roots varied from 8.2 to 64.0. They reported that
Table 19. Sorption of Al and Ca by Plant Roots from the Bi-Cationic Solution (pH 4.0)

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Treatment m.e./l.</th>
<th>m.e./100 g. Dry Roots*</th>
<th>Final Adsorption</th>
<th>Net Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td>Pineapple</td>
<td>0</td>
<td>0.16</td>
<td>0.00</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.10</td>
<td>0.15</td>
<td>-0.44</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.13</td>
<td>1.10</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.89</td>
<td>0.00</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.62</td>
<td>0.09</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.24</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.65</td>
<td>0.00</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.09</td>
<td>0.00</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.94</td>
<td>0.04</td>
<td>1.12</td>
</tr>
<tr>
<td>Kaimi</td>
<td>0</td>
<td>0.38</td>
<td>0.00</td>
<td>-0.11</td>
</tr>
<tr>
<td>Clove</td>
<td>5</td>
<td>0.24</td>
<td>4.16</td>
<td>-0.25</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.39</td>
<td>6.32</td>
<td>-0.28</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>2.93</td>
<td>0.00</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.08</td>
<td>3.42</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.54</td>
<td>5.75</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>3.80</td>
<td>0.00</td>
<td>5.72</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.99</td>
<td>1.94</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.84</td>
<td>4.46</td>
<td>1.90</td>
</tr>
</tbody>
</table>

*Values are averages of two replications.
Table 20. Sorption of Al and K by Plant Roots from the Bi-Cationic Solution (pH 4.0)

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Treatment m.e./l.</th>
<th>m.e./100 g. Dry Roots</th>
<th>Final Adsorption</th>
<th>Net Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>K</td>
<td>Al</td>
<td>K</td>
</tr>
<tr>
<td>Pineapple</td>
<td>0</td>
<td>0</td>
<td>0.07</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.19</td>
<td>0.68</td>
<td>-0.22</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.09</td>
<td>1.04</td>
<td>-0.43</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.39</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.19</td>
<td>1.02</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.85</td>
<td>1.21</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.38</td>
<td>0.40</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.61</td>
<td>0.80</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.29</td>
<td>0.97</td>
<td>0.23</td>
</tr>
<tr>
<td>Kaini</td>
<td>0</td>
<td>0</td>
<td>0.23</td>
<td>4.49</td>
</tr>
<tr>
<td>Clover</td>
<td>0.1</td>
<td>0.45</td>
<td>11.18</td>
<td>-0.20</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.24</td>
<td>13.31</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3.29</td>
<td>9.80</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>2.80</td>
<td>13.83</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.14</td>
<td>15.77</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>5.20</td>
<td>8.76</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>4.62</td>
<td>12.75</td>
<td>3.34</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.16</td>
<td>14.19</td>
<td>2.50</td>
</tr>
</tbody>
</table>

*Values are averages of two replications.*
low figure was associated with sets of plants that had recently received additions of nutrient solutions. Cations which were not present in the external medium diffused out of roots into external medium giving rise to the negative values of Tables 19 and 20. The amounts of Al and Ca adsorbed and absorbed were conditioned by their concentrations in solution (Table 19). For example, the amount of Ca adsorbed and absorbed by kaimi clover roots, from solutions containing 0.1 m.e. Al per liter, increased 1.7-fold when Ca in the outside media increased from 5 to 25 m.e. per liter. Similarly, the amount of Al adsorbed and absorbed by kaimi clover roots, from solutions containing 5.0 m.e. Ca per liter, increased about 2.7 times when Al in the outside media increased from 0.1 to 1.0 m.e. per liter. Pineapple roots behaved similarly. There was mutual competition between Al and Ca for adsorption and absorption and amounts adsorbed and absorbed were influenced by their respective concentrations in solutions. If the concentration of Al was kept constant, then Al adsorption and absorption decreased with increasing concentration of Ca in the solution. Aluminum had the same effect on Ca.

McLean and Baker (1953) reported that C.E.C. of alfalfa was twice as high as red top grass and Ca absorption by alfalfa was almost twice as high as red top. Likewise, Aoki and Morita (1966) reported that the C.E.C. ratio of orange to peach was 3 with a corresponding Ca adsorption ratio of 3.2. In both
cases the Ca absorption and adsorption ratios approximates the C.E.C. ratio. In the experiment reported here, kaimi clover roots (high C.E.C.) adsorbed and absorbed more Al and Ca than did pineapple roots (low C.E.C.). The C.E.C. of kaimi clover roots was three times more than pineapple roots; however, the ratios of Al adsorption by kaimi clover roots to Al adsorption by pineapple roots varied from 1.7 to 3.3 and Al absorption ratios varied from 1.7 to 2.8. On the average, these values were quite close to the C.E.C. ratios as far as adsorption was concerned, but were slightly lower for absorption. The ratios of Ca adsorption and absorption by kaimi clover roots to Ca adsorption and absorption by pineapple roots were much greater than the C.E.C. ratio. Sometimes, Ca adsorption on kaimi clover roots was 40 times greater than on pineapple roots. It appears that pineapple roots adsorbed and absorbed Ca very slowly under the experimental conditions and Al depressed Ca adsorption and absorption by pineapple roots but had relatively less effect on Ca adsorption and absorption by kaimi clover roots.

The results in Table 20 demonstrate that Al adsorption and absorption were decreased by increasing the K concentration. Exceptions to the generalization were seen for both species when no Al had been added. For example, Al adsorption and absorption by kaimi clover roots decreased by 40 and 31 percent when K concentrations were increased from 0 to 1.0 m.e. per liter.
This trend was also observed for pineapple roots. Viets (1944) reported increased uptake of K when Ca or Al was supplied in addition to K in the external medium. In the experiment reported here, Al level of 0.1 m.e. increased K adsorption and absorption by both plant species. However, the amount of K adsorbed and absorbed again decreased, if Al concentration was increased from 0.1 to 1.0 m.e. (Table 20). The Viets effect, influence of polyvalent cations on the uptake of monovalent cations, is not observable unless conditions permit oxidative metabolism. The primary effect of polyvalent cations may be either on plasma membranes or on surface metabolism, intimately related to the permeability of protoplasm. This may be a possible explanation for the stimulating effect of Al on the K adsorption and absorption by roots.

The ratios of potassium adsorption by kaimi clover and pineapple varied from 12.8 to 21.9, but K absorption ratios of kaimi clover to pineapple roots were only 0.4 to 0.8. Aluminum adsorption and absorption ratios of kaimi clover to pineapple roots varied from 2.18 to 3.28 and from 4.64 to 10.87, respectively. It is interesting to note that although K adsorption on kaimi clover roots exceeded adsorption on pineapple roots, the reverse was true for K absorption. Epstein and Hagen (1952), and Overstreet and Jacobson (1952) proposed a working hypothesis for mineral sorption by plant roots. A membrane or region exists in
the cytoplasm of root cells which is impermeable to free ions, but permeable to complexes formed by the reaction of ions with compounds designated as HR and R OH. The compounds HR and R OH are produced metabolically at the external interface where they can combine with anions and cations forming complex as follows:

\[
M^+ + HR \rightleftharpoons MR + H^+
\]
\[
A^- + R OH \rightleftharpoons RA + OH^-
\]

where \( M^+ \) represents a cation and \( A^- \) an anion. The complexes MR and RA then diffuse across this region.

It may be that each type of carrier can bind a specific type of cation and that kaimi clover roots produce metabolically less of the K-binding carrier as compared with pineapple roots. If such is the case, kaimi clover would have absorbed less K than pineapple roots, even though K adsorption on kaimi clover roots was many times greater than on pineapple roots.

Simple correlations between the amounts of a cation adsorbed and absorbed are reported in Table 21. The correlation coefficients were highly significant and \( r^2 \) values indicate that 80 to 98 percent of the variability in cation uptake within a species was accounted for by variations in cation adsorption within that species. These data suggest that cation absorption is related to the adsorption of that cation.
Table 21. Simple Correlations Among the Amount of a Cation Adsorbed and Absorbed by a Given Plant Species

<table>
<thead>
<tr>
<th>Cations Absorbed</th>
<th>Bi-Cationic Solution (Al+Ca)</th>
<th>Cations Adsorbed</th>
<th>Bi-Cationic Solution (Al+K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pineapple</td>
<td>Kaimi Clover</td>
<td>Pineapple</td>
</tr>
<tr>
<td>Al</td>
<td>0.994**</td>
<td>0.991**</td>
<td>0.981**</td>
</tr>
<tr>
<td>Ca</td>
<td>0.978**</td>
<td>0.992**</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>0.903**</td>
<td>0.926**</td>
</tr>
</tbody>
</table>

**Significant at P = 0.01.
Adsorption and absorption of cations by excised roots from the soil suspension. Two series of one percent soil suspensions from Al-saturated Kapaa soil materials were prepared. To the first series of soil suspensions Ca(OH)$_2$ was added equivalent to 0, 10, 20, and 60 percent Ca saturation and to the second series of soil suspensions KOH was added equivalent to 0, 1, and 10 percent K saturation. The amounts of Al, Ca, and K remaining in supernatant solutions of soil suspensions were previously discussed. The adsorption and absorption of Al and Ca by excised roots from the first series of soil suspensions and of Al and K from the second series of soil suspensions were investigated and reported in Tables 22 and 23, respectively.

The amounts of Ca or K adsorbed and absorbed by pineapple and kaimi clover roots increased with increasing Ca(OH)$_2$ or KOH added. These treatments decreased Al adsorbed and absorbed. The amount of Al adsorbed and absorbed by plant roots decreased because of two reasons: (1) pH of the soil suspension increased with increments of Ca(OH)$_2$ or KOH added, which decreased Al solubility, and (2) Ca or K concentrations in solution competed with Al for adsorption and absorption by roots.

The adsorption and absorption of Al by kaimi clover roots were from 1.35 to 1.46 and from 1.63 to 2.34 times greater than by pineapple roots, respectively. The Ca adsorption and absorption by kaimi clover roots were also from 1.96 to 2.22 and from
Table 22. Influence of Percentage Ca Saturation Added as Ca(OH)$_2$ in 1 Percent Kapaa Soil Suspension on the Sorption of Al and Ca by Plant Roots

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage Ca Saturation*</th>
<th>pH</th>
<th>Final Adsorption m.e./100 g</th>
<th>Dry Roots**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td>Pineapple</td>
<td>0</td>
<td>4.3</td>
<td>6.27</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.8</td>
<td>3.92</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.3</td>
<td>1.88</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>6.0</td>
<td>1.26</td>
<td>1.09</td>
</tr>
<tr>
<td>Kaimi</td>
<td>0</td>
<td>4.3</td>
<td>8.62</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.8</td>
<td>5.28</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.3</td>
<td>2.74</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>6.0</td>
<td>1.72</td>
<td>2.42</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
Table 23. Influence of Percentage K Saturation Added as KOH in 1 Percent Kapaa Soil Suspension on the Sorption of Al and K by Plant Roots

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage K Saturation*</th>
<th>pH</th>
<th>m.e./100 g. Dry Roots***</th>
<th>Final Adsorption</th>
<th>Net Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>K</td>
</tr>
<tr>
<td>Pineapple</td>
<td>0</td>
<td>4.3</td>
<td>6.27</td>
<td>0.41</td>
<td>6.42</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.7</td>
<td>3.66</td>
<td>0.94</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.1</td>
<td>2.36</td>
<td>1.30</td>
<td>2.73</td>
</tr>
<tr>
<td>Kaimi</td>
<td>0</td>
<td>4.3</td>
<td>8.62</td>
<td>8.25</td>
<td>10.45</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.7</td>
<td>6.48</td>
<td>10.57</td>
<td>4.91</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.1</td>
<td>5.03</td>
<td>12.36</td>
<td>3.57</td>
</tr>
</tbody>
</table>

*These are the amounts of K added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
1.78 to 2.20 times more than by pineapple roots, respectively (Table 22). These ratios were lower than the C.E.C. ratio of kaimi clover to pineapple roots. From the bi-cationic solutions (Al+Ca), kaimi clover roots sometimes adsorbed and absorbed 40 times greater amounts of Ca than was adsorbed and absorbed by pineapple roots. But kaimi clover roots adsorbed and absorbed only about two times more Ca from soil suspension than was adsorbed and absorbed by pineapple roots.

The adsorption and absorption of Al by kaimi clover roots from the soil suspension (Al+K) were from 1.37 to 2.13 and from 1.46 to 2.26 times greater than adsorbed and absorbed by pineapple roots, respectively. The K absorption by kaimi clover roots was lower than by pineapple roots, even though K adsorption on kaimi clover roots was more. This agrees with data already presented in the section on "Adsorption and absorption of cations by excised roots from bi-cationic solutions (pH 4.0)".

The adsorption and absorption of Al by roots was higher when Ca was the complementary cation than from the soil suspension in which K was the complementary cation. The release of exchangeable Al ions to the solution is increased with increasing bonding strength of complementary cations. Apparently Ca is held by soil colloids with greater bonding energy than K and thus is more effective than K in making Al available.

When the soil suspensions were adjusted to pH 4.3 with HCl
(Tables 24 and 25), it was found that Ca or K adsorption and absorption by roots were lower than from the soil suspension in which pH was allowed to vary (Tables 22 and 23). With increasing Ca or K saturation, the adsorption and absorption of Al decreased in both cases; there was a smaller decrease in the case of soil suspensions which were adjusted to pH 4.3. This is attributed to the favorable pH for Al solubility in soil suspensions and the Al in turn blocked Ca or K adsorption and absorption.

**Influence of percentage Ca and K saturation in Kapaa soil on plant yield and chemical composition**

A greenhouse experiment was conducted in order to ascertain the effect of percentage Ca and K saturation on the yield and Al, Ca, and K contents of the plants. Two series of treatments were used. In the first series, Ca and K were used as hydroxide to bring the soil to different levels of Ca and K saturations. The pH varied from pot to pot, and no attempt was made to manipulate it. The term "hydroxide series" was used for these treatments. In the second series, pH was adjusted to 4.9 (original pH of the soil) by using various combinations of calcium sulphate and calcium hydroxide. Potassium sulphate equivalent to 1 and 10 percent K saturation was used. The term "sulphate series" refers to these treatments. Corn and kaimi clover were grown as test crops for 26 and 38 days, respectively.
Table 24. Influence of Percentage Ca Saturation Added as Ca(OH)$_2$ in 1 Percent Kapaa Soil Suspension Adjusted to pH 4.3 on the Sorption of Al and Ca by Plant Roots

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage Ca Saturation*</th>
<th>m.e./100 g. Dry Roots**</th>
<th>Final Adsorption</th>
<th>Net Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td>Pineapple</td>
<td>0</td>
<td>6.43</td>
<td>0.00</td>
<td>6.42</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.78</td>
<td>0.12</td>
<td>5.68</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>4.25</td>
<td>0.30</td>
<td>5.14</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.72</td>
<td>0.68</td>
<td>4.15</td>
</tr>
<tr>
<td>Kaimi</td>
<td>0</td>
<td>8.77</td>
<td>0.00</td>
<td>10.45</td>
</tr>
<tr>
<td>Clover</td>
<td>10</td>
<td>8.67</td>
<td>0.75</td>
<td>9.55</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>8.19</td>
<td>1.27</td>
<td>8.90</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>6.47</td>
<td>1.78</td>
<td>7.67</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
Table 25. Influence of Percentage K Saturation Added as KOH in 1 Percent Kapaa Soil Suspension Adjusted to pH 4.3 on the Sorption of Al and K by Plant Roots

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage K Saturation</th>
<th>m.e./100 g. Dry Roots**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Final Adsorption</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Pineapple</td>
<td>0</td>
<td>6.43</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.45</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.82</td>
</tr>
<tr>
<td>Kaimi</td>
<td>0</td>
<td>8.77</td>
</tr>
<tr>
<td>Clover</td>
<td>1</td>
<td>8.16</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.60</td>
</tr>
</tbody>
</table>

*These are the amounts of K added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
In the hydroxide series, growth of both plant species was at low K (Figs. 19 and 20 and Table 26). Corn did not grow when Ca was low and K was high, and there was very little growth of kaimi clover in this treatment. Symptoms of extreme Ca deficiency were evident in plants growing at high K at all levels of Ca.

In the sulphate series, growth of both plant species was severely depressed by the low Ca, high K treatment. The appearance of plants at harvest time is shown in Figs. 21 and 22, and yield and composition data are shown in Table 27. There were Ca deficiency symptoms in corn and kaimi clover grown in low Ca and high K soil. Plants were more vigorous in the sulphate series than in the hydroxide series.

Yield data. A summary of data for yield and chemical composition of plants from the hydroxide and sulphate series are presented in Tables 26 and 27. Data in the hydroxide series clearly indicate that an increase in K from 1 to 10 percent saturation reduced yields of both plant species significantly (Table 26). When K was held constant, yields increased with increasing levels of Ca, but this increase was not significant. Furthermore at low K, high Ca depressed yield and K percentage of corn.

In the sulphate series when K was held constant an increase in Ca saturation increased the yield of both plant species. Corn yield was increased significantly by increasing K at medium and
Figure 19. Effect of Percentage Ca and K Saturations in Kapaa Soil (Hydroxide Series) on the Growth of 26 Days Old Corn
Figure 20. Effect of Percentage Ca and K Saturations in Kapaa Soil (Hydroxide Series) on the Growth of 38 Days Old Kaimi Clover
Figure 21. Effect of Percentage Ca and K Saturations in Kapaa Soil (Sulphate Series) on the Growth of 26 Days Old Corn
Figure 22. Effect of Percentage Ca and K Saturations in Kapaa Soil (Sulphate Series) on the Growth of 38 Days Old Kaimi Clover
Table 26. The Influence of Percentage Ca and K Saturation in Kapaa Soil (Hydroxide Series) on Yield and % Al, Ca, K, and P of Plant Tops

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Dry Matter (g. per pot)</th>
<th>Element in Dry Matter**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>ppm Al</td>
</tr>
<tr>
<td>Ca</td>
<td>K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.2</td>
<td>3.18</td>
</tr>
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<td>20</td>
<td>1</td>
<td>5.8</td>
<td>4.12</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>6.5</td>
<td>3.05</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
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</tr>
<tr>
<td>20</td>
<td>10</td>
<td>6.4</td>
<td>1.21</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>7.0</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Corn Top (26 Days Old)

Kaimi Clover Top (38 Days Old)

*These are the amounts of Ca and K adsorbed, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
Table 27. The Influence of Percentage Ca and K Saturation in Kapaa Soil (Sulphate Series) on Yield and % Al, Ca, K, and P of Plant Tops

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Dry Matter (g. per pot)</th>
<th>Element in Plant Dry Matter**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>K</td>
<td></td>
<td>ppm Al % Ca % K % P</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
<td>3.39</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>4.9</td>
<td>3.92</td>
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<td>5.60</td>
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<td>5</td>
<td>10</td>
<td>4.9</td>
<td>0.95</td>
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<td>20</td>
<td>10</td>
<td>4.9</td>
<td>4.40</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
<td>8.80</td>
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<tr>
<td>Corn Top (26 Days Old)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
<td>3.39</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>4.9</td>
<td>3.92</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>4.9</td>
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<td>4.9</td>
<td>0.95</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>4.9</td>
<td>4.40</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
<td>8.80</td>
</tr>
<tr>
<td>Kaimi Clover Top (38 Days Old)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
<td>3.23</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>4.9</td>
<td>4.12</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>4.9</td>
<td>4.28</td>
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<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
<td>3.40</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
high Ca, but significantly depressed at low Ca. However, regardless of Ca levels, the yield of kaimi clover decreased with high K.

**Ca and K content of plants.** It has been shown by many workers that an application of a specified element to the soil may increase the percentage of that element in the plant. An increase in plant Ca with increasing soil Ca was observed for both plant species in both the sulphate and hydroxide series. For example when soil K was low, Ca percentage in kaimi clover increased from 0.5 to 1.7 with increasing Ca. If Ca in the soil was kept constant, then K concentration in the plant increased with increasing K levels in the soil.

Many workers have demonstrated by water culture and soil culture techniques that K and Ca content of plant tissues vary widely with species. In this investigation, Ca content was greater in kaimi clover than in corn, but for K the case was reversed (Tables 26 and 27). For instance in the sulphate series (Table 27) when soil Ca was high and K was low, corn contained 0.7 percent Ca and 3.3 percent K, while kaimi clover contained 1.5 percent Ca and 2.5 percent K. The factors that control absorption of cations are numerous, and the reasons for differences in mineral composition of plants are not clearly understood. However, Elgabaly and Wiklander (1949) suggested that the greater the C.E.C. of roots, the greater would be the divalent cation/mono-
valent cation ratio in the plant. The K/Ca ratios in corn and kaimi clover agree with the above statement. Plots of these ratios (Figs. 23 and 24) show that the ratios tend to be higher for corn (low C.E.C.) than for kaimi clover (high C.E.C.).

Although the proportion of K to Ca in soils is usually small, K tends to control the availability of cations to many plants. Its absorption is comparatively so efficient that luxury consumption at the expense of other cations is a common occurrence. This point is amply illustrated in Fig. 23 where low yields were associated with high potassium in the plant tissue which gave rise to high K/Ca ratios.

Dry matter yields of both plant species were associated with Ca contents of the plants. For example, corn yield increased from 3.4 to 4.6 g. per pot with a corresponding increase of Ca from 0.3 to 0.7 percent (Table 27). Plant Ca vs. dry matter yields are plotted for kaimi clover and corn in Figs. 25 and 26. In one instance kaimi clover yield was low even though Ca content of the plant was relatively high (Fig. 25). This seems to have been related to low P uptake. When soil K was low, K became the limiting factor for corn growth. Increasing plant Ca had little effect on corn yield under these conditions (Fig. 26). However, when K was no longer limiting, yield increased sharply with increasing plant Ca. Kaimi clover, which evidently has a much lower K requirement, grew best at the highest levels of plant Ca.
Figure 23. Relationship Between K:Ca Ratio and Yield of Kaimi Clover

SOIL

○ = 1% K OF C.E.C.
△ = 10% K OF C.E.C

YIELD (g./POT)

△ LOW PLANT P

K/Ca (KAIMI CLOVER)
Figure 24. Relationship Between K:Ca Ratio and Yield of Corn
Figure 25. Relationship Between Plant Ca Percentage and Yield of Kaimi Clover
Figure 26. Relationship Between Plant Ca Percentage and Yield of Corn
One of the most outstanding features of the data relating to corn yield and composition is the difference between the sulphate series (low pH) and the hydroxide series (relatively high pH) in yield and Ca percentage of the tissues. For ease of inspection some of the data from Tables 26 and 27 are presented below.

<table>
<thead>
<tr>
<th>Percentage Ca Saturation</th>
<th>Soil pH</th>
<th>Yield (g. per pot)</th>
<th>Plant Ca (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.9</td>
<td>4.40</td>
<td>0.31</td>
</tr>
<tr>
<td>60</td>
<td>4.9</td>
<td>4.80</td>
<td>0.46</td>
</tr>
<tr>
<td>20</td>
<td>6.4</td>
<td>1.21</td>
<td>0.20</td>
</tr>
<tr>
<td>60</td>
<td>7.0</td>
<td>2.38</td>
<td>0.28</td>
</tr>
</tbody>
</table>

In general, the yield was better in the sulphate series than in the hydroxide series. This seems to be related to better Ca uptake from the sulphate series. Two possible explanations for this relationship are: (1) Since soil pH was low in the sulphate series it is assumed that Al was an important complementary cation. The release of exchangeable Ca ions to the solution increased with increasing bonding strength of the complementary cations. Apparently Al is held by soil colloids with greater bonding energy than K and thus is more effective than K in making Ca available. (2) It is also possible that Ca as CaSO$_4$ is more active than Ca-clay.
When the K level in the soil was kept constant, then percentage K in the plant decreased with increasing Ca level in the soil (Tables 26 and 27). But, it should be noted that decrease of percentage K in the plant may not be due to Ca, but because of increased yield obtained with increasing levels of Ca in the soil. Although the percentage K in the plant decreased with increasing Ca levels in soil, the total K in the plant generally increased (Tables 28 and 29). This agrees with the work reported by Olsen (1941-43).

Al and P contents of plants

Kaimi clover contained high Al concentration in the top as compared with corn (Tables 26 and 27). But its roots contained similar amounts or even less Al than corn (Appendix Tables 18 and 19). The total amount of Al in the whole plant remained high in corn regardless of soil pH. There was no apparent trend in Al percentage in plant tops from the hydroxide as compared to the sulphate series. However, Al yield was slightly higher in the sulphate series than in the hydroxide series. Plants in the sulphate series (low pH), absorbed greater amounts of Al than in the hydroxide series, but Al percentage in the plant tops was diluted by higher yields in the sulphate series. Data in Appendix Tables 18 and 19 demonstrate that soil pH controlled Al concentration in the plant root to a greater extent than in the top (Tables 26 and 27).
Table 28. The Influence of Percentage Ca and K Saturation in Kapaa Soil (Hydroxide Series) on the Total Al, Ca, K, and P Content of Plant Tops

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Element in Plant Dry Matter (mgs./pot)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Ca</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.2</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>5.8</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>6.5</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>6.0</td>
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<tr>
<td>20</td>
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<td>6.4</td>
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<tr>
<td>60</td>
<td>10</td>
<td>7.0</td>
</tr>
<tr>
<td>Kaimi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clover Top</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.2</td>
</tr>
<tr>
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<td>5.8</td>
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<tr>
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<td>6.5</td>
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<td>6.4</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>7.0</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
Table 29. The Influence of Percentage Ca and K Saturation in Kapaa Soil (Sulphate Series) on the Total Al, Ca, K, and P Content of Plant Tops

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Element in Plant (mgs./pot)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Corn Top</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>4.9</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>4.9</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>4.9</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>4.9</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
</tr>
<tr>
<td>Kaimi Clover Top</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>4.9</td>
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<tr>
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<td>4.9</td>
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<td>10</td>
<td>4.9</td>
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<td>4.9</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloids.

**Values are averages of two replications.
Kaimi clover plants had slightly higher P concentration than corn. Except for kaimi clover grown in soil with high Ca and high K (pH 7.0), pH did not influence the P percentage of plants. It is a generally held opinion that the pH range from 6.0 to 7.5 conditions are most favorable for P availability. But in this experiment, P concentration in plants remained relatively constant with increasing yield and soil pH. It is possible that the plant root is controlling soil pH and thus increases phosphate solubility adjacent to the root. Fox (personal communication) also found that several plant species took up little fertilizer P from highly weathered latosols limed to pH 7.

**Distribution of Al, Ca, and K in the plant.** Cation distribution within the plant depends considerably on individual ions. More than 80 percent of K or Ca absorbed were in plant tops. However, most of the Al was associated with the roots (Tables 30 and 31). Localization of Al may result from: (1) Al absorbed by the roots may move upward in the xylem, then returned to the roots via the phloem in a manner similar to Na (Cooil et al., 1965). This possibility is doubted because of lower Al solubility and mobility as compared to Na. (2) The membrane in the cells of certain extra-stelar tissues of the root may serve to exclude Al from the vascular system. This possibility was speculated for high Na in the roots by Gauch and Wadleigh (1945). Later, this was discounted for Na by some workers, but it is a still open
**Table 30. Percentage of Plant Cation in the Plant Top**

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Uptake of Cations in Whole Plant</th>
<th>% of Absorbed Cation in the Plant Top</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mgm.</td>
<td>mgm.</td>
</tr>
<tr>
<td><strong>Corn</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.2</td>
<td>3.15</td>
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<td>5.8</td>
<td>4.82</td>
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<td>60</td>
<td>1</td>
<td>6.5</td>
<td>2.41</td>
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<td>10</td>
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<td>-</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>6.4</td>
<td>1.34</td>
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<tr>
<td>60</td>
<td>10</td>
<td>7.0</td>
<td>2.49</td>
</tr>
<tr>
<td><strong>Kaimi Clover</strong></td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.2</td>
<td>2.28</td>
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<td>20</td>
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<td>5.8</td>
<td>2.89</td>
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<td>10</td>
<td>6.4</td>
<td>0.68</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>7.0</td>
<td>0.095</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca and K added, but not necessarily adsorbed on soil colloids.*
Table 31. Percentage of Plant Cation in the Plant Top

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Uptake of Cations in Whole Plant</th>
<th>% of Adsorbed Cation in the Plant Top</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mgm.</td>
<td>mgm.</td>
</tr>
<tr>
<td>Corn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
<td>2.99</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>4.9</td>
<td>4.82</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
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</tr>
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<td>4.9</td>
<td>0.86</td>
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<td>10</td>
<td>4.9</td>
<td>3.17</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
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</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4.9</td>
<td>1.97</td>
</tr>
<tr>
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<td>1</td>
<td>4.9</td>
<td>4.47</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
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</tr>
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<td>10</td>
<td>4.9</td>
<td>0.64</td>
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<td>20</td>
<td>10</td>
<td>4.9</td>
<td>2.19</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
<td>2.41</td>
</tr>
</tbody>
</table>

*These are the amounts of Ca and K added, but not necessarily adsorbed on soil colloids.
possibility for high Al in plant roots. (3) The high Al of the root may be the result of contamination from the soil.

It was apparent that plants differ in their capacity to transfer Al to the top. The percentage of Al transferred to kaimi clover top was two times greater than corn top.

The significance of Al in nutrient uptake has been sufficiently investigated so that it is reasonably certain that high Al in the nutrient media is responsible for low P and Ca absorption. Several mechanisms may be involved here: (1) Al may precipitate P in the root, (2) Al may inhibit root proliferation, (3) Al may physically or chemically block the pathway by which cations are absorbed, and (4) Al which accumulates adjacent to the root or in the free space of root may repel other nutrient cations as they approach the plasma membrane.

In the present experiment, corn with its relatively high Al content into the root and relatively low C.E.C., responded more to the highest Ca level of the soil than did kaimi clover (high C.E.C.). For example, increasing Ca from 20 to 60 percent equivalent saturation almost doubled the yield of corn while kaimi clover responded slightly to the highest level of Ca.
SUMMARY

The uptake of K, Ca, and Al by plants was studied in three steps: (1) adsorption by excised roots, (2) absorption by excised roots, and (3) uptake by the intact plants.

Cation-exchange capacities of the plant roots were as follows: Pineapple (Annanas comosa), 7.0; sugarcane (Saccharum officinarum), 9.5; corn (Zea mays), 13.6; and kaimi clover (Desmodium canum), 20.0 m.e. per 100 g. dry roots. Cation adsorption on root surfaces was observed to be a function of plant species, cations involved and cation concentrations in the saturating media. The adsorption of Ca and Al on roots of all species increased with increasing cation-exchange capacities. However, K was preferentially adsorbed on corn roots. Cation adsorption increased with increasing cation concentration of the saturating media. The effects of cations upon the adsorption of other cations were reciprocal. At equivalent cation concentrations of the saturating solution, cation adsorption by all roots decreased with increasing cation valency. The Al adsorption was influenced by the complementary cation, being higher with Ca than with K. Roots adsorbed slightly lower amounts of Ca or K from soil suspensions at initial pH than from the soil suspensions at variable pH. Although Al adsorption decreased in both cases with increasing Ca or K added in the soil suspensions, there was a smaller
decrease in the case of the soil suspensions adjusted to initial pH.

The apparent exchange constant (Kc) values varied widely depending upon the concentrations of Al and Ca or K present. Relatively greater root affinity for Ca or K occurred when Ca and K concentrations were low in the equilibrating solutions.

Aluminum depressed the adsorption and absorption of Ca by excised pineapple and kaimi clover roots, but the low concentration of Al stimulated the adsorption and absorption of K. The K adsorption was higher on kaimi clover than on pineapple roots, but the order was reversed for its absorption. A highly significant correlation was observed between adsorption and absorption of individual cations and absorption of individual cations within each plant species. But there was little or no relationship between adsorption and absorption when several species were compared. This suggests that absorption of cations may be related to adsorption but the amount of an appropriate carrier produced by roots is the factor most immediately related to absorption.

The uptake of Al, Ca, and K by intact plants was investigated in a pot experiment with kaimi clover and corn. It was found that when the soil pH was allowed to vary from 5.2 to 7.0, depending upon K and Ca applications as hydroxides, K added in excess of 1 percent saturation decreased the yield of both plant species at all levels of Ca. At pH 4.9, corn yield increased with
increasing K saturation when Ca saturation was 20 or 60 percent, but was markedly depressed by increasing K saturation when Ca saturation was 5 percent. However, regardless of Ca levels, the yield of kaimi clover decreased at the high K level. Generally, yields of both plant species were associated with Ca contents of the plants. When soil K was low, K became the limiting factor for corn growth. However, when K was no longer limiting, yield increased sharply with increasing plant Ca. Kaimi clover, which evidently has a much lower K requirement, grew best at the highest levels of Ca.

The distribution of cation in the root and in the top was shown to vary considerably with the individual ions. More than 80 percent of the K and Ca absorbed was in the plant top, but most of the Al was associated with the roots. Apparently, plants differ in their capacity to transfer Al to their aerial portions. The net translocation of Al in kaimi clover was twice that in corn.
### Appendix Table 1
Effect of Saturating and Desaturating Solution-Root Contact Time on Cations Adsorption by Sugarcane Roots

<table>
<thead>
<tr>
<th>Saturating Solution-Root Contact Time in Seconds</th>
<th>Adsorbed Cations in m.e./100 g. Dry Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Desaturating Solution-Root Contact Time in Seconds</td>
</tr>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td></td>
<td>10</td>
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<td>20</td>
<td>8.9</td>
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<td>60</td>
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<tr>
<td>120</td>
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</tr>
<tr>
<td>300</td>
<td>10.4</td>
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### Appendix Table 2
Effect of Saturating and Desaturating Solution-Root Contact Time on Cations Adsorption by Pineapple Roots

<table>
<thead>
<tr>
<th>Saturating Solution-Root Contact Time in Seconds</th>
<th>Adsorbed Cations in m.e./100 g. Dry Roots</th>
<th>Desaturating Solution-Root Contact Time in Seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
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<td>60</td>
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<td>60</td>
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<td>11.7</td>
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<td>10.6</td>
<td>17.7</td>
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<tr>
<td>300</td>
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<td>18.0</td>
</tr>
<tr>
<td>Cation Treatment (0.1 m.e./l.)</td>
<td>Replication</td>
<td>Cations in m.e./100 g. Dry Roots</td>
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<td>-------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td></td>
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<td>Adsorption</td>
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<td>6.18</td>
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<tr>
<td></td>
<td>B</td>
<td>5.93</td>
</tr>
<tr>
<td>K</td>
<td>A</td>
<td>7.82</td>
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<tr>
<td></td>
<td>B</td>
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### Appendix Table 4

**Adsorption of Ca on Plant-Roots from Mono-Cationic Solution**

<table>
<thead>
<tr>
<th>Treatment m.e./l. Ca</th>
<th>Exchangeable Ca in m.e./100 g. Dry Roots</th>
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</thead>
<tbody>
<tr>
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<tr>
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<tr>
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<td>3.12</td>
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### Appendix Table 5

**Adsorption of K on Plant-Roots from Mono-Cationic Solution**

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<th>Treatment m.e./l. K</th>
<th>Exchangeable K in m.e./100 g. Dry Roots</th>
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<td>Pineapple</td>
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### Appendix Table 6

**Adsorption of Al on Plant-Roots from Mono-Cationic Solution (pH 4.0)**

<table>
<thead>
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<th>Treatment m.e./l. Al</th>
<th>Al Adsorbed in m.e./100 g. Dry Roots</th>
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</thead>
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<tr>
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Appendix Table 7
Adsorption of Ca:Al Ratios on Plant Roots from Tri-Cationic Solution (pH 4.0)

<table>
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<th>Cation Treatment m.e./l.</th>
<th>Ca</th>
<th>K</th>
<th>Ca:Al Ratios Adsorbed on Plant Roots</th>
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<td>Pineapple</td>
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<td>0.01</td>
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<td>1.35</td>
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<td>25.0</td>
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Appendix Table 8

Influence of the Added Ca(OH)$_2$ on Percentage Ca Saturation of Soil-Colloids and Ca Status in the Supernatant Solution

<table>
<thead>
<tr>
<th>Ca(OH)$_2$ Added Equivalent to Ca Saturation</th>
<th>Actual % Ca Saturation of Soil Colloids</th>
<th>m.e. Ca/liter of the Supernatant Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Kapaa</td>
</tr>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>8</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
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</tr>
<tr>
<td>60</td>
<td>32</td>
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</tbody>
</table>
### Appendix Table 9
Influence of the Added KOH on Percentage Saturation of Soil Colloids and K Status in Soil Solution

<table>
<thead>
<tr>
<th>KOH Added Equivalent to % K Saturation</th>
<th>Actual % K Saturation of Soil Colloids</th>
<th>m.e. K/liter of the Supernatant Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Akaka</td>
<td>Kapaa</td>
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<td>0.00</td>
<td>0.00</td>
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<td>2.6</td>
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<td>11.2</td>
<td>1.8</td>
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</table>
## Appendix Table 10

**Al and Ca Content of Pineapple Roots After Equilibrating in Bi-Cationic Solution (Al+Ca) for 24 Hours**

<table>
<thead>
<tr>
<th>Treatment m.e./l.</th>
<th>m.e./100 g. Dry Roots*</th>
<th>Adsorbed</th>
<th>Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td>Ca</td>
</tr>
<tr>
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<td>0.16</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.10</td>
<td>0.15</td>
<td>1.12</td>
</tr>
<tr>
<td>25</td>
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<td>1.30</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
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<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.62</td>
<td>0.09</td>
<td>2.24</td>
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<tr>
<td>25</td>
<td>0.24</td>
<td>0.20</td>
<td>1.66</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>1.65</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>1.09</td>
<td>0.00</td>
<td>3.21</td>
</tr>
<tr>
<td>25</td>
<td>0.94</td>
<td>0.04</td>
<td>2.68</td>
</tr>
</tbody>
</table>

**Al and Ca Content of Pineapple Roots Before Starting Experiment**

<table>
<thead>
<tr>
<th>m.e./100 g. Dry Roots*</th>
<th>Adsorbed</th>
<th>Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Ca</td>
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<td>0.20</td>
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</tr>
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</table>

*Values are averages of two replications.
Appendix Table 11
Al and Ca Content of Kaimi Clover Roots After Equilibrating in Bi-Cationic Solution (Al+Ca) for 24 Hours

<table>
<thead>
<tr>
<th>Treatment m.e./l.</th>
<th>m.e./100 g. Dry Roots*</th>
<th>Adsorbed</th>
<th>Absorbed</th>
</tr>
</thead>
<tbody>
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<td>1.00</td>
</tr>
<tr>
<td>25</td>
<td>0.39</td>
<td>6.32</td>
<td>0.97</td>
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<td>2.93</td>
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<td>5.21</td>
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<td>5</td>
<td>1.08</td>
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</table>

Al and Ca Content of Kaimi Clover Roots Before Starting Experiment

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<th>m.e./100 g. Dry Roots*</th>
<th>Adsorbed</th>
<th>Absorbed</th>
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</thead>
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<tr>
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<td>1.25</td>
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*Values are averages of two replications.
Appendix Table 12
Al and K Content of Pineapple Roots After Equilibrating in Bi-Cationic Solution (Al+K) for 24 Hours

<table>
<thead>
<tr>
<th>Treatment m.e./l.</th>
<th>m.e./100 g. Dry Roots*</th>
<th>Adsorbed</th>
<th>Absorbed</th>
</tr>
</thead>
<tbody>
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<td>K</td>
<td>Al</td>
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<td>1.19</td>
<td>1.02</td>
<td>1.73</td>
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<td>1.57</td>
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<td>2.41</td>
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</table>

*Values are averages of two replications.

Al and K Content of Pineapple Roots Before Starting Experiment

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*Values are averages of two replications.
### Appendix Table 13
Al and K Content of Kaimi Clover Roots After Equilibrating in Bi-Cationic Solution (Al+K) for 24 Hours

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<th>Treatment m.e./l.</th>
<th>m.e./100 g. Dry Roots* Adsorbed</th>
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<th>Absorbed</th>
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<th></th>
</tr>
</thead>
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<td>K</td>
<td>Al</td>
<td>K</td>
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<td>0.1</td>
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### Al and K Content of Kaimi Clover Roots Before Starting Experiment

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<tr>
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<td>0.56</td>
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*Values are averages of two replications.
Appendix Table 14
Influence of Percentage Ca Saturation Added as Ca(OH)$_2$ in 1 Percent Kapaa Soil Suspension on Al and Ca Content of Plant Roots After Absorption Experiment

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage Saturation*</th>
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<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed Al</th>
<th>Adsorbed Ca</th>
<th>Absorbed Al</th>
<th>Absorbed Ca</th>
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Al and Ca Content of Plant Roots Before Starting Experiment

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<th>Plant Species</th>
<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed Al</th>
<th>Adsorbed Ca</th>
<th>Absorbed Al</th>
<th>Absorbed Ca</th>
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</tbody>
</table>

*These are the amounts of Ca added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
## Appendix Table 15
Influence of Percentage K Saturation Added as KOH in 1 Percent Kapaa Soil Suspension on Al and K Content of Plant Roots After Absorption Experiment

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage pH Saturation*</th>
<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed</th>
<th>Absorbed</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>K</td>
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<table>
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<tr>
<th>Al and K Content of Plant Roots Before Starting Experiment</th>
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</thead>
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<td>Plant Species</td>
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<td></td>
</tr>
<tr>
<td></td>
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<tr>
<td>Pineapple</td>
</tr>
<tr>
<td>Kaimi</td>
</tr>
<tr>
<td>Clover</td>
</tr>
</tbody>
</table>

*These are the amounts of K added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
Appendix Table 16
Influence of Percentage Ca Saturation Added as Ca(OH)$_2$ in 1 Percent Kapaa Soil Suspension Adjusted to pH 4.3 on Al and Ca Content of Plant Roots After Absorption Experiment

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage Saturation*</th>
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<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed</th>
<th>Absorbed</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
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<td></td>
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<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
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Al and Ca Content of Plant Roots Before Starting Experiment

<table>
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<tr>
<th>Plant Species</th>
<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed</th>
<th>Absorbed</th>
</tr>
</thead>
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<tr>
<td></td>
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<td>Ca</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
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<tr>
<td>Kaimi</td>
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<tr>
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<td>1.25</td>
<td>5.34</td>
</tr>
</tbody>
</table>

* These are the amounts of Ca added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
Appendix Table 17
Influence of Percentage K Saturation Added as KOH in 1 Percent Kapaa Soil Suspension Adjusted to pH 4.3 on Al and K Content of Plant Roots After Absorption Experiment

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Percentage K Saturation*</th>
<th>pH</th>
<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed Al</th>
<th>Adsorbed K</th>
<th>Absorbed Al</th>
<th>Absorbed K</th>
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Al and K Content of Plant Roots Before Starting Experiment

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<th>Plant Species</th>
<th>m.e./100 g. Dry Roots**</th>
<th>Adsorbed Al</th>
<th>Adsorbed K</th>
<th>Absorbed Al</th>
<th>Absorbed K</th>
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<tr>
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<td>1.25</td>
<td>5.32</td>
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</table>

*These are the amounts of K added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
## Appendix Table 18
The Influence of Percentage Ca and K Saturation in Kapaa Soil (Hydroxide Series) on Yield, % Al, Ca, and K of Plant Roots

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Dry Matter (g./pot)</th>
<th>Element in Dry Matter**</th>
</tr>
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<tbody>
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<td>K</td>
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<td>% Al</td>
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<tr>
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<td>5.2</td>
<td>1.23</td>
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<td>60</td>
<td>1</td>
<td>6.5</td>
<td>1.32</td>
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<tr>
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<td>7.0</td>
<td>0.87</td>
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<td>1.24</td>
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<td>5.8</td>
<td>1.24</td>
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*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
Appendix Table 19
The Influence of Percentage Ca and K Saturation in Kapaa Soil (Sulphate Series) on Yield, % Al, Ca, and K of Plant Roots

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Dry Matter (g./pot)</th>
<th>Element in Plant Dry Matter**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Corn Roots</td>
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<td>1</td>
<td>4.9</td>
<td>1.02</td>
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<td>4.9</td>
<td>1.51</td>
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<td>4.9</td>
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<td>10</td>
<td>4.9</td>
<td>0.28</td>
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<td>20</td>
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<td>4.9</td>
<td>1.28</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>4.9</td>
<td>2.34</td>
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<td>0.22</td>
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<td>4.9</td>
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<td>0.19</td>
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*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
Appendix Table 20
The Influence of Percentage Ca and K Saturation
in Kapaa Soil (Hydroxide Series)
on the Uptake of Al, Ca, and K

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>pH</th>
<th>Yield of Element in Plant (mgs/pot)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Ca</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.2</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>5.8</td>
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<tr>
<td>60</td>
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<td>6.5</td>
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<td>10</td>
<td>6.0</td>
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<tr>
<td>20</td>
<td>10</td>
<td>6.4</td>
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<tr>
<td>60</td>
<td>10</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Kaimi Clover Roots

|                        |     | Al  | Ca  | K  |
|                        |     |     |     |    |
| 5                      | 1   | 5.2 | 1.79| 1.54| 22.36|
| 20                     | 1   | 5.8 | 2.48| 2.10| 21.20|
| 60                     | 1   | 6.5 | 1.24| 2.38| 16.16|
| 5                      | 10  | 6.0 | -   | -   | -    |
| 20                     | 10  | 6.4 | 0.48| 0.24| 13.11|
| 60                     | 10  | 7.0 | 0.061|tr.| 1.33 |

*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloid.
**Values are averages of two replications.
### Appendix Table 21

The Influence of Percentage Ca and K Saturation in Kapaa Soil (Sulphate Series) on the Uptake of Al, Ca, and K

<table>
<thead>
<tr>
<th>Percentage Saturation</th>
<th>pH</th>
<th>Yield of Element in Plant (mgs/pot) **</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td><strong>Ca</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.9</td>
<td>2.74</td>
</tr>
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<td>4.9</td>
<td>4.56</td>
</tr>
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<td>60</td>
<td>4.9</td>
<td>7.76</td>
</tr>
<tr>
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<td>4.9</td>
<td>0.72</td>
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<td>4.9</td>
<td>2.87</td>
</tr>
<tr>
<td>60</td>
<td>4.9</td>
<td>6.76</td>
</tr>
</tbody>
</table>

| **K**                |     |             |             |             |
|----------------------|-----|             |             |             |
| **Corn Roots**       |     |             |             |             |
| 5                    | 4.9 | 1.58        | 1.25        | 20.35       |
| 20                   | 4.9 | 3.56        | 2.01        | 24.50       |
| 60                   | 4.9 | 4.02        | 2.44        | 22.74       |
| 5                    | 4.9 | 0.42        | 0.20        | 6.71        |
| 20                   | 4.9 | 1.76        | 1.25        | 25.58       |
| 60                   | 4.9 | 1.92        | 1.50        | 21.22       |

| **Kaimi Clover Roots** |     |             |             |             |
|-----------------------|-----|             |             |             |

*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloid.

**Values are averages of two replications.
Appendix Table 22
The Influence of Percentage Ca and K Saturation in Kapaa Soil (Hydroxide Series) on Dry Matter Yield Ratio of Plant Top to Root

<table>
<thead>
<tr>
<th>Percentage Saturation*</th>
<th>Dry Yield in Plant (g./pot)</th>
<th>Corn</th>
<th>Kaimi</th>
<th>Clover</th>
</tr>
</thead>
<tbody>
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<td>Ca K</td>
<td></td>
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</tr>
<tr>
<td>5 1</td>
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<td></td>
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<td>2.88</td>
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<td>20 10</td>
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*These are the amounts of Ca and K added, but not necessarily adsorbed on the soil colloid.
LITERATURE CITED


