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ALUMINUM TOXICITY IN SOME HIGHLY WEATHERED SOILS OF THE TROPICS

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This study is consistent with the hypothesis that Al toxicity is primarily an inhibition of Ca uptake and that Al is one of several cations which may induce a Ca deficiency. The logarithms of the solution cation ratios $(Ca)^{1/2}/(Al)^{1/3}$ and $(Ca)^{1/2}/(H)$ were well correlated with rootgrowth in systems dominated by Ca and Al. These ratios were superior to either Ca activity in explaining variations in rootgrowth in such systems. Reductions in rootgrowth induced by K and Mg reported in the literature were related to similar ratios such as $(Ca)^{1/2}/(Mg)^{1/2} + (K)$.

The results indicate a nonspecific competition between interfering ions, and Ca, similar to that which occurs for exchange sites on an inert exchanger. On this basis, the reduction in rootgrowth associated with high solution concentrations of Al or other competing ions may be caused by a lack of Ca at the growing root tip. The competitive action of cations such as Al or Ca is not confined to the root tip, but also extend to the ability of the plants to absorb Ca.

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ALUMINUM TOXICITY IN SOME HIGHLY WEATHERED SOILS OF THE TROPICS

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Presented to the Faculty of the Graduate School

of Cornell University for the Degree of

Doctor of Philosophy

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By
Hubert G. Zandstra

~~December, 1971~~
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BIOGRAPHICAL SKETCH

Hubert G. Zandstra was born in Makassar, Indonesia, on October 28, 1940.

He graduated form the State College of Tropical Agriculture, Deventer, The Netherlands in 1961 and from the "Sugar School", Amsterdam, The Netherlands in 1962. He received the degree of B. Sc. (Agr.) in 1964 and an M. Sc. in 1966, both from McGill University, Montreal, Canada. In 1966 he joined the staff of the Canada Department of Agriculture Research Station at Melfort, Saskatchewan. In September 1968 he was granted educational leave and enrolled in the Graduate School at Cornell with a major in Soil Science and minors in Biometry and International Agricultural Development.

Mr. Zandstra married the former Ilse Ingrid Zalite in 1966. They have two sons.

The author is a member of the Agricultural Institute of Canada, Canadian Society of Soil Science, The American Society of Agronomy, Soil Science Society of America, The Colombian Society of Soil Science and The International Society of Soil Science.

To

Ilse and Ma

PREFACE

Highly weathered soils of the lowland tropics cover about 19 percent of the land area in the world, but include one third of the arable land of the world. These soils are the principal soils of the humid and seasonally wet-dry tropics. Virtually the whole part of Colombia, S. A., east of the Andes is occupied by these soils. This area constitutes 50 percent of the total area of Colombia.

Highly weathered soils, under natural conditions, are generally acid, low in bases, highly saturated with aluminum and of very low phosphorus fertility. Most of these soils have excellent physical characteristics and are suitable for mechanization. Because of their infertility, they have been rarely utilized for crop production and they generally support human populations of very low densities. The development of productive agricultural systems for extensive areas of well drained, acid, infertile soils will require a better understanding of the various aspects of soil acidity and its effects on plants.

Most of the ideas for the research presented in this thesis were derived from my visit to the Eastern Plains of Colombia in 1969. During this visit the frequent discussions with Dr. James M. Spain, Dr. Shaw and Mr. Eric Owen laid the ground-work for many ideas pursued in the next two years.

I am greatly indebted to Dr. D. R. Bouldin, chairman of my special

committee, for the guidance he provided throughout this study. He gave freely of his time to establish the continuing dialogue from which this thesis was derived. I also thank Dr. M. Drosdoff and Dr. S. R. Searle for serving on my special committee and for their frequent advice.

The field work for this thesis was conducted in 1970 and 1971 at the Carimagua Research Station of the Instituto Colombiano Agropecuario (ICA). I thank Dr. Hugo Manzano and Dr. Alfredo León for their cooperation with this research. Their encouragement and advice has been greatly appreciated.

During my stay in Colombia, I received much support from Dr. James M. Spain of the Centro Internacional de Agricultura Tropical, CIAT. Without his support and guidance, the field work for this thesis would have been impossible. I am greatly indebted for the many fruitful discussions with Dr. Spain which have given me a better understanding of the problems of agricultural development.

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INTRODUCTION

Damage to plants associated with high concentrations of soluble aluminum has been the subject of much research since the turn of the century (Miyake, 1916; Pierre, 1931; Hester, 1935). The earlier work is extensively reviewed by Hutchison (1943) in his treatise on the biogeochemistry of aluminum and related elements. Excellent later reviews by Pearson (1966) and Jackson (1967) describe the main effects of aluminum toxicity on root-growth, calcium nutrition and phosphorus nutrition of the plants. From these works it is also evident that of the several ionic forms of aluminum in solution, the trivalent form has generally been recognized as the active agent of aluminum toxicity.

The first section of this introduction discusses briefly the forms of Al present in soil and their contribution to Al^{3+} in the soil solution. This is followed by a discussion of the effects of Al toxicity on plants and some concluding remarks.

1. Aluminum in the soil and soil solutions

Three fairly distinct pools of aluminum can be recognized in the soil. These will be referred to as solution, exchangeable and matrix aluminum. Although these pools are fairly distinct, they interact strongly with each other and under many conditions approach a time invariant condition that can reasonably be referred to as equilibrium, where equilibrium is used in the

sense that changes occur slowly. These three pools are generally not in equilibrium with each other in a thermodynamic sense.

a. Matrix aluminum

The matrix aluminum refers to the aluminum which is component part of the soil matrix, as for example, the aluminum in the silicates and oxides which are the solid phases of the soil. In a thermodynamic sense the matrix Al probably is included in a number of unstable configurations, since equilibrium conditions are approached very slowly where transformations of these compounds are concerned.

For example, if a base is added to a solution containing Al, the resulting precipitate will not be a well crystallized solid phase whose solubility or rate of dissolution can be predicted with a high degree of precision (Lindsay, 1956; Clark, 1966). Furthermore, this precipitate will not be the thermodynamically stable phase and it will only slowly be transformed to the estable phase (Frink and Peech, 1962; Turner and Ross, 1970). If, on the other hand, a well crystallized, thermodynamically stable Al silicate or hydrated oxide is suspended in a solution maintained at pH 4.0, the solution will equilibrate only very slowly with the solid, and some months may be required for the solution to reach equilibrium with the solid phase (Frink and Peech, 1962).

Despite these theoretical problems, a reasonable amount of evidence supports the approximation that the solubility of the matrix Al can be

expressed as:

$$(Al) \quad (OH)^3 = Ksp \qquad (1)$$

where the use of parenthesis indicates activities, Ksp refers to the apparent solubility of the matrix Al, and Al is trivalent. This convention will be maintained throughout this thesis, so that ionic valences are generally omitted.

As indicated above, Ksp will not be a universal constant. Substantial research by Lindsay (1956), Frink and Peech (1962), Turner (1965) and Clark (1966a), among others, has shown the solubility of Al hydroxides in soils to decrease with time after formation, decreasing soil pH, increasing degree of crystallization and decreasing amounts of freshly precipitated Al hydroxides in the soil. This research indicates, however, that within certain limits, equation (1) can be used to interpret data in a useful and sound fashion. In effect then, in the remainder of this thesis, the solubility of the matrix Al will be described by equation (1).

b. Exchangeable aluminum

Another of the pools referred to is called exchangeable Al. By and large this pool is defined as the amount of Al extracted from the soil by some more or less empirical procedure, usually involving an unbuffered salt solution. The presence of exchangeable Al has been extensively discussed in early works by Mattson (1929 and 1940), Paver and Marshal (1934) and Harward and Coleman (1954). They established that the presence of exchangeable Al

in the soil is a result of dissociation and dissolution of the matrix aluminum. In a thermodynamically stable state, the exchangeable Al is thus in equilibrium with the matrix Al as well as the third pool of Al, the solution phase Al.

The major significance of the exchangeable pool lies in its kinetic potential to buffer the solution phase. In effect, the activity of the exchangeable Al reflects the activity of the matrix Al, but the matrix Al is less accessible kinetically to the solution phase. If, for example, the Al in the solution phase is removed by some process, the exchangeable Al almost instantaneously replenishes the solution phase Al. A much longer time would be required if only the matrix Al were available, as it dissolves relatively slowly. In effect then, the exchangeable Al can be viewed as a gigantic "surge tank" whose potential is set by the solubility of the matrix phase and whose capacity is set by the size of the pool of exchangeable ions.

A second important property of the exchangeable pool is the general recognition that exchangeable Al contributes, in effect, the major fraction of the acidity of acid soils. On removal of exchangeable Al by neutralization, a great many problems (but by no means all) associated with soil acidity generally disappear. Thus the exchangeable Al appears to be a major and important target of any liming program.

c. Soil solution aluminum

Finally, and unfortunately, the soil solution Al is no simpler to work with than the other two pools. One of the main difficulties arises from the uncertainty about the relative importance of various ionic species of Al in solution. Most chemical methods determine the total Al concentration in solution to which several ionic species may be contributing. The activity of the trivalent ion needs to be calculated on the basis of the dissociation constant of the various species. Several dissociation mechanisms have been proposed and extensively debated (Faucherre, 1954; Brosset et al, 1954; Lindsay, 1956; Frink and Peech, 1963a; Fripiat et al, 1965). From these studies it is evident that condensed basic polymers are present in aged or concentrated solutions and in solutions whose pH has been raised to pH 5 or above by adding base. The effect of these polymers on the calculated activity of trivalent Al in the soil solution appears to be relatively unimportant under the conditions considered in this thesis (Frink and Peech, 1963a). Recently, Richburg and Adams (1970) preferred a polymeric hydrolysis product because it was possible to select a hydrolysis constant which resulted in a virtually constant pKsp of Al hydroxide over a wide range of pH values. The solubility of Al hydroxides probably does not remain constant so that there is not much reason to favour their hydrolysis mechanism over others calculated for the same reaction.

On the basis of the foregoing, the activity of Al in the soil solution is considered to be controlled by:

$$pKsp = 3pOH + pAl,$$

where the prefix p refers to the negative logarithm of the activity or the solubility product involved. The trivalent Al activity is determined from the analytically determined total solution Al using the following relations:

$$(Al) = \frac{(AlOH)\ (H)}{K_H}$$

and: Total Al = AlOH + Al, where K_H is the hydrolyses constant.

As discussed above, any changes in the soluble Al pool will be immediately reflected by changes in the exchangeable Al. In addition, any change in solution concentration caused by other ions will be responded to by changes in the exchangeable phase. Description of the solution phase of Al without taking into account the exchangeable Al is therefore of limited usefulness.

The use of ion activity ratios in solution has allowed the development of exchange relations on the basis of mass action law, Donnan equilibrium or Gouy theory (Schofield and Taylor, 1955; Bolt, 1967). Turner, Clark and Nichols extensively discussed the soil-solution exchange relation for Al and Ca in a series of papers from 1958 to 1967.

Using theories of ion exchange, they described the contribution of exchangeable Al to soil solution Al as a function of the dominant ions in the system and calculated values for the exchange constants for Ca and Al. This work will be more extensively discussed together with experimental results in Chapter III.

2. Effects of aluminum toxicity on plants

a. Rootgrowth

At low levels of Al toxicity the rate of growth of main and lateral roots is reduced. The reduced rate of growth leads generally to thicker main roots with short, thick lateral roots. At higher toxicity levels the apical meristem will cease to function giving rise to stimulation of primordia all along the root and even just behind the apex. In such cases lateral roots fail to develop beyond a stubby appendix, often failing to break through the cortex of the main root. The resulting appearance of the roots has been described as coral-like. (See Jackson, 1967; Clarkson, 1968).

Investigations by Clarkson (1965a and b and 1968) and Sampson et al (1965) showed that the presence of Al severely interfered with cell division. Reduction in root elongation was found to correspond closely with a reduction in mitotic figures in apical meristems of roots. Their findings indicated that there was failure of genetic DNA synthesis even though nucleic acid metabolism as a whole was not disturbed by aluminum.

Evaluation of levels of Al in the soil that are toxic to plants and lead to reduced rootgrowth is of great agronomic importance. This research has been confounded by differences in species and varietal tolerance of plants (Foy et al, 1967) and by difficulties in selecting a suitable index of soil Al (Adams and Pearson, 1967). Of the indices used, exchangeable Al and percent Al saturation were not satisfactory when different soil types were considered. Adams and Lund (1966) determined the activity of Al in

soil solution and related this measure to rootgrowth. The relative merits of these and other Al toxicity indices will be extensively discussed in relation to experimental results in Chapter II.

b. Effects of aluminum toxicity on calcium nutrition of plants

Calcium deficiency is in general conceptually regarded as an aspect of acid soil infertility, distinct and fairly independent of Al toxicity. This concept was supported by evidence that roots can not grow unless Ca is directly supplied to the growing root (Ca can not effectively be translocated to the root from other parts of the plant) and that sometimes increasing Ca concentrations improve rootgrowth in the presence of toxic Al (Lund, 1970). However, in some cases Ca additions have not improved rootgrowth (Hallsworth et al, 1957; Clarkson, 1965a; Ríos and Pearson, 1964). In attempts to separate Al toxicity per se from Ca deficiency per se, two types of approaches were used: 1) It was reasoned that if the problem was one of Ca deficiency, addition of neutral Ca salts would improve plant performance without reducing the effects of Al, or 2) If the problem was one of Al toxicity, removal of Al by addition of a base not containing Ca should improve plant performance.

The similarity of Ca deficiency symptoms to those of Al toxicity has been frequently noted (Bollard and Butler, 1966) and the role of Ca in preventing a wide variety of metal ion toxicities is well recognized (Jones and Lunt, 1967). In addition, uptake of Ca in strongly depressed by Al (Johnson and Jackson, 1965; Lance and Pearson, 1969). Recently, Soileau et

al (1969) suggested that Al toxicity and Ca deficiency are closely related and utilized the term "Al-induced Ca deficiency" in the discussion of their results. Differentiation between Al toxicity and Ca deficiency has thus been difficult and the possibility that both terms refer to a single phenomenon must be considered.

c. Phosphorus nutrition

An important effect of high soil solution concentration of Al is the interference of Al with P adsorption and translocation (Jackson, 1967). In most crop plants Al accumulates in cortical cell walls of roots in non-exchangeable form (Clarkson, 1966) and little is transported to the above ground parts (Fried and Peech, 1946; Foy et al, 1967). Clarkson (1967) concluded that the absorbed Al can fix large amounts of P by an adsorption - precipitation reaction. Occurrence of Al-phosphates within the endodermis and within the cell has been described (Wright and Donahue, 1953). Translocation of P to shoots was also reduced in the presence of Al (Wright and Donahue, 1953 and Clarkson, 1966).

d. Tolerance to Aluminum toxicity

Some Al tolerant species have shown high accumulation of Al in above-ground parts (Hutchison, 1943; Chenery, 1946). The cell sap of these plants was found to have a pH between 3.6 and 4.8 (Chenery, 1948). Jones (1961) recognized three groups of plants with respect to Al accumulation: 1) Acidiphilous plants that accumulate a large amount of Al, such as those described by Chenery (op. cit.); 2) Alkaliphilous plants in which the cell sap

is dominantly buffered by organic acids, thus allowing translocation of some Al in complexed forms; and 3) Alkaliphilous plants with a phosphate dominated buffer system, which do not translocate much Al. Most crop plants of major importance fall into the last two categories, and Jones (op. cit.) felt that their tolerance to high Al levels in soil was related to their ability to translocate Al to the above-ground parts by forming soluble complexes with Al.

Foy et al (1967) showed that differences in tolerance among varieties of wheat and barley were not related to differences in Al contents of plant tops. His extensive studies of differential Al tolerance of crop plants led Foy and coworkers (Foy and Brown, 1963; Fleming and Foy, 1968) to conclude that Al tolerance is related to root cation exchange capacity, the amount of Al adsorbed on the root, and reduced Ca uptake. These results concur with those of Vose and Randall (1962) who related tolerance to Al toxicity to root CEC of ryegrass varieties.

3. Concluding remarks

The various effects of Al toxicity on rootgrowth and calcium and phosphorus nutrition must be considered separately if an understanding is to be gained of their relative importance and the mechanisms involved. Indices selected should have applicability over a wide variety of soils. A better understanding of the mechanisms of Al toxicity may eventually lead to a better understanding of differences in tolerance of plants to Al and screening techniques for plant selection and breeding purposes.

One major effect of Al toxicity appear to be on rootgrowth. This in turn influences uptake of water and all other ions (Lance and Pearson, 1969). In particular, the reduced Ca uptake associated with Al toxicity may be closely related to the reduction of rootgrowth.

Studies contained in this thesis are confined to the effects of Al toxicity on rootgrowth and Ca uptake. Chapter I consists of a description of the area, soil and climate of the site at which field experiments were conducted, and from which soil samples were taken. This chapter also contains a description of the samples of soils from Puerto Rico used in these studies. In Chapter 2, the relationship between indices of soil Al and root growth are studied, and a mechanism for root damage is proposed. Chapter 3 compares soil solution and exchangeable Al indices in an attempt to select a toxicity index which poses no great analytical difficulties and promises wide applicability. In Chapter 4, results of field and greenhouse experiments are discussed, together with data from the literature with emphasis on the influence of soil acidity on Ca nutrition. The conclusions of Chapters 2, 3 and 4 are reviewed and summarized in Chpater 5.

I. DESCRIPTION OF SOILS AND AREA OF FIELD WORK

The majority of studies reported in this thesis were conducted with soils obtained from the Carimagua Research Station of the "Instituto Colombiano Agropecuario" in the Eastern plains of Colombia. The other soils from the Colombian plains were sampled in the same general area. In addition to soil samples from Colombia, samples of four soil series from selected sites in Puerto Rico were used for soil chemical studies (Chapter 3).

1. Soils from the Eastern Plains of Colombia

Geology:

After the Andean uplift, the geosyncline created between the new mountains and the Guayana shield was gradually filled with materials of Andean origin during the tertiary and quaternary periods (Van Wambeke *et al*, 1964). The Eastern plains soils studied in this thesis are all located in the high savannah region. These soils were formed on deposits from the early Pleistocene (Samper *et al*, 1959).

The high plains consists of a strip of approximately 3.000.000 ha of well drained non-dissected smooth land extending from Puerto López almost to the Orinoco river. South of this area the landscape is more dissected by erosion and presents strongly rolling landscape.

The whole area varies in altitude from 100 to 200 m above sea level. Drainage is through well-defined channels (caños) with gentle slopes, generally going from west to east. The landscape is generally well drained, although certain low spots with poor drainage exist.

Climate:

This climatic description of the Carimagua region is based on 7 years data collected at Orocué, which is approximately 30 km North of Carimagua. Average monthly temperature varies less than 2°C around a yearly average of 28.1°C (Fig. 1.1). Differences between daily maxima and minima, are however, substantial. The average yearly maximum temperature was approximately 32°C compared to an average yearly minimum temperature of 22°C (Van Wambeke et al, 1964).

Precipitation data at Orocué indicate a yearly average of 1730 mm. This precipitation occurs in one rainy season, beginning in April and ending around the middle of November (Fig. 1.1). Precipitation has been measured at Carimagua since April, 1970. Rainfall data collected during the experimental period are presented in Fig. 1.1.

The climatic classification of the area according to Koeppen-Geiger (1954) is Aw (savannah climate), and according to Koeppe (1968) is a "wet and dry tropical climate".

Vegetation:

The ecological map of Colombia (Espinal and Montenegro, 1963) classifies the vegetation in the Carimagua region as dry tropical forest using the

Holdridge system. The actual vegetation is dominantly savanna with gallery forest along the drainage ways. The high well-drained savannas are covered by native grasses and some legumes. The dominant grass species is Trachyporon vestitus or paja de savannah. Other frequently occuring species are Axonopus purpusii (guaratara) and Paspalum pectinatum (Van Wambeke et al, 1964).

Soils:

The soils of the Llanos have been described by Samper (1959), Guerrero (1965), Van Wambeke et al (1964) and most recently, Guerrero (1971). The latter author concluded that most soils of the high savannas belong to the orders of Oxisols and Ultisols using the new U.S. soil taxonomy. These soils are highly weathered, with medium to heavy textures. They are very acid

(pH_{CaCl_2} : 4.0 - 4.3, pH_{KCl} : 3.6 - 4.0, pH_{H_2O} : 4.6 - 5.0),

highly Al satured (Vargas, 1964), low in exchangeable bases and P. Organic matter contents range from 3% to 5% in the surface horizons. The natural fertility of these soils is very low, mainly due to high levels of Al and very low P fertility.

Description of Carimagua profile:

A profile pit dug near the area of field experimentation has been described by Guerrero (1971), (appendix 1). Guerrero classified the soil as a kaolonitic, isohyperthermic, Typic Haplustox. Chemical analyses (Table 1.1) indicate the high Al saturation and low effective cation exchange capacity of the soil.

Mineralogical composition of the clay fraction and particle size

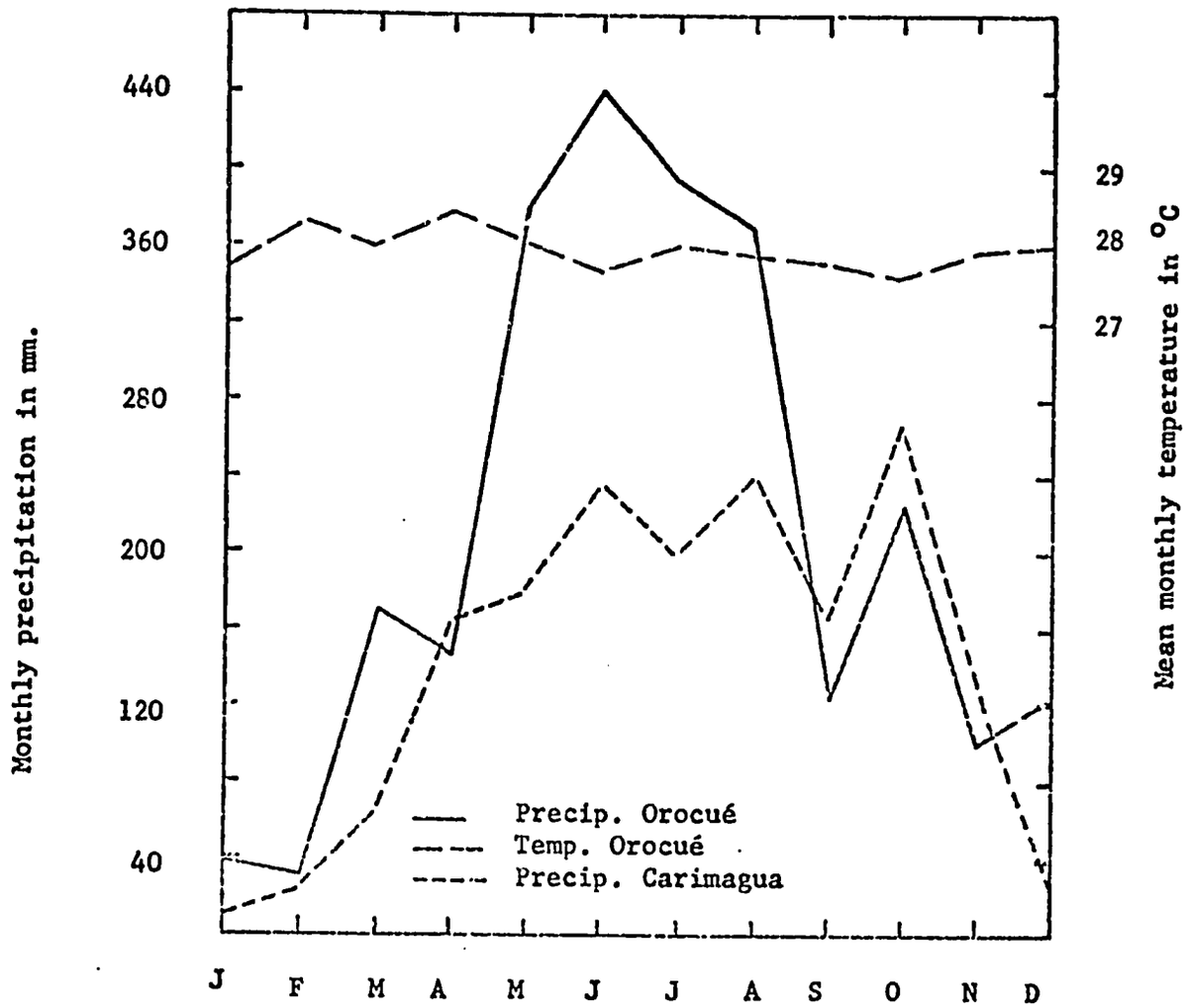

Figure 1.1: Average monthly temperature and precipitation at Orocué and monthly precipitation from October, 1970 to and including September, 1971, at Carimagua.

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Table 1.1: Soil chemical analyses of Carimagua profile. Adapted from Guerrero (1971).

Depth	pH		Organic carbon	CEC[1)]	Exchangeable					Sum of[2)] Cations	Base[3)] Saturation
	H_2O	KCl			Ca	Mg	K	Na	Al		
	1:1	1:1	%	me/100g							%
0 - 8	4.8	3.6	3.1	13.0	0.4	0.1	0.1	0.2	3.4	4.2	23.5
8 - 22	4.7	3.6	1.7	10.1	0.2	0.1	0.1	0.2	3.2	3.8	15.8
22 - 46	4.4	3.8	1.1	8.8	0.2	0.1	0.1	0.1	1.9	2.4	20.8
46 - 132	4.9	4.1	0.6	6.0	0.1	0.1	0.1	0.1	0.6	1.0	40.0
132 - 140	5.4	4.3	–	7.0	0.2	0.1	0.1	0.2	0.3	0.9	67.0

1) By ammonium acetate at pH 7
2) Not including H
3) Of effective CEC or sum of cations.

Table 1.2: Mineral content* of the clay fraction (<2μ) of the Carimagua soil profile (Unpublished data, R. M. Weaver, Agronomy Department, Cornell University)

Depth	Mica	Vermiculite	Chlorite (integrade)	Kaolinite	Gibbsite	Amorphous
cm	%					
8 - 20	8	4	25	29	1	20
20 - 57	8	3	20	34	1	21
82 - 112	10	3	21	31	1	21
112 - 135	11	3	23	37	1	21

* Does not include Pyrophyllite which was detected by x-ray diffraction.

Table 1.3: Particle size distribution and dithionite extracteable Fe_2O_3 and Al_2O_3 of the Carimagua soil profile.

Depth	2000 - 50μ	50 - 2μ	<2μ	Fe_2O_3	Al_2O_3
cm.	%				
8 - 20	10.1	54.5	29.6	4.2	1.8
20 - 57	9.7	51.6	32.0	4.7	2.1
82 - 112	8.2	51.2	33.8	4.9	1.9
112 - 135	8.2	44.6	40.1	5.4	1.8

* Based on recovered separates plus dithionite-extractable Fe_2O_3 and Al_2O_3.

analyses of selected horizons made by Dr. R. M. Weaver are presented in Tables 1.2 and 1.3, respectively. The mineralogical analyses were made according to the methods described by Alexiades and Jackson (1966). Particle size distribution was determined by the pipette method after removal of Fe_2O_3 and Al_2O_3 by dithionite extraction.

2. Soil samples from Puerto Rico

Soil samples were collected from experimental sites of the Cornell-Puerto Rico soil fertility project. Although no profile description of these sites is available at this time, a tentative classification has been made on the basis of data from the Soil Survey Investigations report No. 12, and field inspection at the sites. Samples used in this thesis belong to the following series: Piñas sandy loam from the Fundador site is a well-drained, permeable, acid soil tentatively classified as Psammentic Haplotox, sandy, isohyperthermic.

Humatas clay, Corozal site: A deep, well-drained soil with only fair permeability because of clay accumulation in the subsoil. Tentative classification: Typic Tropohumult, clayey, kaolonitic, isohyperthermic.

Catalina clay from the Barranquitas. A deep, well-drained, permeable soil which had been limed and fertilized for a number of years. Subsoil horizons are acid. Tentative classification: Typic Haplorthox clayey, oxidic, isohyperthermic.

Los Guineos silty clay from the Jayuya site. A permeable, deep, well-drained soil with slightly acid topsoil and very acid subsoil horizons, tentatively classified as Typic Tropohumult, clayey mixed, isohyperthermic.

II EFFECTS OF ALUMINUM IN SOIL SOLUTION ON ROOT GROWTH OF CORN AND SORGHUM

1. General

Reduction of root growth by soluble aluminum in acid soils has been related to exchangeable Al and percent Al saturation of the cation exchange complex with only limited success, particularly when different soil types were considered (Adams and Pearson, 1967). Adams and Lund (1966) found a reasonably consistant relation between the activity of Al in the displaced soil solution and root growth. The relation, although a great improvement over that with exchangeable aluminum, varied among soil types. These differences were in some cases considerable: an activity of 10^{-5} M Al in the Bladen subsoil reduced relative root length by about 70%, but in the Dickson subsoil, reduction in relative rootlength at the same Al activity was approximately 35%.

Recently, Soileau et al (1969) considered Al toxicity and Ca deficiency to be closely related. They used the term "aluminum induced calcium deficiency" in the discussion of their results. Lund (1970) studied the effects of Ca on root growth of soybeans and found that reductions in rootgrowth from high solution Al activities were lessened by increasing the Ca activity in solution. To interpret his results Lund (op. cit.) used the ratios

$\frac{a_{Ca}}{a_H}$ for the effects of pH, $\frac{a_{Ca}}{\Sigma a_{cations}}$ for the effects of Mg and K, $\frac{a_{Ca}}{a_{Al}}$ for the effects of Al on root growth.

The experiments discussed in this chapter were designed to evaluate the hypothesis that the toxic effect of aluminum in the soil on root growth is directly related to the activity of aluminum in the soil solution. In considering this hypothesis other possible aluminum indices will be discussed.

2. Methods

Techniques for the study of root growth were described by Nelson and Brady (1953), Ragland and Coleman (1959) and Rios and Pearson (1964). These researchers grew plants or seedlings in fertile, non-toxic soil and placed these on top of the soil or solution to be studied. These methods allowed development of healthy roots in the non-toxic medium and reduced indirect physiological effects on rootgrowth (Adams and Pearson, 1967). The technique described in this study was designed for the rapid study of root growth using small amounts of soil and solution. Primary roots of recently germinated seedlings were used to reduce indirect physiological effects on rootgrowth.

a. Soil preparation

Samples of 150 g Carimagua topsoil were combined with 300 ml of 10^{-3}M, 5 x 10^{-3}M or 10^{-2}M $CaCl_2$. Various amounts of $Ca(OH)_2$ were added and thoroughly mixed through the suspensions. These treatments are listed in Table 2.1 for experiment 1, and in Table 2.2 for experiment 2. During 10 days, soils were continuously aerated with acid washed air and stirred twice daily. After 10 days pH was determined by placing the glass electrode in the soil suspension and the reference electrode in the supernatant solution.

Supernatant solutions were removed by suction, centrifuged and analysed for Al by the aluminon procedure (Mclean, 1965 pp 988-989), for Ca and

Mg by atomic adsorption in solutions containing 0.5% La. The activities of Al, Ca and Mg were calculated assuming the monomeric hydrolysis mechanism for Al (Lindsay et al, 1959) using pH = 5.02 and the Debye-Huckel equation with distance-of-closest approach constants reported by Kielland (1937). Approximations were repeated until the difference between successive estimates of the activity coefficients was less than 0.002. No correction for ion pair formation was thought necessary as the system employed Cl^- as the counter balancing ion.

The soil was rinsed until the conductivity of the wash solution was less than 0.05 millimohs. The soil was then dried at 45°C until moist, broken up with a spatula, further dried at 45°C and ground by mortar and pestle. Subsamples of the soil were used in the rootgrowth experiments.

b. Germination of seedlings

Seeds were germinated between sheets of filter paper placed on a glass plate and moistened with a solution of 10^{-3} M $CaCl_2$. The entire assembly was wrapped in black plastic, except at the base, which was placed in a tray with distilled water. The glass plate was set at an angle of about 20° from the vertical during germination of the seeds. After germination, seedlings were rinsed by floating them in a try with distilled water. At the initiation of the experiment, the lenght of primary roots of corn seedlings varied from 3.5 to 4.5 cm and of sorghum seedlings from 2.5 to 3.5 cm. In experiment 1 insufficient care was taken in the selection of seedlings with similar lengths of primary roots. In experiment 2 variations in initial root length within replicates was kept small. The varieties used were Pioneer X-306 for corn and DeKalb R.S. 610 for sorghum.

c. Measurement of root growth

Polyethylene drying tubes, of 20 cm length and with an inner diameter of 1.4 cm, were fitted with a device designed to aerate and stir the solution, and at the same time circulate the solution through a layer of soil. This device consisted of a hypodermic needle stuck through a rubber stopper. The stopper was cut to fit a glass tube in a manner that allowed free entrance of liquid at the base of the tube (Fig. 2.1). In each tube, 27 ml of prepared equilibrium solution was recombined with 5 g of the dried soil (see soil preparation). The composition of the equilibrium solutions is described in table 2.1 (Expt. 1) and table 2.3 (Expt. 2). During the addition of solution and soil, air under pressure of a 40 cm water column was passed through the hypodermic needles. The rapid flow of air created sufficient suction at the base of the glass tube to carry with it lenses of liquid, which were released into the bulk solution at the top of the glass tube. The amount of solution passing up-ward through the glass tubes, estimated by observation of the size and frequency of the liquid lenses, varied from 4 to 10 ml/min. This insured percolation of the solution through the soil for the duration of the experiment. After the soil suspension had cleared, pregerminated seeds were placed in the inverted caps of the drying tubes on top each tube. Experiments were continued for 60 hours during which several measurements of rootlength were made. The 60 hour period was found to allow substantial differentiation of rootgrowth.

3. Results

In the experiments reported here, the more severely damaged roots appeared swollen and grew crookedly. The root tip was blunt, often appearing

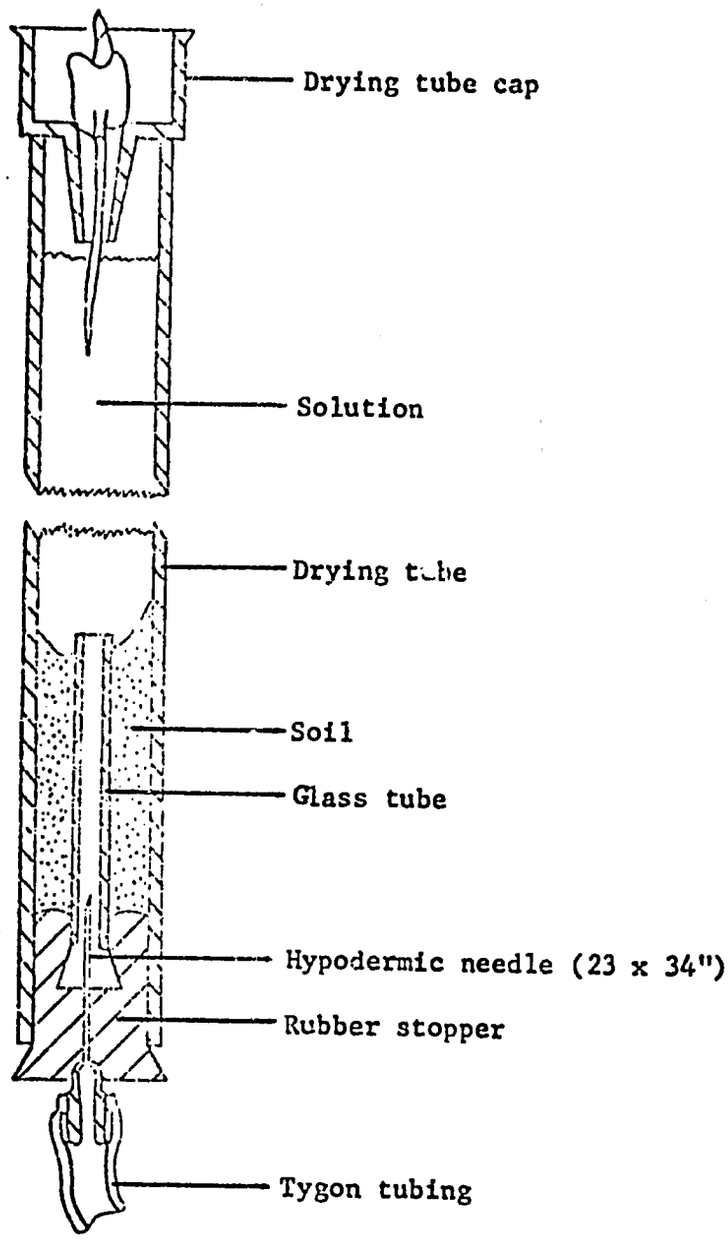

Figure 2.1: Assembly for rootgrowth studies used in Experiments 1 and 2.

to be compound. The root cap was often split and partially sloughed off. The epidermis and cortex showed deep lengthwise cracks and because of their transparent, glossy appearance the stele could easily be distinguished. In some cases swollen root primordia could be found all along the root, often causing cracking of the cortex without emerging from it. Root elongation ceased after as few as 36 hours in corn seedlings and 24 hours in sorghum seedlings. In some cases, root elongation was so small that most of it could be accounted for by cell elongation alone.

a. Experiment 1

Because of variations in initial root length of corn seedlings, initial rate of root growth varied widely. This led to wide variations within treatments in root length measured after 60 hours of growth. Inspection of roots at the end of the experiment indicated that the proximity to the roots apex of swollen lateral root primordia was little affected by the initial root length. This distance provides a useful index of root growth inhibition by effects of soil acidity as initiation of lateral root primordia progresses from the seed downward and is a function of extent of inhibition of the apical meristem.

Results showed substantial effects of $Ca(OH)_2$ but only minor effects of $CaCl_2$ (Table 2.1). Statistical analyses showed that effects of $CaCl_2$ treatments on root growth were not significant (Table 2.2). Because increases in $CaCl_2$ levels decreased pH and substantially increased Al activity in solution (Table 2.1), the lack of effect of $CaCl_2$ was considered anomalous under the hypothesis that the activity of Al alone regulates effects on root growth.

b. Experiment 2

To further evaluate the primary hypothesis a second experiment was designed which included more $Ca(OH)_2$ levels. In this experiment increases in calcium chloride concentration of the equilibrium solution decreased solution pH, and increased Ca and Al activity as expected, but the effects of these changes in solution composition on root growth were minor (Table 2.3) and statistically non-significant. In the corn experiment, however, there was a significant interaction sums of squares (Table 2.2).

Figures 2.2 A and B illustrate that rootgrowth was not simple function of pH or Al activity, but depended as well on the concentration of $CaCl_2$. In both figures, rootgrowth showed greater tolerance to low solution pH and high Al activity at the higher $CaCl_2$ level. The hypothesis that rootgrowth reductions in acid soil are related to pH or the activity of Al in the soil solution must therefore be rejected or modified.

Comparing the two figures, it is evident that solution pH as well as Al activity show close relationships to rootgrowth at fixed $CaCl_2$ levels. It appears, therefore, that a soil solution index, related to pH or Al activity, but not affected by changes in $CaCl_2$ concentration is required to account for the observed lack of effect of $CaCl_2$ on root growth.

Cation activity ratios of the general category:

$$\frac{(C_1^{\,v})^{1/v}}{(C_2^{\,w})^{1/w}}$$

(C is concentration)

(v and w are ionic valences)

or, in logarithmic form: $1/w\ pC_2^{\,w} - 1/v\ pC_1^{\,v}$, are independent of soil solution ratio and variations in salt concentration so long as no extensive

Table 2.1: Effect of added $Ca(OH)_2$ and $CaCl_2$ concentration of the added solution on the pH and activity of Al in the equilibrium supernatant solution and the proximity of swollen root primordia to the root tip (Expt. 1).

Treatment			pH	aAl	D*
No	$Ca(OH)_2$ me/100g	$CaCl_2$ $M/1x10^3$		$M/1x10^5$	cm
1	0.0	1	4.02	10.7	4.4
2	0.0	5	3.98	14.2	3.4
3	0.0	10	4.02	15.7	4.5
4	1.75	1	4.83	0.2	10.4
5	1.75	5	4.65	0.7	10.6
6	1.75	10	4.46	1.8	9.5
7	3.50	1	5.71	0.1	12.9
8	3.50	5	5.41	0.3	11.2
9	3.50	10	5.14	0.5	10.5

* Distance of swollen root primordia closest to the root-tip.

Table 2.2: Analyses of variance of effects of $CaCl_2$ and $Ca(OH)_2$ on proximity of swollen root primordia to the roottip and additional rootgrowth of corn and sorghum seedlings.

	Experiment 1			Experiment 2				
	Root primordia, Corn			Additional rootlength, $\Delta L/60$ hrs.				
				Corn			Sorghum	
Sources	df	SS	F	df	SS	F	SS	F
Total	36	3113.7		48	2316.9		569.33	
Mean	1	2664.3		1	1685.1		209.58	
$Ca(OH)_2$	2	373.3	85.28**	5	606.9	282.0**	356.70	1108.0**
$CaCl_2$	2	7.0	1.61ns	1	0.007	0.017ns	0.01	0.16ns
Interaction	4	10.8	1.24ns	5	8.2	3.79**	0.42	1.31ns
Replicates	3	5.7	0.87ns	3	2.5	1.94ns	0.49	2.52ns
Error	24	52.5		33	14.2		2.12	

** significant at $p = 0.01$
ns non-significant

Table 2.3: Effects of $Ca(OH)_2$ additions and $CaCl_2$ solution concentration on equilibrium solution parameters and rootgrowth of corn and sorghum seedlings (Expt. 2).

Treatment									
no	$Ca(OH)_2$ me/100g	$CaCl_2$ $M/1x10^3$	pH	pCa	pAl	pH-1/2pCa $(M/1)^{1/2}$	1/3pAl-1/2pCa $(M/1)^{3/2}$	ΔL^*-corn cm/60hr	ΔL^*-sorghum cm/60hr
1	0.0	1	4.02	3.33	3.97	2.35	-0.34	2.3	0.5
2	0.0	10	4.02	2.38	3.80	2.83	0.07	3.7	0.5
3	0.22	1	4.07	3.12	3.80	2.51	-0.28	2.5	0.3
4	0.22	10	3.97	2.38	3.66	2.74	0.00	3.0	0.5
5	0.44	1	4.15	3.01	4.00	2.65	-0.17	3.1	0.3
6	0.44	10	4.00	2.38	3.72	2.81	0.05	3.0	0.4
7	0.87	1	4.34	2.93	4.47	2.87	0.02	5.5	0.7
8	0.87	10	4.11	2.36	3.98	2.93	0.13	5.1	0.9
9	1.75	1	4.83	2.88	5.79	3.40	0.50	10.2	2.6
10	1.75	10	4.46	2.31	4.76	3.29	0.40	9.0	2.3
11	3.50	1	5.71	2.91	6.90	4.26	0.85	12.0	8.0
12	3.50	10	5.14	2.26	6.07	4.01	0.89	11.6	8.0

* Additional rootlength 60 hrs after placement of seedlings into solutions.

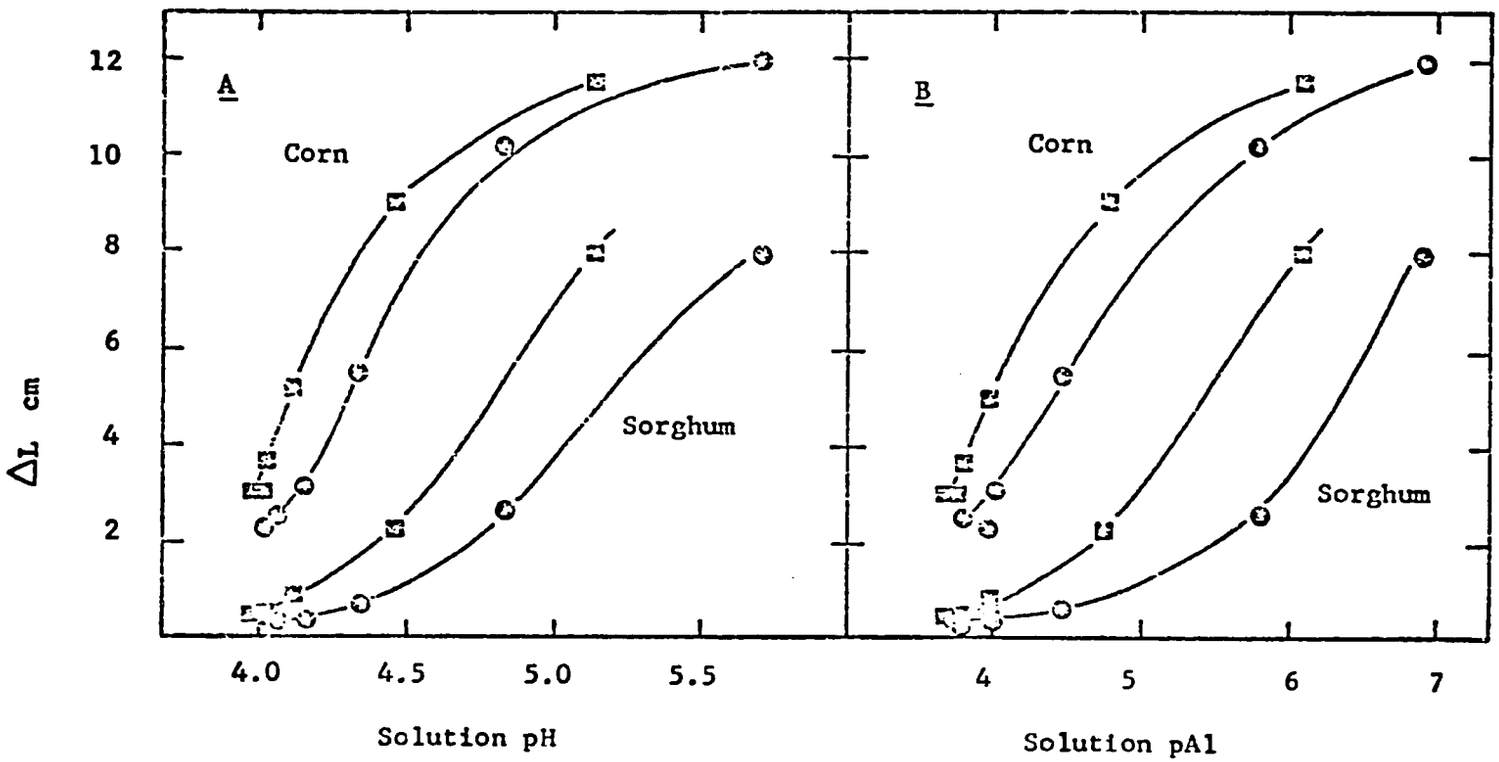

Figure 2.2: Effect of pH and pAl of equilibration solutions on rootgrowth (ΔL) of corn and sorghum seedlings. Circles refer to 10^{-3}M $CaCl_2$ equilibration. Squares refer to 10^{-2} M $CaCl_2$ equilibration.

are made in the suite of exchangeable cations (c.f. Schofield, 1947; Beckett, 1964; Lindsay and Peech, 1959). These ratios have been used extensively to describe the dependence of the activity of ions in the soil solution on the exchangeable ions (Turner and Clark, 1965; Frink and Peech, 1963 b).

As illustrated in figures 2.3A and 2.3B, the variables pH - 1/2pCa and 1/3pAl - 1/2pCa were well correlated with root growth regardlessof the concentration of added $CaCl_2$ at all $Ca(OH)_2$ levels.

4. Discussion

The relation between the parameters pH and pH - 1/2pCa can be represented by:

$$pH = (pH - 1/2pCa) - 1/2pCa,$$

giving rise to a series of parallel curves of pH verses rootgrowth, each for its particular Ca activity. The difference between the two relations of rootgrowth verses pH in figure 2.2A, accounts very well for the differences in pCa in solution as evidenced by the collapse of the two curves into one when the measure pH - 1/2pCa is related to rootgrowth. A similar argument applies to pAl, as:

$$pAl = 3(1/3pAl - 1/2pCa) - 3/2pCa,$$

accounting for the shift in curves in figure 2.2B. The parameter $\frac{aCa}{aAl}$ (Lund, 1970) can be transformed to pAl - pCa which relates to 1/3pAl-1/2pCa as follows:

$$pAl - pCa = 3(1/3pAl - 1/2pCa) - 1/2pCa,$$

or $$pAl - pCa = 2(1/3pAl - 1/2pCa) + 1/3pAl.$$

This means that the relation of pAl - pCa to rootgrowth could be shifted by variations in either Ca or Al activities.

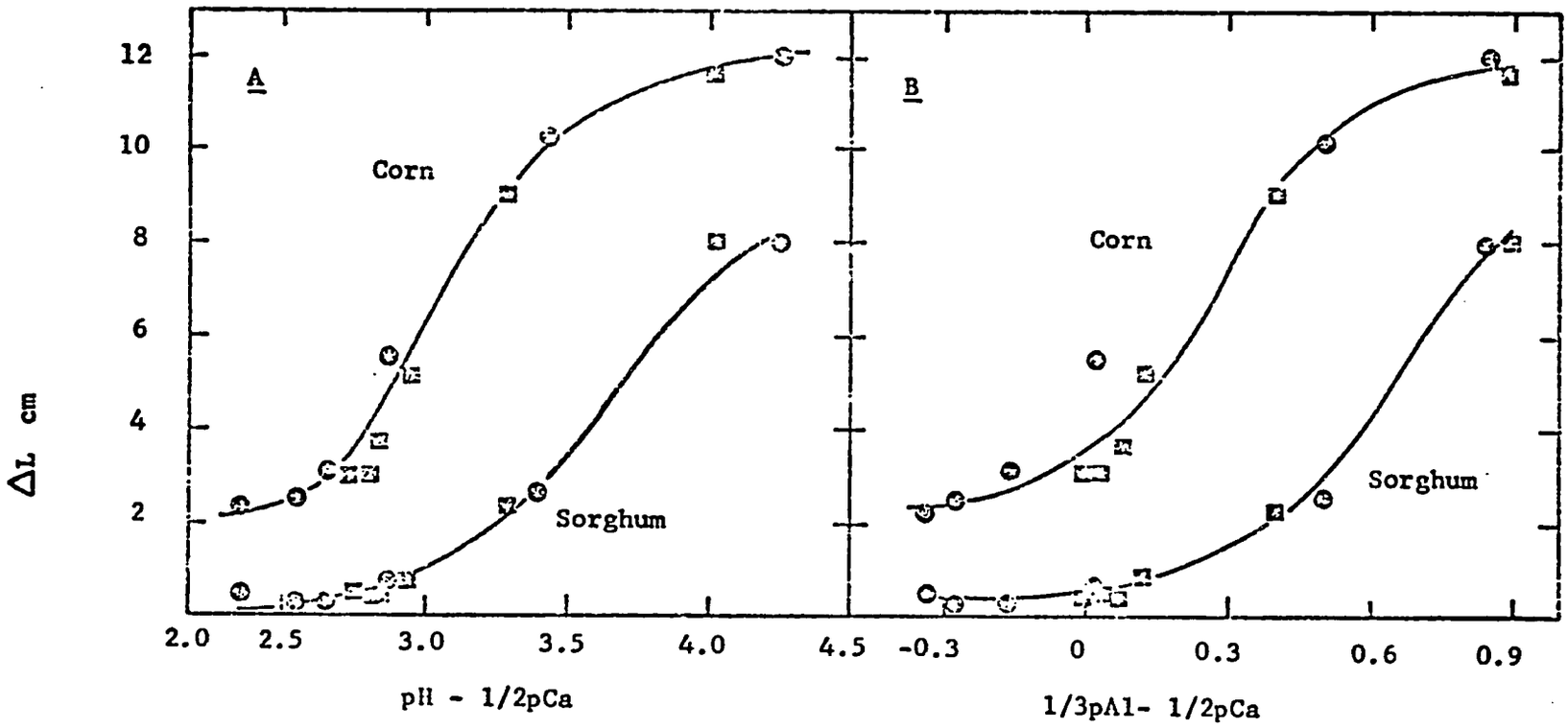

Figure 2.3: The relation of pH - 1/2pCa and 1/3pAl - 1/2pCa with rootgrowth (ΔL) of corn and sorghum seedlings. Circles and squares refer to 10^{-3} and 10^{-2} M $CaCl_2$ equilibrations, respectively.

The variables pH - 1/2pCa and 1/3pAl - 1/2pCa are in effect activity ratios and their correlation with rootgrowth suggest that perhaps root growth may be reduced by a deficiency of Ca induced by an excess of another ion. This may account for the ameliorating effect of increasing Ca activity on reduction in rootgrowth induced by a low solution pH (Arnon and Johnson, 1942). In addition, Clarkson (1965b) found that symptoms of typical Al toxicity could be obtained using indium, gallium and lanthanum salts.

Recent data published by Lund (1970) allow for a comparison of these variables. Table 2.4 and figure 2.4A indicate that the parameter pH-1/2pCa fits the data of his experiments 2 and 3 very well. (Treatment 5 is an exception but this value appears to be erroneous, which is evident from comparison with treatment 7). The parameter used by Lund: $\frac{aH}{aCa}$, may be inverted and transformed to the negative logarithm to give pH - pCa. As: pH - pCa = 2(pH - 1/2pCa) - pH, pH - pCa is not a unique function of pH-1/2pCa. The relation of rootgrowth with pH - 1/2pCa (Fig. 2.4A) may then be replaced by a series of relations with pH - pCa, each representing a selected pH value. Except for treatment 5 (not plotted), the rates of rootgrowth fit the curve representing the appropriate pH quite well (Fig. 2.4B).

In experiments 4 and 5, Lund (op.cit.) studied the interaction of Ca and Mg and Ca and Mg + K (Table 2.5). Plotting rootgrowth against $\frac{(Ca)}{\Sigma(M_i)}$ two curves were required, depending on whether or not Mg was the only cation (Fig. 2.5A). As the availability of Ca will be affected by the introduction of another dominant ion, the ratio $\frac{(Ca)^{1/2}}{(Mg)^{1/2} + (K)}$ was calculated (Table 2.5) and plotted against rate of rootgrowth (Fig. 2.5B). The good agreement obtained between the calculated activity ratio and rootgrowth in figure 2.5B

Table 2.4: Effect of Ca concentration and pH on soybean taproot elongation in nutrient solutions (From: Lund, 1970).

Treatment no	pH	Ca ppm	pH - 1/2pCa**	pH - pCa**	$\Delta L/\Delta t$* mm/hr
1	5.60	0.05	2.65	0.30	2.66
2	5.60	0.50	3.15	0.70	2.87
3	5.60	2.50	3.50	1.40	2.70
4	4.75	0.05	1.80	1.15	0.11
5	4.75	0.50	2.30	0.15	0.91
6	4.50	0.05	1.55	1.40	0.04
7	4.50	0.50	2.05	0.40	1.36
8	4.50	2.50	2.40	0.30	2.38
9	4.00	2.50	1.90	0.20	0.44
10	4.00	5.00	2.05	0.10	1.26

* Rate of elongation during 48 hours after placement of roots into solution.

** No activities were calculated.

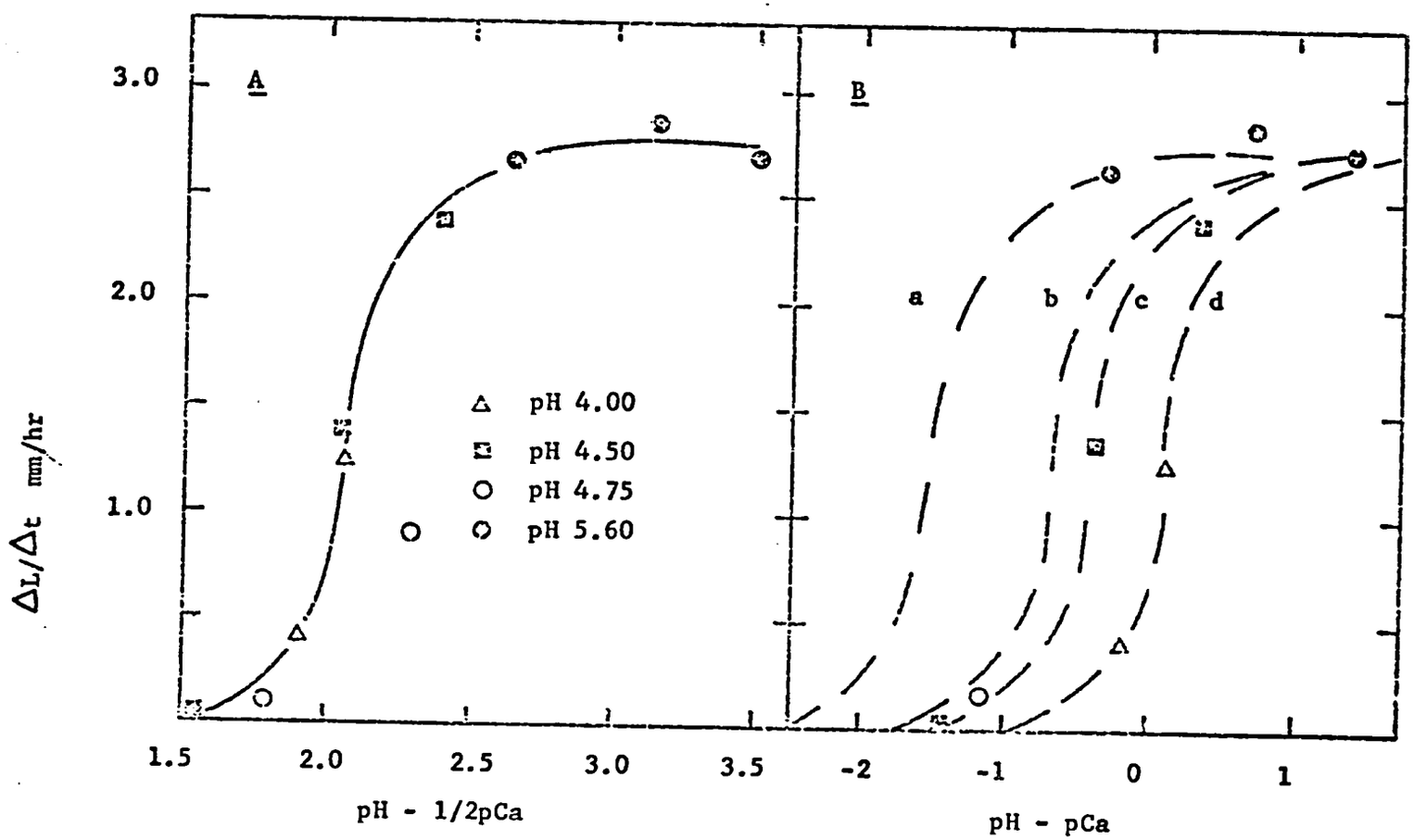

Figure 2.4: Tap root elongation rate of soybean ($\Delta L/\Delta t$) in relation to pH - 1/2pCa and pH - pCa. In figure B, calculated curves are at pH 5.6 (a), pH 4.75 (b), pH 4.5 (c) and pH 4.0 (d). (Data from Lund, 1970).

indicates the importance of ionic valence in the effects of interfering ions on rootgrowth. The resulting fit may to some extent be regarded as fortuitous as in $\frac{(Ca)^{1/2}}{(Mg)^{1/2} + (K)}$ no allowance is made for the difference in exchange behavior between Mg and K ions. To do so the parameter would become: $\frac{(Ca)^{1/2}}{(Mg)^{1/2} + c(K)}$. It appears from these results that c may be close to 1.0.

The results discussed show that effects of Al toxicity, low Ca:Mg ratio, low pH and Ca deficiency on rootgrowth, can all the related to the same type of soil solution function:

$$\frac{(Ca)^{1/2}}{\Sigma c_i \ (M_i)^{1/v_i}}$$

were M_i is any cation, $v > 0$ its charge and c_i a constant.

This indicates that all these effects are either induced Ca deficiences at the growing root tip, or a series of cation toxicitie which can be minimized by the presence of Ca. Because of the specificity of Ca in these relations, they could reasonably be called induced Ca deficiencies.

Comparison of the effects of Mg and K on rootgrowth (Table 2.5) shows that a given activity of K inhibits root growth much less than the same activity of Mg in solution. Levels of Mg activity which strongly interfered with root growth at a Ca activity of approximately 0.8×10^{-3} M were approximately 16×10^{-3} M. Substantially lower Al activities of 10^{-4} M to 6×10^{-5} M showed similar rootgrowth inhibition at similar Ca activities in solution (See table 2.3), treatments 5 and 7). The activity ratio $\frac{(Ca)}{\Sigma(M_i)}$ does not take into account the substantial effects of ionic valence evident in the above mentioned

Table 2.5: Effect of concentration of Ca, Mg and K on taproot elongation in nutrient solutions (From: Lund, 1970).

Treatment				$\frac{(Ca)^{**}}{\Sigma(M_i)}$	$\frac{(Ca)^{**}}{(Mg)^{1/2} + (K)}$	$\Delta L/\Delta t^{*}$ mm/hr
no	Ca me/l	Mg me/l	K me/l			
1	2	38	0	0.05	0.22	1.56
2	4	36	0	0.10	0.32	2.59
3	8	32	0	0.20	0.48	3.25
4	2	19	19	0.02	0.25	2.07
5	4	18	18	0.04	0.37	2.69
6	8	16	16	0.09	0.56	3.15

* Rate of elongation during 48 hours after placement of roots into solutions.
** Parentheses denote approximate activities.

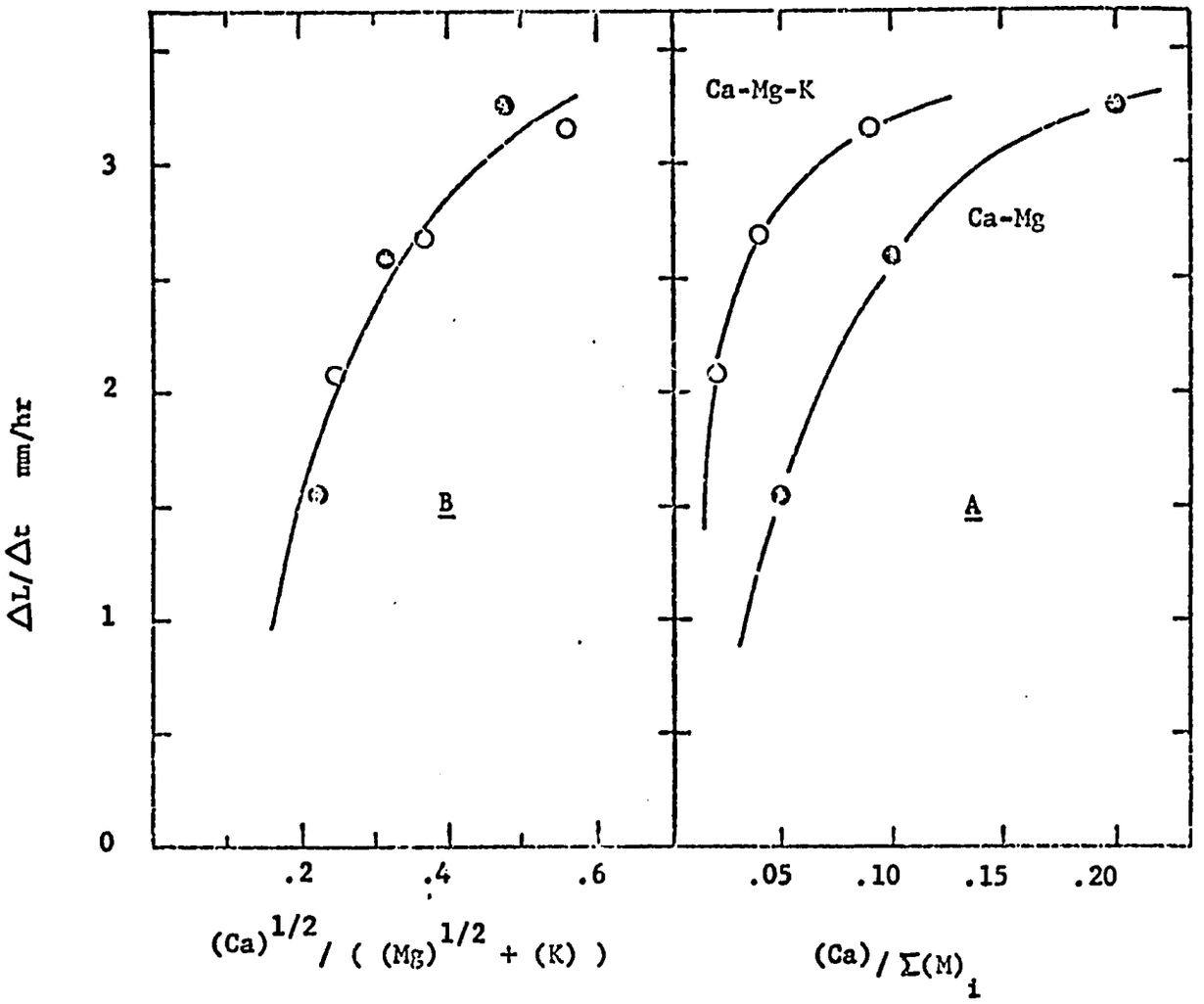

Figure 2.5: Comparison of two ion activity ratios in their relation to soybean tap root elongation rate ($\Delta L/\Delta t$) obtained in a Ca-Mg solution and a Ca-Mg-K solution (Data from Lund, 1970).

results, and is therefore not applicable to soil solutions in which the relative dominance of mono - di - or ti - valent ions varies.

Relating reduction in rootgrowth to relative Ca - intensity can be experimentally trying if more than one or two ions are affecting Ca intensity at the same time. In natural soils it is generally possible to select a suitable parameter based on a single cation as reference ion. In acid soils, 1/3pAl - 1/2pCa is suitable but analytically demanding.

For aluminum hydroxide:

$$3p(OH) + pAl = pKsp,$$

$$14 - pH = \frac{pKsp}{3} - 1/3\ pAl,$$

or

$$1/3pAl = pH + \frac{pKsp}{3} - 14$$

The ratio 1/3pAl - 1/2pCa may thus be replaced by pH - 1/2pCa if the pKsp of aluminum hydroxide is reasonably constant. The ratio pH - 1/2pCa is easily measured in soils and relatively independent of salt concentration.

5. Conclusions

The effects of Al on rootgrowth were not governed solely by the activity of Al in solution. Rootgrowth was related to relative Ca intensity measures such as pH - 1/2pCa, 1/3pAl - 1/2pCa and $\frac{(Ca)^{1/2}}{(Mg)^{1/2} + (K)}$. This suggests the operation of an exchange mechanism of interfering ions with Ca, which controls damage to roots due to high activities of H, Al, Mg or any other cation. The measure $\frac{(Ca)}{\Sigma(M_i)}$ did not take into account the important effects of ionic valence of the interfering cation.

Considering the results of this study and of others discussed in this

chapter, the following mechanism of the effects of Al, H, Mg and other cations on rootgrowth is proposed: Reduced rootgrowth is a result of a lack of Ca at the growing roottip. The inability of the meristematic cells to avail themselves of enough Ca is caused by a barrier zone in which ion activities are regulated by exchange phenomena.

III ALTERNATIVE MEASURES OF ALUMINUM TOXICITY

1. Introduction

Both Al and Ca in the soil solution were related to rootgrowth by the variable 1/3pAl - 1/2pCa in the preceding chapter. Since the Al activity in the soil solution is difficult to measure, alternative ways to estimate this variable are considered in this chapter.

If the solubility of $Al(OH)_3$ is constant, an equivalent function can be calculated as follows:

$$(Al)\ (OH)^3 = Ksp$$

or

$$3p(OH) + Al = pKsp \qquad (1)$$

Since

$$(H)\ (OH) = K_w$$

$$pH + p(OH) = pK_w \qquad (2)$$

Substituting (1) in (2) and rearranging,

$$pH - pK_w - 1/3pKsp = 1/3pAl \qquad (3)$$

Substracting 1/2pCa from both sides of (3),

$$pH - 1/2pCa = pK_w - 1/3pKsp + 1/3pAl - 1/2pCa$$

or

$$1/3pAl - 1/2pCa = pH - 1/2pCa - pK_w + 1/3pKsp \qquad (4)$$

Since pK_w and pKsp are known, the function 1/3pAl - 1/2pCa can be estimated from measured values of pH and Ca in the soil solution. This is more easily done than measuring the Al activity in solution.

Extensive studies by Turner and coworkers (1962a, 1962b, 1963, 1965, and 1967) and Clark and coworkers (1965, 1966a, 1966b) showed values for

pKsp to vary between 33 and 36 in a wide variety of soils. Such variations could change 1/3pAl - 1/2pCa values by up to one unit for similarly measured values of pH - 1/2pCa (eq.4). The relation between rootgrowth of corn and sorghum seedlings and 1/3pAl - 1/2 pCa extended over 1.2 units (Fig. 2.2B). A change of one unit of 1/3pAl - 1/2pCa could therefore make the difference between a highly toxic and a non-toxic rooting environment.

To improve on the relation between pH - 1/2pCa and percent base saturation, Turner and Clark (1965) formulated a "corrected lime potential" (CLP):

$$CLP = pH - 1/2pCa - 1/3(33.8 - pKsp)$$

This measure corrected for variations in the $Al(OH)_3$ solubility products using the solubility of gibbsite as a bases for comparison. The CLP requires, however, determination of pH, pCa and pAl and offers no advantage over 1/3pAl - 1/2pCa in this respect.

Richburg and Adams (1970) showed the solubility product of $Al(OH)_3$, calculated as pKsp, assuming the monomeric hydrolyses mechanism

$$\frac{(Al^{3+})\ (OH^-)}{(AlOH)^{2+}} = K_I\ ,$$

to be a linear function of pH. Further, they found the pH - pKsp relation of Norfolk sandy loam to be 0.5 pKsp units higher than that Lucedale clay loam. Comparison of the relations between pH and the pKsp of $Al(OH)_3$ in mineral and organic soils, showed differences in pKsp varying from 1.5 to 0.4 pKsp units depending on pH (Clark and Nichol, 1966). However, little information is available on the pH - pKsp relacions of highly weathered soils of the tropics.

Another alternative to measuring Al and Ca activities in solution would be to evaluate their concentration on the exchange complex and estimate the solution activities using ion exchange relations. This approach has several procedural advantages; it allows a more accurate determination of Al in soil with pH values close to or above pH 5: virtually all exchangeable Al is in trivalent form even at higher pH values (Frink and Peech, 1963b), making dissociation calculations unnecessary; activities of the ions in the exchanger phase cannot be estimated and are thus included in the exchange constant (Erikson, 1952), making the estimation of activity coefficients unnecessary; no equilibration or soil solution extraction procedures are required, evading problems associated with dilution of the soil solution, equilibration time and electrolyte concentration of the equilibrium solution.

The usefulness of this approach depends largely on the extent to which estimated exchange constants vary within and among soil types. Turner and Clark (1965) found the constant to be similar for a wide variety of Canadian soils. Exchange constants calculated for 12 mineral soils from results of Clark and Nichol (1966) showed substantial variation. These soils varied in organic matter contents from 4.1 to 19.6 percent. There was, however, no evidence of a relation between the value of the exchange constant and percent organic matter (r=.25). In addition, exchanges constants calculated for organic soils were similar to those for mineral soils.

Studies discussed in this section were designed to evaluate the constancy of the $Al(OH)_3$ solubility - pH relation and the variation in the exchange constant of Ca for Al in some highly weathered soils of the tropics. The results were considered on the basis of their applicability towards a practical index of aluminum toxicity.

2. Materials and Methods

Three equilibration experiments were conducted. Experiment 1 and 2 were designed to evaluate the effects of equilibrium solution concentration and additions of $Ca(OH)_2$ on the solubility of $Al(OH)_3$, neutralization of exchangeable Al by $Ca(OH)_2$ and the exchange characteristics of Ca and Al in Carimagua topsoil. Experiment 3 consisted of a comparison of the $Al(OH)_3$ solubility and the exchange characteristics of Al and Ca in samples of four selected highly weathered soils from Puerto Rico.

a. Experiments 1 and 2

Experiments 1 and 2 were, in effect, successive experiments with the same soil. The sequence of events is summarized as follows:

a) $CaCl_2$ and $Ca(OH)_2$ were added to large samples (150 g) of soil. The supernatant solutions were analyzed, but the exchangeable fraction was not determined at this time.

b) Following washing and drying of the soil, subsamples of the large samples of soil from step (a) were extracted with KCl and the exchangeable ions were determined.

c) Another subsample of the washed and dried soil was equilibrated with a $CaCl_2$ solution and the equilibrium solutions were analyzed.

Thus experiment 1 consists of the supernatant from (a) and the exchangeable ions from (b). It should also be noted that the soil samples used in the second rootgrowth experiment in Chapter 2, were subsamples of the washed and dried soil described here. Details of the experimental procedures outlined above are described in the following paragraphs.

Samples of 150 g dried and ground Carimagua topsoil were equilibrated

with 300 ml of 10^{-3} M, 5 x 10^{-3} M and 10^{-2} M $CaCl_2$. Calcium hydroxide was added at zero, 0.22, 0.44, 0.87, 1.5, 3.5 and 7.0 me/100 g soil. After 10 days of equilibration with frequent stirring and aeration, supernatants were removed by suction. Supernatants were centrifuged at 1250 x g for 20 minutes and analyzed for Ca, Mg and Al (for more details, see methods of Chapter 2). The centrifugation at 1250 x g was selected because no further reduction of Al concentration was obtained from centrifugation at higher speeds (Appendix 2). After removal of the supernatant solutions, the soil was rinsed four times with 450 ml distilled, deionized water, so that the conductivity of the wash solution was less than 0.05 millimhos. The soil was dried at 45° and ground with mortar and pestle.

A 10 g sample of dry soil was placed in a 250 ml plastic centrifuge bottle and briefly handshaken with 40 ml N CKl. The suspension was centrifuged at 500 rpm for 5 min. and filtered into a 250 ml volumetric flask. The soil was extracted with five additional aliquots of 40 ml KCl and combined extracts were made up to 250 ml. This solution was analyzed for Ca and Mg by atomic adsorption in a 0.5%.La solution and for Al by titration (McClean, 1965 pp 992-993).

Ten gram samples of the washed and dried soil of experiment 1 were combined with 20 ml of 10^{-3} M $CaCl_2$ and intermittently shaken. On the third day the soil was allowed to settle and solution pH was determined by placing the glass electrode in the soil suspension and the reference electrode in the clear supernatant solution. The supernatant solution was removed by centrifugation at 1250 x g for 20 minutes and analyzed for total Al by the aluminon method (McClean, 1965 pp 988-989) and for Ca by atomic adsorption in a 0.5% La solution.

In experiment 2, the addition of $CaCl_2$ caused some changes in the composition of the exchange complex. However, appropriate corrections were made, based on the difference in the composition of the added solution and the equilibrium solution.

b. Experiment 3

Air dried and ground samples from topsoil and lower horizons of four Puerto Rican soils were selected for this study. The soils used were:

Piñas sandy loam	(Psammentic Haplortox)
Humatas clay	(Typic Tropohumult)
Catalina clay	(Tropeptic Haplortox)
Los Guineas silty clay	(Typic Tropohumult)

as described in Chapter 1. From each sample, 10 g of soil were equilibrated for three days with 20 ml 10^{-3} M $CaCl_2$. Determinations of pH and Ca, Mg and Al concentrations in the supernatant solution were made as described before. A separate 10 g subsample was extracted with N KCl for determination of exchangeable Al, Ca and Mg, as in experiment 2. The exchangeable Ca values wei corrected for the change in $CaCl_2$ concentration of the supernatants during equilibration.

c. Calculation of soil solution exchange constant

A number of equations have been used to describe the cation exchange equilibrium in soils. Bolt (1967) reviewed the various models of the exchange process, the assumptions made and the limitations of the resulting equations. The equation selected here is based on the formulation introduced by Eriksson (1952). Turner (1952) modified Eriksson's relation to:

$$\frac{(Al)^2 [Ca]^3}{(Ca)^3 [Al]^2 C} = K_E , \qquad (5)$$

in which parenthesis refer to activities in solution, square brackets to moles exchangeable and C to the exchange capacity ($C = 2[Ca] + 3[Al]$). In this study, the exchange equation was used to estimate the solution variable 1/3pAl - 1/2pCa from exchangeable Al and Ca. For this purpose the equation

$$\frac{(Al)^{1/3}}{(Ca)^{1/2}} = K \frac{[Al]^{1/3}\ C^{1/6}}{[Ca]^{1/2}} \qquad (6)$$

was selected, which when rearranged gives:

$$\frac{(Al)^{1/3}\ [Ca]^{1/2}}{(Ca)^{1/2}\ [Al]^{1/3}\ C^{1/6}} = K \qquad (7)$$

comparing equation (5) and (7) shows that equation (7) equals equation (5) taken to the 6th power, so that $K_E = K^6$. It should be noted that Turner and Clark generally use the logarithmic form pK_E in their publications. To make the results of Turner and Clark more easily comparable with experimental results reported in this section, their results were recalculated on the basis of equation (7).

In this chapter, various calculated measures are discussed. These are summarized below:

The activity of Al^{3+} was calculated assuming the monomeric dissociation mechanism (Frink and Peech, 1963a), and using the Debye - Huckel equation. No corrections were made for ion association because equilibration solutions were dominantly chloride systems.

<u>The solubility product of $Al(OH)_3$</u> was calculated in the logarithmic form: $pKsp = p(Al) + 3p(OH)$.

<u>The solution ratio</u> of Ca and Al was: $Rsol = \frac{(Al)^{1/3}}{(Ca)^{1/2}}$ where parentheses indicate molar activities.

<u>The exchange ratio</u> of Ca and Al was:

$Rex = \frac{[Al]^{1/3}\ C^{1/6}}{[Ca]^{1/2}}$, where square brackets represent moles exchangeable cation per 100 g soil and C is the sum of exchangeable cations in me/100 g soil.

The exchangeable constant $K = \frac{Rsol}{Rex}$ relates to the constant K_E of equation (5) used by Turner et al (1963) as $K = K_E^{1/6}$.

Percent Ca saturation was calculated as $\frac{Ca}{\sum M_i}$

Exchangeable Mg^+ was thus added into the sum in the denominator.

3. Results and discussion

a. The solubility of $Al(OH)_3$

An increase in equilibrium solution pH was associated with increased solubility of $Al(OH)_3$, and thus a decrease in pKsp, in all three experiments. This is reflected in the negative slope of the regression between pKsp, and pH figures 3.1 and 3.2. These results are similar to those of Frink and Peech (1962) and Richburg and Adams (1970). Where-as the former authors accepted differences in the pKsp of $Al(OH)_3$ as a consequence of variation in degree of crystallinity and type of freshly precipitated $Al(OH)_3$, the latter authors feel that differences in pKsp are a consequence of erroneous assumptions made in using the monomeric hydrolysis mechanism. Richburg and Adams (1970) gave preference to a polymeric hydrolysis product because it was possible to select a hydrolysis constant which resulted in a virtually constant pKsp over a wide variety of pH values. As it appears possible to select an arbitrary hydrolysis constant for the monomeric mechanism which will result in a virtually constant pKsp for $Al(OH)_3$ (e.g. $pK_H = 3.5$), the results presented by Richburg and Adams do not constitute conclusive evidence for the proposed polymeric mechanism. Moreover, critical studies of the formation of gibbsite have established the initial formation of a more soluble, amorphous solid phase, which

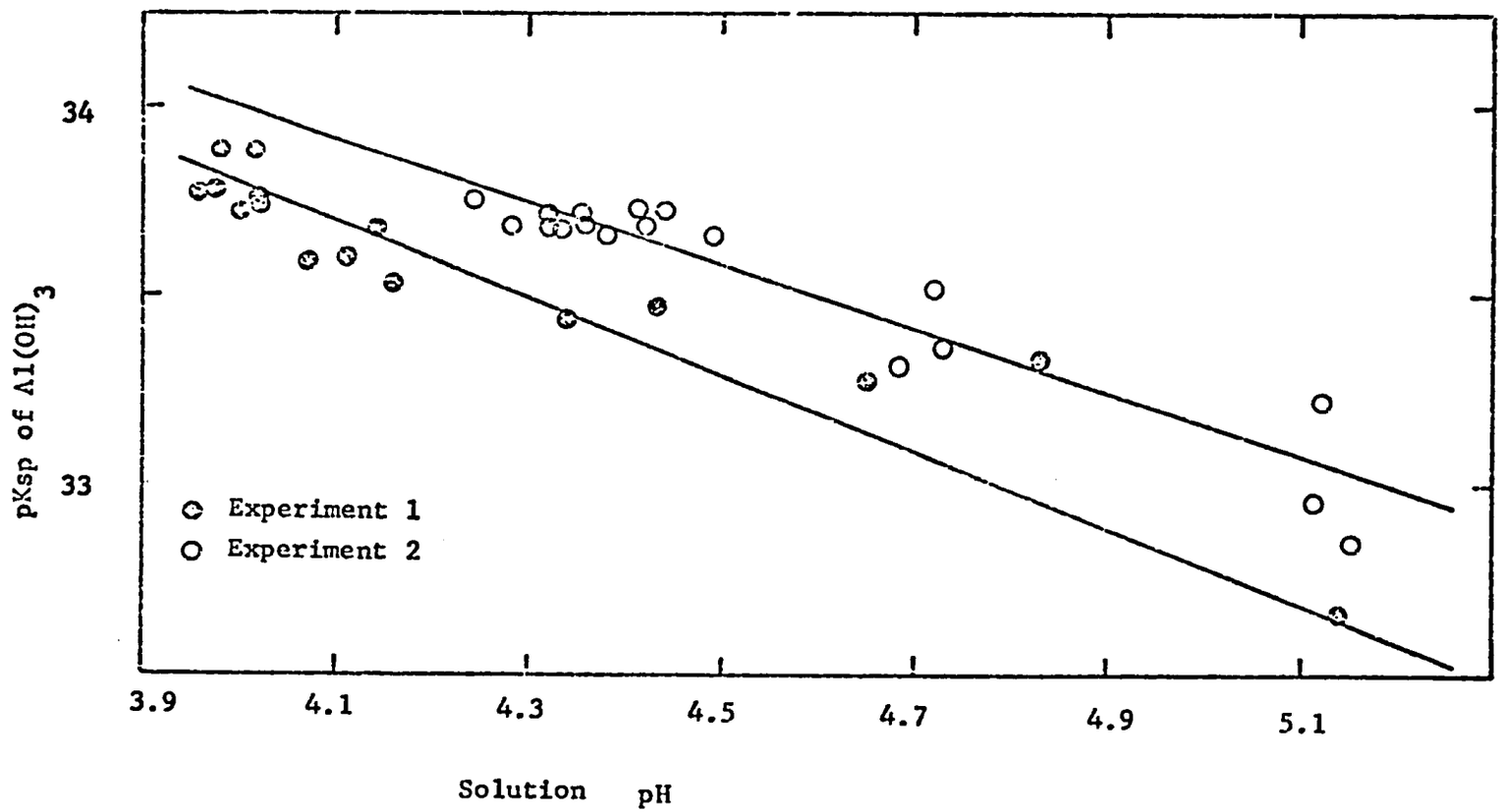

Figure 3.1 The relations between solution pH and $Al(OH)_3$ solubility in Carimagua soil. Data of tables 3.1 and 3.2.

(The data points (5.41, 32.26) and (5.71, 31.78) of experiment 1 were not included in the graph).

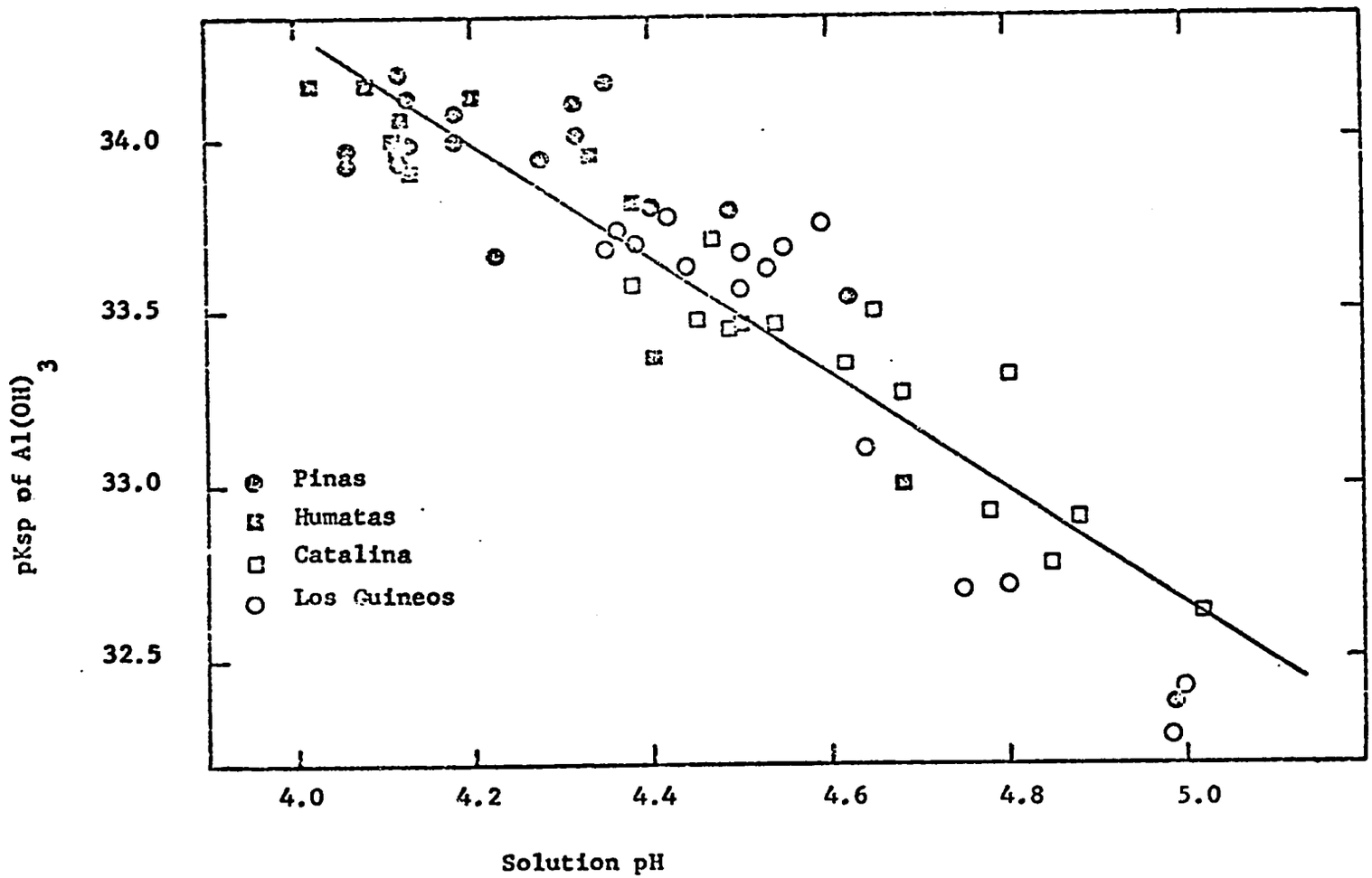

Figure 3.2: The relation between solution pH and $Al(OH)_3$ solubility in four Puerto Rican soils (Experiment 3).

by a gradual process rearranges towards the less soluble, more crystalline gibbsite (Frink and Sahwney, 1967 ; Turner and Ross, 1970).

Results of experiment 2 showed higher pKsp values than those of experiment 1 (Fig 3.1) indicating that the washing and drying step reduced the solubility of $Al(OH)_3$ precipitated in experiment 1. This constitutes further evidence that the solubility product of $Al(OH)_3$ precipitate in soils is not to be considered the solubility of gibbsite, but instead, is dominated by the most soluble form of $Al(OH)_3$ present. Comparison of figure 3.1 with pKsp values listed in table 3.1 and 3.2 showed no effects of $CaCl_2$ concentration, independent of its effect on pH, on the pKsp values for experiment 1.

Solubility products obtained from samples of soils from Puerto Rico (Exp. 3) decreased more with pH and showed more variation among samples than those encountered in experiments 1 and 2 (Fig. 3.2). This is borne out by increased slope of the regressions of pKsp on pH and the lower R^2 values obtained for the soil samples from Puerto Rico (Table 3.3). Statistical comparison of the calculated regressions using the method described by Rao (1952, pp 112) showed differences in the pH - pKsp relations between these four soil types to be significant at the 10% probability level (Table 3.4).

The usefulness of the pH - pKsp relation for the purpose of predicting values of 1/3pAl - 1/2pCa was evaluated by considering the 95% confidence limit of a predicted pKsp value (Steel and Torrie, 1960 p175). Using the combined regression equation, at pH 4.7, the predicted pKsp would be 33.15 ±0.96. As in equation 4,

$$1/3pAl - 1/2pCa = pH - 1/2pCa - pK_w + 1/3pKsp,$$

Table 3.1: Effects of initial $CaCl_2$ concentration of the equilibrium solution and added $Ca(OH)_2$ on the solubility of $Al(OH)_2$ and Al - Ca exchange relations in Carimagua topsoil (Experiment 1, means of 2 replicates).

Treatment								
No.	$CaCl_2$ mM/l	$Ca(OH)_2$ me/100g	pH	pKsp	R_{sol}	R_{ex}	K_{ex}	%Ca Saturation
1	1	0	4.02	33.89	2.18	3.66	.60	6.8
2	5	0	3.98	33.89	1.28	2.80	.45	11.3
3	10	0	4.02	33.75	.84	2.33	.36	15.8
4	1	.22	4.07	33.59	1.94	4.48	.44	4.7
5	5	.22	3.97	33.77	1.14	3.35	.34	8.0
6	10	.22	3.96	33.77	.99	2.54	.39	13.5
7	1	.44	4.16	33.53	1.49	3.48	.45	7.5
8	5	.44	4.02	33.76	1.01	2.78	.36	11.3
9	10	.44	4.16	33.72	.88	2.34	.38	15.6
10	1	.87	4.34	33.44	.95	2.44	.39	14.4
11	5	.87	4.14	33.67	.82	2.13	.39	18.5
12	10	.87	4.11	33.60	.73	1.97	.37	21.1
13	1	1.75	4.83	33.33	.34	1.32	.26	39.4
14	5	1.75	4.65	33.28	.36	1.27	.29	41.6
15	10	1.75	4.43	33.47	.37	1.27	.29	41.7
16	1	3.50	5.71	31.78	.14	.74	.19	73.8
17	5	3.50	5.41	32.26	.12	.75	.16	72.2
18	10	3.50	5.14	32.65	.13	.74	.17	72.8
19	1	7.00	6.98	-	-	.20	-	98.8
20	5	7.00	6.87	-	-	.16	-	99.5
21	10	7.00	6.71	-	-	.12	-	99.6

Table 3.2: Effects of $CaCl_2$ and $Ca(OH)_2$ pretreatments on the solubility of $Al(OH)_2$ and Al - Ca exchange relations in 10^{-3} M $CaCl_2$ (Experiment 2, Carimagua topsoil after washing and drying, means of 2 replicates).

No.	Pretreatment $CaCl_2$ mM/l	Pretreatment $Ca(OH)_2$ me/100g	pH	pKsp	R_{sol}	R_{ex}	K_{ex}	%Ca Saturation
1	1	0	4.24	33.75	1.50	2.18	0.53	6.5
2	5	0	4.32	33.68	1.20	2.45	0.49	10.3
3	10	0	4.36	33.69	1.02	2.18	0.47	15.5
4	1	0.22	4.28	33.67	1.44	3.17	0.46	4.5
5	5	0.22	4.32	33.72	1.22	2.76	0.44	7.7
6	10	0.22	4.35	33.73	1.04	2.33	0.44	13.1
7	1	0.44	4.33	33.68	1.26	2.75	0.46	7.2
8	5	0.44	4.38	33.66	1.08	2.47	0.44	11.0
9	10	0.44	4.41	33.73	0.89	2.21	0.40	15.4
10	1	0.87	4.42	33.68	1.00	2.17	0.46	13.9
11	5	0.87	4.44	33.73	0.86	1.99	0.43	17.9
12	10	0.87	4.49	33.65	0.76	1.89	0.40	20.7
13	1	1.75	4.72	33.52	0.49	1.29	0.38	38.7
14	5	1.75	4.73	33.36	0.50	1.27	0.40	41.2
15	10	1.75	4.68	33.31	0.57	1.27	0.44	42.0
16	1	3.50	5.15	32.85	0.30	0.73	0.42	72.8
17	5	3.50	5.12	33.23	0.22	0.75	0.29	72.9
18	10	3.50	5.10	32.95	0.27	0.76	0.36	74.1
19	1	7.0	5.75	-	-	0.20	-	99.6
20	5	7.0	5.76	-	-	0.16	-	99.9
21	10	7.0	5.77	-	-	0.12	-	99.9

using the prediction equation,

$$pKsp = 41.0 - 1.67pH$$

at pH 4.7, means that 95% of the predicted values of 1/3pAl - 1/2pCa would fall within $\frac{2 \times 0.96}{3} = 0.64$ units of 1/3pAl - 1/2pCa. As the relation between root growth and 1/3pAl - 1/2pCa extends over 1.2 units (Fig. 2.2B), this confidence interval covers too wide a range for useful differentiation of soil samples with respect to their aluminum toxicity. To predict within a range of 0.20 units, which would allow reasonably good differentiation, the probability level of the confidence interval would need to be reduced to approximately 50%.

b. Exchange constant for Ca and Al

Calculated solution and exchange measures of experiments 1 and 2 are given in tables 3.1 and 3.2. These variables calculated for individual samples from Puerto Rican soils are given in appendix table 3.2. Results of chemical analyses used to calculate these values for experiments 1 and 2 are given in appendix tables 3.3. and 3.4.

Experiments 1 and 2:

Linear regressions of Rsol on Rex calculated from data of table 3.1 and 3.2, respectively, are presented in figure 3.3. and table 3.5. Both regressions showed intercepts that were significantly different from zero, but had very similar slopes. The average value of the exchange constant K, determined from the regression equations; K = 0.52 for experiment 1 and 0.51 for experiment 2, compared well with the average values obtained by Turner et al (1963) for a Wyoming bentonite (0.56) and by Turner and Clark (1965) for a wide variety of Canadian soils (0.56). Exchange constants obtained from untreated samples from four profiles in the Eastern plains of Colombia had a mean of 0.55 with a

Table 3.3: Table of linear regressions of pKsp on pH (Experiments 1, 2, and 3).

No.	Soil type	N	Estimated Intercept	Estimated slope	R^2	$s_{y.x}$ 1)
Colombian soils						
1	Carimagua, Expt. 1	18	38.03	-1.04	.94	0.143
2	Carimagua, Expt. 2	18	37.49	-1.87	.88	0.095
Puerto Rican Soils						
3	Pinas sandy loam	17	40.21	-1.48	.69	0.241
4	Humatas clay	16	40.95	-1.67	.85	0.143
5	Catalina clay	13	40.57	-1.57	.83	0.148
6	Los Guineos clay	15	44.31	-2.93	.87	0.203
7	3,4,5, and 6 comb.	61	41.00	-1.67	.85	0.200

1) $s_{y.x} = \sqrt{EMS}$

Table 3.4: Analyses of variance of the residual sums of squares of the pooled regression of pKsp on pH for four Puerto Rican soils.

Source	d.f.	Residual SS	M.S.	F	$F_{0.10}$
Pooled regression	59	2.370			
Individual regressions	53	1.930	0.0364		
Deviation from combined model	6	0.439	0.0732	2.01	1.89

standard deviation of 0.025 (Appendix table 3.5).

The intercepts obtained in figure 3.3 represent a systematic variation in the constant K as calculated by $K = \frac{Rsol}{Rex}$. These values are presented in tables 3.1 and 3.2. Analyses of variance showed that additions of $Ca(OH)_2$ and the $CaCl_2$ concentration of the equilibration solution had highly significant effects on the value of K (Table 3.6). The significant interaction of $Ca(OH)_2$ levels with $CaCl_2$ levels was due to a decreased effect of $CaCl_2$ on K at higher base saturations (Tables 3.1 and 3.2). Several hypotheses are advance to explain this phenomenon:

(a) It was noted that a substantial amount of Ca was lost in the washing cycle between experiment 1 and 2 (See discussion of the next section). The inclusion of this amount of Ca into the exchange relation did not change the values of K at high base saturation, and increased the values of K at low base saturations, in effect, further decreasing the intercept.

(b) Comparing tables 3.1 and 3.2, it is evident that Rsol in substantially higher at high pH levels in experiment 2 than in experiment 1, indicating an understimation of the Al activity at the higher pH levels. This may relate to the high solubilities of $Al(OH)_3$ obtained in these samples. As the deviations are more strongly evident at the high pH levels, analytical errors due to the presence of large amounts of freshly precipitated $Al(OH)_3$ or interferences from Ca, may have affected the results. It is of interest in this regard, to note that untreated samples of Puerto Rico soils generally showed positive intercepts for the regression of Rsol on Rex. The freshly precipitated $Al(OH)_2$ formed in the Carimagua soils as consequence of the addition of $Ca(OH)_2$ may have contributed substantially to this anomaly.

(c) The exchange relation employed (Eq. 7) is empirical and according to Bolt (1967) can not be expected to be truly constant over a wide range of conditions.

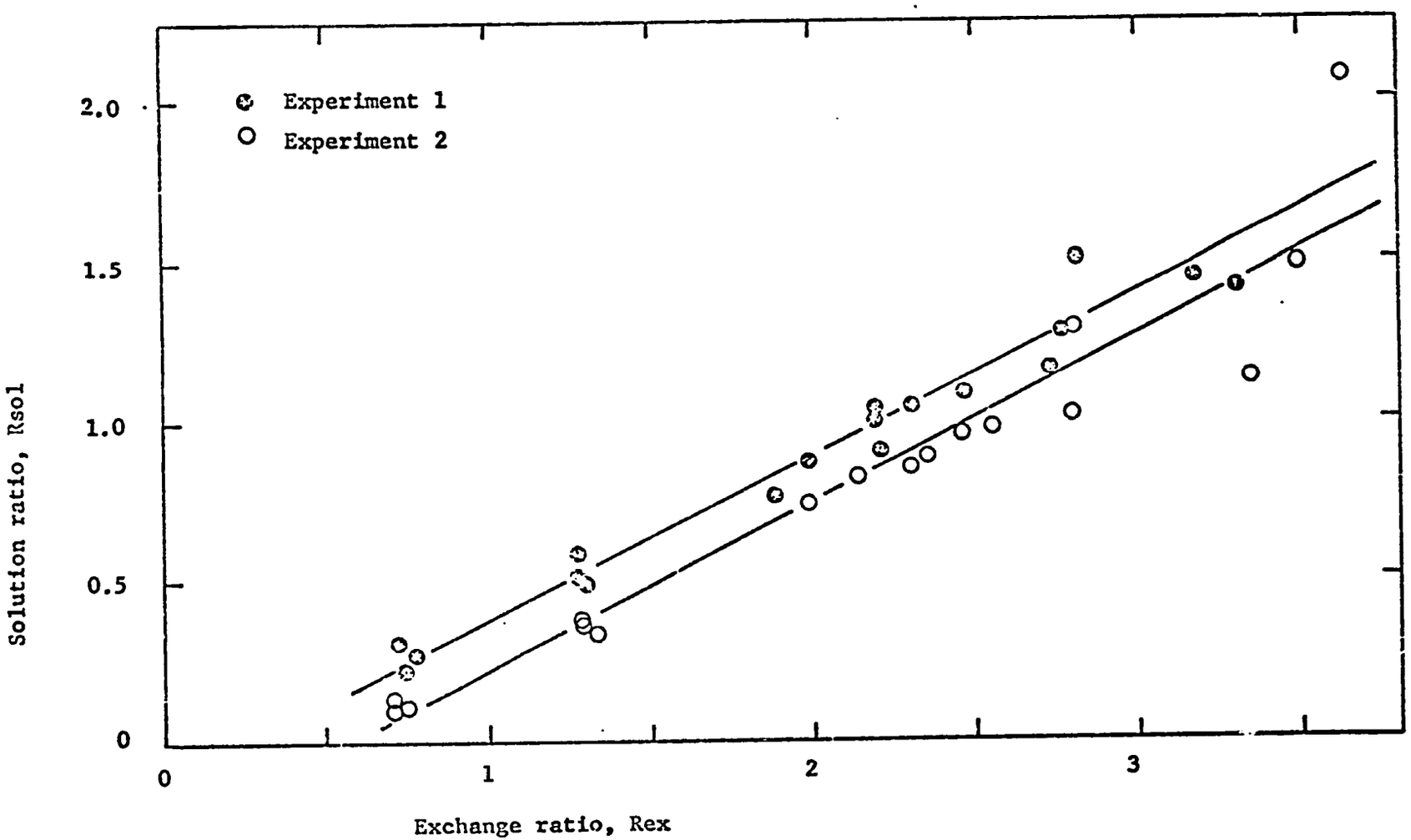

Figure 3.3: The regression of Rsol on Rex for Carimagua topsoil determined in Experiments 1 and 2 (Data from tables 3.1 and 3.2).

Table 3.5: Table of regressions of R_{sol} on R_{ex} (Experiments 1, 2 and 3).

No.	Soil type	N	Estimated Intercept	Estimated Slope	R^2	$s_{y.x}$ 1)
Colombian soils						
1	Carimagua, Expt. 1	18	-0.30**	.52	.92	.173
2	Carimagua, Expt. 2	18	-0.13*	.51	.97	.072
Puerto Rican soils						
3	Piñas sandy loam	18	0.15	.52	.70	.226
4	Humatas clay	16	0.33**	.42	.93	.076
5	Catalina clay	13	0.30	.49	.54	.233
6	Los Guineos clay	15	0.12	.56	.97	.120
7	3, 4, 5, and 6 combined	62	0.21**	.51	.85	.179
8	3, 4, 5, and 6 combined zero intercept model	62	-	.60	.97	.199

* Significant at p = .05
** Significant at p = .01
1) $s_{y.x} = \sqrt{EMS}$

Table 3.6: Analyses of variance of the effects of $Ca(OH)_2$ additions and initial concentration of $CaCl_2$ on the value of the exchange constant K. (Experiment 1, Table 3.1).

		Experiment 1		Experiment 2	
Source	d.f.	SS	F	SS	F
Total	36	.433		.124	
Mean	1	.003		.005	
Replicates	1	.001	0.69	.009	10.38**
$Ca(OH)_2$ level	5	.330	54.69**	.063	13.93**
$CaCl_2$ level	2	.026	10.84**	.009	5.10*
Interaction	10	.052	4.29**	.022	2.40*
Residual	17	.021		.015	

* Significant at p = 0.05
** Significant at p = 0.01

Table 3.7: Analyses of variance of the residual sums of squares of the pooled regression of R_{sol} on R_{ex} for four Puerto Rican soils.

Source	d.f.	Residual SS	M.S.	F	$F_{0.10}$
Pooled regression	60	1.930			
Individual regressions	54	1.689	0.0313		
Deviation from combined model	6	0.242	0.0403	1.29	1.89

A more detailed explanation of the variation in the value K encountered is not evident and would require further study of the exchange relation of Ca for Al.

Experiment 3:

The regressions of Rsol on Rex for four Puerto Rican soils were very similar. In each case the intercept was small, and in fact only significantly different from zero for the Humatas clay (Table 3.5). Analysis of variance, using the method described by Rao (1952 pp 112), showed no significant differences among regressions, indicating that a single, pooled regression suffices to represent the four soils (Table 3.7).

The intercepts of the regression equations in table 3.6 should be considered deviations from the theoretical intercept and are probably due to methodological errors. Forcing equation (7) of table 3.5 through zero (i.e. no intercept model), increases both the slope and the estimated standard error. The R^2 value increased because its calculation is based on sums of squares uncorrected for the mean, whereas the R^2 values of the intercept models are based on corrected sums of squares (c. f. Searle, 1971 pp 95).

As rootgrowth was related to $(Ca)^{1/2} / (Al)^{1/3}$ in solution, the regression of the inverse of Rsol on the inverse of Rex would be used for prediction purposes. Using the zero intercept model, this regression was calculated as:

$$1/Rsol = 1.38/Rex \qquad (r^2 = .92).$$

The standard error was 0.3177 and the 95% confidence interval of a future value of 1/Rsol at the mean of 1/Rex was 1.28. The relation of 1/Rex

to root growth established in Chapter II, extended over approximately 8 units (Fig. 2.3B). The prediction of the solution ratio of Ca and Al on the exchange complex should therefore, allow good differentiation between soils with respect to Al toxicity as it affects rootgrowth.

c. <u>The effects of $Ca(OH)_2$ and $CaCl_2$ on exchangeable Al and Ca in Carimagua soil.</u>

The results of experiments 1 and 2 were illustrated in figure 3.4 where the amounts of KCl extracteable Ca and Al and CEC (Ca + Al + Mg) of the samles, following washing with distilled water, are plotted against the amount of $Ca(OH)_2$ added. On the basis of equivalent neutralization, the simplest hypothesis which can be formulated is that the amount of KCl extractable $Al(Al_{ex})$ decreases by one me for each me of $Ca(OH)_2$ added, and that the KCl extractable Ca (Ca_{ex}) increases concomittantly. This assumes no contribution of $CaCl_2$ to Ca_{ex}, and no loss of Al_{ex} by exchange for Ca subsequent removal with the supernatant solution. The hypothesis expressed thus tends to underestimate the neutralizing effects to be expected. In the presence of exchangeable Al this hypothesis can be presented in the form of the following reaction:

$$3Ca^{2+} + 6(OH) + 2AlX_3 \text{ —— } 2Al(OH)_3 + 3CaX_2$$

where X is a homoionic exchanger.

Taking into account the amount of Ca originally present:

$$Ca_{ex_1} = Ca_o + Ca_1,$$

$$Al_{ex} = Al_o - Ca_1,$$

where Ca_{ex_1} = Amount of calcium extracted by KCl following washing with distilled water,

Ca_o = Exchangeable Ca in untreated soil,

Ca_1 = Amount of Ca added as $Ca(OH)_2$,

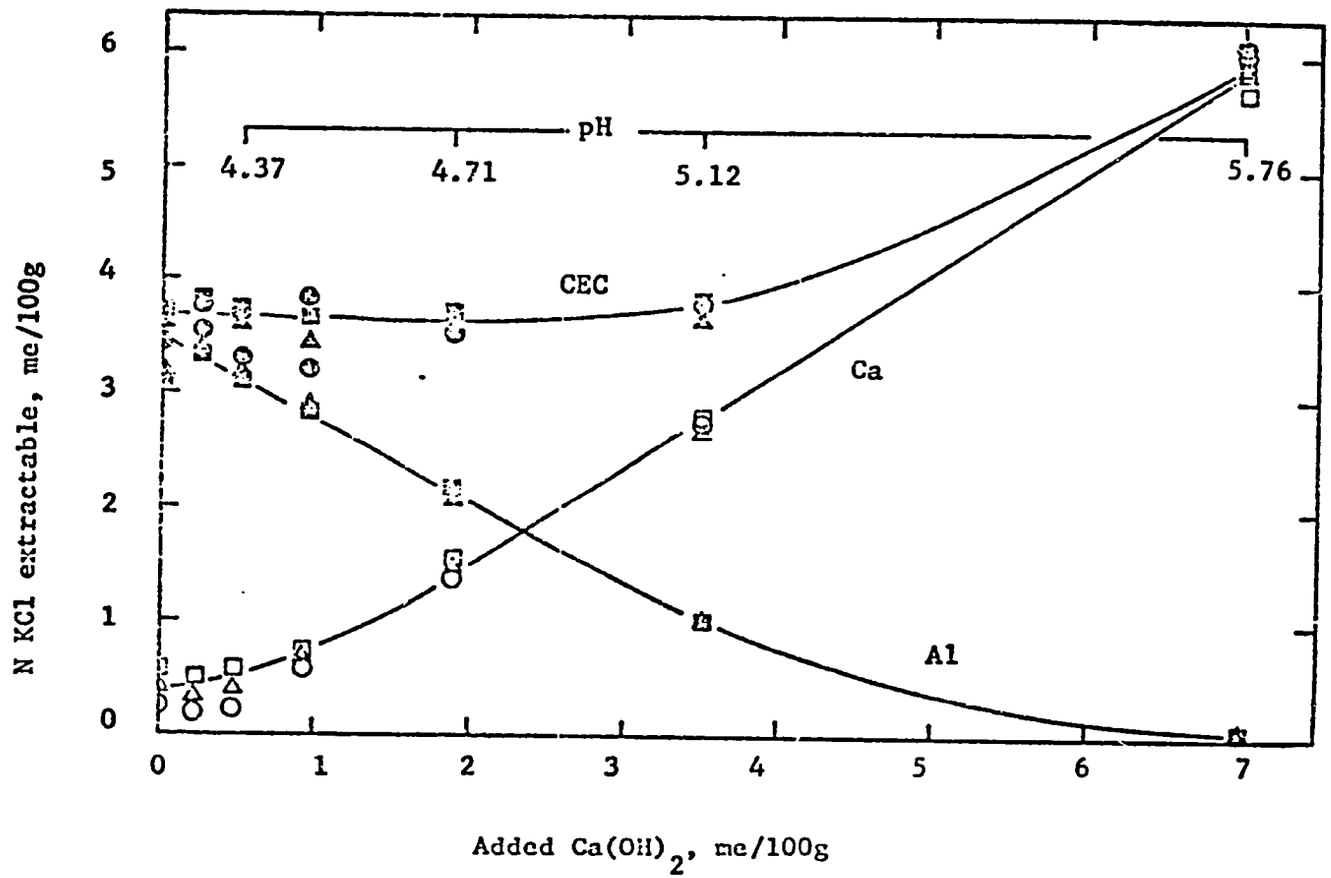

Figure 3.4: Effect of added $Ca(OH)_2$ on CEC, pH in 10^{-3}M $CaCl_2$ and extractable Al and Ca, after washing and drying (Expt. 1). Squares, triangles, and circles represent 10^{-4}, 5×10^{-3} and 10^{-3}M $CaCl_2$ equilibrations respectively.

and subscripts to Al have similar meanings.

Examination of figure 3.4 reveals that neither the decrease in Al nor the increase in Ca is nearly as large as expected, making the hypothesis of equivalent neutralization unacceptable in the form stated above.

Hypotheses which can be advanced to explain these resul. , are as follows; (a) errors in addition of $Ca(OH)_2$ and (b) leaching of cations from the soil during washing.

To evaluate (a), the recovered Ca was calculated as;

$$\text{Recovered Ca} = Ca_{ex} + VCa_s,$$

where V is the volume of the supernatant solution per 100 g soil and Ca_s the concentration of Ca in this volume. The recovered Ca was plotted against the Ca added ($Ca_a = Ca(OH)_2 + CaCl_2$), both in me/100 g soil (Fig. 3.5). This figure indicates that 87% of the added Ca is recovered, regardless of whether or not it was added as $CaCl_2$ or as $Ca(OH)_2$. It seems unlikely that a 13% error should have been made in additions of both $CaCl_2$ and $Ca(OH)_2$, thus eliminating the first hypothesis.

The second hypothesis suggests that part of the Ca recovered in the equilibrium solution, and thus held on the clay complex, is removed by repeated washing with distilled water. Under this hypothesis the exchangeable Ca can be evaluated by:

$$Ca_{ex_2} = Ca_o + Ca_a - VCa_s$$

Plotting this quantity in me/100 g against me/100 g $Ca(OH)_2$ added, resulted in a relation showing excellent recovery for added $Ca(OH)_2$ (Fig. 3.6).

Calculating the CEC as:

$$CEC_2 = Ca_{ex_2} + Al_{ex} + Mg_{ex}$$

and plotting this quantity against $Ca(OH)_2$ added, indicates higher CEC's at the high $CaCl_2$ levels and an increase of CEC with increasing $Ca(OH)_2$ additions. It appears therefore, that the lack of neutralization of exchangeable Al may be related to neutralization of pH dependent charge by added $Ca(OH)_2$. An explanation for these observations, and in particular for the reduction in CEC and loss of exchangeable Ca, on washing is not evident, and further study of this phenomena is needed. It is of interest in this respect that van Raij (1971) found that in soils in which kaolinite and Al - and Fe oxides constitute the dominant clay fraction, the surface charge is dependent on electrolyte concentration and pH. In addition, results of Vargas (1964) show a similar lack of neutralization of exchangeable Al by added $Ca(OH)_2$, for a Carimagua soil sample, as well as for 19 samples of unlimed soils collected throughout the Eastern plains of Colombia (Fig. 3.7).

4. Conclusions

The prediction of 1/3pAl - 1/2pCa by measurement of pH - 1/2pCa and the use of an empirical relation between pH and the pKsp of $Al(OH)_3$ was found to be of little practical value for differentiating soil samples with respect to their Al toxicity. The poor prediction was a result of differences in the pH-pKsp relations encountered among different soils and of analytical difficulties in the determination of pKsp.

The exchange constant for the relation:

$$\frac{(Al)^{1/3}}{(Ca)^{1/2}} = K \frac{[Al]^{1/3}\, c^{1/6}}{[Ca]^{1/2}} \qquad \text{(see equation 7)}$$

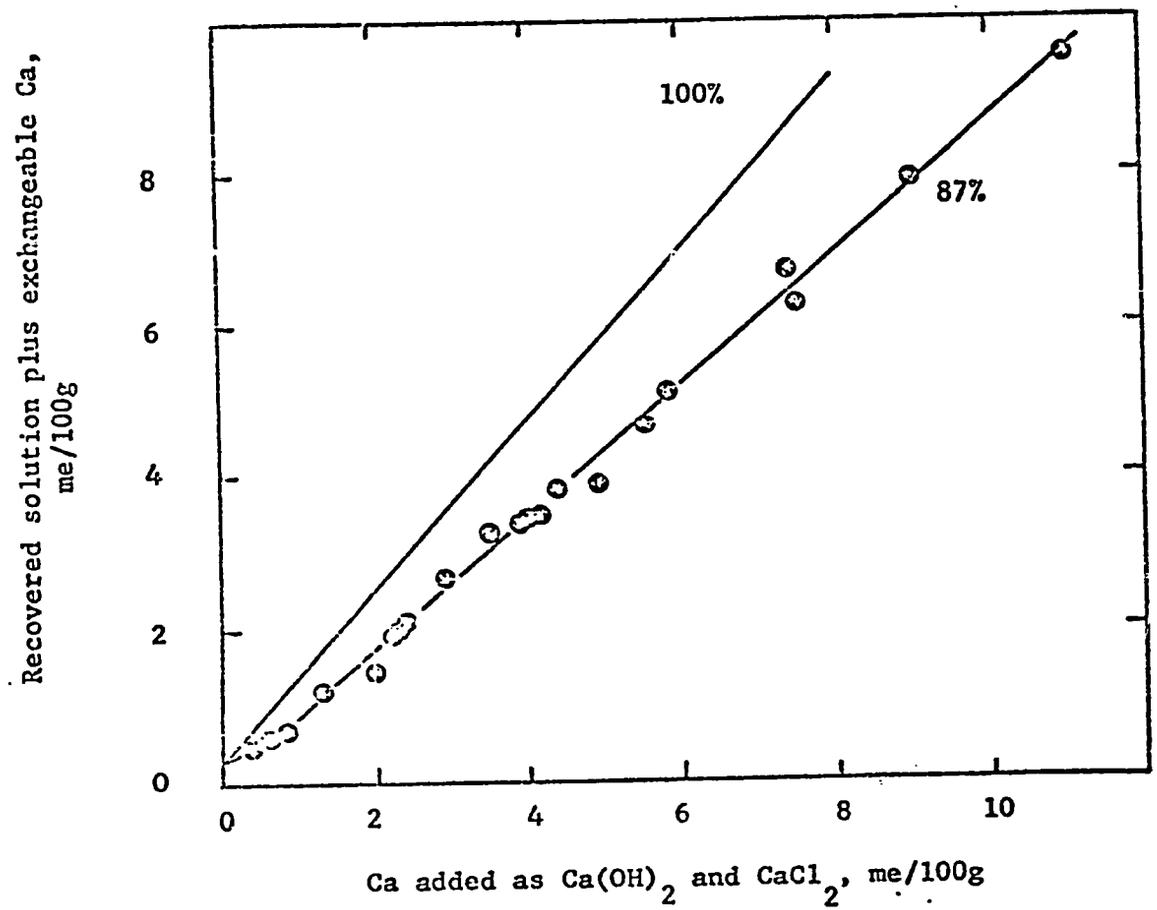

Figure 3.5: The amount of added Ca recovered in solution and in exchangeable form after washing and drying (Experiment 1).

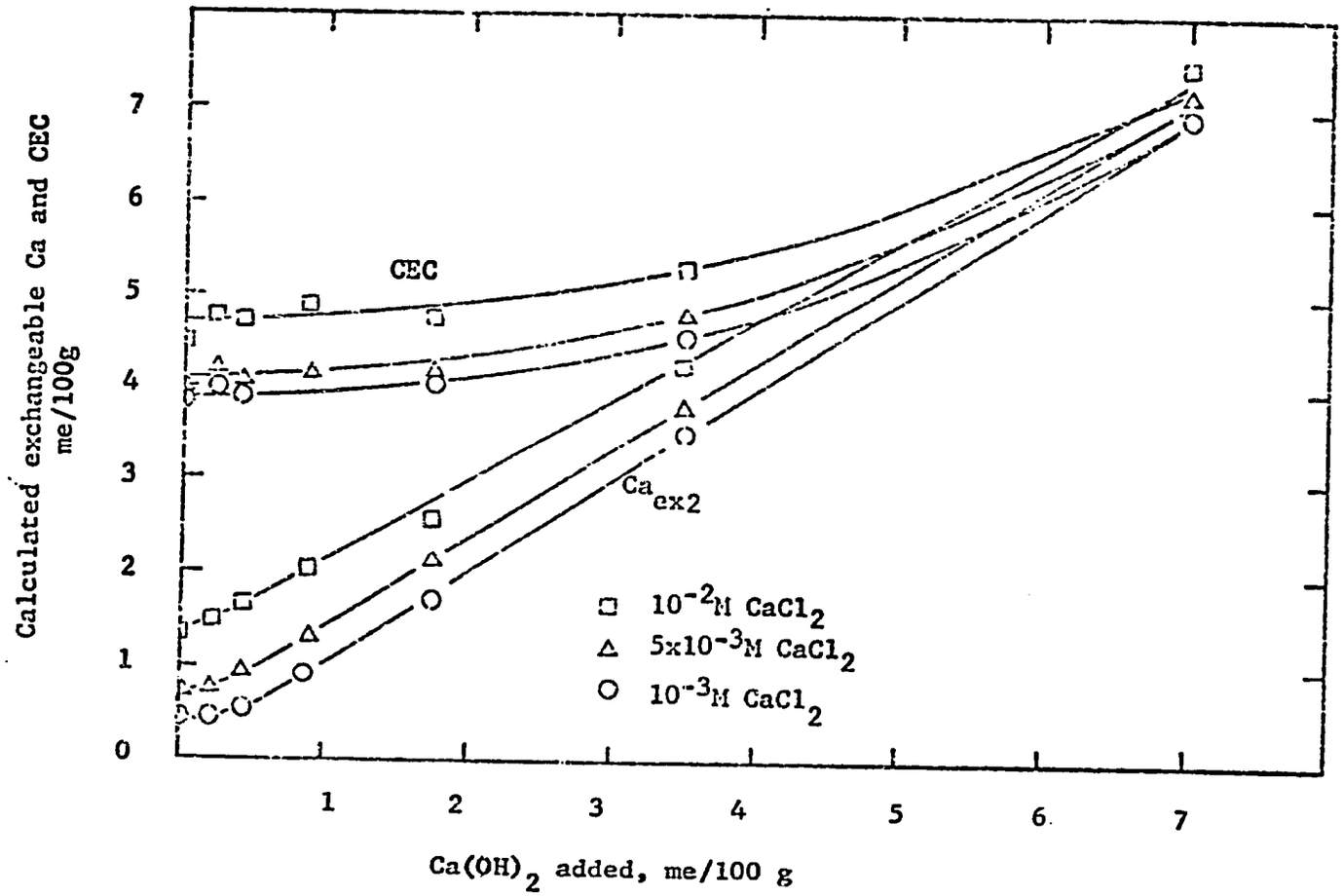

Figure 3.6: The effect of added $Ca(OH)_2$ on the calculated amounts of exchangeable Ca (Ca_{ex2}) and CEC.

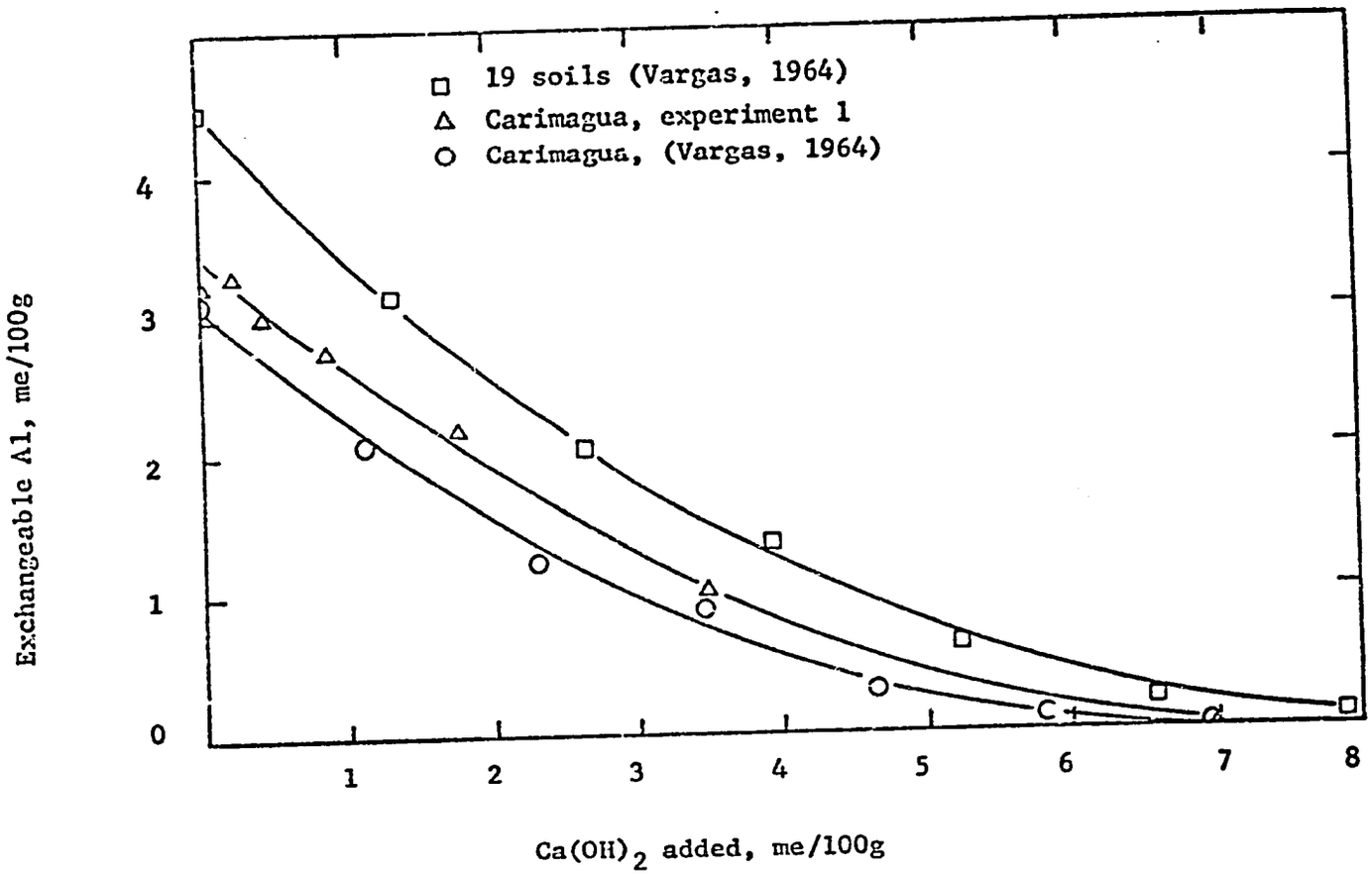

Figure 3.7: Neutralization of exchangeable Al in soils from the Eastern Plains of Colombia.

appeared to be applicable to a variety of soils and allowed good prediction of the solution parameter by measurement of exchangeable Al and Ca.

Exchangeable Ca and Al, in the relation

$$\frac{[Ca]^{1/2}}{[Al]^{1/3}C^{1/6}},$$

appeared to be a useful index of aluminum toxicity as it affects rootgrowth in soils in which more than 80% of the exchange complex is saturated with Ca plus Al.

The addition of $Ca(OH)_2$ to the Carimagua top soil did not result in loss of equivalent amounts of exchangeable Al. Evidently some of the $Ca(OH)_2$ was utilized in neutralization of pH - dependent acidity. In addition, increasing the concentration of $CaCl_2$ appeared to lead to increases in net negative charge of the soil.

IV THE EFFECTS OF ALUMINUM ON CALCIUM UPTAKE FROM CARIMAGUA SOIL

1. Introduction

One of the benefits commonly attributed to liming acid soils is the correction of Ca deficiency. Low Ca contents observed in plants grown on acid soils led Schmehl et al (1952) to propose an antagonistic effect of Al, Mn and H on the absorption of Ca. More recently, Soileau et al (1969) suggested, similarly, the existence of Al induced Ca deficiency. These observations agree with detailed studies of Johnson and Jackson (1964), who found large reductions in Ca uptake when Al concentration in solution was increased.

On the other hand, the presence of large amounts of Ca in soils and a lack of response from the addition of neutral Ca salts, have, at times, discredited this concept (Fried and Peech, 1946; Adams and Pearson, 1967). The benefits of liming, were in such cases attributed to decreases in soluble Al or Mn. Very convincing evidence against the importance of Ca deficiency as an aspect of acid soil infertility was presented by Vlamis (1953). He obtained similar benefits to root and shoot yields from the addition of Na(OH) and K(OH) as from $Ca(OH)_2$, and emphasized the importance of soluble aluminum.

Calcium deficiency in plants is found at a wide range of Ca levels in solution depending on the type and concentration of other ions in solution (Johnson and Jackson, 1964; Jones and Lunt, 1967). Howard and Adams (1965) found that Ca deficiency was related to the Ca/total - cation ratio of the

soil solution. They concluded that ion antagonistic effects on Ca uptake were not restricted to Mg but were the result of the total cation concentration in solution. Adams and Pearson (1967) feel, however, that this ratio, or a similar ratio on the exchange complex, can only be considered a good measure of Ca availability in soils, in the absence of toxic levels of H, Al or Mn ions.

Results of Chapter II indicated that inhibitory effects on rootgrowth are substantially dependent on the ionic valence of the interfering ion. This may also be the case with Ca uptake, as indicated by results from Johnson and Jackson (1964) who showed that Al was more effective than Mg or K in reducing Ca uptake from solutions. The ratio $(Ca)/(M_i)$ can not be expected to account for the effects of ionic valence observed.

Reductions of Ca uptake by interfering ions have been described for Al, Mn, Mg, K, Na, NH_4 and H (Jackson, 1967), and although active absorption processes have been described, these appear to be either non-specific, or not of a dominant nature. Results of Wiersum (1966) and Lazaroff and Pitmann (1966) show that Ca uptake is related to respiration rate. Al-Abbas and Barber (1963) found a good relation between Ca uptake and an estimate of the amount of Ca moving to the root by mass flow plus the amount of Ca contacted by root growth. These results suggest a great dependence of Ca uptake on root growth.

According to the measure employed by Barber, increases in soil solution concen tration of Ca should materially increase Ca uptake, given comparable root growth and transpiration. This did not occur when Fried and Peech (1946) applied lime and gypsum to a Mardin silt loam. They found Ca contents of

alfalfa leaves and Ca uptake by ryegrass little increased from gypsum applications, even though soil solution concentrations of Ca were more than quadrupled (Table 4.1). As the addition of neutral salts does not effect root growth (Chapter II), these results are in complete disagreement with the notion that Ca uptake is related to Ca activity in the soil solution. Comparison of Ca uptake with pH-1/2pCa, however, showed no divergence of gypsum treatments from lime treatments (Fig. 4.1).

Another indication of the applicability of a Ca intensity measure for the interpretation of cation interference with Ca uptake, independent of root growth, can be obtained from published results of short term adsorption and uptake experiments.

Johnson and Jackson (1964, Fig. 1 and 2) found lower values for short term adsorption (up to 2 hrs.) of Ca^{45} at pH 4 than at pH6:

pH	Ca	pH - 1/2pCa	adsorption
4.1	0.001N	2.3	$6.5 Mx10^{-7}$
6.0	0.001N	4.3	$12.3 Mx10^{-7}$

The calculated values for pH - 1/2pCa relate closely to short term adsorption, which tends to suggest that this adsorption is controlled by exchange reactions.

Using the data of figure 5 of the same work, Ca uptake by excised barley roots was compared to 1/3pAl - 1/2pCa. To do this, a value for the Al activity in the "no Al" treatment had to be assumed. This value was calculated by relating treatment 5 (Table 4.2) to the graph established by the first 4 treatments. Using this value for pAl, 1/3pAl - 1/2pCa was calculated for the remaining treatments. The resulting values show a close relation between 1.3pAl - 1/2pCa and Ca uptake by the roots (Fig. 4.2).

Table 4.1: Calcium uptake by Alfalfa and Ryegrass from Mardin silt loam treated with lime and gypsum. Data of Fried and Peech (1946).

No.	Treatments*	Soil analyses pH	Ca ppm	pH-1/2pCa	% Ca in Alf. leaves	Ca in tops of Ryegrass, g.
1	Check	4.80	16	3.10	1.68	0.038
2	1/2 to gypsum	4.65	64	3.25	2.01	0.049
3	2 to gypsum	4.40	428	3.30	1.95	0.061
4	5 to lime	6.30	130	5.05	3.88	0.155
5	5 to lime + 2 to gypsum	6.00	595	5.10	3.81	0.137
6	5/3 to lime	5.40	49	3.90	3.04	0.100

* Per 2,000,000 lbs soil, oven dry basis.

Table 4.2: Calcium uptake by exised wheat roots in relation to Ca - Al solution measures. Data from Johnson and Jackson (1964).

No.	Treatments Ca me/l	Al me/l	Estimated activities pCa	pAl	1/3pAl-1/2pCa	uptake** moles Cax10^7
1	0.2	0.3	4.05	4.15	-0.650	2.7
2	1.7	0.3	3.40	4.15	-0.325	4.1
3	5.0	0.3	2.70	4.15	-0.025	10.1
4	10.0	0.3	2.40	4.15	0.175	11.9
5	0.2	"no Al"	4.05	5.75*	-0.125	8.0
6	1.0	"no Al"	3.40	5.75	0.200	11.0
7	5.0	"no Al"	2.70	5.75	0.550	15.6
8	10.0	"no Al"	2.40	5.75	0.700	18.2

* Calculated from treatments 1 to 4
** After distilled water washing.

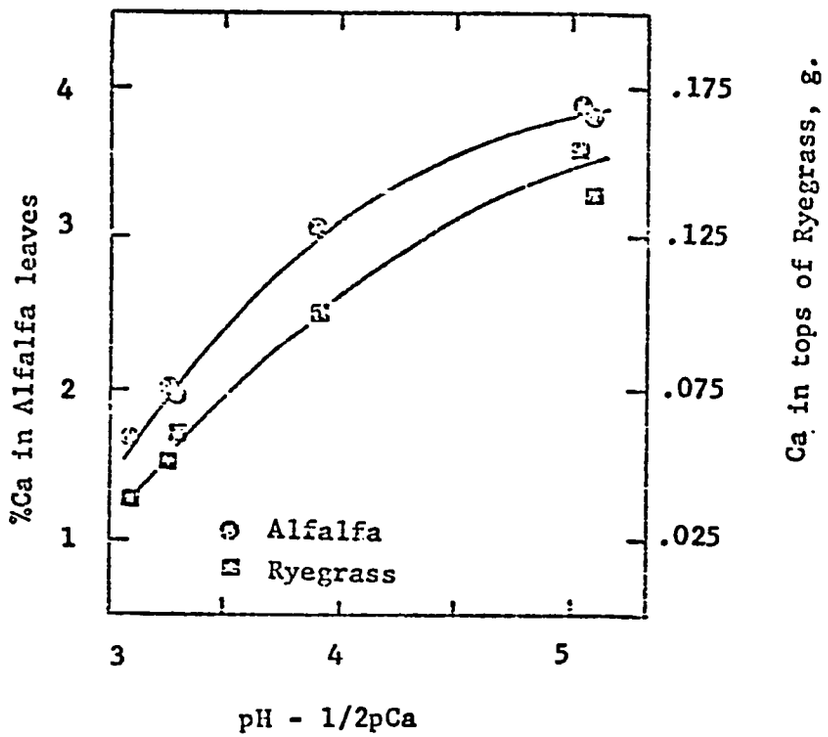

Figure 4.1: Calcium uptake by alfalfa and Ryegrass in relation to pH - 1/2pCa (from Fried and Peech, 1946).

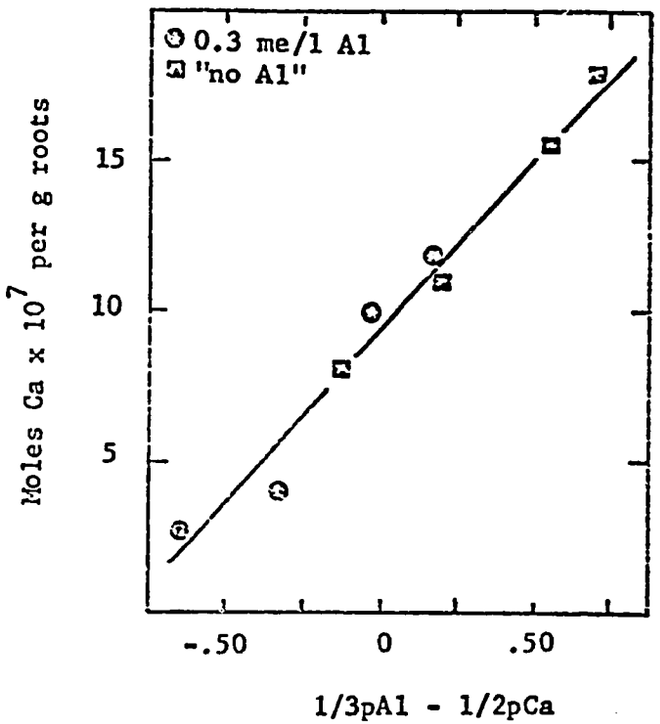

Figure 4.2: Calcium uptake by wheat roots in relation to 1/3pAl - 1/2pCa (from Johnson and Jackson, 1964).

These results are consistent with the hypothesis that Ca uptake is not solely dependent on the activity of Ca in solution. Uptake of Ca is more closely related to intensity measures such as 1/3pAl-1/2pCa or pH-1/2pCa. This appears to indicate that the Ca-saturation of the root free space can have a dominant effect on Ca uptake. Oberlander (1966) and Ulrich and Oberlander (1964) supported the possibility of a rate limiting step in cation translocation across the free space of roots on the basis of kinetic considerations. The lack of increase in Ca uptake obtained from additions of neutral Ca salts is consistent with the tendency for the abovementioned ratios to remain constant in the soil solution and on exchanger surfaces after additions of neutral salts (Schofield, 1947).

Summarizing, it appears that Ca uptake may be reduced by a wide variety of interfering cations and that reductions in root growth may be an effect of Ca deficiency which may further reduce uptake of Ca by the plant. In Chapter II proposed mechanisms of Al toxicity of the Carimagua soil on root growth assumed that root growth was reduced because of a Ca deficiency at the root tips. To further evaluate this assumption, in this Chapter, effects of Al toxicity on root growth are compared to Ca uptake by tops. In addition, various Ca - intensity measures are compared in relation to root growth and Ca uptake.

2. Greenhouse experiment

a. Materials and methods

A bulk sample from the top 20 cm of the Carimagua soil was air dried, pulverized and passed through a 5 mm screen. Ten treatments (Table 4.3) were applied to 8 kg soil and thoroughly mixed in a drum. Two kg soil was placed in tar covered asbestos pots, thus making 4 replicates. Soils were wetted up

to field capacity and pots were covered with plastic for one week. After this, soils were allowed to dry partially for one week. The content of each pot was removed, thoroughly mixed and returned to the same pot. Six seeds of corn (Var. H253) were placed at 3 cm depth and pots were watered up to field capacity. Pots were watered when necessary to prevent moisture stress. When seedlings had reached the three leaf stage, the number of plants was thinned to two plants per pot. Three weeks after seeding 20 pmm N was applied as NH_4NO_3, by pipetting the solution onto the soil surface. Phosphorus was applied at 50 pmm P by pipetting the solution of KH_2PO_4 in the centre of the pots at a depth of 7 cm. The Nitrogen application was repeated six weeks after seeding.

The experiment was harvested after 9 weeks. All top growth was dried, weighed, ground and analyzed for Ca, Mg and P. Roots were separated from the soil by seiving and subsequent washing. Roots were dried at 100°C and weighed.

Soil samples were collected, air dried and ground. Ten grams soil were equilibrated with 20 ml 10^{-3}M $CaCl_2$ for 3 days. Determination of pH and Ca, Mg and Al contents of the supernatant solution and calculation of activities and activity ratios were made as described in Chapter II.

b. Results

Soon after germination, treatments 5 and 1 showed symptoms of Ca deficiency. The second and third leaves had a chlorotic appearance, particularly toward the top and edges of the leaves. Leaves were curled and appeared as if damaged by frost. Separation of younger leaves from the whorl was often difficult because of the wilted, thin consistency of the leaf tips. This often led to tearing or loss of the tip. At later growth stages, leaf edges of

Table 4.3: Treatments applied to Carimagua topsoil in greenhouse experiment.

Treatment	Chemicals added on a dry soil basis me/100g					
	CaO	MgO	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
1	-	-	-	-	-	-
2	1.75	-	0.21	-	-	-
3	3.50	-	0.21	-	-	-
4	-	1.75	-	-	-	-
5	-	3.50	-	-	-	-
6	-	1.75	-	-	-	0.25
7	1.75	-	-	0.21	-	0.25
8	1.75	-	0.21	-	0.25	-
9	-	-	0.21	-	0.25	-
10	-	-	-	0.21	-	0.25

Table 4.4: Yield of dry matter of tops and roots (g/pot) and uptake of Ca, Mg and P (mg/pot) by corn of the greenhouse experiment.

Treatment	D.M. wt. tops	D.M. wt. roots	Uptake in tops		
			Ca	Mg	P
1	8.38c	4.94de	6.5de	19.4c	18.0cde
2	10.70ab	6.16bc	13.5c	25.9bc	22.6ab
3	10.51ab	8.01a	19.8ab	23.8bc	20.4bc
4	10.20ab	5.33cd	4.8de	42.5a	18.7cd
5	8.04c	4.15e	3.3e	44.4a	15.3e
6	10.70ab	5.53bcd	5.5de	48.3a	19.1c
7	11.61a	6.45b	21.6a	32.1b	25.1a
8	11.36a	6.07bc	16.8b	30.0b	21.4bc
9	9.51bc	4.98de	8.1d	27.3bc	15.9de
10	10.69ab	6.22bc	12.3c	29.7b	20.2bc

* Means not followed by the same letter are significantly different at the 5% level.

treatments 1 and 5 showed cupping and tearing.

After approximately 5 weeks new leaves in most treatments had a wet glassy appearance, as if cuticular wax were lacking, which started from the leaf tip and progressed towards the base of the leaves. The symptoms appeared considerably later in treatments 7 and 10, and did not appear in treatment 6. In later developed leaves the glassy appearance was extended to the whole leaf. Foliar application of a solution containing 1% of both $Cu(NO_3)_2$ and $Zn(NO_3)_2$ did not alleviate symptoms.

During early growth, substantial differences in plant height and vigor were evident. After approximately 5 weeks, growth in most treatments slowed down considerably and treatments evened up until at harvest (9 weeks after seeding) only small differences in dry matter yields were obtained (Table 4.4). Only treatments 1 and 5 had significantly lower dry matter yields than all other treatments, except treatment 9, on the basis of Duncan's multiple range test (Steel and Torry, 1960).

Effects of CaO additions:

Dry matter yield of tops and roots and yield of Ca, P and Mg were all significantly increased by CaO additions (Table 4.4). Dry matter yields of tops and yields of Mg and P did not increase between the first and second increment of CaO, even though root yields and Ca uptake were significantly increased. As the soil was exhaustedly cropped, some other factor had probably become limiting, as was indicated by the slow growth towards the end of the experiment. Additions of CaO increased equilibrium solution pH and Ca activities, as well as all Ca-intensity values calculated (Table 4.5). The Al-activity in solution decreased. Values of pH-1/2pCa and 1/3pAl - 1/2pCa

of the check plots were very low and the poor root growth obtained was expected on the basis of results obtained in Chapter II. Observation of the root systems showed that inhibition of rootgrowth had virtually eliminated the thin, long fibrous roots from the system (treatments 1, 5 and 9). This was very evident though large amounts of these fine roots had been lost during washing of treatments with well-developed root systems.

Effects of MgO addition:

The first increment of MgO significantly increased yield of tops and Mg uptake. There was a substantial increase in root yield and a decrease in Ca uptake. Uptake of P was not affected. The second increment of MgO significantly decreased yield of tops and roots as well as P uptake from the levels obtained at the first increment of MgO (treatments 4 and 5 of Table 4.4). Calcium uptake was further decreased and Mg uptake was slightly increased.

The increased yields of treatment 4 were not related to increase Ca uptake. Comparing Ca uptake with dry matter yields of tops and roots indicated that all treatments receiving MgO differed from other treatments in this relation (Fig. 4.4). This appears to be a case of a treatment induced change in the function y = f(Ca) where y is yield and f(Ca) is a function of the calcium uptake (Black and Scott, 1956). No clear explanation of the higher efficiency of absorbed Ca to produce dry matter in the presence of large amounts of Mg, appears evident.

Equilibrium solution analyses showed the expected increase in pH and reductions in Ca and Al activities from additions of MgO. Of the Ca intensity measures calculated, pH - 1/2pCa increased, and 1/3pAl - 1/2pCa initially increased slightly and then decreased (Table 4.5). The measures 1/2pMg -

Table 4.5: Chemical analyses of supernatants of the 10^{-3} M $CaCl_2$ equilibration of samples from the greenhouse experiment.

Treatment No.	pH	Ca $M/Lx10^3$	Al $M/Lx10^6$	pH - 1/2pCa $(L/M)^{1/2}$	1/3pAl-1/2pCa $(M/L)^{1/6}$	1/2pMg-1/2pCa	$p(Mg^{1/2}+Al^{1/3})$ 1/2pCa
1	4.40	0.250	0.98	2.60	-0.131	0.038	-0.356
2	4.81	0.464	0.24	3.14	0.207	0.242	-0.077
3	5.06	0.595	0.13	3.45	0.362	0.307	0.032
4	4.87	0.104	0.17	2.87	-0.071	-0.292	-0.495
5	5.13	0.072	0.13	3.07	-0.108	-0.459	-0.641
6	4.76	0.174	0.26	2.89	-0.013	-0.284	-0.470
7	4.69	0.582	0.27	3.07	0.243	0.274	-0.042
8	4.70	0.572	0.35	3.08	0.201	0.231	-0.084
9	4.39	0.352	1.18	2.65	-0.086	0.060	-0.318
10	4.40	0.349	0.99	2.68	-0.060	0.062	-0.303

1/2pCa and $P(Mg^{1/2} + Al^{1/3})$ - 1/2pCa decreased substantially from additions of MgO.

Effects of neutral salts:

The addition of $CaCl_2$ and $CaSO_4$ increased yields of tops and roots in all cases. The increase over the same treatment without neutral salts was generally small and only significant for treatment 10. Additions of $CaSO_4$ increased yields of tops and roots more than additions of $CaCl_2$. The difference was significant for treatments 9 and 10 (Table 4.3).

Uptake of Ca was significantly increased by the addition of $CaCl_2$ only in treatment 8 (compare 8 vs 2). Addition of $CaSO_4$ increased Ca uptake significantly in treatments 7 and 10. Addition of $CaSO_4$ to soil that received 1.75 me/100 MgO did not result in a significant increase of Ca uptake. The $CaSO_4$ treatments increased Ca uptake significantly more than the $CaCl_2$ treatments (compare treatment nos. 7 vs 8 and vs 10).

Neutral salts did not significantly affect Mg uptake and P uptake. The addition of $CaCl_2$ did, however, result in a significantly lower P uptake than the addition of $CaSO_4$.

Treatments 6, 7 and 8 had pH values lowered by approximately 0.1 unit from the same treatments not receiving neutral salts. Little or no change in pH was observed from addition of neutral salts to the unlimed soil (treatments 9 and 10). Equilibrium solution concentrations of Ca were increased by neutral salt addition. The Al activity was, however, hardly increased by added $CaSO_4$. Addition of CaO did decrease Al activities as expected.

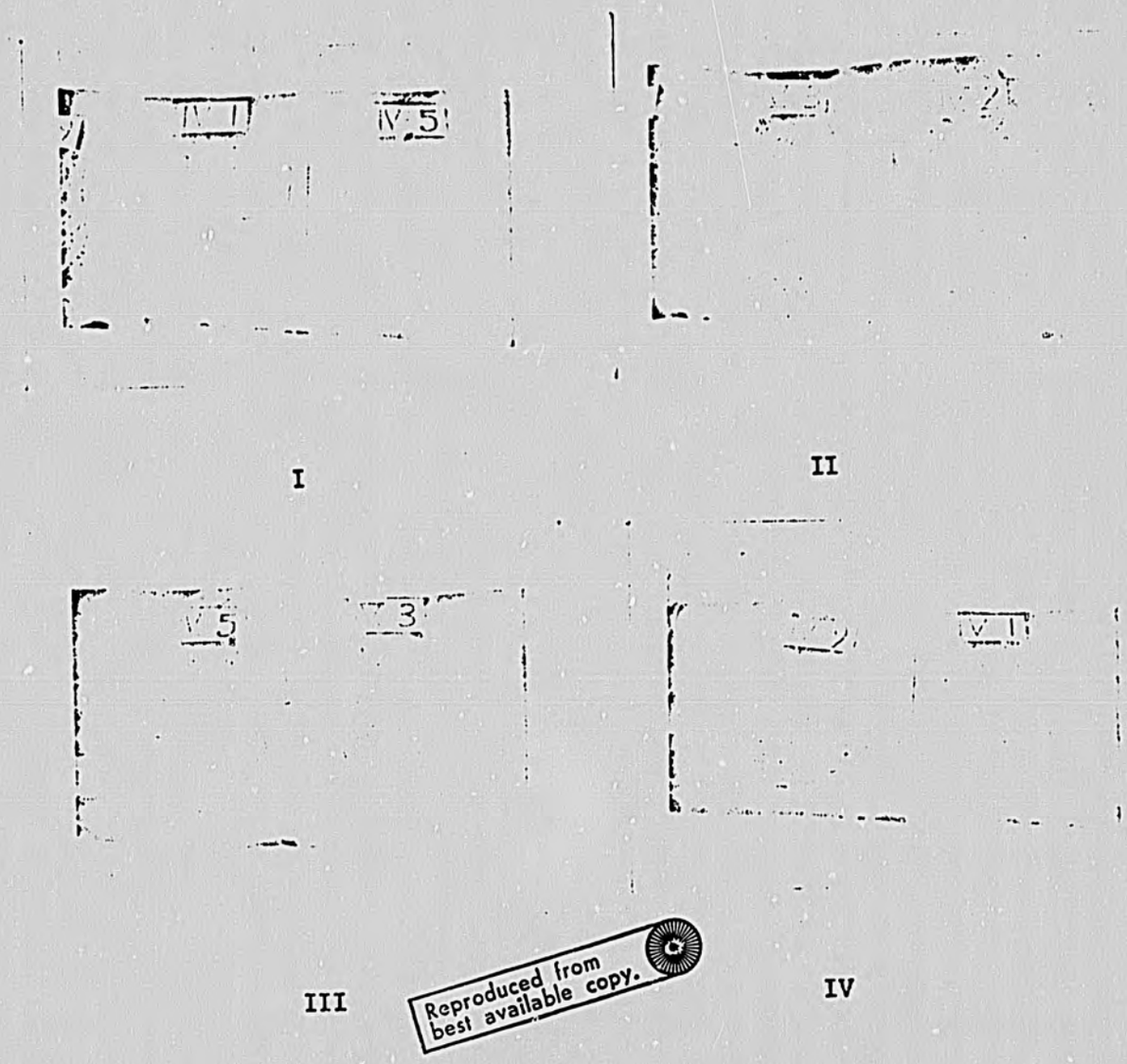

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Figure 4.3: The effects of selected treatments on root-systems of corn grown in the greenhouse. Arabic numbers refer to treatments as listed in table 4.3.
I: Check (1) verses 3.5 me/100 g MgO,
II: 3.5 (1) verses 1.75 me/100 g CaO,
III: 3.5 me/100 MgO (1) verses 3.5 me/100g CaO,
IV: 0.25 me/100g $CaCl_2$ (1) verses check.

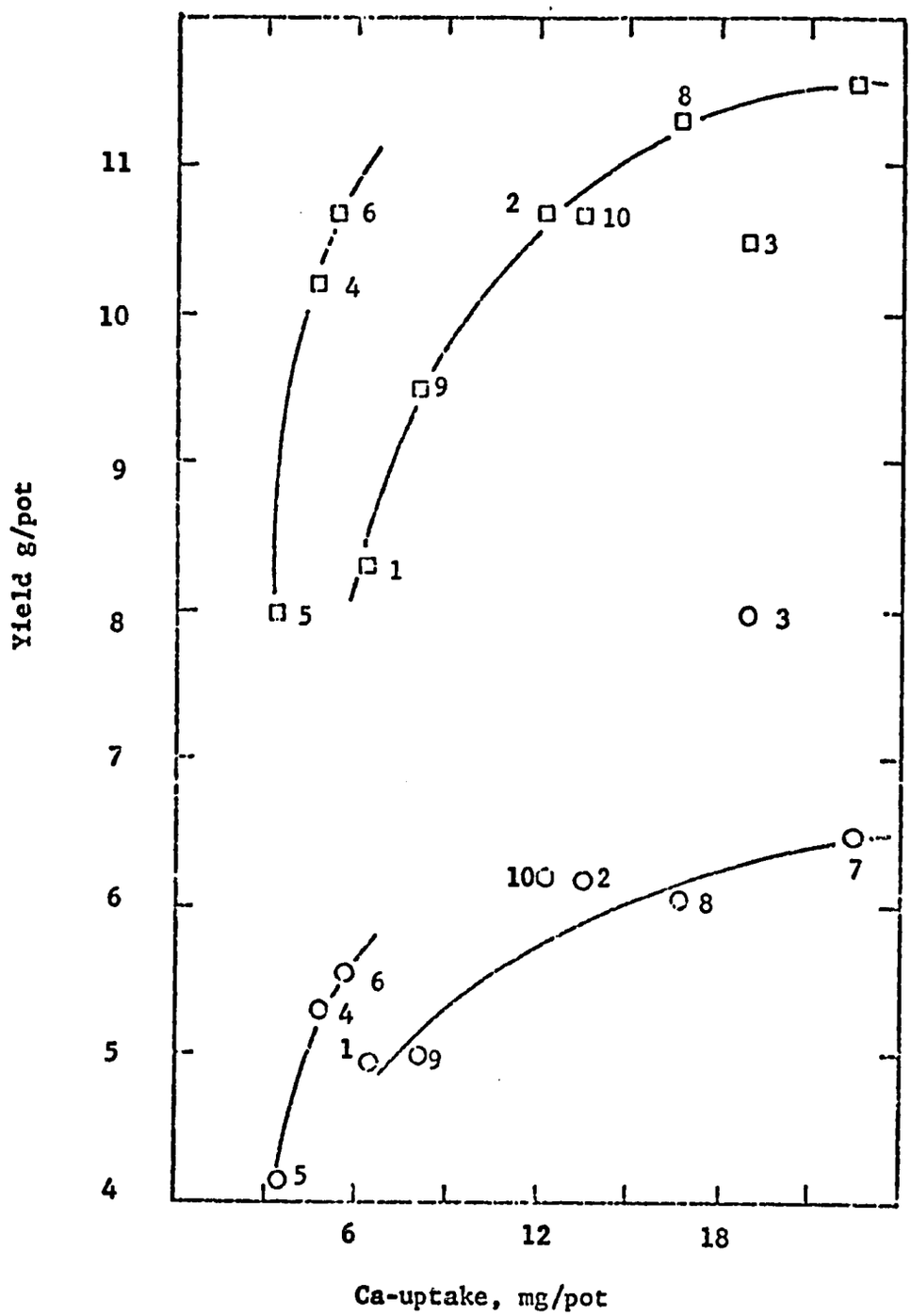


Figure 4.4: The relation of Ca-uptake to dry matter yields of tops (squares) and roots (circles) of corn from the greenhouse experiment.

The pH - 1/2pCa values did not appear to be much affected by neutral salt additions, although some increase was noticeable where no lime was applied. Addition of $CaCl_2$ had little effect on 1/3pAl - 1/2pCa at the 1.75 me/100 $Ca(OH)_2$ level (treatment 8), but increased this measure where no lime was added (treatment 9). Treatments 6, 7 and 10, which received $CaSO_4$, showed increased values of 1/3pAl - 1/2pCa compared to similarly limed treatments not receiving neutral salts. Additions of $CaSO_4$ increased 1/3pAl - 1/2pCa more than the additions of $CaCl_2$. The effects of neutral salts on $p(Mg^{1/2} + Al^{1/3})$ - 1/2pCa were similar to those on 1/3pAl - 1/2pCa, except that the high Mg activity in solution reduced differences between treatments 4 and 6.

The effects of neutral salts were different for chloride than for sulfate. Calcium intensity was little affected by $CaCl_2$ additions where the soil was already partially base saturated, but was increased in unlimed soil. These results are similar to those obtained in Chapter III and to results obtained by Clark (1965). Addition of $CaSO_4$ increased Ca intensity measurements through a decrease in Al activity in the equilibrium solution. This effect was relatively small and may have been caused by the formation of basic aluminum sulfates. Similar, but much more substantial effects, were obtained by Reeve and Sumner (1970) who attributed a "self-liming effect" to gypsum added to Natal soils. Singh and Brydon (1969) reported the formation of $Al_4(OH)_{10}SO_4.5H_2O$ with a solubility product of 10^{-117} in solutions of $AlSO_4$ in the presence of montmorrilonite.

c. Discussion

Uptake of Ca by top growth was very small compared to the exchangeable

Ca present in the soil. Even in the check treatment only approximately 5% of the exchangeable Ca was recovered in the top growth. In the treatment receiving 3.5 me CaO/100 g soil this percentage dropped to 0.75%. Treatments received between 3000 and 4000 ml of water during the experiment. Assuming 75% of this to have been used for transpiration, and assuming similar Ca contents for tops and roots, the Ca concentration of the soil solution would need to be approximately 1.0×10^{-4} M for the check treatment. For the treatment receiving 3.5 me CaO/100 g soil the soil solution concentrations would have had to be 3×10^{-4} M Ca. A reasonable estimate of the soil solution concentration of the check plot is 1.0×10^{-4} M Ca, and of the 3.5 me CaO treatment is 4.5×10^{-4} M Ca.

The check treatment and, more so, treatments receiving MgO may not have been able to depend entirely on mass flow for the Ca-supply to their roots. Using the ratio of dry root weight to root volume of 1:25 (Al-Abbas and Barber, 1964), the soil volume occupied by roots would at least have been 4%. Assuming that roots absorbed 50% of the exchangeable Ca from this soil volume, would already account for 2.4 mg Ca in the case of the check treatment.

It may thus be assumed that more Ca was present at the root-soil interface than was taken up by the plants. In treatments receiving CaO or neutral Ca salts, mass flow will have led to accumulation of Ca at the root-soil interface. Among these treatments there are still substantial differences in Ca contents of top growth and root yields. This suggests the existence of some interfering mechanism which inhibits Ca uptake from the root-soil interface. These results agree with Al-Abbas and Barber (1964) who obtained estimates of mass flow substantially larger than plant uptake of Ca at suboptimal Ca-uptake levels.

The relation between Ca uptake and root growth (Fig. 4.4) was different for treatment that received MgO. As Mg contents of all treatments were higher than Ca contents, there was no indication of a Mg deficiency. The high Mg levels appear to have changed the Ca requirement of the corn in these treatments. No physiological explanation of this phenomenon is evident. Within groups of treatments receiving MgO or CaO yields of roots and tops were closely related to Ca uptake. This is consistent with the hypothesis formulated in Chapter II, in which reduced root growth by high solution levels of Al or other cations is considered to be an induced Ca - deficiency.

The increased uptake of Ca when neutral salts were added may have been enhanced by the intensive manner in which the soil was cropped. Such differences in Ca uptake may not occur under field conditions. Comparing Ca uptake with pH-1/2pCa indicated poor agreement where MgO was added. This measure is thus a poor choice in cases where a substantial part of the base saturation is attributable to other than Ca and Al ions. A practical examples of such a case would be a soil derived from serpentine rock (Martin et al, 1953), or other soils with low Ca:Mg ratios. The measure 1/3pAl - 1/2pCa showed similar disadvantages.

The activity of Ca relative to Mg was very small in soils that received MgO as indicated by the low 1/2pMg - 1/2pCa values obtained (Table 4.5). Estimation of the intensity of Ca in these soils should therefore include Mg as a reference ion.

The measure $p(Mg^{1/2} + Al^{1/3})$ - 1/2pCa combines the activities of Mg and Al in a rather arbitrary fashion to serve as a reference for the Ca activity (see discussion of Chapter II). The resulting ratio related closely to Ca

uptake except in treatments receiving $CaSO_4$ or $CaCl_2$ (Fig. 4.5A), in which intensive cropping favoured uptake of Ca from neutral salts.

No determinations of soil solution Ca activity were made. Activities of Ca in the 10^{-3}M $CaCl_2$ equilibrium supernatants, although more nearly an intensity measure, did provide an indication of the relative merit of a measure of soil solution Ca activity. Figure 4.5B shows that the equilibrium activity of Ca relates closely to Ca uptake by corn tops for treatments 1 to 6. Treatment 7 and 10, which received $CaSO_4$, showed higher Ca uptake. Treatments 8 and 9, however, showed low adsorption in relation to Ca activity. In these latter treatments, addition of CaCl, resulted in increases in Al activity as well as Ca activity in solution. The increased Al activity appears to have reduced Ca uptake by the corn in a similar manner as found by Johnson and Jackson (1964).

The activity of Ca in displaced soil solution will fluctuate more widely from additions of neutral Ca salts or changes in soil solution concentration than the equilibrium activity employed above. It may therefore substantially overstimate availability of Ca under such circumstances.

d. Conclusions

Addition of CaO to Carimagua soil significantly increased Ca uptake by corn. Additions of MgO decreased Ca uptake. Neutral salts generally increased uptake of Ca. The intensive cropping system applied to the soil appears to have encouraged uptake of Ca from added neutral salts.

Reductions in root growth were related to the relative nutritional status of the plant with respect to Ca. The relation between yield of roots

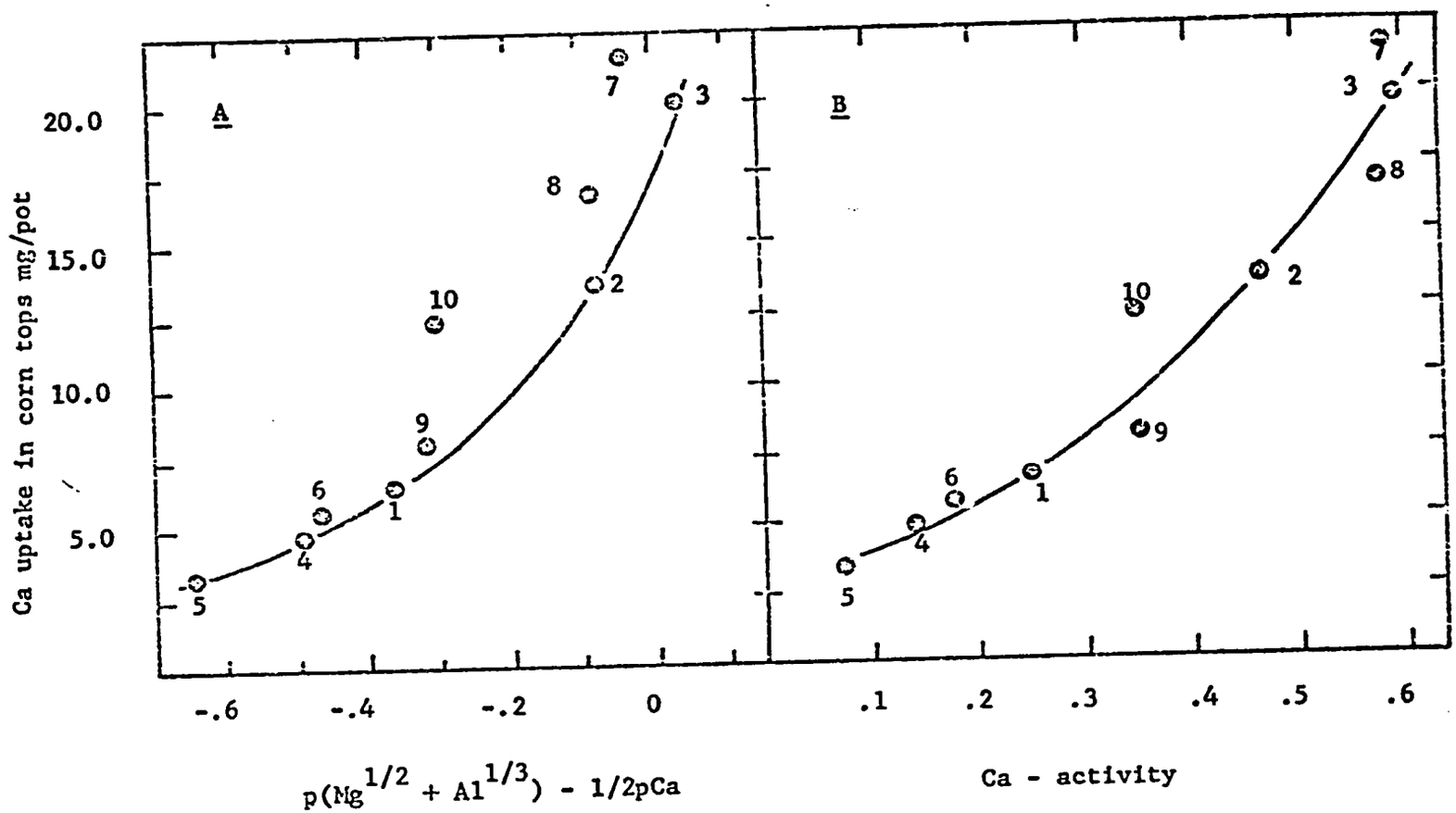


Figure 4.5: The relation of Ca uptake by corn to $p(Mg^{1/2} + Al^{1/3}) - 1/2pCa$ (A) and the activity of Ca (B), determined by 10^{-3}M $CaCl_2$ equilibration. Numbers refer to treatments of greenhouse experiment.

or tops and Ca - uptake for treatments receiving MgO differed from this relation for treatments receiving CaO or neutral Ca salts.

In most treatments, Ca uptake could be more than accounted for on the basis of mass flow only. The lack of Ca - uptake does therefore, not appear to be due to a shortage of Ca at the soil - root interface. The relation between Ca uptake and 1/3pAl - 1/2pCa was inadequate where Mg became a dominant ion in the soil solution system. The measure $p(Mg^{1/2} + Al^{1/3})$ - 1/2pCa related closely to Ca uptake and was changed only to a small extent by additions of $CaCl_2$ and $CaSO_4$.

The activity of Ca in solution of a 1:2 equilibration with 10^{-3} M $CaCl_2$ related very well with Ca uptake in treatments that received no neutral Ca salts. In treatments receiving $CaCl_2$ this measure underestimated Ca uptake by corn even though soils were very intensively cropped.

3. Field experiments

a. Materials and methods

Two randomized complete block designs were established with four replicates and five liming treatments in plots of 4.5 by 10 meters. The experiments were laid out on freshly broken savanna.

On October 6 and 7, 1970, lime was applied in rates of 0,1,2,4, and 8 to/ha of agricultural grade CaO as follows. The area was disced and staked. A minor element mix (see below) was applied to the entire plot area. Half of the lime was applied to each plot and the area was disced twice and plowed to 20 cm depth. After this, the area was restaked, the remaining half of the lime was applied and the plot area was disced twice. The minor element mix

contained:

10 Kg/ha $ZnSO_4$	250 Kg/ha $MgSO_4$
10 Kg/ha $CuSO_4$	10 Kg/ha Borax

On October 8, 1970 one experiment was seeded to corn (var H253) with 5 rows per plot spaced at 90 cm. On October 17, the other experiment was seeded to sorghum (var P25) with 9 rows per plot, placed 50 cm apart. Both crops received 19 Kg/ha N as urea, 50 Kg/ha P as triple super phosphate and 37 Kg/ha K as muriate of potash, at seeding time. These fertilizers were placed 4 cm beside and 4 cm below the seed. Corn plots were side-dressed with 50 Kg/ha N as urea at 4 and 8 weeks after seeding. The sorghum experiment was side-dressed with 50 Kg/ha N as urea at 4 and 7 weeks after seeding.

The corn experiment was thinned to approximately 45000 plants/ha, 5 weeks after seeding. At this time, samples of topgrowth were collected for plant analyses. Seedling samples for the sorghum experiment were collected 8 weeks after seeding. Samples were stored in plastic bags, washed with distilled water, dried at 100°C, weighed, ground and analyzed for Ca by atomic adsorption and P by the ammonium vanadate method.

Four weeks after lime application, soil samples were taken from the corn experiment by taking three cores to a depth of 20 cm from the two center rows of each plot. Soil samples were dried, ground and analyzed for equilibrium and exchangeable Ca and Al measures, according to the method described fro experiment 2, Chapter 3. Composite samples of the four replicates were used for rootgrowth studies of the same varieties of corn and sorghum used in the field experiment. The rootgrowth studies were conducted as described in Chapter 2, using a 10^{-3} M $CaCl_2$ solution for equilibration of the soil

samples. Sorghum plots were sampled 8 weeks after lime application using the same methods as used for the corn experiment.

Eight weeks after seeding, at tasseling time, leaf samples were collected from the corn experiment by taking the center third of the leaf opposite and below the major ear. Every third plant of the center 7 meters of the center three rows were sampled until 20 leaf samples were collected. Samples were dried, ground and analyzed for Ca and P by the same methods used for seedling samples. The sorghum experiment was sampled 10 weeks after seeding. Thirty leaves were sampled from the three center rows of each plot. Samples were processed and analyzed as for the corn experiment.

During the growing season, severe insect attacks (mainly Spodoptera frigiperda and Diatrea spp) made frequent applications of insecticides necessary. Insecticides used were 2:1 DDT-methyl parathion mixture at 1 1/2 gal/ha applied whenever insect populations built up beyond control by regular applications of Sevin, a slow release granulated insecticide (1.5 Kg/ha). Even though 12 applications were made during the growing season, insect damage to corn was severe.

Because of insect damage and drought, the corn crop was harvested as total dry matter of topgrowth 94 days after seeding. The center 7 meters of the best 2 of the center 3 rows of each plot were harvested by cutting stalks 5 cm above the ground. Total fresh weight was taken and 3 to 5 representative stalks were chopped up as a subsample for dry matter determination.

Insect damage in the sorghum crop was considerably less. The crop matured in 112 days and was harvested after 121 days. The center 4 meters

of the center 5 rows of each plot was harvested by cutting off the panicles including only 1 cm of the stalk. The total harvested weight was corrected by a threshing percentage. This percentage was determined by threshing a 500 g sample of panicles in a head row thresher.

As soon as possible after the dry season, both experiments were reseeded to the same crop after plowing and discing (April 16 and 17, 1971). No lime or minor elements were applied. Rates and placement of N, P and K fertilizers were the same as in 1970. Seedling samples were taken 4 and 6 weeks after seed ing for the corn and sorghum experiment, respectively. No leaf samples were collected at tasseling time. Both experiments received a side-dressing of 50 Kg/ha N as urea 5 and 10 weeks after seeding. Further plot maintenance, including insect control was similar to that in 1970.

The corn experiment was harvested on August 16, 1971. All ears produced in the three center rows were harvested, except for a border of 1.5 m at either end of the plot. Cobs with less than 50% seed set, rotten cobs and those severely damaged by birds, as well as cobs smaller than 3 cm were disgarded. Yields were calculated on an air dry basis, using a 75% threshing percentage determined on a sample of harvested cobs. The sorghum experiment was harvested on August 19, 1971 as in 1970, and yields were calculated using the same threshing percentage (80%).

b. Results and discussion

In both years, corn and sorghum crops emerged as a complete stand. The corn stand was, however, continuously reduced throughout the growing season because of insect damage. In both years the sorghum stand became very uneven shortly after emergence, and a large number of seedlings were retarded or

died. This effect was very irregular and more evident at low lime rates. Because no such effects were encountered in another sorghum experiment receiving broadcast applications of basic slag, it appeared that the reason for poor development of young seedlings was their inability to reach the banded phosphorus fertilizer. Inspection of the affected seedlings showed that the primary roots had died before they reached more than 5 cm in lenght. For good establishment of sorghum on the Carimagua soil, phosphate fertilizer should therefore probably be placed with the seed. Results of the second replicate of the sorghum experiment were excluded from analyses and calculations, as soil analyses and experimental results indicated that errors were made in lime application in this replicate. Results of soil analyses for the corn and sorghum experiment are summarized in appendix tables 4.31 and 4.32 respectively.

Corn experiments:

During early growth, corn plants showed much more differences between treatments in 1970 than in 1971, as in evident from the dry matter yield of seedlings sampled in both years (Table 4.6). This was probably caused by seeding the experiment directly after lime application, and very shortly after breaking and plowing of the savannah. In 1970, plants receiving 2 to/ha or less lime appeared chlorotic with narrow leaves and were badly stunted. Calcium contents of seedlings were substantially lower than in 1971 but increased dramatically at higher lime rates. The relation between Ca contents of seedlings and dry matter yields presented in figure 4.6, supports the hypothesis that the response to lime additions is at least in part due to a correction of Ca deficiency of the crop. Differences in Ca contents of the crop were maintained throught the growing season as shown by differences in

Table 4.6: The effects of lime applications on Ca uptake by corn seedlings, Ca content of leaf samples taken at tasseling time and yield of corn.

Lime rate CaO-lime	Seedling samples: Dry matter g/plant	Seedling samples: Percent Ca	Seedling samples: Ca uptake mg/plant	Leaf samples percent Ca	Final harvest yield to/ha
1970					
0	0.49a	0.33a	1.70a	0.32a	2.37a[1)]
1	0.76a	0.46b	3.45a	0.36ab	3.35a
2	1.08a	0.41ab	3.95a	0.48bc	3.49a
4	2.66b	0.60c	15.92b	0.55cd	4.75b
8	4.26c	0.79d	33.32c	0.66d	5.74b
1971					
0	3.78a	0.58a	21.9a	-	1.15a[2)]
1	4.75bc	0.75b	35.5b	-	2.04b
2	5.21c	0.84c	44.0c	-	2.00b
4	5.18c	0.93d	48.1c	-	2.18b
8	4.43b	1.07c	47.3c	-	2.24b

1) Total dry matter yield of topgrowth
2) Grain yield

Ca contents of leaf samples taken at tasseling time. The 1970 experiment was harvested as total dry matter because severe insect damage throughout the growing season had damaged virtually all cobs. Cobs on the 0,1 and 2 to/ha treatments were very small and showed poor seed set. Cobs of the 8 to/ha plots were of a fair size and had good seed set. Total dry matter yields of above ground parts increased with increasing lime levels (Table 4.6).

In 1971, increases in grain yield as well as Ca uptake by seedlings were not substantial at rates over 2 to/ha of lime. Plots receiving 4 or 8 to/ha contained a large number of plants which showed a rosette type growth and white banding between the center vein and the edges of the leaves. Samples of the check plot and the 8 to/ha lime plots were analyzed for Zn contents and showed a significant reduction from 25.5 to 20.0 ppm Zn for these two treatments, respectively (Appendix Table 4.30). These values appear to be in the critical range for Zn deficiency as Zn contents of corn seedlings of a similar age which had received 20 Kg/ha additional $ZnSO_4$, ranged from 46 to 78 ppm. This may have decreased responses to lime additions at higher lime rates. It may also account for the significant reduction in dry matter weight of seedlings which accompanied a significant increase in Ca content of the 8 to/ha treatment in 1971 (Table 4.6 and figure 4.6). Grain yields varied from 1.15 to 2.24 to/ha, but no significant response was obtained beyond the 1 to/ha lime rate[1]. These grain yields are

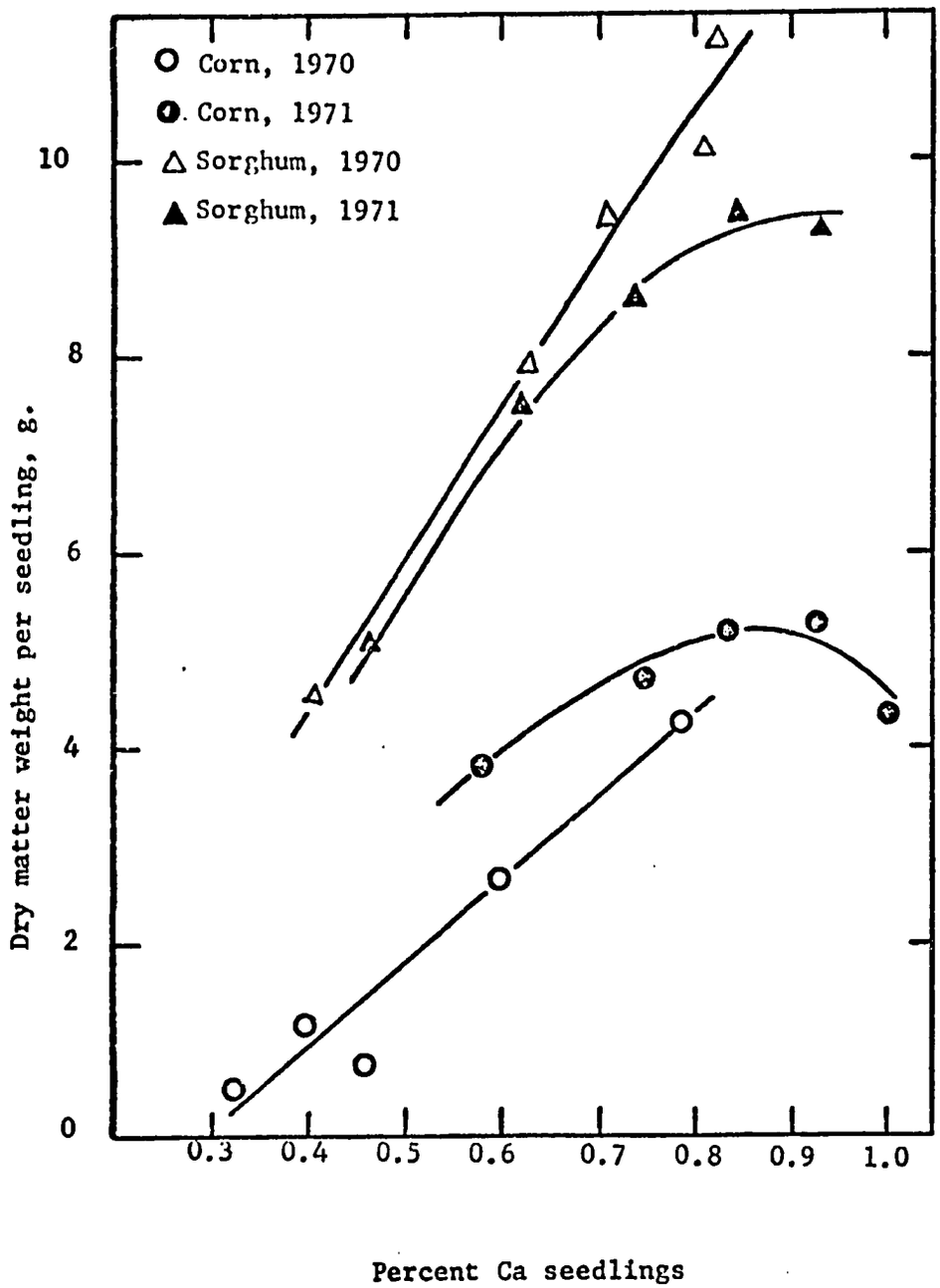
1)The mean of the grain yield for corn for the 1 to/ha lime rate was substantially increased by one plot with an extraordinary high yield for this experiment. The yield figure was, however, verified and in accord with the previously noted vigour of the plot. As neither soil analyses nor Ca or P contents of the seedlings indicated any abnormalities, the yield was included in the mean. The mean of the three remaining plots was 1.62 to/ha (C. F. Appendix Table 4.24).

considered poor for the area. Substantially higher yields have been obtained employing high rates of phosphate fertilizers (200 Kg P/ha), suggesting that the crop may have suffered from P deficiency. Phosphorus analyses of seedlings ranged from 0.21% to 0.28% in 1970 and from 0.26% to 0.28% in 1971. Leaf sampled taken at tasseling time in 1970, ranged in P contents from 0.22% to 0.25% (c.f. Appendix Tables 4.9, 4.23 and 4.11). These P contents do not appear to be in the critical range and the benefits of high rates of P applications noted in other experiments may have been of an indirect nature.

Field inspection of the root systems showed little or no root penetration below the depth of liming (20 cm). Density of corn roots was noticeably reduced only in the 0 and 1 to/ha lime plots. The root system in the zero lime plots showed blunt root apices and a tendency for short, thick, lateral roots. The absence of fine, fibrous roots was striking at the 0 and 1 to/ha lime rates.

Sorghum experiments:

Results of sorghum experiments were generally similar in 1970 and 1971 (Table 4.7). Dry matter weight of seedlings, percent Ca of seedlings and Ca uptake by seedlings were all substantially increased by lime additions in both years. Grain yields increased substantially with increased lime additions in both years, but the increase in 1971 failed to reach the significance level. In both years, Ca contents of seedlings related closely to their dry matter yields (Fig. 4.6) as was the case for the corn experiments. Although yield depression occurred at the high lime levels, the response



Figures 4.6: The relation between Ca content of seedlings of corn and sorghum and their dry matter yields in field experiments at Carimagua.

Table 4.7: Effects of lime applications on Ca uptake by sorghum seedlings, percent Ca of leaf samples taken at inflorescence and grain yields of sorghum for the 1970 and 1971 experiments.

Lime rate CaC-lime to/ha	Seedling samples Dry Matter g/plant	Percent Ca	Ca uptake mg/plant	Leaf Samples Percent Ca	Grain yield to/ha
1970					
0	4.5a	0.41a	19.0a	0.42a	1.09a
1	7.9b	0.63ab	50.1b	0.65b	1.56b
2	9.4bc	0.71b	67.7bc	0.72bc	1.84bc
4	10.1bc	0.81b	82.0cd	0.81cd	1.87bc
8	11.2c	0.82b	91.0d	0.86d	2.15c
1971					
0	5.0a	0.46a	23.3a	-	1.86a
1	7.5b	0.62b	45.7b	-	2.13a
2	8.6b	0.74b	63.1b	-	2.10a
4	9.3b	0.93c	86.6c	-	2.68a
8	9.4b	0.85c	79.8c	-	2.68a

in dry matter yields to increased Ca contents was smaller in 1971 than in 1970. Analyses of seedling samples showed again significantly lower Zn contents in seedlings from the 8 to/ha plots (24 pmm Zn) compared to those from the check plots (35 pmm Zn, see appendix table 4.30). Density of sorghum roots was noticeably reduced in the 0,1 and 2 to/ha lime plots. The presence of living roots was reduced as many roots had died and turned purple or black. The roots system of plants receiving no lime was reduced to a shallow crown of dead roots, with only a few thick, newly initiated roots which were alive.

Phosphorus contents of sorghum seedlings were substantially lower than those corn, indicating that plants may have suffered from P-deficiency . Seedling samples in 1970 decreased from 0.22% for the check plots to 0.13% for the 8 to/ha treatments. In 1971 these values were 0.17% and 0.19%, respectively. Leaf samples collected at flowering time contained between 0.20% and 0.21% P (c. f. Appendix Tables 4.16, 4.28 and 4.18).

Soil analyses:

Analyses of $CaCl_2$ supernatant solutions and KCl extracts for individual samples are presented in appendix tables 4.31 and 4.32. Averages and calculated soil chemical measurements are listed in table 4.8. These values indicate that the check plots were more Ca saturated and showed a higher pH in 10^{-3} M $CaCl_2$ than the samples used in Chapters 2 and 3. This may be because the experiment was located closer to the lake and its surrounding forest, but is more probably due to contamination from adjacent plots, or from the banded triple superphosphate.

As expected, liming increased exchangeable Ca, pH, pH - 1/2pCa and 1/3pAl - 1/2pCa. The relation between pH and exchangeable Al was very similar to that obtained by liming Carimagua soil in the laboratory in Chapter 3. The exchange relation of Ca and Al calculated from Rex and Rsol (As defined in Chapter 3) for the samples from the corn and sorghum experiment were similar to those obtained in Chapter 3. Using the zero intercept model, the estimated slopes of the regression of Rsol on Rex were 0.53 (N=11, R^2 = 0.976) for the corn experiment and 0.51 (N=9, R^2= 0.982) for the sorghum experiment. These values compare closely to those of 0.52 and 0.51 obtained in experiments 1 and 2 of Chapter 3.

Because yields of corn and sorghum were clearly limited by factors other than liming, these results are not suitable for firm reccommendation of lime levels. The responses of the corn experiment, in 1970, to high lime levels were probably a result of a lack of reaction of the lime with the soil.

Root growth:

Comparison of pH - 1/2pCa with root growth (Table 4.8) showed similar relations to those obtained in Chapter 2. Maximum root-growth of corn was obtained at pH - 1/2pCa values of approximately 3.5. For sorghum this value of pH - 1/2pCa was approximately 4.1.

Rootgrowth compared closely to Ca uptake by seedlings except for the corn experiments in 1970 (Fig. 4.7). This experiment was sampled 5 weeks after lime application, and seeded one day after lime application. Most of the lime had therefore not reacted with the soil during most of the period of seedling development. The rootgrowth studies, on the other hand, were

Table 4.8: The effects of lime additions on soil chemical measures of Carimagua topsoil samples from liming experiments in the field.

Lime rate CaO-lime to/ha	10^{-3} $CaCl_2$ equilibrium supernatant pH	1/3pAl - 1/2pCa	pH - 1/2pCa	KCL extractable, me/100g Ca	Mg	R_{ex} [1]	Rootgrowth mm/60hrs.
corn experiment							
0	4.50	-0.06	2.72	0.94	3.34	2.02	3.8a
1	4.60	0.13	2.87	1.77	2.24	1.37	5.5b
2	4.99	0.49	3.33	3.04	1.37	0.84	8.4c
4	5.75	-	4.17	5.91	0.39	0.28	8.9c
8	6.23	-	4.66	7.55	0.04	0.14	9.0c
sorghum experiment							
0	4.51	-0.08	2.70	0.75	3.53	2.29	0.6a [1]
1	4.78	0.26	3.10	2.21	2.29	1.14	2.1b
2	4.96	0.37	3.27	2.78	1.77	0.94	4.8c
4	5.95	-	4.37	7.65	0.07	0.15	6.7d
8	6.49	-	4.98	8.57	0.00	0.08	6.3d

1) The root growth study for sorghum was done with soil samples of the corn experiment, and should therefore, be compared to the soil analyses listed for the corn experiment.

2) $R_{ex} = [Al]^{1/3} c^{1/6} / [Ca]^{1/2}$, where square brackets indicate moles exchangeable (c.f. Chapter 3).

conducted at equilibrium conditions, so that the poor agreement obtained for the 1970 corn experiment could be expected. The comparison of Ca uptake to root growth in figure 4.7 again indicates that the effects of Al toxicity on root growth are closely related to Ca uptake by the plant.

c. Conclusions

Yield responses of corn and sorghum to added lime were limited by a lack of other nutrients such as Zn and possibly P. Added lime increased Ca uptake by seedlings of both crops in both years, and yields of seedlings were closely related to Ca contents of seedlings. Differences in Ca contents due to added lime were also evident in leaf samples taken later in the growing season. Ca uptake by seedlings of corn and sorghum compared closely to root growth measurements.

These results are consistent with the hypothesis that Al toxicity on the Carimagua soil is in effect, an Al induced Ca-deficiency which results in substantially reduced root growth and low Ca uptake by the above ground parts.

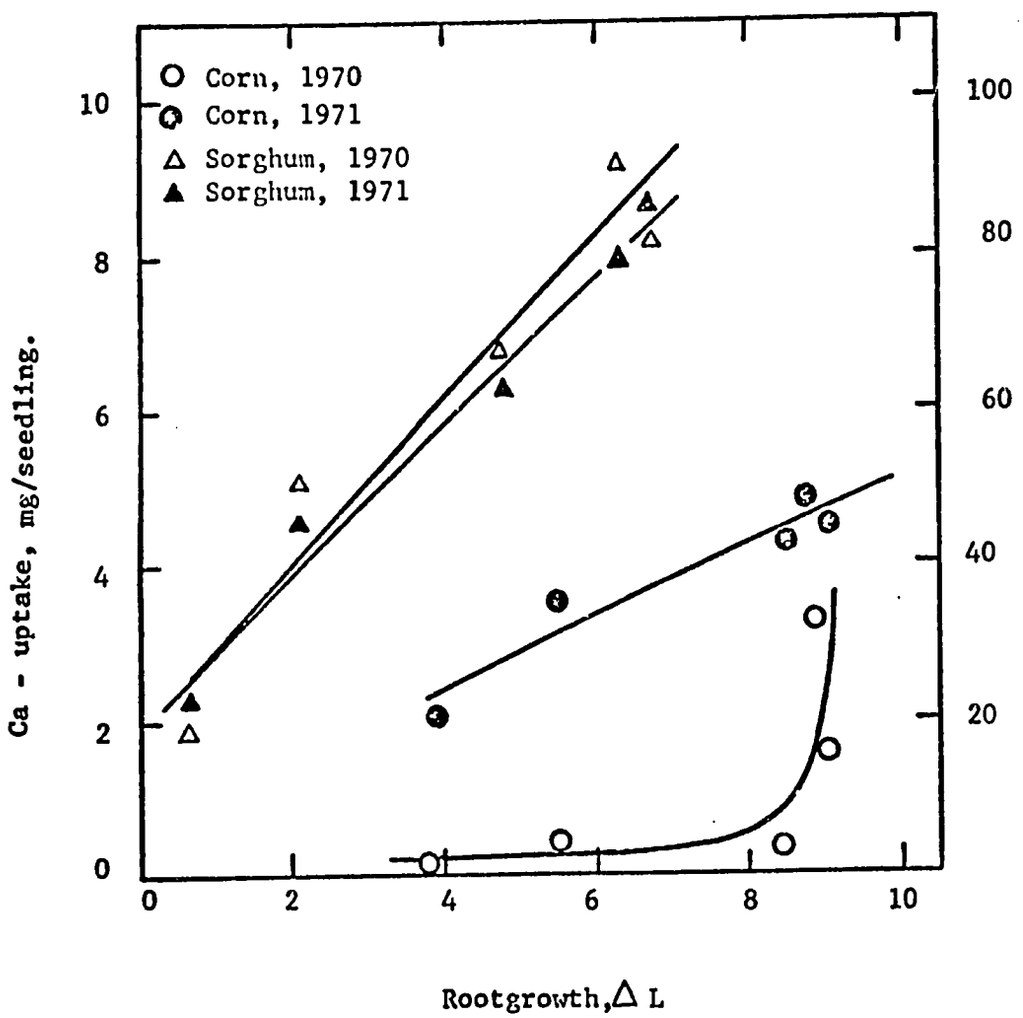


Figure 4.7: The comparison between rootgrowth determined in 10^{-3} M $CaCl_2$ equilibrium solutions of samples taken from field experiments on Carimagua soil and Ca-uptake by corn and sorghum seedlings sampled from these field experiments.

V. SUMMARY

The work presented in the precenting chapters is consistent with the hypothesis that Al toxicity is primarily an inhibition of Ca uptake and that Al is one of several cations which may induce a Ca deficiency. The logarithms of the solution cation ratios $(Ca)^{1/2}/(Al)^{1/3}$ and $(Ca)^{1/2}/(H)$ were well correlated with rootgrowth in systems dominated by Ca and Al. These ratios were superior to either Ca activity or Al activity in explaining variations in rootgrowth in such systems. Reductions in rootgrowth induced by K and Mg reported in the literature were related to similar ratios such as $(Ca)^{1/2}/(Mg)^{1/2}+(K)$.

The results indicate a non specific competition between interfering ions, and Ca, similar to that which occurs for exchange sites on an inert exchanger. On this basis, the reduction in rootgrowth associated with high solution concentrations of Al or other competing ions, may be caused by a lack of Ca at the growing root tip. The competitive action of cations such as Al or Ca is not confined to the root tip, but also extend to the ability of the plants to absorb Ca, as was shown in Chapter 4.

The soil solution measure which suitably related to effects of Al toxicity, low Ca: Mg ratio.low pH and Ca deficiency was of the general function $(Ca)^{1/2}/\ C_i(M_i)^{1/v_i}$ (Chapter 2). In the case of Al toxicity the denominator of this function is largely dependent on the concentration of trivalent Al. This measure is therefore, not readily affected by changes in the concentration of other mono or divalent cations in solution and unless these ions become

dominant, the general function may be reduced to $(Ca)^{1/2}/(Al)^{1/3}$

Due to their lower valence, Mg and K are much less effective than Al in reducing rootgrowth. When Al is precipitated by addition of $Mg(OH)_2$, KOH or NaOH, the resulting influence on plant growth becomes complicated to analyze because the simple ratio $(Ca)^{1/2}/(Al)^{1/3}$ becomes inadequate (the system is not predominated by Ca and Al). In these cases more complicated functions of Al plus the associated cations must be used in the denominator. In case the original Ca content is high enough, low levels of these bases may improve rootgrowth, primarily by precipitating Al, but as the amount of added base is increased, the concentration of the added ion may become high enough to induce a Ca deficiency.

Because of variations in the solubility of $Al(OH)_3$ in different soils, the ratio $(Ca)^{1/2}/(H)$ is not generally equivalent to the ratio $(Ca)^{1/2}/(Al)^{1/3}$. A more accurate and convenient estimate of the solution ratio $(Ca)^{1/2}/(Al)^{1/3}$ was based on the ratio $[Ca]^{1/2}/[Al]^{1/3}C^{1/6}$ utelizing exchangeable Ca and Al, as described in Chapter III. The applicability of this measure is under similar constraints as mentioned for the solution measure $(Ca)^{1/2}/(Al)^{1/2}$. These constraints do not generally limit the applications of these measures in highly weathered soils of the tropics. There are, however, soils in which Mn may dominate a substantial percent of the CEC. In these cases, the induced Ca deficiency will be better explained if Mn is included into the reference-denominator of the ratio. Similar difficulties arise in soils derived from serpentine rock, which generally are highly Mg saturated.

Although cations such as Mn and Mg appear to interfere similarly with rootgrowth and Ca uptake of crops, their effects should not be considered

entirely similar to those of Al. Very little Al is translocated to the above ground parts of crop plants, whereas Mn and Mg contents in top growth are substantially increased at increased soil solution concentration of these ions. In these latter cases additional physiological disturbances may be expected to occur.

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Appendix 1.1: Profile description of Carimagua profile.

Description: Pit by R. Guerrero and S. W. Buol.

Date: August 4, 1969

Location: Approximately 300-500 meters west of the Carimagua ranch house, near and along the fence of the experimental field.

Vegetation: Treeless savanna; herding area.

Physiography: Apparently intermediate position.

Parent Material: Mixed acid alluvial sediments.

Slope: 0-1%.

Drainage: Well drained (to somewhat poorly drained?).

Erosion: None.

Depth to Water Table: Deep.

Remarks: Possibly water table at this place is influenced by the short distance to the Carimagua lake (400 meters). An apparent catena was observed along the ditch to the lake.

0 - 8 cm Very dusky red (2.5YR 2/2); silty clay loam; weak, coarse, massive that breaks into moderate, fine, subangular blocky structure; hard when dry, slightly sticky when wet; many medium and fine roots; clear, smooth boundary.

8 - 22 cm Dark reddish brown (5YR 3/4); clay loam; weak, medium subangular blocky structure, friable when moist; many fine roots; pockets and tongues of organic material transported from first horizon; gradual, smooth boundary.

22 - 46 cm Yellowish red (5YR 4/8); clay loam; moderate fine subangular blocky structure; slightly sticky when wet; many roots but less than above, channels and tongues of organic materials from first horizons; gradual, wavy boundary.

46 -132 cm Yellowish red (5YR 5/8) with few, faint, fine (10YR 6/6) brownish yellow mottlings; light silty clay loam; weak, fine, subangular blocky structure; friable when moist; common, fine roots; diffuse, wavy boundary.

132-140 cm Yellowish red (5YR 5/8) with common strong brown (7.5YR 5/8) and red (10 R 5/8) medium, faint mottlings; silty clay; slightly sticky, few, fine roots.

Appendix 3.1

Effect of centrifugation speed on concentration of Al determined in $CaCl_2$ - equilibrium solutions by the Aluminon method. (Mclean, 1965 pp 988-989).

At the time of development of experimental techniques it was noted that some supernatant solutions showed substantially higher Al concentration than expected on the basis of their pH. These samples generally had pH values from 4.7 to 5.2 and had been centrifuged at 300xg. To evaluate the effect of centrifugation, nine selected supernatants were centrifuged at 300xg, then at 1250xg and finally at 5000xg.

The results (Appendix table 1) showed that in solutions with higher pH values, the measured Al concentration was substantially reduced by centrifugation at 1250xg after centrifugation at 300xg. The solutions with pH values of 4.5 or below showed little change in measured concentration. A paired t-test showed a highly significant difference between the means at 300xg and 1250xg.

Centrifugation at still higher speeds did not result in further reductions of measured Al concentrations in high or low pH samples. A paired-t-test showed no significant difference between the means at 1,250xg and 5,000xg. On this basis it was concluded that centrifugation at 1,250xg was sufficient to remove finely precipitated $Al(OH)_3$ present in these supernatant solutions.

Appendix table 3.1:

The effect of centrifugation speed on measured Al concentrations in $CaCl_2$ equilibrium solutions.

		Centrifugation method		
Sample no.	pH	300xg	1250xg	5000xg
1	4.77	1.19	0.37	0.33
2	4.40	1.52	1.41	1.48
3	4.73	1.22	0.37	0.41
4	4.83	1.96	0.74	0.44
5	4.50	1.74	1.74	1.85
6	5.05	1.11	0.44	0.52
7	4.50	1.37	1.26	1.45
8	4.84	1.07	0.56	0.44
9	4.90	1.48	0.67	0.52
mean	:	1.41	.84	.83
mean difference	:	0.57	.015	
paired t-test	:	4.09**	.308ns	

Appendix table 3.2:

Equilibrium pH, pKsp of $Al(OH)_3$, R_{sol}, R_{ex} and the exchange constant for Ca and Al (K_{ex}) of four Puerto Rican soils, determined in 10^{-3} M $CaCl_2$ equilibration.

Sample no	pH	pKsp	R_{sol}	R_{ex}	K_{ex}
Pinas sandy loam:					
F39A	4.62	33.54	0.693	1.070	0.647
F39B	4.40	33.80	0.865	1.389	0.623
F39D	4.12	33.93	1.534	2.524	0.608
F39E	4.22	33.66	1.495	2.809	0.532
F39F	4.06	33.96	1.743	2.607	0.669
F39G	4.06	33.93	1.888	2.868	0.658
F12B	4.98	32.37	0.643	0.649	0.991
F12D	4.35	34.18	0.684	1.248	0.548
F12E	4.18	34.06	1.174	1.796	0.654
F12F	4.18	33.98	1.216	1.915	0.635
F12G	4.13	33.98	1.357	1.910	0.711
F02B	4.90	32.97	0.486	2.061	0.235
F18A	4.32	34.00	0.987	1.642	0.601
F18B	4.12	34.19	1.298	2.231	0.581
F23A	4.49	33.79	0.788	1.486	0.530
F23B	4.32	34.09	0.859	1.058	0.812
F30A	4.28	33.94	1.136	1.898	0.598
F30B	4.13	34.11	1.348	2.432	0.554
Humatas clay:					
C32A	4.52	33.46	0.690	0.935	0.738
C32B	4.08	34.15	1.150	2.035	0.565
C32D	4.12	33.95	1.296	2.292	0.565
C32E	4.13	33.90	1.336	2.426	0.551
C32F	4.11	34.00	1.263	2.356	0.536
C38B	4.38	33.82	0.876	1.466	0.598
C38D	4.10	34.06	1.454	2.526	0.576
C38E	4.02	34.14	1.503	2.825	0.532
C38F	4.02	34.15	1.538	2.845	0.541
C21A	4.40	33.37	1.019	1.145	0.890
C21B	4.01	34.40	1.105	1.901	0.581
C06B	4.20	34.12	0.991	1.705	0.581
C43B	4.33	33.95	0.793	1.317	0.602
C15B	4.20	34.00	1.117	1.913	0.584
C11A	4.68	33.00	0.715	0.891	0.802
C11B	4.04	34.25	1.371	2.234	0.614

Appendix table 3.2, continued.

Sample no	pH	pKsp	R_{sol}	R_{ex}	K_{ex}
Catalina clay:					
B24D	4.80	33.31	0.442	0.731	0.605
B24E	4.65	33.48	0.808	1.206	0.670
B24F	4.45	33.47	1.334	2.078	0.642
B24G	4.38	33.57	1.601	1.426	1.123
B40A	5.02	32.64	0.572	1.108	0.517
B40B	4.54	33.47	0.788	1.209	0.651
B40D	4.68	33.27	0.733	0.958	0.766
B40E	4.62	33.35	0.610	0.516	
B40F	4.49	33.45	1.000	1.063	0.940
B40G	4.47	33.71	1.138	2.168	0.525
B13B	4.88	32.90	0.569	0.679	0.838
B38A	4.85	32.76	0.726	0.714	
B38B	4.78	32.93	0.854	1.068	0.799
Los Guineos clay:					
J02A	4.75	32.70	0.836	1.001	0.835
J02B	4.55	33.68	0.713	1.294	0.552
J02D	4.42	33.76	1.102	1.811	0.608
J02E	4.38	33.70	1.767	2.747	0.643
J02F	4.35	33.68	2.243	3.802	0.590
J07A	5.00	32.42	0.530	0.759	0.698
J07B	4.59	33.75	0.640	1.268	0.505
J07D	4.44	33.64	1.358	2.244	0.605
J07E	4.45	33.56	2.448	3.966	0.617
J07F	4.36	33.71	2.458	4.230	0.581
J04A	4.96	32.28	0.733	0.820	0.894
J04B	4.50	33.77	0.860	1.605	0.536
J11A	4.80	32.72	0.890	1.094	0.813
J12A	4.64	33.10	0.951	1.366	0.696
J12B	4.53	33.62	0.905	1.551	0.584

Appendix table 3.3: Selected chemical properties of $CaCl_2$ and $Ca(OH)_2$ treated Carimagua topsoil samples (Chapter 3, experiment 1.).

Treatment		Replicate	KCl extractable, me/100g			$CaCl_2$ equilibrium solution			
$CaCl_2$ $Mx10^3$	$Ca(OH)_2$ me/100g		Ca	Mg	Al	pH	Ca $M/Lx10^3$	Mg $M/Lx10^3$	Al $M/Lx10^3$
1	0	1	0.25	0.01	3.45	4.00	0.61	0.22	0.20
5	0	1	0.40	0.01	3.25	3.96	1.94	0.55	0.35
10	0	1	0.55	0.01	3.10	3.99	6.89	0.30	0.51
1	0.22	1	0.15	0.05	3.67	4.08	1.08	0.15	1.32
5	0.22	1	0.30	0.04	3.39	3.98	4.26	0.04	0.56
10	0.22	1	0.50	0.03	3.39	3.97	5.42	0.04	0.60
1	0.44	1	0.25	0.05	3.25	4.16	1.32	0.15	0.21
5	0.44	1	0.40	0.04	3.13	4.02	4.39	0.04	0.40
10	0.44	1	0.60	0.03	3.02	4.00	7.62	0.04	0.64
1	0.87	1	0.55	0.05	3.25	4.34	1.61	0.14	0.08
5	0.87	1	0.65	0.04	2.86	4.13	4.44	0.04	0.22
10	0.87	1	0.80	0.03	2.85	4.11	7.90	0.04	0.37
1	1.75	1	1.37	0.02	2.10	4.97	2.01	0.09	0.003
5	1.75	1	1.45	0.01	2.05	4.68	4.89	0.18	--
10	1.75	1	1.50	0.01	2.10	4.44	8.66	0.32	0.05
1	3.50	1	2.77	0.02	1.00	5.78	1.67	0.06	0.001
5	3.50	1	2.65	0.02	0.95	5.28	5.08	0.16	0.002
10	3.50	1	2.82	0.02	1.05	5.16	11.17	0.30	0.004
1	7.0	1	6.00	0.02	0.05	7.12	1.73	0.25	--
5	7.0	1	5.85	0.02	0.03	6.68	5.27	0.25	--
10	7.0	1	5.65	0.02	0.01	6.85	9.29	0.24	--

Appendix table 3.3, continued

Treatment $CaCl_2$ $Mx10^3$	Treatment $Ca(OH)_2$ me/100g	Replicate	KCl extractable, me/100g Ca	Mg	Al	pH	$CaCl_2$ equilibrium solution Ca $M/Lx10^3$	Mg $M/Lx10^3$	Al $M/Lx10^3$
1	0	2	0.25	0.01	3.35	4.05	0.61	0.16	0.20
5	0	2	0.42	0.01	3.15	4.01	3.44	0.20	0.35
10	0	2	0.62	0.01	3.10	4.05	7.56	0.39	0.51
1	0.22	2	0.20	0.04	3.37	4.06	1.03	0.15	0.33
5	0.22	2	0.30	0.04	3.39	3.97	4.30	0.04	0.57
10	0.22	2	0.55	0.03	3.30	3.96	7.35	0.04	0.78
1	0.44	2	0.30	0.05	3.42	4.15	1.32	0.15	0.21
5	0.44	2	0.40	0.03	3.04	4.03	4.39	0.03	0.42
10	0.44	2	0.55	0.03	3.13	4.00	7.35	0.04	0.62
1	0.87	2	0.55	0.05	3.19	4.34	1.61	0.13	0.08
5	0.87	2	0.65	0.04	2.89	4.15	4.39	0.04	0.02
10	0.87	2	0.75	0.03	2.88	4.12	7.62	0.04	0.40
1	1.75	2	1.42	0.02	2.15	4.70	1.55	0.09	0.007
5	1.75	2	1.52	0.01	2.10	4.62	4.54	0.18	0.02
10	1.75	2	1.62	0.01	2.25	4.42	8.97	0.41	0.08
1	3.50	2	2.77	0.02	1.00	5.65	1.61	0.59	0.001
5	3.50	2	2.65	0.02	1.05	5.55	4.89	0.17	0.002
10	3.50	2	2.75	0.02	1.00	5.12	8.97	0.27	0.006
1	7.0	2	5.92	0.02	0.05	6.84	1.94	0.04	--
5	7.0	2	5.85	0.02	0.02	7.05	5.27	0.12	--
10	7.0	2	5.75	0.02	0.01	6.58	9.63	0.24	--

Appendix table 3.4: Selected chemical properties of Carimagua topsoil samples, pre-treated with $CaCl_2$ and $Ca(OH)_2$, after washing and drying. (Chapter 3, experiment 2).

Pre-treatment		Replicate	KCl extractable, me/100g			10^{-3} $CaCl_2$ equilibrium solution			
$CaCl_2$ M/Lx10^3	$Ca(OH)_2$ me/100g		Ca	Mg	Al	pH	Ca M/Lx10^3	Mg M/Lx10^3	Al M/Lx10^6
1	0	1	0.25	0.01	3.45	4.25	0.54	0.06	57.8
5	0	1	0.40	0.01	3.25	4.31	0.71	0.04	46.2
10	0	1	0.55	0.01	3.10	4.40	0.79	0.04	30.2
1	0.22	1	0.15	0.05	3.67	4.27	0.56	0.06	53.7
5	0.22	1	0.30	0.04	3.39	4.32	0.62	0.05	37.0
10	0.22	1	0.50	0.03	3.39	4.32	0.75	0.04	28.9
1	0.44	1	0.25	0.05	3.25	4.32	0.58	0.06	36.3
5	0.44	1	0.40	0.04	3.13	4.38	0.69	0.05	30.7
10	0.44	1	0.60	0.03	3.02	4.42	0.85	0.05	14.1
1	0.87	1	0.55	0.05	3.25	4.42	0.60	0.06	20.5
5	0.87	1	0.65	0.04	2.86	4.43	0.75	0.05	16.7
10	0.87	1	0.80	0.03	2.85	4.49	0.82	0.04	12.9
1	1.75	1	1.37	0.02	2.10	4.72	0.81	0.05	4.4
5	1.75	1	1.45	0.02	2.05	4.70	1.01	0.04	6.3
10	1.75	1	1.50	0.01	2.10	4.68	1.09	0.04	6.7
1	3.50	1	2.77	0.02	1.00	5.15	0.84	0.04	1.1
5	3.50	1	2.65	0.02	0.95	5.13	1.09	0.04	0.7
10	3.50	1	2.82	0.01	1.05	5.13	1.17	0.04	1.8
1	7.0	1	6.00	0.02	0.05	5.75	1.17	0.04	-
5	7.0	1	5.85	0.02	0.03	5.76	1.17	0.04	-
10	7.0	1	5.65	0.01	0.01	5.80	1.31	0.04	-

Appendix table 3.4, continued.

Pre-treatment $CaCl_2$ / $CaCl_2$	Pre-treatment $Ca(OH)_2$ me/100g	Replicate	KCl extractable, me/100g Ca	KCl extractable, me/100g Mg	KCl extractable, me/100g Al	10^{-3} $CaCl_2$ equilibrium solution pH	Ca M/Lx10^3	Mg M/Lx10^3	Al M/Lx10^6
1	0	2	0.25	0.01	3.35	4.24	0.56	0.06	54.8
5	0	2	0.42	0.01	3.15	4.34	0.63	0.04	34.4
10	0	2	0.62	0.01	3.10	4.33	0.76	0.04	32.5
1	0.22	2	0.20	0.04	3.37	4.30	0.56	0.06	51.9
5	0.22	2	0.30	0.04	3.39	4.32	0.64	0.05	38.9
10	0.22	2	0.55	0.03	3.30	4.38	0.75	0.05	33.3
1	0.44	2	0.30	0.05	3.42	4.35	0.58	0.07	38.1
5	0.44	2	0.40	0.03	3.04	4.38	0.75	0.05	35.2
10	0.44	2	0.55	0.03	3.13	4.40	0.78	0.04	32.6
1	0.87	2	0.55	0.05	3.19	4.42	0.64	0.06	21.5
5	0.87	2	0.65	0.04	2.89	4.45	0.72	0.04	17.8
10	0.87	2	0.75	0.03	2.88	4.50	0.82	0.04	15.9
1	1.75	2	1.42	0.02	2.15	4.72	0.84	0.05	4.8
5	1.75	2	1.52	0.01	2.10	4.71	0.94	0.04	6.3
10	1.75	2	1.62	0.01	2.25	4.68	1.09	0.04	15.9
1	3.50	2	2.77	0.02	1.00	5.14	0.91	0.04	2.6
5	3.50	2	2.65	0.02	1.05	5.10	1.09	0.04	1.1
10	3.50	2	2.75	0.02	1.00	5.07	1.17	0.04	1.8
1	7.0	2	5.92	0.02	0.05	5.76	1.09	0.04	-
5	7.0	2	5.85	0.02	0.02	5.75	1.13	0.04	-
10	7.0	2	5.75	0.02	0.01	5.75	1.22	0.03	-

Appendix table 3.5:

Equilibrium pH, pKsp of $Al(OH)_3$, R_{sol}, R_{ex} and the exchange constant for Ca and Al (K_{ex}) of selected samples from the Eastern plains of Colombia.

$Al(OH)_3$ POTENTIAL AND EXCHANGE RELATION

No.	pH-$CaCl_2$	pKsp	R_{sol}	R_{ex}	K_{ex}
C118	4.21	33.46	1.597	3.152	0.507
C119	4.38	33.31	1.574	3.298	0.477
C201	4.30	33.73	1.422	2.991	0.475
C202	4.25	33.60	1.581	3.057	0.517
C204	4.30	33.63	1.605	2.236	0.718
C401	4.45	33.35	1.495	2.633	0.568
C507	4.12	33.82	1.927	3.491	0.552

Appendix table 4.1: Analysis of variance of dry matter yields (g/pot) of top growth of corn grown in the greenhouse.

Treatment no.	Replicates 1	2	3	4	Mean
1	9.07	8.15	8.60	7.69	8.38 c
2	9.77	10.55	11.78	10.72	10.71 ab
3	10.28	10.16	11.41	10.21	10.51 ab
4	10.60	10.87	9.83	9.51	10.20 ab
5	9.08	7.61	9.54	5.92	8.04 c
6	10.76	12.12	10.05	9.89	10.70 ab
7	14.03	11.48	9.15	11.78	11.61 a
8	11.95	11.72	10.71	11.06	11.36 a
9	8.72	10.20	10.41	8.73	9.51 bc
10	9.80	10.94	11.01	11.00	10.69 ab

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	39	83.588		
Treat.	9	50.558	5.617	5.18
Reps.	3	3.753	1.251	1.15
Error	27	29.276	1.084	

c.v. = 0.102

Appendix table 4.2: Analysis of variance of dry matter weight (g/pot) of roots of corn grown in the greenhouse.

Treatment no.	Replicates 1	2	3	4	Mean
1	5.72	4.21	5.12	4.72	4.94 de
2	7.02	5.18	5.30	7.15	6.16 bc
3	8.64	8.29	7.40	7.70	8.01 a
4	6.19	5.67	4.35	5.12	5.33 cd
5	3.90	3.82	5.00	3.90	4.15 e
6	5.73	5.64	4.42	6.34	5.53 bcd
7	6.92	6.91	5.71	6.27	6.45 b
8	6.36	6.57	5.66	5.68	6.07 bc
9	5.89	4.76	5.50	3.79	4.98 de
10	5.57	7.12	5.78	6.44	6.22 bc

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	39	56.859		
Treat.	9	40.314	4.479	9.29
Reps.	3	3.041	1.014	2.10
Error	27	13.004	0.482	

c.v. = 0.120

Appendix table 4.3: Analysis of variance of calcium uptake (mg/pot) by corn grown in the greenhouse.

Treatment	Replicates 1	2	3	4	Mean
1	4.99	6.68	7.40	7.00	6.52 de
2	12.70	16.46	10.60	14.26	13.50 bc
3	19.84	16.36	22.36	20.82	19.84 ab
4	5.94	4.35	4.72	4.38	4.85 de
5	2.54	2.74	4.58	3.55	3.35 e
6	3.65	6.06	6.03	6.23	5.49 de
7	27.07	18.37	19.21	21.79	21.61 a
8	12.07	18.17	19.92	16.92	16.77 b
9	7.50	8.16	9.37	7.15	8.13 d
10	9.50	12.14	13.87	13.64	12.30 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	39	1690.31		
Treat.	9	1545.78	171.75	34.41
Reps.	3	9.775	3.258	0.65
Error	27	134.76	4.991	

c.v. = 0.199

Appendix table 4.4: Analysis of variance of magnesium uptake (Mg/pot) by corn grown in the greenhouse.

Treatment no.	Replicates 1	2	3	4	Mean
1	23.6	20.4	17.2	16.4	19.4 c
2	33.2	25.6	20.6	24.1	25.9 bc
3	28.8	17.7	24.3	24.5	23.8 bc
4	36.0	40.2	45.2	48.5	42.5 a
5	47.2	46.4	35.3	48.8	44.4 a
6	55.9	51.9	31.2	54.4	48.8 a
7	35.0	29.4	27.4	36.5	32.1 b
8	33.5	23.4	30.0	32.2	30.0 b
9	26.2	33.2	25.3	24.4	27.3 bc
10	24.5	27.4	34.1	33.0	29.7 b

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	39	4317.98		
Treat.	9	3298.49	366.50	12.03
Reps.	3	197.31	65.77	2.15
Error	27	822.19	30.45	

c.v. = 0.170

Appendix table 4.5: Analysis of variance of phosphorus uptake (mg/pot) by corn grown in the greenhouse.

Treatment no.	Replicates 1	2	3	4	Mean
1	21.8	16.7	15.5	18.1	18.0 cde
2	20.5	22.2	26.5	21.4	22.6 ab
3	21.1	20.8	19.4	20.4	20.4 bc
4	18.0	17.4	18.7	20.9	18.7 cd
5	16.8	14.4	17.2	12.7	15.3 e
6	21.5	18.2	17.6	19.3	19.1 c
7	27.4	23.5	22.9	26.5	25.1 a
8	21.5	19.9	21.4	22.8	21.4 bc
9	13.1	18.4	16.7	15.3	15.9 de
10	17.6	20.8	19.8	22.6	20.2 bc

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	39	439.44		
Treat.	9	317.91	35.32	8.10
Reps.	3	3.79	1.26	0.29
Error	27	117.73	4.36	

c.v. = 0.106

Appendix table 4.6 : Analysis of variance of dry matter weight of seedlings (g) sampled from the 1970 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	0.30	0.54	0.45	0.69	0.49 a
2	0.44	0.62	0.95	1.04	0.76 a
3	0.76	1.02	1.30	1.25	1.08 a
4	2.62	2.69	2.35	3.01	2.66 b
5	5.74	4.60	3.72	3.00	4.26 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	45.338		
Treat.	4	40.433	10.108	25.46
Reps.	3	0.143	0.048	0.12
Error	12	4.762	0.040	

c.v. = 0.340

Appendix table 4.7: Analysis of variance of calcium content (%Ca) of seedlings sampled from the 1970 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	0.30	0.34	0.38	0.32	0.33
2	0.50	0.48	0.48	0.39	0.46
3	0.35	0.45	0.42	0.42	0.41
4	0.45	0.70	0.64	0.60	0.60
5	0.78	0.76	0.68	0.94	0.79

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	0.6000		
Treat.	4	0.5141	0.1285	21.47
Reps.	3	0.0140	0.0047	0.78
Error	12	0.0718	0.0060	

c.v. = 0.149

Appendix table 4.8: Analysis of variance of calcium uptake by seedlings (mg/plant) sampled from the 1970 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	1.0	2.9	1.7	2.2	1.7 a
2	2.2	3.0	4.6	4.0	3.4 a
3	2.7	4.8	3.0	5.3	3.9 a
4	11.8	18.8	15.0	18.1	15.9 b
5	44.8	34.9	25.4	28.2	33.3 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	3117.72		
Treat.	4	2854.45	713.61	35.72
Reps.	3	23.57	7.86	0.39
Error	12	239.71	19.97	

c.v. = 0.383

Appendix table 4.9: Analysis of variance of phosphorus contents of seedlings (% P) sampled from the 1970 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	0.29	0.31	0.27	0.27	0.28
2	0.30	0.30	0.26	0.23	0.27
3	0.26	0.26	0.21	0.22	0.24
4	0.24	0.20	0.21	0.19	0.21
5	0.30	0.32	0.23	0.24	0.27

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	0.0281		
Treat.	4	0.0146	0.0036	13.20
Reps.	3	0.0101	0.0034	12.18
Error	12	0.0033	0.0003	

c. v. = 0.065

Appendix table 4.10: Analysis of variance of calcium contents of leaves (%Ca) sampled at tasseling time from the 1970 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	0.28	0.34	0.31	0.34	0.32 a
2	0.39	0.38	0.39	0.28	0.36 ab
3	0.36	0.50	0.51	0.56	0.48 bc
4	0.70	0.52	0.42	0.56	0.55 cd
5	0.72	0.52	0.78	0.62	0.66 d

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	0.4244		
Treat.	4	0.3117	0.0779	8.60
Reps.	3	0.0040	0.0013	0.14
Error	12	0.1087	0.0090	

c. v. = 0.2008

Appendix table 4.11: Analysis of variance of phosphorus contents of leave (%P) sampled at tasseling time from the 1970 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	0.24	0.24	0.25	0.28	0.25
2	0.26	0.26	0.25	0.25	0.26
3	0.25	0.24	0.25	0.24	0.25
4	0.24	0.24	0.24	0.21	0.23
5	0.22	0.22	0.22	0.23	0.22

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	0.00506		
Treat.	4	0.00303	0.00076	4.52
Reps.	3	0.00001	0.000005	0.02
Error	12	0.00201	0.00017	

c. v. = 0.0535

Appendix table 4.12: Total dry matter yields (to/ha) of above ground parts of corn in the 1970 corn - experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	2.07	1.86	2.81	2.75	2.37 a
2	2.82	3.12	3.85	3.59	3.35 a
3	2.87	3.17	4.18	3.74	3.49 a
4	5.75	4.56	4.29	4.40	4.75 b
5	7.35	4.96	4.91	5.75	5.74 b

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	35.289		
Treat.	4	27.675	6.919	12.88
Reps.	3	1.173	0.391	0.72
Error	12	6.442	0.537	

c. v. = 0.186

Appendix table 4.13: Analysis of variance of dry matter weight of seedlings (g) sampled from the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	3.68	5.55	4.30	4.51 a
2	5.65	9.55	8.40	7.87 b
3	7.15	10.83	10.30	9.43 bc
4	10.95	11.00	8.55	10.17 bc
5	11.15	11.90	10.55	11.20 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	104.07		
Treat.	4	81.47	20.37	13.86
Reps.	2	10.85	5.42	3.69
Error	8	11.75	1.47	

c. v. = 0.140

Appendix table 4.14: Analysis of variance of calcium contents of seedlings (%Ca) sampled from the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	0.49	0.50	0.24	0.41 a
2	0.51	0.77	0.60	0.63 ab
3	0.64	0.80	0.68	0.71 b
4	0.76	0.83	0.83	0.81 b
5	0.78	0.65	1.02	0.82 b

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	0.4987		
Treat.	4	0.3329	0.0832	4.37
Reps.	2	0.0137	0.0068	0.35
Error	8	0.1522	0.0190	

c. v. = 0.205

Appendix table 4.15: Analysis of variance of calcium uptake (mg/plant) by seedlings sampled from the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	18	28	11	19.0 a
2	29	73	50	50.1 b
3	46	87	70	67.7 bc
4	83	92	71	82.0 cd
5	87	78	108	91.0 d

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	12411		
Treat.	4	9752	2437	11.10
Reps.	2	902	451	2.05
Error	8	1757	220	

c. v. = 0.239

Appendix table 4.16: Analysis of variance of phosphorus contents (%P) of seedlings sampled from the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	0.20	0.23	0.24	0.22
2	0.17	0.14	0.16	0.16
3	0.15	0.14	0.14	0.14
4	0.15	0.13	0.14	0.14
5	0.14	0.12	0.14	0.13

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	0.0181		
Treat.	4	0.0162	0.0041	22.3
Reps.	2	0.0004	0.0002	1.13
Error	8	0.0014	0.0002	

c. v. = 0.085

Appendix table 4.17: Analysis of variance of calcium contents of leaves (%Ca) sampled at inflorescence from the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	0.32	0.38	0.56	0.42 a
2	0.59	0.56	0.72	0.65 b
3	0.56	0.70	0.92	0.72 bc
4	0.72	0.66	1.05	0.81 cd
5	0.76	0.85	0.96	0.86 d

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	0.5669		
Treat.	4	0.3531	0.0883	17.82
Reps.	2	0.1742	0.0871	17.58
Error	8	0.0396	0.0049	

c. v. = 0.102

Appendix table 4.18: Analysis of variance of phosphorus contents of leaves (%P) sampled at inflorescence from the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	0.21	0.19	0.19	0.20
2	0.22	0.19	0.17	0.19
3	0.20	0.20	0.17	0.19
4	0.18	0.21	0.24	0.21
5	0.22	0.23	0.21	0.22

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	0.00604		
Treat.	4	0.00191	0.00048	0.98
Reps.	2	0.00028	0.00014	0.29
Error	8	0.00385	0.00048	

c. v. = 0.109

Appendix table 4.19: Analysis of variance of grain yields (to/ha) of the 1970 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	1.30	0.96	1.00	1.09 a
2	1.57	1.84	1.28	1.56 b
3	1.81	2.01	1.72	1.84 bc
4	1.89	1.69	2.04	1.87 bc
5	1.93	2.39	2.13	2.15 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	2.385		
Treat.	4	1.946	0.487	10.08
Reps.	2	0.052	0.026	0.53
Error	8	0.386	0.048	

c. v. = 0.129

Appendix table 4.20: Analysis of variance of dry matter weight (g) of seedlings sampled from the 1971 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	4.00	3.22	4.28	3.61	3.78 a
2	4.87	4.75	4.41	4.97	4.75 bc
3	5.95	5.01	5.34	4.55	5.21 c
4	5.65	4.68	5.21	5.17	5.18 c
5	4.65	4.06	4.07	4.94	4.43 b

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	8.556		
Treat.	4	5.650	1.412	9.70
Reps.	3	1.161	0.389	2.65
Error	12	1.745	0.145	

c.v. = 0.082

Appendix table 4.21: Analysis of variance of calcium contents of seedlings (%Ca) sampled from the 1971 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	0.54	0.58	0.62	0.58	0.58 a
2	0.73	0.81	0.73	0.73	0.75 b
3	0.84	0.91	0.84	0.78	0.84 c
4	0.84	1.04	0.91	0.94	0.93 d
5	1.04	1.14	1.10	1.01	1.07 e

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	0.6003		
Treat.	4	0.5529	0.1382	91.08
Reps.	3	0.0292	0.0097	6.41
Error	12	0.0182	0.0015	

c. v. = 0.047

Appendix table 4.22: Analysis of variance of calcium uptake by seedlings (mg/plant) sampled from the 1971 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	21.6	18.7	26.5	20.9	21.9 a
2	34.9	38.5	32.2	36.3	35.5 b
3	50.0	45.6	44.9	35.5	44.0 c
4	47.5	48.7	47.4	48.6	48.1 c
5	48.4	46.2	44.8	49.9	47.3 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	2100.1		
Treat.	4	1918.2	479.6	44.05
Reps.	3	12.9	4.3	0.30
Error	12	169.0	14.1	

c.v. = 0.095

Appendix table 4.23: Analysis of variance of phosphorus contents of seedlings (%P) sampled from the 1971 corn experiment.

Treatment No.	Replicates 1	2	3	4	Mean
1	0.31	0.31	0.22	0.29	0.28
2	0.23	0.31	0.27	0.25	0.27
3	0.27	0.23	0.26	0.27	0.26
4	0.27	0.26	0.25	0.24	0.25
5	0.27	0.27	0.29	0.27	0.27

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	0.01302		
Treat.	4	0.00217	0.00054	0.65
Reps.	3	0.00090	0.00030	0.36
Error	12	0.00995	0.00083	

c.v. = 0.109

Appendix table 4.24: Analysis of variance of grain yields (to/ha) of the 1971 corn experiment.

Treatment no.	Replicates 1	2	3	4	Mean
1	1.26	0.86	1.75	0.73	1.15 a
2	1.55	1.43	3.30	1.87	2.04 b
3	2.32	1.59	2.20	1.87	2.00 b
4	2.44	2.08	2.48	1.75	2.19 b
5	2.24	2.04	2.44	2.24	2.24 b

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	19	6.766		
Treat.	4	3.145	0.786	6.21
Reps.	3	2.101	0.701	5.53
Error	12	1.519	0.0127	

c.v. = 0.185

Appendix table 4.25: Analysis of variance of dry matter weight of seedlings (g) sampled from the 1971 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	4.41	5.16	5.55	5.04 a
2	6.86	8.53	6.99	7.46 b
3	10.37	7.99	7.35	8.57 b
4	8.38	9.03	10.39	9.27 b
5	9.83	9.17	9.16	9.39 b

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	48.531		
Treat.	4	38.670	9.668	7.86
Reps.	2	0.024	0.012	0.00
Error	8	9.837	1.230	

c.v. = 0.140

Appendix table 4.26: Analysis of variance of calcium contents (%Ca) of seedlings sampled from the 1971 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	0.48	0.44	0.46	0.46 a
2	0.64	0.56	0.65	0.62 b
3	0.71	0.75	0.76	0.74 b
4	0.94	0.90	0.96	0.93 c
5	0.86	0.99	0.70	0.85 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	0.47440		
Treat.	4	0.42327	0.10582	17.04
Reps.	2	0.00148	0.00074	0.11
Error	8	0.04965	0.00621	

c.v. = 0.109

Appendix table 4.27: Analysis of variance of calcium uptake by seedlings (mg/plant) sampled from the 1971 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	21.6	22.7	25.5	23.3 a
2	43.9	47.8	45.4	45.7 b
3	73.6	59.9	55.9	63.1 b
4	78.8	81.3	99.7	86.6 c
5	84.5	90.8	64.1	79.8 c

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	8826.7		
Treat.	4	7988.4	1997.1	19.49
Reps.	2	18.7	9.4	0.09
Error	8	819.5	102.4	

c. v. = 0.169

Appendix table 4.28: Analysis of variance of phosphorus contents of seedlings (%P) sampled from the 1971 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	0.18	0.16	0.18	0.17
2	0.17	0.19	0.12	0.16
3	0.17	0.17	0.17	0.17
4	0.18	0.19	0.17	0.18
5	0.22	0.17	0.19	0.19

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	0.00617		
Treat.	4	0.00184	0.00046	1.04
Reps.	2	0.00081	0.00041	0.92
Error	8	0.00352	0.00044	

c. v. = 0.120

Appendix table 4. 29: Analysis of variance of grain yields (to/ha) of the 1971 sorghum experiment.

Treatment no.	Replicates 1	3	4	Mean
1	2.65	0.78	2.15	1.86 a
2	2.46	2.42	1.50	2.13 a
3	2.92	1.74	1.64	2.10 a
4	2.70	2.83	2.42	2.65 a
5	2.83	2.65	2.56	2.68 a

Analysis of variance

Source	d.f.	Sums of squares	Mean square	F
Total	14	5.191		
Treat.	4	1.587	0.397	1.42
Reps.	2	1.380	0.690	2.48
Error	8	1.222	0.278	

c. v. = 0.231

Appendix Table 4.30: The effects of 0 and 8 to/ha lime treatments on Zn contents (ppm Zn) of seedlings in corn and sorghum experiments of 1971.

Replicates No.	Corn seedlings		Sorghum seedlings	
	0 to/ha lime	8 to/ha lime	0 to/ha lime	8 to/ha lime
1	26	19	34	24
2	25	21		
3	27	20	38	23
4	24	20	34	25
Paired t-test	t=6.11**		t=6.35*	
t,.05	3.18		4.30	
t,.01	5.84		9.92	

* significant at p=0.05
** significant at p=0.01

Appendix table 4.31: Selected chemical analyses of topsoil samples taken in 1970 from the corn experiment.

Lime rate to/ha	Replicates 1	2	3	4	Mean
			pH in 10^{-3} M $CaCl_2$		
0	4.50	4.60	4.45	4.47	4.50
1	4.68	4.51	4.71	4.51	4.60
2	5.31	5.02	4.80	4.82	4.99
4	6.00	5.79	6.08	4.96	5.75
8	7.19	5.64	6.11	5.97	6.23
			Exchangeable Al		
0	3.14	3.05	3.49	3.70	3.34
1	2.29	2.77	1.93	3.29	2.24
2	0.62	1.21	1.97	1.95	1.37
4	0.05	0	0	1.25	0.39
8	0	0.18	0	0	0.04
			Exchangeable Ca		
0	0.95	1.33	0.85	0.63	0.94
1	1.98	1.48	2.58	1.06	1.77
2	4.15	3.33	2.35	2.35	3.04
4	6.25	6.50	7.88	3.03	5.91
8	10.00	5.00	7.05	8.15	7.55
			R_{sol}		
0	1.22	0.83	1.19	1.32	1.14
1	0.62	0.85	0.52	0.95	0.73
2	-	0.25	0.47	0.23	0.32
			R_{ex}		
0	1.91	1.61	2.11	2.48	2.02
1	1.20	1.47	1.00	1.83	1.37
2	0.54	0.75	1.04	1.04	0.84
4	0.20	0.05	0.05	0.85	0.28
8	0.05	0.33	0.14	0.05	0.14
			pH-1/2pCa		
0	2.71	2.85	2.66	2.67	2.72
1	2.94	2.79	3.01	2.75	2.87
2	3.67	3.38	3.12	3.16	3.33
4	4.44	4.39	4.53	3.32	4.17
8	5.74	4.00	4.54	4.38	4.66

Appendix table 4.32: Selected chemical analyses of topsoil samples taken in 1970 from the sorghum experiment.

Lime rate to/ha	Replicates 1	2	3	4	Mean[1)]
	pH in 10^{-3} M $CaCl_2$				
0	4.48	6.01	4.48	4.57	4.51
1	4.71	6.15	4.81	4.83	4.78
2	5.05	4.80	4.93	4.89	4.96
4	5.67	5.52	5.83	6.35	5.95
8	6.43	5.01	7.20	5.85	6.49
	Exchangeable Al				
0	3.76	0	3.61	3.24	3.53
1	2.83	0	1.90	2.15	2.29
2	2.09	2.22	1.27	1.96	1.77
4	0.23	0.87	0	0	0.07
8	0	1.28	0	0.02	0
	Exchangeable Ca				
0	0.75	6.60	0.55	0.95	0.75
1	2.10	8.40	2.30	2.25	2.21
2	2.45	2.00	3.30	2.60	2.78
4	5.90	3.65	7.05	10.00	7.65
8	8.65	3.50	10.00	7.05	8.57
	R_{sol}				
0	1.24	-	1.44	0.95	1.21
1	0.49	-	0.53	0.62	0.55
2	0.31	0.50	0.49	0.50	0.43
	R_{ex}				
0	2.31	0.05	2.63	1.94	2.29
1	1.27	0.05	1.04	1.10	1.14
2	1.05	1.17	0.77	1.01	0.94
4	0.34	0.64	0.05	0.05	0.15
	pH - 1/2pCa				
0	2.63	4.43	2.61	2.86	2.70
1	3.00	4.57	3.17	3.13	3.10
2	3.32	3.11	3.26	3.22	3.27
4	4.06	3.88	4.23	4.83	4.37
8	4.89	3.35	5.75	4.29	4.98

1) Mean of replicates 1, 3 and 4.