

200 T19

✓
SOIL ACIDITY AND LIMING
IN NATAL / SR

200 T19 A

NEVILLE GEORGE REEVE .

(M.Sc. Agric. (Natal))

N.T. Octa Thesis (Ph.D. in Soil Science) — University
of Natal, Pietermaritzburg, 1970. —
Loan copy in Agricultural Library.

(Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy
in the
Department of Soil Science
University of Natal)

339 SA 128 TX
Pietermaritzburg, 1970. (October) 1970. ^{to} ^{to}

PP



D

CONTENTS

ABSTRACT	1
INTRODUCTION	3
1 EFFECTS OF ALUMINIUM TOXICITY AND PHOSPHORUS FIXATION ON CROP GROWTH ON OXISOLS IN NATAL	5
2 LIME REQUIREMENTS OF NATAL OXISOLS BASED ON EXCHANGEABLE ALUMINIUM	20
3 CATION EXCHANGE CAPACITY AND EXCHANGEABLE ALUMINIUM IN NATAL OXISOLS	32
4 AMELIORATION OF SUBSOIL ACIDITY IN NATAL OXISOLS	47
GENERAL DISCUSSION	60
APPENDICES	
1 Sample localities of the soils studied	65
2 Detailed results of pot experiment in paper 1	66
3 Detailed chemical analysis of eight Natal Oxisols	68
4 Miscellaneous data cited in paper 4	72
ACKNOWLEDGEMENTS	75
LITERATURE CITED	76

ABSTRACT

1. Effects of Aluminium Toxicity and Phosphorus Fixation on Crop Growth on Oxisols in Natal

Simple, routine methods for estimating exchangeable Al and P fixing capacity of acid soils are described. A glass-house study on eight Oxisols revealed marked growth response of 'trudan' (Sorghum sudanense) to amelioration by lime, gypsum and Ca silicate which is ascribed to elimination of Al toxicity rather than to improved P availability. Growth response to ameliorants took place up to the point of elimination of exchangeable Al after which a significant reduction in yield occurred. P fixation is shown to be a major fertility limitation in the soils studied. Since no apparent relationship between P fixing capacity and exchangeable Al existed and since lime did not decrease P fixation despite its ability to eliminate soluble Al, it is concluded that P fixation is an adsorption reaction rather than a precipitation reaction. Although the soils studied are all capable of fixing large quantities of P considerable variation exists between them. Fertilizer recommendations based only on an estimate of the available P in the soil per se could thus be in serious error.

2. Lime Requirements of Natal Oxisols based on Exchangeable Aluminium

The exchangeable Al status of eight Natal Oxisols is a suitable criterion for the measurement of lime requirement defined as the amount of lime necessary for maximum crop production. The principal function of lime in these soils is to eliminate Al toxicity; it has little or no effect on P availability. A "critical value" for exchangeable Al below which 'trudan' did not respond to lime application was found. On the average the amount of lime necessary for maximum growth and exchangeable Al control was approximately one sixth the amount required to raise the soil pH to 6.5.

3. Cation Exchange Capacity and Exchangeable Aluminium in Natal Oxisols

Positive charges in acid soils reduce CEC at low electrolyte concentration probably by double layer interaction. The resultant net CEC (determined by washing soil free of salt with water) is the effective CEC under field conditions and the difference between net CEC and exchangeable bases is accordingly a convenient measure of exchangeable Al. A reaction scheme is proposed which relates the large pool of non-exchangeable Al (extractable with \underline{N} $\text{NH}_4\text{OAc-pH4}$) in these soils to the relatively small amounts of exchangeable Al; this reaction scheme is governed primarily by net CEC and exchangeable bases rather than by pH.

4. Amelioration of Subsoil Acidity in Natal Oxisols.

The large pH dependent CEC in Natal Oxisols effectively limits the downward movement of lime. Although heavy fertilisation, particularly with acid forming nitrogenous fertilizers increases the rate of movement, relatively small amounts of Ca salts having little ability to neutralise subsoil exchangeable Al could be leached from limed topsoil. In contrast, bases equivalent to 80% of that applied leached rapidly from gypsum treated topsoil. Although gypsum did not eliminate subsoil exchangeable Al, it was considerably more efficient than lime in this respect. However, gypsum caused severe loss of exchangeable Mg which could have serious nutritional consequences if not corrected.

INTRODUCTION

Soils of the Highlands of Natal constitute a major soil group within the region. Derived mainly from shale (Griffin, Clovelly, Lidgetton and Farmhill series), dolerite (Balmoral series) or shale/dolerite mixtures (Hutton and Farningham series), these soils occur at altitudes mostly above 1200m, in areas having an average annual rainfall of nearly 1000mm and average maximum and minimum daily temperatures of 16.4 and -1.9°C in midwinter and 24.2 and 12.2°C in midsummer. The natural vegetation is grassland (Themeda-Trachypogon) with numerous patches of Yellow Wood (Podocarpus) forest on steep slopes, in ravines and along stream banks (van der Eyk, MacVicker and de Villiers, 1969). The clay fraction of these soils is mostly kaolinite with free sesquioxides, gibbsite and some 2:1 layer minerals, (mainly pedogenic chlorite; de Villiers, 1964; Verster and de Villiers, 1968; de Villiers and Jackson, 1967).

"The combined effects of a humid climate and long exposure are evident in the acid, highly leached and highly weathered soils of this zone... These deep, permeable and well aggregated soils are stable under cultivation. Due to their high infiltration capacity surface runoff is negligible. Under grass they remain moist for a greater part of the year and plant available moisture is high. From the standpoint of their excellent physical characteristics and favourable moisture regime, they are prime arable soils with a very low erosion hazard, provided normal conservation practices are applied in accordance with the steepness of the land. Although the low natural nutrient content associated with their strongly acid character represents a major limiting factor to profitable cropping..., it has been demonstrated...that these and other soils of the Highlands and Midland Mistbelt are potentially highly productive if heavily fertilized... By virtue of abundant rainfall, low incidence of drought and low general erosion hazard, this zone is pre-eminently suited to intensive agricultural utilisation... The economics of

intensification will, however, remain uncertain until research has provided a firmer foundation than that which presently exists for assessing fertility status, making accurate fertilizer recommendations, ameliorating soil acidity, and preventing further acidification of soils under cultivation" (van der Eyk, et al., 1969).

With the above motivation, this work is directed primarily towards understanding the nature and effects of soil acidity in the Highlands with a view to practical amelioration thereof, on the grounds that the harmful effects of soil acidity must be corrected as a prerequisite to the establishment of a sound fertility status.

The soils selected for study, classified after Verster and de Villiers (1968) as oxisols, represent a cross section of the soils found in the Highlands of Natal and were sampled at widely separated sites within the sub-region (appendix 1). Profile descriptions and other information regarding the soil series involved are given by van der Eyk, et al., (1969) and are therefore not presented here. Since the work undertaken falls naturally into a number of distinct though related topics, it is convenient to present the findings in the form of a series of scientific papers.

PAPER 1

EFFECTS OF ALUMINIUM TOXICITY AND PHOSPHORUS
FIXATION ON CROP GROWTH ON OXISOLS IN NATAL

Two fundamental factors limit fertility in acid soils, viz. impoverished nutrient status and the presence of toxic substances. In particular, P presents special difficulties in that it is subject to rapid fixation, principally by Fe and Al compounds (Smith, 1965) either by precipitation (Kittrick and Jackson, 1955) or by a surface chemisorption reaction (Hsu, 1965). Soluble Al is widely held to be the major toxic substance in acid soils (Ragland and Coleman, 1959; Hourigan, et al., 1961; Shoop, et al., 1961; Kehoe and Curnow, 1963; Abruna, Vicente-Chander, and Pearson, 1964) although Mn may also reach toxic concentrations, particularly under waterlogged conditions (Graven, Attoe, and Smith, 1965).

Although toxic effects may be eliminated by liming, P fixation is not easily reduced. Lime has been shown to improve P availability as measured by extraction (Awan, 1964) and exchange resin (Taylor and Gurney, 1965) while Pierre and Browning (1935), Hourigan, et al., (1961) and Okruszko, Warren, and Wilcox (1962) report a depressing effect of lime on yield consistent with reduced P availability. Anions such as silicate, oxalate, citrate, bicarbonate, and tartrate have been shown to decrease P fixation (Deb and Datta, 1967; Taylor, 1961; Nagarajah, Posner, and Quirk, 1968; Hunter, 1965) while Raupach and Piper (1959) found that although silicate effected a marked lowering of P fixation in laboratory tests, pot experiments failed to substantiate the observation.

Al toxicity and P fixation are frequently studied independently of one another creating the impression that in soils where one is a problem the other is not. However, if the Al compounds in a soil

are sufficiently active to subtend toxic concentrations of soluble Al in the soil solution then P fixation in that soil is to be expected. The converse is not necessarily true, but is not unlikely. The object of this paper is to investigate the relative magnitude and importance of P fixation and Al toxicity in a number of acid Natal soils.

MATERIALS AND METHODS

Eight Oxisols representative of the most important soil series in the Highland Sourveld of Natal were sampled (0-15cm; appendix 1). Some selected properties of these soils are presented in Table 1. Exchangeable Al was determined by the method of Skeen and Sumner (1965) and CEC was determined by saturating with KCl, correcting for occluded salt by weighing and extracting with NH_4Cl . Lime requirements were determined by the SMP buffer method (Shoemaker, McLean, and Pratt, 1961). No relationship exists between lime requirement and CEC, exchangeable Al, percentage clay, or pH; lime requirement is, however, highly correlated with percentage C indicating that organic matter is a major source of buffering in these soils.

Assessment of exchangeable Al - Determination of exchangeable Al in acid soils by conventional extraction procedures is complicated by dissolution of non-exchangeable Al which depends on pH, concentration and nature of the extractant, and duration of extraction (Pratt and Bair, 1961; Skeen and Sumner, 1967a, 1967b). Skeen and Sumner (1965, 1967a, 1967b) propose a technique for estimating "truly" exchangeable Al involving a series of successive extractions carried out under controlled conditions. The technique allows a correction to be made for non-exchangeable Al extracted. Although sound, this method is laborious and not suitable for use on a large scale. However, Al determined in the first of a series of such extractions was highly

Table 1. Selected properties of eight Oxisols from Natal

Soil	Exchangeable cations							C	Clay	pH		Lime req.†
	CEC	Ca	Mg	K	Na	Al	Mn			CaCl ₂ §	H ₂ O	
	-----meq/100gsoil-----							ppm	-----%-----			m.ton/ha
Griffin	5.5	1.1	1.1	0.6	0.2	2.0	8.7	6.8	30.2	4.4	5.2	19.5
Clovelly	6.4	2.1	1.7	0.3	0.1	2.0	5.2	3.3	42.0	4.4	5.0	15.0
Lidgetton	7.3	2.3	2.0	1.1	0.1	1.7	7.0	4.4	51.7	4.5	5.3	15.0
Farmhill	5.6	2.2	1.3	0.7	0.1	0.4	10.4	4.2	57.9	4.6	5.4	13.5
Hutton	6.0	1.0	0.9	0.6	0.1	2.7	7.0	4.1	41.6	4.7	5.3	15.0
Farningham A	4.5	0.8	0.6	0.4	0.2	2.1	10.4	3.7	52.0	4.6	5.2	12.0
Farningham B	6.7	3.7	2.2	0.5	0.1	0.0	15.6	4.5	49.7	5.0	5.6	13.5
Balmoral	5.3	1.7	1.6	0.2	0.1	1.4	31.2	1.9	37.0	4.7	5.3	9.0
r‡	0.55					0.28		0.90***	-0.11	-0.51		

† lime requirement to pH6.5; SMP buffer

‡ correlation between lime requirement and indicated properties

§ 0.002M CaCl₂

correlated with the final exchangeable Al value ($r = 0.922^{***}$). A single two minute extraction in a reciprocating shaker with 0.2N NH_4Cl (1:10 soil : solution ratio) was therefore adopted as a working index to exchangeable Al. Al determined in this way will be termed the exchangeable Al index (EAI) of a soil to distinguish from exchangeable Al as determined by Skeen and Sumner (1965). For soils containing no exchangeable Al (e.g. Farningham B, Table 1) a small EAI value will be obtained due to dissolution of non-exchangeable Al for which no correction is made. This slight overestimation is not, however, considered serious. Air drying did not affect the EAI values of these soils.

Assessment of P "fixing" capacity - For the purpose of this paper it is desired to obtain a measure of that fraction of added P which is "available". To this end P treated soils were extracted with a reagent commonly used to measure "available" P and the amount not extracted was regarded as "fixed". The relatively strong Bray No. 2 solution (0.03N NH_4F in 0.1N HCl) was used to minimise weakening by reaction with unreacted lime and to promote maximum dissolution of Ca phosphates in limed soil. Although the fluoride solution would be expected to extract some Al-P this does not imply that Al compounds necessarily play no part in the fixation of the remainder.

5g air dry soil was treated with 5ml P solution of varying strength, allowed to stand overnight (16 hours) and then extracted with 20ml Bray No. 2 reagent for exactly one minute in a reciprocating shaker. The suspensions were then immediately centrifuged and P determined in the supernatant. Up to the maximum amount of P added (400 ppm) a linear relationship exists between P added and P extracted for all soils except the Balmoral where a slight deviation from linearity occurs at the higher rates of application (Fig.1). Similar desorption isotherms were constructed for soils which had previously been equilibrated with CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and a commercial CaSiO_3 .

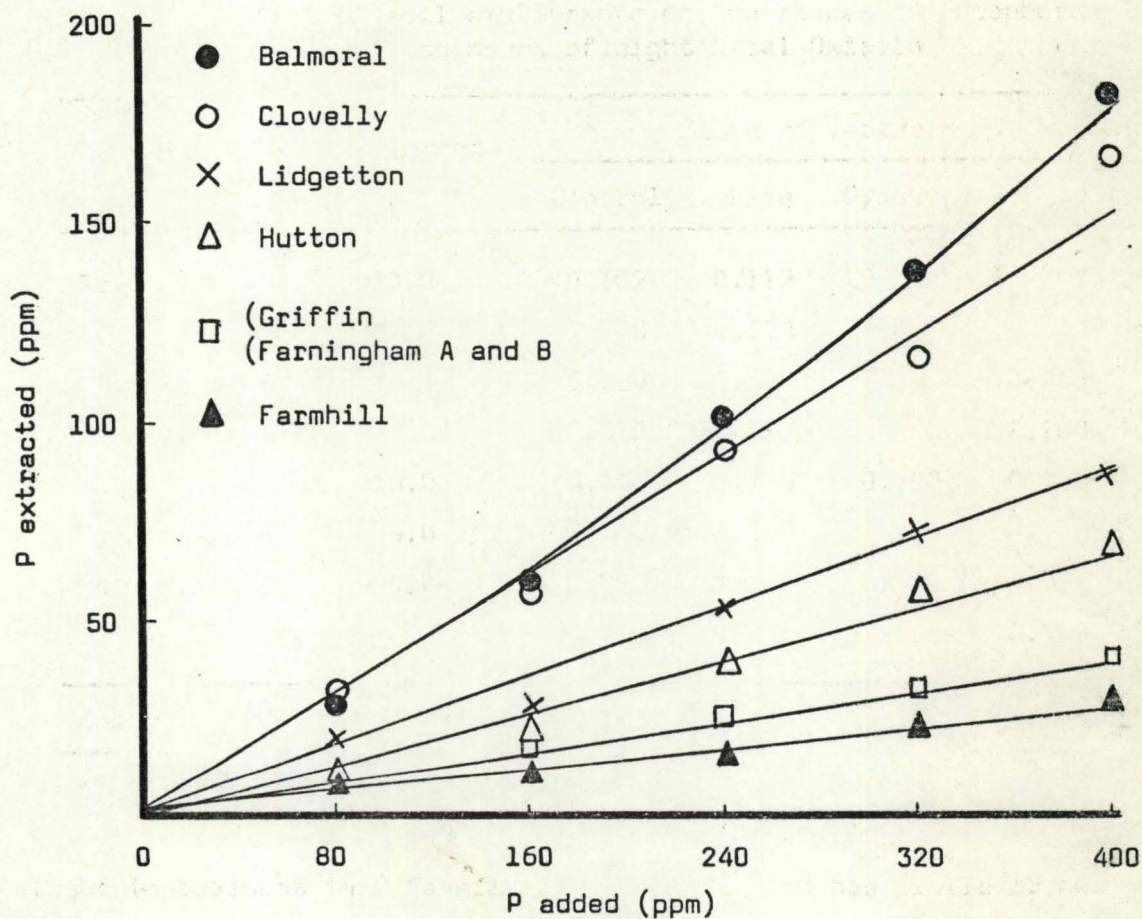


Fig.1 Phosphorus desorption isotherms of eight Natal Oxisols. P extracted from untreated soils was in all cases less than 5 ppm.

product known as Silene¹, all at rates equal to the amount of lime required to raise the pH of the soils to 6.0 (SMP buffer). Slopes of the resultant isotherms representing the fraction of added P which is "available" are presented in Table 2. Gypsum and Silene effect a

Table 2. Effect of soil ameliorants on the slopes of phosphorus desorption isotherms of eight Natal Oxisols

Soil	Ameliorant dressing*	Slope of isotherm			
		Control	Lime	Gypsum	Silene
Griffin	13.0	0.102	0.112	0.150	0.138
Clovelly	10.0	0.390	0.350	0.438	0.363
Lidgetton	10.0	0.220	0.212	0.282	0.238
Farmhill	9.0	0.070	0.088	0.150	0.100
Hutton	10.0	0.163	0.150	0.250	0.207
Farningham A	8.0	0.100	0.100	0.165	0.138
Farningham B	9.0	0.113	0.138	0.194	0.158
Balmoral	6.0	0.390	0.355	0.435	0.400
Means	9.4	0.193	0.188	0.258	0.217

* metric tons/ha

slight improvement in P "availability" while lime has little or no effect. Since the desorption isotherms are linear (Fig.1) a single point on an isotherm will suffice as a measure of its slope. Values for single points at the 80 ppm P treatment level were highly correlated with and have been used as a measure of the slopes of complete isotherms ($r = 0.975^{***}$). For convenience this measure of the "availability" of added P will be termed the P desorption index

¹ Manufactured by Pittsburgh Plate Glass Co., Pittsburg, Pa.

$\text{SiO}_2 = 64.9\%$, $\text{CaO} = 19.5\%$, $\text{R}_2\text{O}_3 + \text{MgO} + \text{NaCl} = 2.3\%$.

(PDI) of a soil. P fixation as assessed by the above method was complete within one hour and did not progress further during four days. PDI values for air dry soil samples were highly correlated with values for field moist samples ($r = 0.979^{***}$) although on the average the former were 26% lower than the latter.

Effects of Al toxicity and P fixation on plant growth - Plant growth on the soils described was studied in the glass-house. The soils were treated with three types of soil ameliorant (CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or Silene) each at four levels of application (equal in weight to 0, 0.33, 0.67, and 1.00 of the amount of lime required to reach pH6.5; table 1) and two levels of P (20 and 80 ppm). Standard N, K, and trace element dressings were applied to all pots at rates of 150 ppm K, 150 ppm N, 20 ppm Mg, 27 ppm S, and 1 ppm each of Mn, Cu, Zn, B, and Mo. A further 100 ppm N was subsequently applied halfway through the growing period. Plastic pots containing 5kg soil were used. Ameliorants were thoroughly mixed with the soil which was equilibrated moist in the pots for 52 days. The "field" moisture capacity of the soils was maintained by weighing. Fertilizers were then thoroughly mixed with the soil, 'trudan' seed (Sorghum sudanense) planted, the crop harvested after 36 days, oven dried, and weighed. The soils were sampled for laboratory analysis.

RESULTS

Main effects of P on crop yield are shown in Fig. 2. Although growth response to P was highly significant in all cases there is considerable variation between soils. Comparison of Figs. 1 and 2 reveals a good correlation between PDI and growth response to P ($r = 0.830^{**}$) indicating that fixation of added P is largely responsible for the observed differences in productivity.

The maximum growth response to lime as measured by the overall

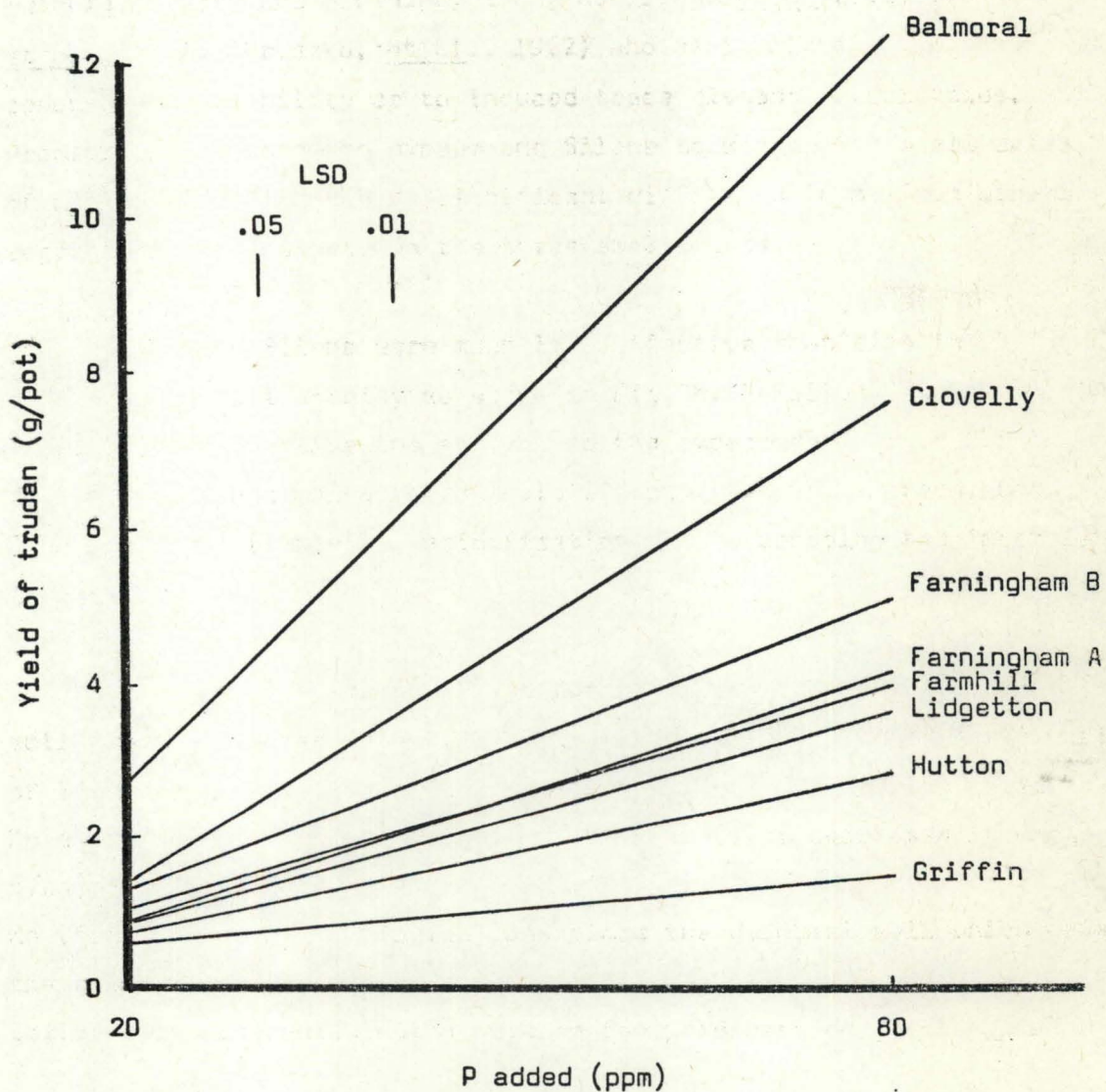


Fig.2 Main effects of phosphorus on yield of trudan on eight Natal Oxisols

main effect occurred at 1/3 lime requirement to pH6.5 followed by a significant reduction in yield at the highest level (Fig.3a). Depression in yield at high levels of lime has been noted by several authors (Pierre and Browning, 1935; Hourigan, et al., 1961; Shoop, et al., 1961; Okruszko, et al., 1962) and variously attributed to reduced P availability or to induced trace element deficiencies. Progressive response to gypsum and Silene took place over all rates of application although no significant difference in maximum growth response was found between the three ameliorants.

Gypsum and Silene were much less effective than lime in neutralizing soil acidity as shown in Fig.3b. Failure of the top level of lime to raise the soil pH to the expected value of 6.5 is attributed to a combination of salt effects (McLean, Dumford, and Coronel, 1966) (Table 1), acidification due to cropping and incomplete reaction.

Extractable Mn was estimated for all soils by extracting moist soil for two minutes with 0.2N NH_4Cl as described for the determination of EAI values. In Fig.3c it is shown that lime eliminated extractable Mn at the first level of application while Silene decreased it and gypsum increased it. Since no relationship exists between extractable Mn (Fig.3c) and yield (Fig.3a) and since the Balmoral soil which gave the highest yields (Fig.2) contained most extractable Mn (Table 1), Mn toxicity is apparently not a problem for this crop on these soils.

Lime essentially eliminated exchangeable Al at the lowest level of application while gypsum and Silene progressively lowered EAI values with increasing rates of application (Fig.3d). Since gypsum has no acid neutralising ability the reduction in EAI is probably the result of sulphate induced Al polymerisation by ligand exchange for hydroxyl groups (Chang and Thomas, 1963) resulting in a "self liming" effect. The reaction is clearly concentration dependent. Silene, however, has

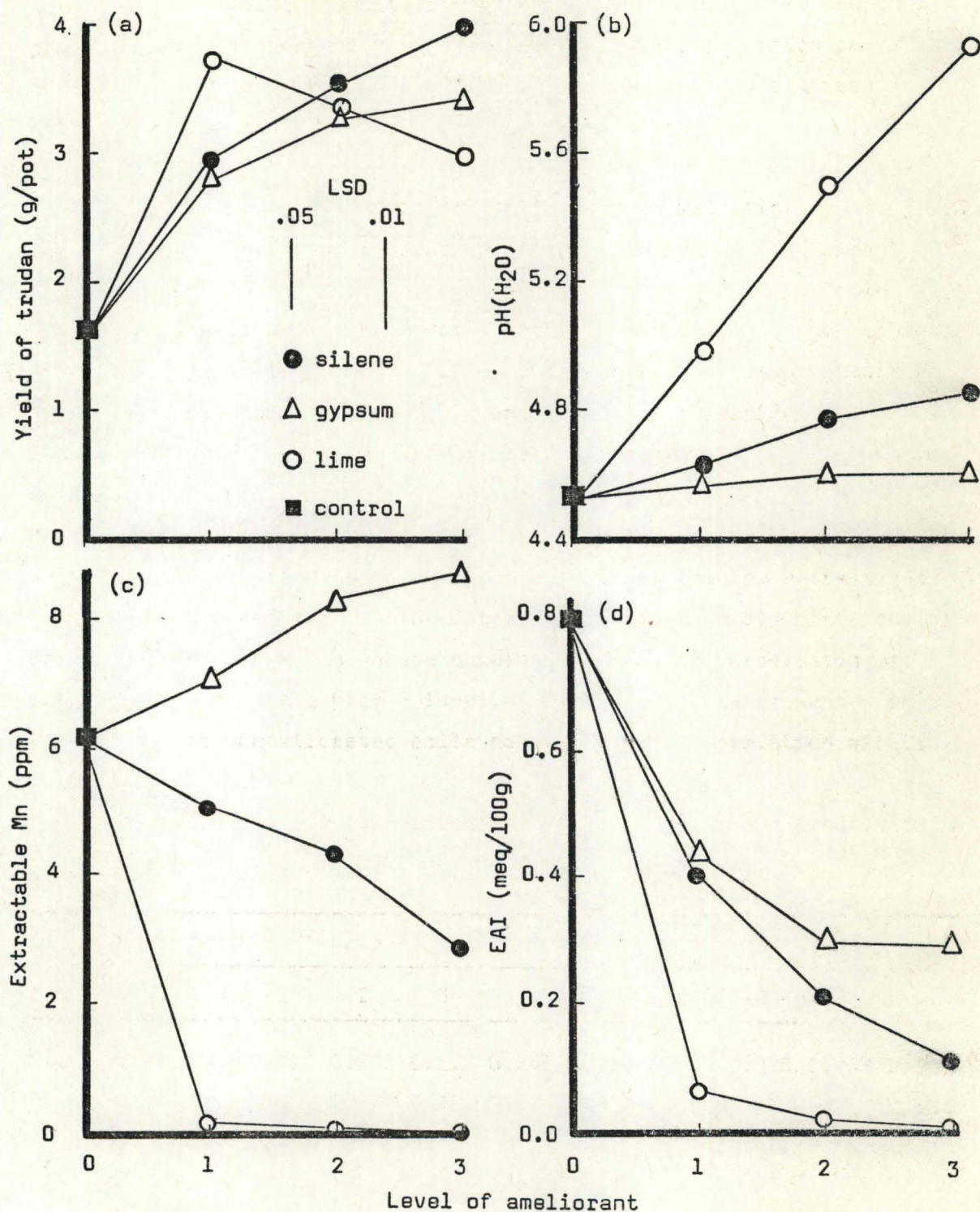


Fig.3 Effect of three soil ameliorants on: (a) yield of trudan (overall main effects); (b) mean pH value; (c) mean extractable Mn value; (d) mean exchangeable Al index of eight Natal Oxisols.

an acid neutralising capacity of 5.9 meq/g ($\text{CaCO}_3 \equiv 20 \text{ meq/g}$) and thus probably acts as a weak liming agent approximately one third as effective as CaCO_3 (cf. Figs. 3b and 3d) rather than as a source of silica (Taylor, 1961).

Comparison of the effects of ameliorants on EAI (Fig.3d) and yield (Fig.3a) reveals a clear inverse relationship which is independent of type of ameliorant (Fig.4). Deviation from linearity at high levels of lime is due to secondary factors already discussed. The increase in yield to the point of near elimination of exchangeable Al (also noted by Shoop, *et al.*, 1961) and the negligible effects of ameliorants on P "availability" (Table 2) indicate that elimination of Al toxicity is the primary function of ameliorants on these soils.

PDI values were determined for the soils at the low P treatment to minimise the contribution of fertilizer P and to avoid differential cropping effects and the values obtained tested for correlation with yields obtained at the high P level. The results are presented in Table 3. For unameliorated soils no significant correlation exists

Table 3. Effect of soil ameliorants on mean phosphorus desorption index (PDI) and correlation coefficient between PDI and yield of trudan on eight Natal Oxisols

	Control	Lime			Gypsum			Silene		
	0 [†]	1	2	3	1	2	3	1	2	3
Mean PDI	0.231	0.212	0.201	0.175	0.245	0.283	0.295	0.220	0.237	0.218
r	0.58	0.80**	0.86**	0.85**	0.65	0.58	0.52	0.74*	0.81**	0.90**

[†] levels of application

between yield and P "availability" due to confounding of P fixation and Al toxicity effects. Upon eliminating the latter by liming, the

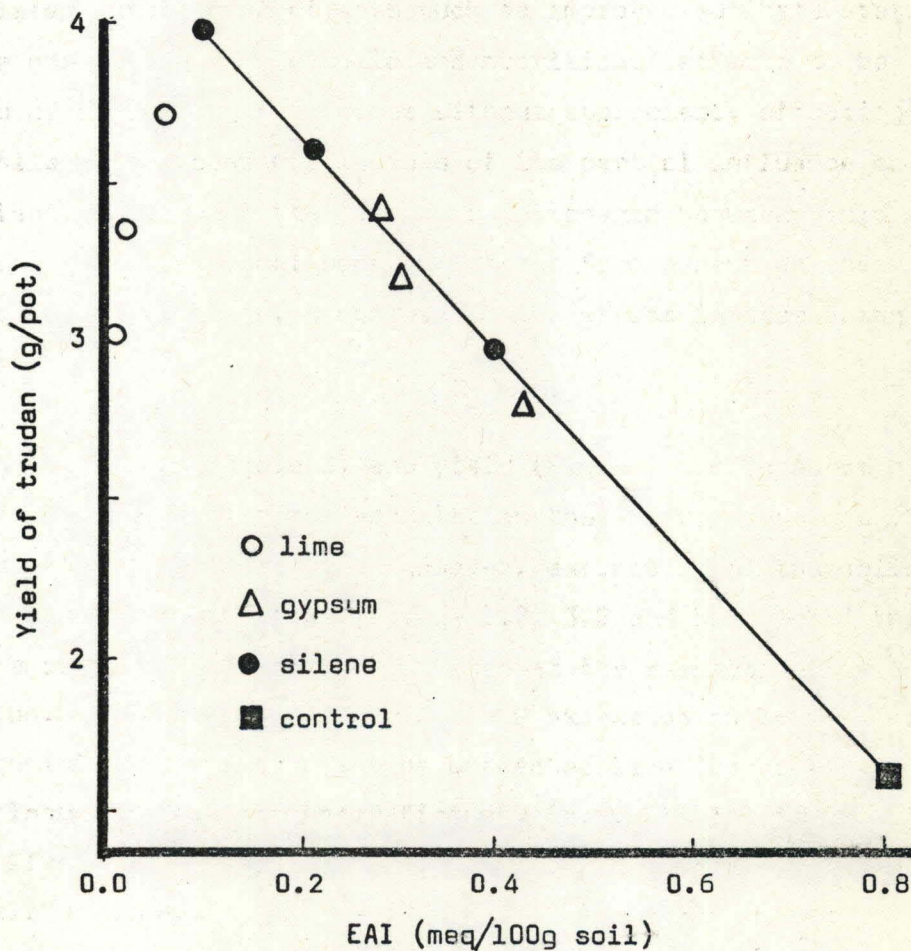


Fig.4 Relationship between EAI and yield of trudan on eight Natal Oxisols.

correlation immediately becomes highly significant. For Silene treated soils the correlation between yield and PDI is consistent with the ability of Silene to progressively lower EAI values with increasing rates of application (Fig.3d). No significant correlation between yield and PDI exists for gypsum treated soils probably due to the inability of gypsum to completely inactivate exchangeable Al and to associated nutritional effects such as improved sulphate status. Thus lime and Silene enable toxic and nutritional effects to be separated by decreasing the former without appreciably affecting the latter while gypsum does not because of its partial influence on both. Nevertheless, in view of the general relationship between yield and EAI (Fig.4) any nutritional benefits gained from gypsum on these soils are, on the average, secondary to its effect in decreasing exchangeable Al.

Both PDI values (Table 3) and yield (Fig.3a) decreased at high levels of lime supporting the speculation that heavy dressings of lime interfere with P availability. However, extraction of the soils with $\text{N NH}_4\text{OAc}$ revealed that on the average 1.7, 3.8 and 5.3 meq of the added lime per 100g soil had not reacted at the respective levels of application. The observed decrease in P extracted could have arisen from weakening of the extractant by unreacted lime (Baker and Hall, 1967). Induced trace element deficiency (e.g. Fig.3c) is therefore the more likely explanation for the observed depression in yield at high levels of lime.

Detailed results of this experiment are presented in appendix 2.

DISCUSSION

Both Al toxicity and P fixation limit plant growth on the soils studied although their relative importance and inter-relationship varies. Thus the Farningham B and Farmhill soils are among the most

active with respect to P fixation yet have the least amounts of exchangeable Al (Fig.1, Table 1). The converse is true for the Clovelly while for soils such as the Hutton, Griffin, Lidgetton, and Farningham A both phenomena are serious limitations. Both P fixation and Al toxicity are primary factors limiting growth as alleviation of one had little influence without simultaneous alleviation of the other. Although the data are not presented here (appendix 2) little growth response to ameliorants occurred at the low level of P while for soils high in exchangeable Al little response to P took place in the absence of ameliorants. Failure to recognise P fixation and Al toxicity as independent limiting factors could well result in an incorrect interpretation of the observed P-ameliorant interaction. The shape of the P desorption isotherms (Fig.1) supports a surface chemisorption mechanism (Hsu, 1965) in which the ease of P desorption is determined by the degree of saturation of the adsorption complex. If the fixation mechanism were precipitation, cations capable of forming insoluble phosphates would be required in solution; fixation would be complete before and negligible after exceeding the solubility product or removing such cations from solution. P fixation by precipitation would be "limited by pH, being negligible at pH5 or above, but there is no such limitation for the activities of amorphous Al hydroxides and Fe oxides which can be of any magnitude at any pH" (Hsu, 1965). Failure of lime to effect a reduction in P fixation despite its ability to eliminate exchangeable Al is thus attributed to the fixation of P by chemisorption on sesquioxide surfaces. Reports claiming improved P availability as the result of lime application are frequently based on plant analysis data. Kehoe and Curnow (1963) point out that improved uptake of P from limed soil may well be due to improved ability of plants to take up P rather than to an improved rate of supply by the soil. Roots subjected to toxic concentrations of Al are frequently stunted, deformed and discoloured; P uptake could be hindered by limited root proliferation or for physiological reasons.

The relatively wide spectrum of P fixing abilities of the soils studied (Fig.1 and 2, Table 2) indicate that fertilizer recommendations based on direct determination of the amount of P required to raise the status of a soil to a desirable level are likely to be more accurate than those based on an estimate of the amount of available P in the soil per se. "Perhaps soil chemists have been too long preoccupied with attempting to assess the elusive amount of available P in soils... Not even a perfect measure of available P would predict the practical answer which is usually required - the amount of phosphatic fertilizer necessary to convert a deficiency to a minimal sufficiency" (Beckwith, 1963). Reference to Fig.1 reveals that approximately five times as much P would be required to raise the Farmhill soil to the same status as the Balmoral. Cognisance of this would not be taken in soil test procedures where an estimate of available P is made and the amount required to attain the desired status is calculated by difference assuming an arbitrary recovery factor. Oxisols invariably test very low with respect to P; it is not unlikely that the recovery factor used in the calculation of P application rates would assume a more significant role than the original test value. It is therefore recommended that soil tests for P should at least be supplemented by some measure of such recovery factors. PDI values appear to afford a satisfactory and convenient measure of this.

PAPER 2

LIME REQUIREMENTS OF NATAL OXISOLS
BASED ON EXCHANGEABLE ALUMINIUM

The application of lime to acid soils is commonly aimed at raising the soil pH to near neutrality in the belief that effects such as low base status, Al toxicity and P fixation will be eliminated. Accordingly, most methods of estimating lime requirement involve a calibration of buffer capacity to a near neutral pH (usually 6.5) in terms of the amount of lime required to raise the pH by an equivalent amount during incubation (Mehlich, 1948; Woodruff, 1948; Shoemaker, McLean, and Pratt, 1961; Adams and Evans, 1962; Peech, 1965). Considering that organic matter contributes significantly towards titratable acidity or pH dependent charge in soils (Helling, Chesters, and Corey, 1964; McLean, Reicosky, and Lakshmanan, 1965) it is not surprising that lime requirement is highly correlated with organic matter content (Keeney and Corey, 1963; Ross, Lawton, and Ellis, 1964; McLean, Dumford, and Coronel, 1966; paper 1) resulting in prohibitively high lime requirement values for soils high in organic matter (paper 1). In fact, two recent surveys (Adams and Pearson, 1967; Fisher, 1969) indicate that it is unnecessary to lime to pH 6.5 or above while several other authors have reported depressed yields as the result of heavy lime applications (Pierre and Browning, 1935; Hourigan, et al., 1961; Shoop, et al., 1961; Okruszko, Warren, and Wilcox, 1962; paper 1) either due to decreased P availability or induced trace element deficiencies.

Although Reeve (1968) showed the SMP buffer method (Shoemaker, et al., 1961) to be suitable for determining lime requirements of Natal Oxisols to pH 6.5, data in paper 1 show this criterion to be

unsuitable for determining lime requirements for maximum yield on these soils. Not only did maximum growth of trudan (Sorghum sudanense) take place when the soils were treated with considerably less lime than that required to reach pH6.5, but near maximum yields were obtained on soils treated with gypsum which did not affect the soil pH. The growth response was attributed to the elimination of Al toxicity, in the case of gypsum by sulphate induced Al polymerisation by ligand exchange for hydroxyl groups resulting in a "self liming" effect. Considerable evidence is available to show that in many acid soils the beneficial effects of liming are largely due to inactivation of exchangeable Al. Ragland and Coleman (1959), Hourigan, et al. (1961), and data of Ross, et al. (1964) show respectively that grain sorghum and alfalfa responded to lime in proportion to the amount of exchangeable Al in the soil. "Critical values" reported for exchangeable Al are 0.2 meq/100g for alfalfa (Moschler, Jones, and Thomas, 1960), 0.1 meq/100g for Ladino clover, Kentucky 31 fescue, and Sericea Lespedeza (Shoop, et al., 1961), 2 meq/100g for Napiergrass (Abruna, Vicente-Chandler and Pearson, 1964), 0.1, 1.0, and 2.5 meq/100g for cotton on three soils "having wide differences in characteristics" (Adams and Lund, 1966), 0.55 meq/100g for barley and 0.09 meq/100g for soybean (G.W. Thomas and W.W. Moschler, respectively. Quoted by Adams and Pearson, 1967.) Although a universal critical value has not emerged this is to be expected owing to different types of soil studied, different methods of Al extraction and different degrees of Al tolerance by different crops. For any given Al extraction procedure it should be possible to establish critical values and corresponding lime requirements on large groups of soils of similar character.

In paper 1 it was shown that the "fixation" of applied P drastically limits crop production in Natal Oxisols and that lime has little effect on this process as measured by chemical methods. If lime requirements for maximum crop production are to be assessed in

terms of exchangeable Al as a toxic factor it is important to show that lime does not affect P availability to the plant.

Since Natal Oxisols have extremely high capacities for P fixation it would be quite unrealistic to attempt to eliminate P status as a variable by saturation when studying the effect of lime. For the purposes of estimating lime requirements a relatively low level of P may be used if the pattern of growth response to lime can be shown to remain unchanged over a reasonably wide range of P status.

MATERIALS AND METHODS

Eight Natal Oxisols described in paper 1 having widely different exchangeable Al contents (Table 1) were studied in three pot experiments.

Table 1. Selected properties of eight Natal Oxisols

Soil	CEC		Exch. cations			Org.C (%)	pH (CaCl ₂)*
	KCl	NH ₄ OAc	Ca	Mg	Al [†]		
	-----meq/100g soil-----						
Griffin	5.5	39.5	1.1	1.1	2.0	6.8	4.4
Clovelly	6.4	18.8	2.1	1.7	2.0	3.3	4.4
Lidgetton	7.3	31.7	2.3	2.0	1.7	4.4	4.5
Farmhill	5.6	22.0	2.2	1.3	0.4	4.2	4.6
Hutton	6.0	21.2	1.0	0.9	2.7	4.1	4.7
Farningham A	4.5	23.0	0.8	0.6	2.1	3.7	4.6
Farningham B	6.7	30.0	3.7	2.2	0.0	4.5	5.0
Balmoral	5.3	14.3	1.7	1.6	1.4	1.9	4.7

* 0.002M CaCl₂

† Determined by the method of Skeen and Sumner (1967)

Experiment No. 1: Only two soils both with high P "fixing" capacities were studied, viz. the Farmhill (low exchangeable Al) and the Farningham A (high exchangeable Al). Two levels of lime were applied: (i) the amount required to raise the soil pH to 6.0 (8 m.tons CaCO_3 /ha for each soil) according to the SMP buffer; (ii) the amount required to eliminate exchangeable Al (1 m.ton/ha for the Farmhill soil and 4 m.ton/ha for the Farningham A soil). Six levels of P (as $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) were applied in 40 ppm increments from 0 through 200 ppm giving a $2 \times 2 \times 6$ factorial in two replications. Other nutrients were applied to each pot at the following rates: 150 ppm K, 150 ppm N, 20 ppm Mg, 27 ppm S, and 1 ppm each of Mn, Cu, Zn, B and Mo. A further 100 ppm N was subsequently applied as a top dressing after two weeks of growth. Plastic pots containing 5kg soil were used. After liming the soil was equilibrated at "field" moisture capacity (by weighing) for 30 days before fertilizing and planting to trudan (Sorghum sudanense). After 36 days the crop was reaped, oven dried and weighed.

Experiment No. 2: It is desired to present certain data from an experiment reported in paper 1 which is pertinent to this paper. The eight soils studied were treated with three types of soil ameliorant (CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and a commercial grade of CaSiO_3) each at four levels of application (equal in weight to 0, 0.33, 0.67 and 1.00 of the amount of lime required to reach pH6.5 as indicated by the SMP buffer (see table 2) and two levels of P (20 and 80 ppm). After harvesting exchangeable Al index (EAI) values were measured by extracting 5g soil with 50 ml 0.2N NH_4Cl for exactly two minutes in a reciprocating shaker (paper 1). Other experimental details were as in experiment 1.

Experiment No. 3: All eight soils were limed in one m.ton/ha increments from 0 through 4 m.tons/ha at a constant level of P (80 ppm). All treatments were duplicated. After harvesting EAI values

were measured as above. Other experimental details were as in experiment 1.

RESULTS AND DISCUSSION

The yield of trudan increases in direct proportion to the level of P added (Fig.1). Thus over a wide range of P status a constant fraction of added P is "available" depending on the P "fixing" capacity of the soil. The application of lime in excess of the amount required to eliminate exchangeable Al as a toxic factor does little or nothing to increase this fraction in agreement with the findings in paper 1 based on chemical extraction techniques.

The relationship between yield and EAI as influenced by different types and levels of ameliorant at two widely different levels of P application is shown in Fig. 2 for the group of eight soils. The pattern of growth response to reduction of exchangeable Al is clearly independent of P status over the range of P applied irrespective of type of ameliorant used. In Fig. 2 the slope of the line relating yield and EAI at the 80 ppm P level of application is four times greater than that at 20 ppm P in accordance with the proportional relationship between yield and P status illustrated in Fig. 1. The apparent P-ameliorant interaction is not, however, due to a decrease in P fixation by the soil. As pointed out earlier (paper 1) P fixation and Al toxicity behave as independent growth limiting factors; the apparent interaction lasts only until Al is eliminated as a toxic factor and is due to an improved ability of the plants to take up P rather than to an improved rate of supply of P by the soil.

The effect of lime on yield for each soil is shown in Fig. 3. Because considerable variation in productivity exists between these soils at the single level of P applied, the results have been presented as percentages of the maximum yield for each soil. The lime

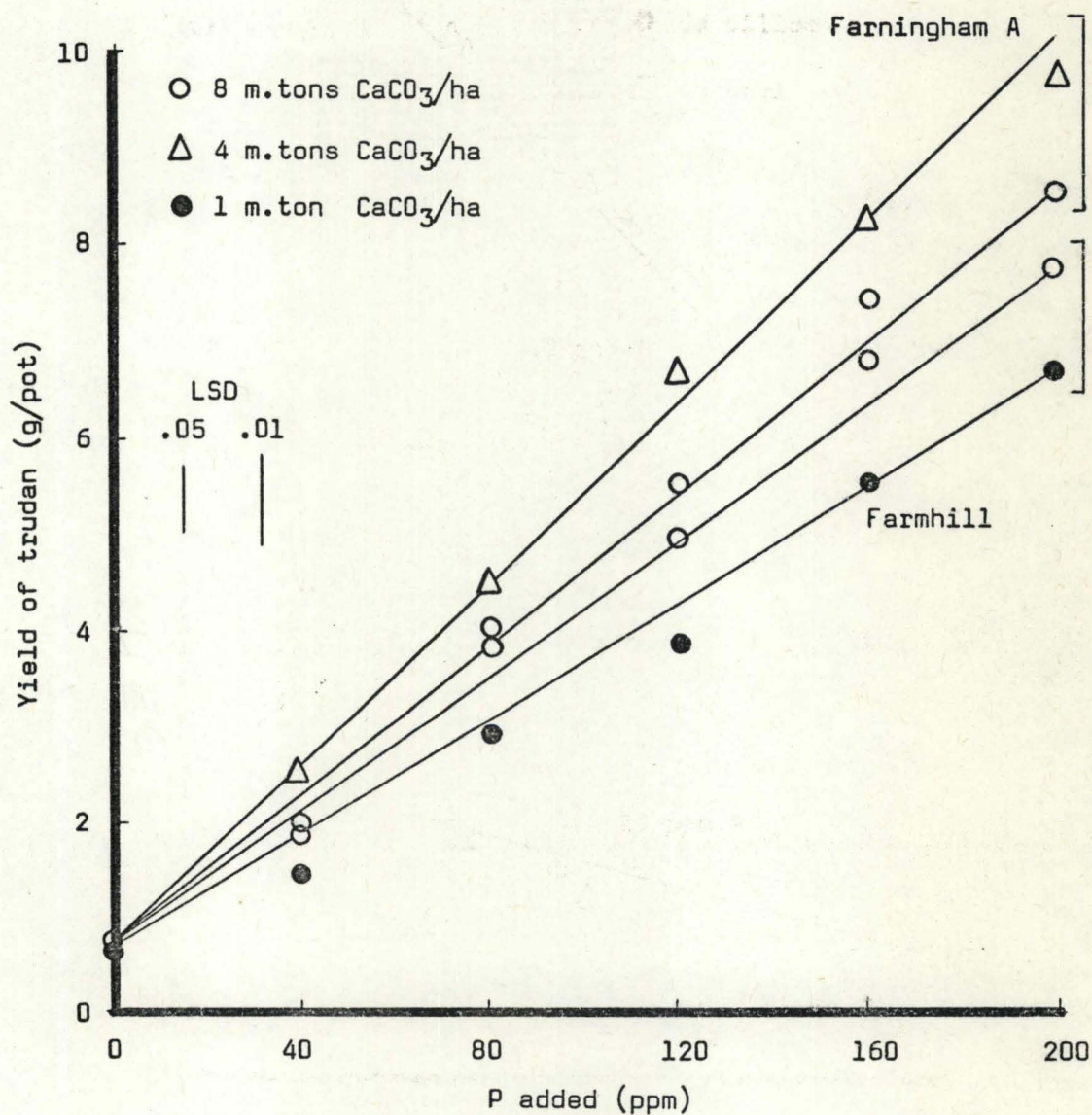


Fig.1 Effect of P on yield of trudan for two Natal Oxisols limed to eliminate exchangeable Al (1 and 4 m.tons/ha and to pH6.0 (8 m.tons/ha)

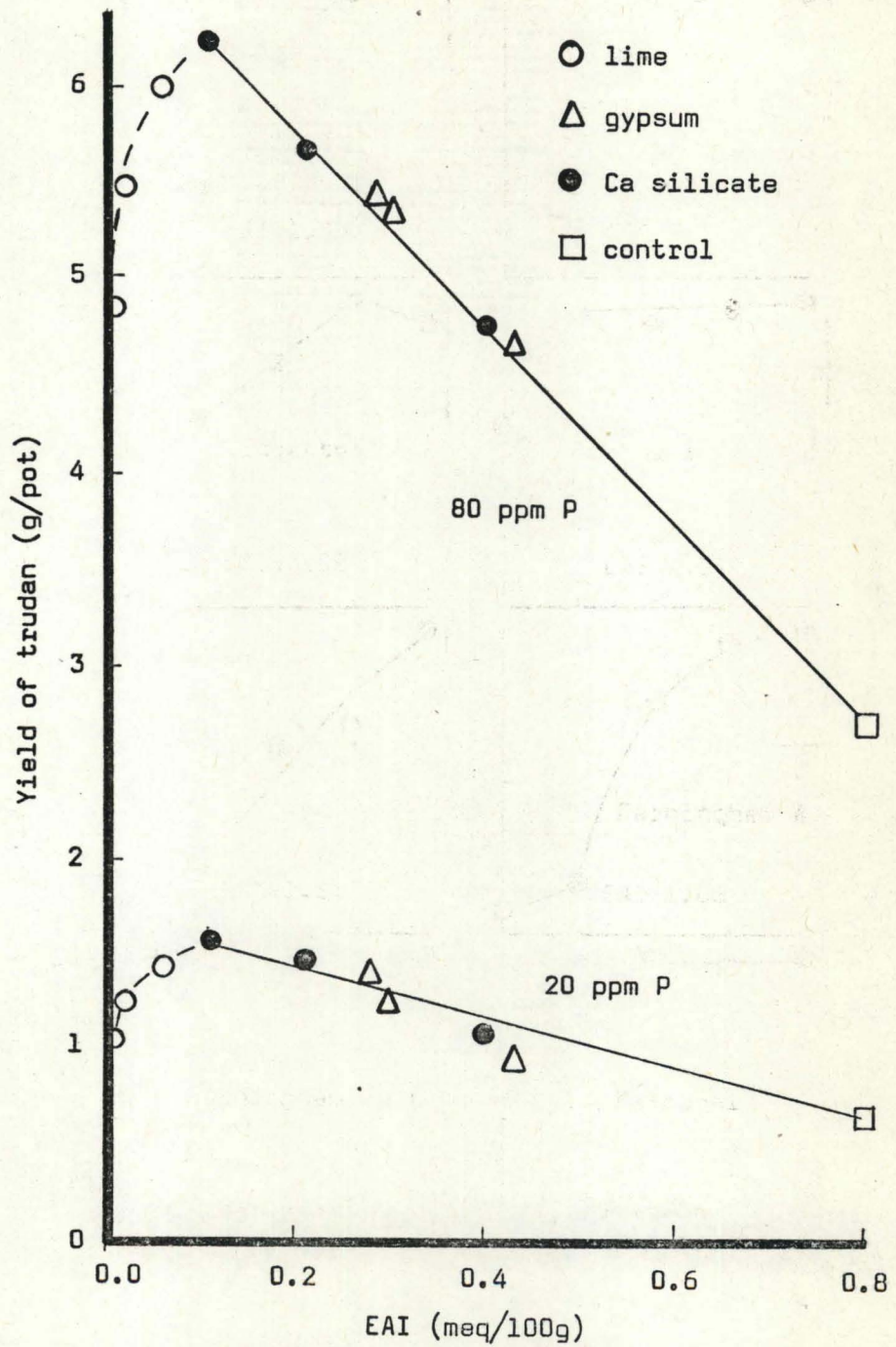


Fig.2 Effect of P on the relationship between EAI and yield of trudan (means of eight Natal Oxisols).

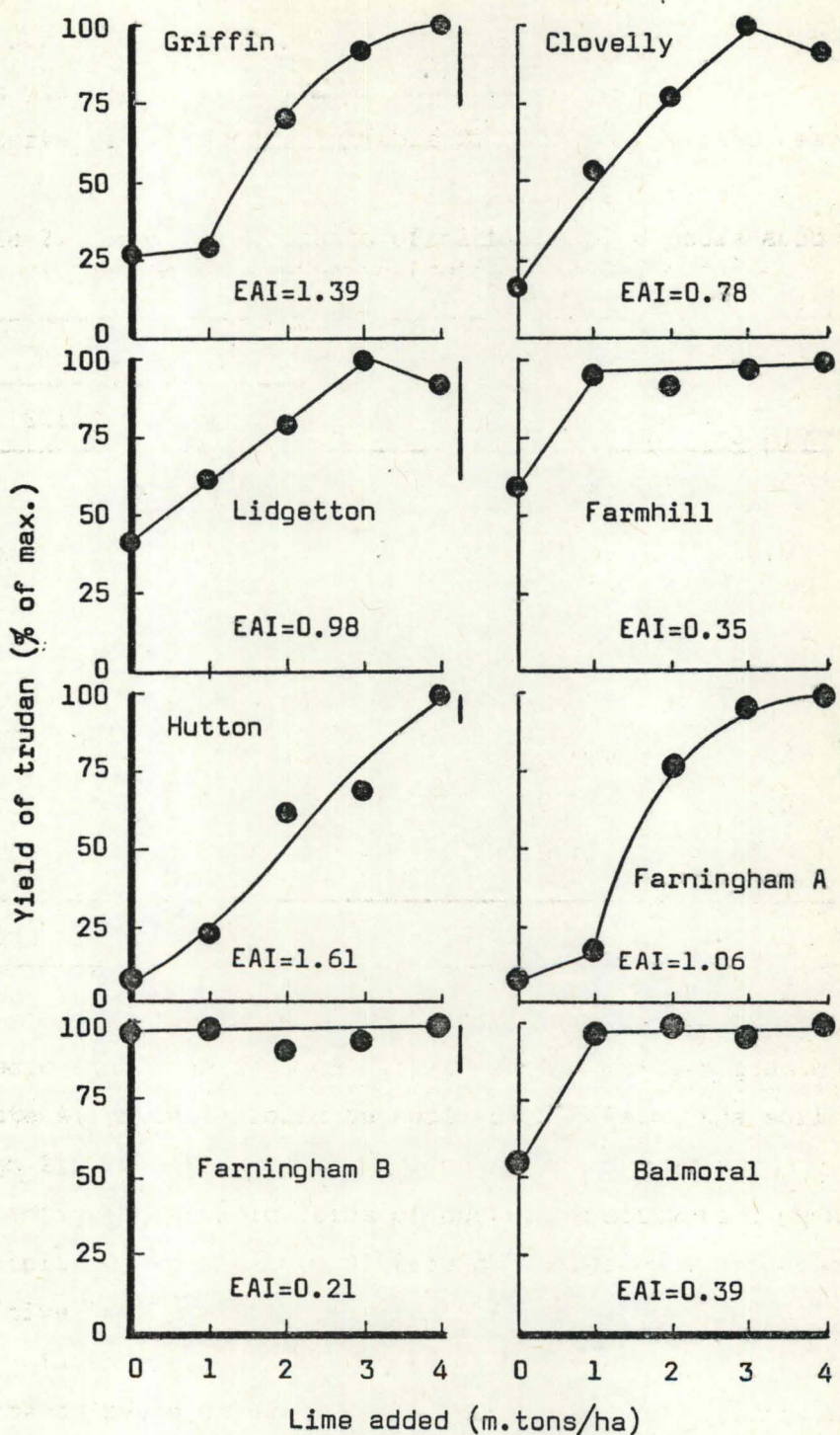


Fig.3 Effect of lime on yield of trudan on eight Natal Oxisols (EAI values (meq/100g) refer to unlimed soil; LSD (0.05) shown as vertical lines).

requirement taken as the amount necessary to give the highest yield is in good agreement with the amount of lime required to reduce the EAI to 0.2 meq/100g (Fig.4). Lime requirements assessed using maximum yield, exchangeable Al and buffer capacity to pH6.0 and 6.5 as criteria are presented in Table 2. On the average nearly six

Table 2. Lime requirements of eight Natal Oxisols according to different criteria (metric ton CaCO_3/ha)

Soil	C r i t e r i o n			
	Max.yield of trudan	Exch. Al (0.2 meq/100g)	pH6.0 (SMP)	pH6.5 (SMP)
Griffin	4.0	4.0	13.0	19.5
Clovelly	3.0	2.8	10.0	15.0
Lidgetton	3.0	3.0	10.0	15.0
Farmhill	1.0	0.8	9.0	13.5
Hutton	4.0	4.6	10.0	15.0
Farningham A	3.0	2.8	8.0	12.0
Farningham B	0.0	0.0	9.0	13.5
Balmoral	1.0	1.0	6.0	9.0
Means	2.4	2.4	9.4	14.1

times more lime than is necessary to obtain maximum growth or to eliminate Al toxicity would be applied in raising the soil pH to 6.5. Although lime requirements for Al toxicity control could be conveniently assessed in terms of buffer capacity to a pH high enough to precipitate exchangeable Al (say pH5.5), such a procedure would be insensitive to the wide variation in Al status occurring in these soils. Table 2 shows no significant correlation between lime requirements based on exchangeable Al and buffer capacity to pH6.0.

Taking the lime requirement of a soil as the amount required to reduce the EAI value to 0.2 meq/100g (Table 2) the data in Fig. 4 may be replotted to show the relationship between EAI and lime

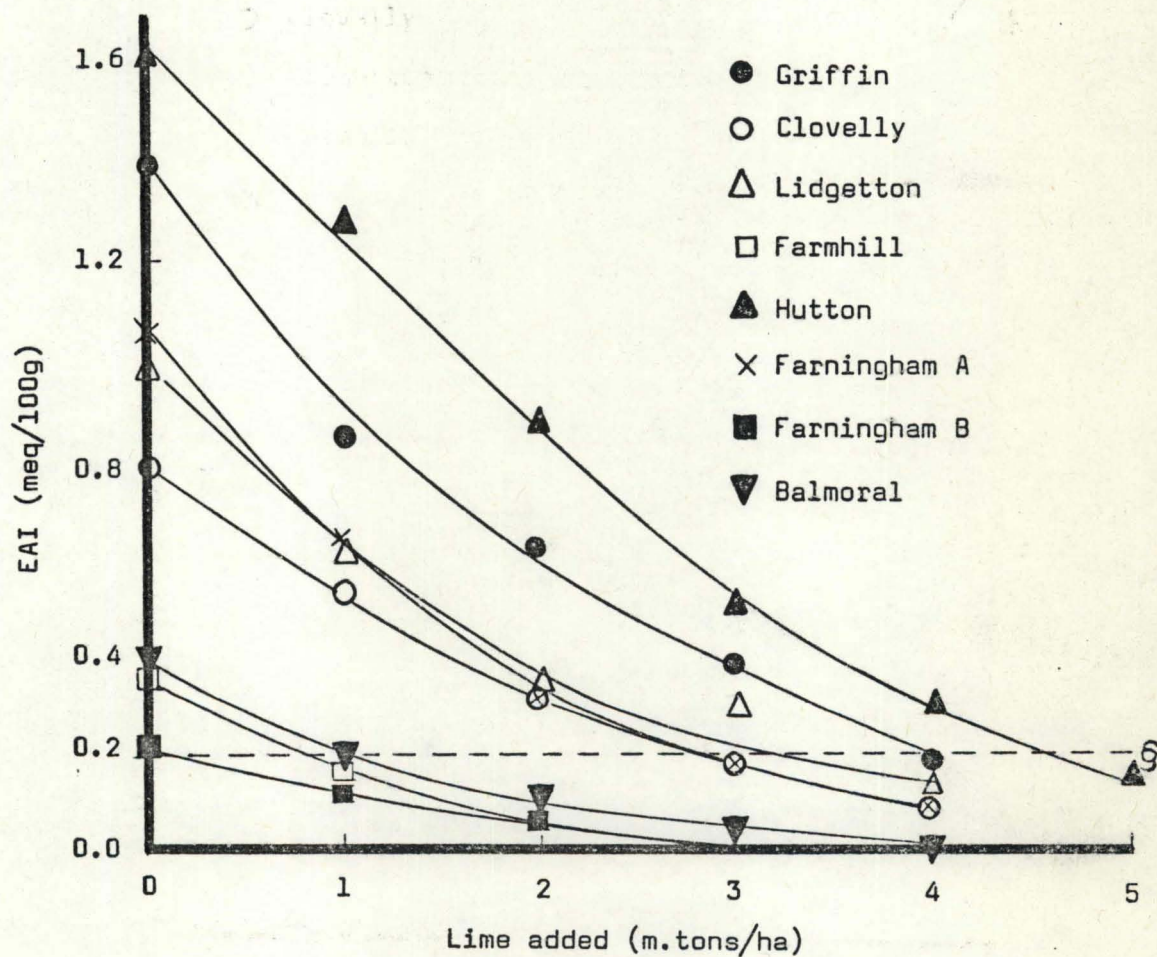


Fig.4 Effect of CaCO_3 on EAI values of eight Natal Oxisols.

S determined separately

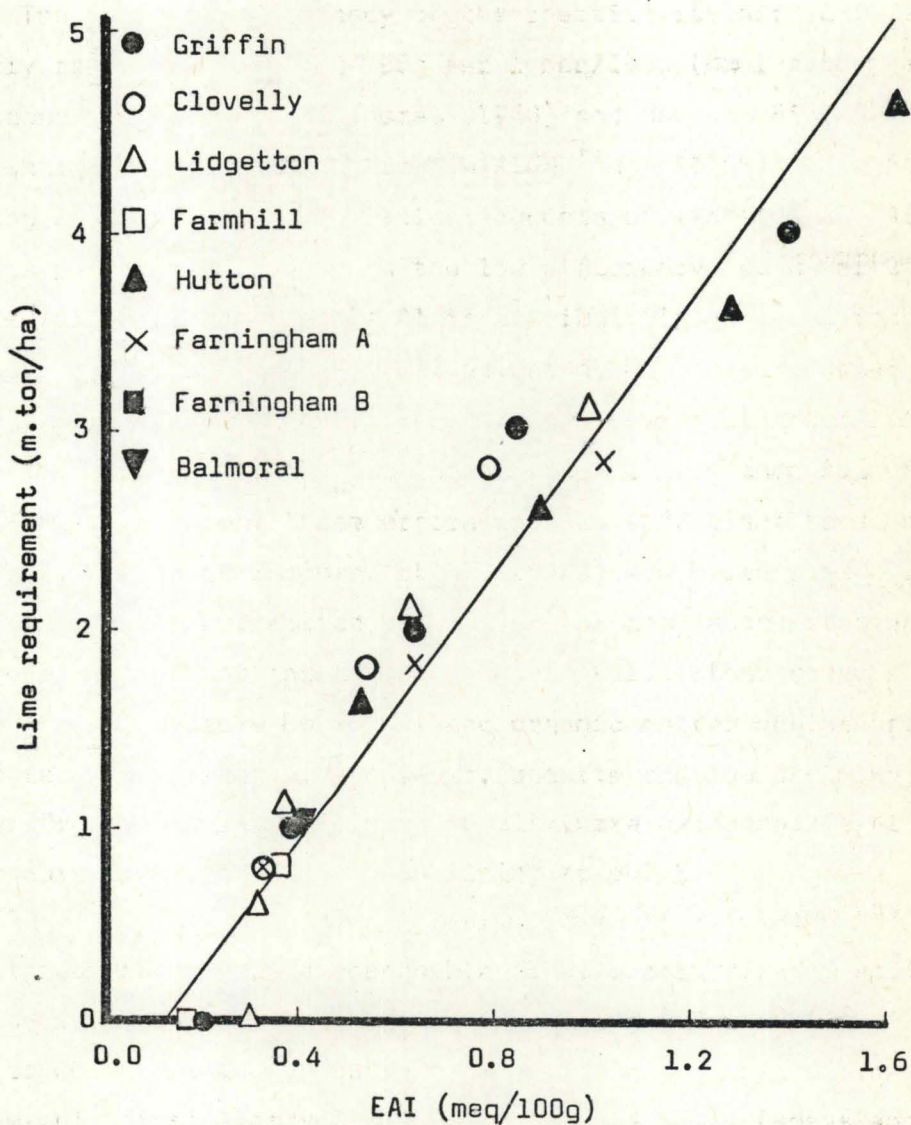


Fig.5 Relationship between EAI and lime required to reduce EAI to 0.2 meq/100g in eight Natal Oxisols.

$$(\text{lime req.} = 3.353 \text{ EAI} - 0.393; r = 0.973^{***})$$

requirement. For partially limed soil the lime requirement value (Table 2) was corrected for the amount of lime added. Fig. 5 shows that the entire range of soils closely follow a common relationship between EAI and the amount of lime required to reduce EAI to 0.2 meq/100g. The apparent efficiency of the reaction is low; EAI values were only reduced by 0.3 meq/100g per 1 meq/100g (\approx 1 m.ton/ha) of CaCO_3 added. In contrast, Thomas (1960) and Hsu and Rich (1960) showed that in certain circumstances AlOH^{2+} and Al(OH)_2^+ can form resulting in greater than equivalent amounts of exchangeable Al neutralised by lime. Although the low efficiency found for the neutralisation of exchangeable Al is attributable partly to incomplete extraction of exchangeable Al (EAI values do not measure total exchangeable Al) and partly to incomplete reaction of added lime (extraction of Ca with $\text{N NH}_4\text{OAc}$ indicated that more than 80% of the added lime had reacted) these errors are not sufficient to account for the effect. Data of Moscher, *et al.* (1960) and McLean, *et al.* (1964) show a similarly low reaction efficiency for the neutralisation of exchangeable Al suggesting that in certain soils other sources of acidity such as hydroxy Fe and Al and organic matter are neutralised more or less concurrently. However, despite the low efficiency, it is clear from Table 2 that liming to eliminate exchangeable Al is considerably more economical than liming to pH6.5.

Although the use of exchangeable Al as a criterion of soil fertility is limited to groups of soils of essentially similar character while the use of activity of Al^{3+} in the soil solution places widely dissimilar soils on a comparable basis (Adams and Lund, 1966) the former is more suited to practical application. Al concentration and hence activity in the "field" soil solution would fluctuate widely according to moisture status and salt content as affected by fertilisation, leaching and plant uptake. As a working index to the Al status of soils for routine advisory or soil survey purposes, a quantity factor is more meaningful than an intensity factor.

PAPER 3

CATION EXCHANGE CAPACITY AND EXCHANGEABLE
ALUMINIUM IN NATAL OXISOLS

Following the belief that acid soils should be limed to a near neutral pH for optimum crop growth, buffering in acid soils has been the subject of much research (reviewed by Coleman and Thomas, 1967). These authors observe that there are two definitions for an acid soil: (a) the pH is < 7 ; and (b) the effective CEC is not completely countered by basic cations. The latter definition would be more informative if a uniform convention for defining the CEC existed. However, numerous publications (Coleman and Thomas, 1967) show that the CEC of acid soils is largely dependent on the method of determination, particularly on the pH of the saturating electrolyte solution. The higher the pH of this solution the higher the measured CEC, the lower the calculated degree of base saturation and the greater the apparent acidity of the soil. The pH dependent charge, equivalent to the titratable or pH dependent acidity (Pratt and Bair, 1962) is due to factors such as (a) deprotonation of weak acid sites on organic matter or freeing of exchange sites as complexed Al is precipitated (Helling, Chesters, and Corey, 1964; McLean, Reicosky, and Lakshmanan, 1965); (b) release of initially blocked isomorphous substitutional negative charge by deprotonation of positive hydroxy alumina (de Villiers and Jackson, 1967); and (c) amphoteric behaviour of iron oxides also by deprotonation (Sumner, 1963a).

Although a knowledge of soil buffering characteristics is of value in understanding the nature of soil acidity and in discriminating, say, between soils of similar pH, the author (papers 1 and 2) and Kamprath (1970) have questioned the use of buffer capacity to pH6.5 as a criterion for lime requirement. In eight Natal Oxisols (papers 1 and 2) liming to pH6.5 was unnecessary and in some cases harmful; crop

response to lime ceased after application of relatively small but sufficient amounts of lime to eliminate exchangeable Al as a toxic factor. No correlation existed between exchangeable Al and buffer capacity as measured by lime requirement to pH6.5 or CEC at pH7. This supports the argument (Coleman, Weed, and McCracken, 1959) that CEC values of general significance in fertility work and in implementing percent base saturation as an unambiguous measure of "effective" acidity should be those operating under field conditions rather than those measured at artificially high pH values.

Since exchangeable Al is the important acidity to be neutralised by liming (salt exchangeable H_3O^+ is not considered to exist in significant amounts; Coleman and Thomas, 1967) its occurrence, formation and measurement are of importance. Determination of exchangeable Al by conventional extraction procedures is complicated by dissolution of non-exchangeable Al which depends on pH, concentration and nature of the extractant and duration of extraction (Pratt and Bair, 1961; Bhumbra and McLean, 1965; Skeen and Sumner, 1967 a,b). There is no clearcut division between the various forms of Al in the soil; pH is considered to be the main factor governing the relationship between exchangeable and non-exchangeable Al (Pionke and Corey, 1967). However, exchangeable Al was not related to pH in Natal Oxisols (papers 1 and 2) suggesting that other factors are involved. The object of this paper is to investigate the measurement of CEC values operative under field conditions and the factors affecting the occurrence of exchangeable Al in Natal Oxisols.

MATERIALS AND METHODS

Eight Natal Oxisols studied in papers 1 and 2 were sampled at 15cm intervals to a depth of 90cm, air dried and gently crushed to pass a 1mm screen. All samples were analysed for exchangeable Al by the method of Skeen and Sumner (1967 a,b) in which a sample of soil is extracted successively with 0.2N NH_4Cl (1:10 soil : solution ratio)

for exactly two minutes per extraction in a reciprocating shaker. Assuming that a constant amount of non-exchangeable Al dissolves in each extract, a plot of Al extracted vs. number of extractions will become linear when all exchangeable Al has been removed enabling a correction for non-exchangeable Al to be applied (Fig.1). The technique was modified for use as follows:

2g soil were placed in a tared 100ml centrifuge tube and extracted as above with 20ml portions 0.2N NH_4Cl . Four batches of five successive extracts were bulked and labelled A, B, C and D. After batch B (10 extractions) the centrifuge tubes were immediately weighed and the extraction continued using 0.2N KNO_3 (Skeen and Sumner, 1967a, showed that K^+ and NH_4^+ , Cl^- and NO_3^- behave similarly in the extraction of Al). Solution A was analysed for exchangeable Ca, Mg, K and Na, solution C for NH_4^+ and Cl^- from which CEC (field pH) and AEC (anion exchange capacity) were calculated after correcting for occluded salt; solutions A, B, C and D were analysed for Al from which exchangeable Al was calculated as above. CEC values were also determined in the following three ways: (a) by saturating with 0.2N NH_4Cl , washing free of Cl^- with distilled water and extracting the adsorbed NH_4^+ with 0.2N KNO_3 ; (b) as in (a) except that the occluded salt was removed by washing with absolute alcohol; (c) by saturating with N NH_4OAc -pH7, washing with alcohol and extracting with 0.2N KCl . The CEC of one subsoil (Farningham A, 60-75cm) was determined by saturating subsamples with 0.2N NH_4Cl , then washing to equilibrium with NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ solutions decreasing in strength from 0.2N to zero, and displacing the adsorbed NH_4^+ with 0.2N KCl . Occluded salt was corrected for by weighing except in one case where the soil was treated with 0.2N $(\text{NH}_4)_2\text{SO}_4$ and washed with water until free of SO_4^{2-} . One soil (Hutton, 0-15cm) was treated with increments of $\text{Ca}(\text{OH})_2$, moist incubated for 10 days, air dried and analysed for exchangeable cations as above and for CEC by the 0.2N $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$ washing/ KNO_3 procedure.

Al extractable with \underline{N} $\text{NH}_4\text{OAc-pH4}$ was determined in a few samples using the successive extraction technique of Skeen and Sumner (1967a,b). Al extractable with \underline{N} $\text{NH}_4\text{OAc-pH4}$ (1:10 soil : solution ratio, single 2 minute shake), pH in both water and \underline{N} KCl, and oxidisable carbon (Walkley-Black) were determined in all samples. NH_4^+ was determined by the Kjeldahl method, Al by the aluminon method, exchangeable bases by flame photometry and Cl^- with an Aminco-Cotlove chloride titrator.

RESULTS

Relevant properties of the eight soils are presented in Table 1 as means for the group (detailed data in appendix 3). Apart from those properties for which ranges are presented, values for individual soils did not differ greatly from the means and with certain exceptions to be discussed, the trends shown in Table 1 are typical of individual soils. Thus with increasing depth in the profile, organic matter, \underline{N} $\text{NH}_4\text{OAc-pH4}$ extractable Al, exchangeable bases and CEC decreased while AEC increased. Exchangeable Al was nearly constant with increasing depth in four soils, decreased in two and increased in the remaining two soils (Table 2). In six soils the pH remained constant with depth, pH (KCl) being approximately 0.9 unit lower than pH(H_2O) while in the remaining two soils (those in which exchangeable Al decreased) pH values increased, pH(KCl) increasing relatively more than pH(H_2O) (e.g. Farningham A, Table 2).

Al soluble in \underline{N} $\text{NH}_4\text{OAc-pH4}$ followed a curvilinear relationship with progressive extraction similar to that of Al removed by $0.2\underline{N}$ NH_4Cl (Fig.1) indicating that the former reagent extracted certain forms of Al relatively easily before dissolving more difficultly soluble forms at a constant rate per extraction. Pionke and Corey (1967) have suggested that Al extracted with acidified \underline{N} NH_4OAc is mostly associated with organic matter. In the soils studied Al

Table 1. pH, organic matter, extractable Al and cation exchange properties (means) of eight Natal Oxisols

Depth (cm)	pH (H ₂ O)	pH (KCl)	ox. C*	Extr. Al†	Exch. Al	Exch. Bases	AEC	"field pH" CEC	Net CEC‡	Net CEC§	pH7 CEC¶	Exch. cations
			%	-----meq/100g-----								
0-15	5.2	4.3	4.3	8.0	1.4	3.8	0.8	6.4	5.6	5.2	27	5.2
15-30	5.2	4.4	3.3	8.9	1.4	2.3	1.3	5.9	4.6	4.1	24	3.7
30-45	5.3	4.5	2.2	8.4	1.3	1.5	1.8	4.8	3.0	2.9	21	2.8
45-60	5.3	4.6	1.6	7.9	1.3	1.2	1.8	4.4	2.6	2.3	20	2.5
60-75	5.3	4.6	1.1	7.3	1.4	0.9	2.2	4.6	2.4	2.3	19	2.4
75-90	5.3	4.7	0.8	6.4	1.3	0.9	2.2	4.5	2.3	2.1	18	2.2

* Ranges (0-15cm) 1.7-7.4, (75-90cm) 0.3-2.0%

† Extracted with $\underline{\text{N}}$ NH₄OAc-pH4.0 (1:10 soil : solution ratio, single 2 min. shake).
Ranges (0-15cm) 4.2-14, (75-90cm) 3.1-11.9 meq/100g.

‡ Net CEC = CEC "field pH" - AEC

§ Net CEC determined by washing with H₂O

¶ Ranges (0-15cm) 14.3-39.2, (75-90cm) 10.3-28.4 meq/100g

Table 2. pH, extractable Al and cation exchange properties (meq/100g) of two Natal Oxisols exhibiting increasing and decreasing exchangeable Al values with increasing depth in the profile

Depth (cm)	Farningham B						Farningham A					
	pH (H ₂ O)	pH (KCl)	Extr.* Al	Exch. Al	Exch. Bases	Net CEC	pH (H ₂ O)	pH (KCl)	Extr.* Al	Exch. Al	Exch. Bases	Net CEC
0-15	5.5	4.5	6.3	0.3	6.3	6.5	5.2	4.3	7.7	2.0	2.0	3.2
15-30	5.5	4.5	7.0	0.4	5.7	6.2	5.1	4.4	6.3	1.4	1.4	2.5
30-45	5.5	4.5	7.0	0.4	4.1	4.9	5.2	4.5	5.6	0.8	1.2	1.4
45-60	5.5	4.6	7.0	0.7	3.0	3.4	5.3	4.8	5.2	0.1	0.9	0.9
60-75	5.5	4.5	7.7	1.1	1.8	3.1	5.3	5.0	4.5	0.0	0.8	0.9
75-90	5.3	4.6	6.7	0.7	1.4	1.8	5.4	5.4	3.5	0.0	0.8	0.7

* Extracted with N NH₄OAc-pH4.0 (1:10 soil : solution ratio, single 2 min. shake)

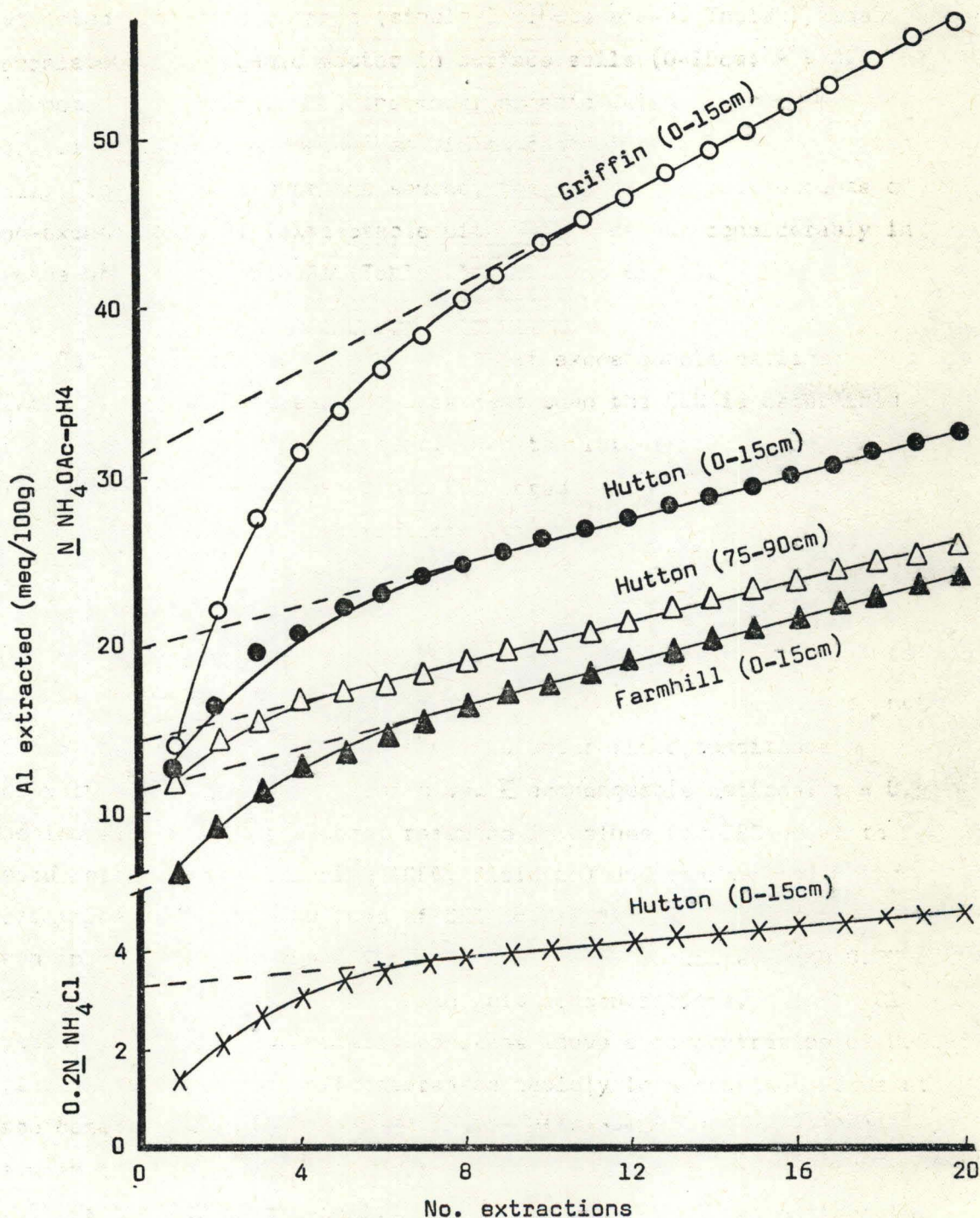


Fig.1 Cumulative amounts of Al extracted from Natal Oxisols with $N \text{ NH}_4\text{OAc-pH4}$ and $0.2N \text{ NH}_4\text{Cl}$. The linear portion of the NH_4Cl curve signifies the dissolution of non-exchangeable Al at a constant rate enabling exchangeable Al to be calculated.

extracted with this reagent (single 2 minute shake, Table 1) was correlated with organic matter in surface soils (0-15cm; $P = 0.05$) but not for subsoils. Furthermore, organic matter decreased far more with increasing depth than did extractable Al (Table 1; Hutton soil, Fig.1). Whatever the source, these soils contain amounts of non-exchangeable Al (extractable with \underline{N} $\text{NH}_4\text{OAc-pH4}$) considerably in excess of exchangeable Al (Tables 1 and 2 and Fig.1).

Comparison of the values for sum of exchangeable cations (Table 1) with CEC reveals no agreement when the CEC is determined at pH7 or at field pH. However, when the latter is corrected for AEC the resulting values for net CEC agree very closely with the sum of exchangeable cations (correlation net CEC vs. Σ exchangeable cations, $r = 0.95$). Contrary to the conclusions of other authors (Lin and Coleman, 1960; Sumner, 1963b) that washing with H_2O or H_2O /alcohol mixtures is undesirable in soils containing positive charges, CEC (H_2O washing; Table 1) gives a very good measure of net CEC which is clearly the effective CEC under field conditions (correlation net CEC/ H_2O washing vs. Σ exchangeable cations, $r = 0.98$). Washing with absolute alcohol resulted in values for CEC equal to those determined by weighing (CEC, field pH) and are not presented (see appendix 3g). The loss of CEC on dilution of the system can be seen in Fig. 2 where the CEC of soil initially saturated with 0.2N NH_4Cl was determined at decreasing salt concentrations. In NH_4Cl systems the CEC is essentially constant above a concentration of 0.05N ; below this concentration it decreases rapidly to a constant value at zero concentration (H_2O washed). The difference (2.5 meq/100g) between the CEC at zero concentration and that on the plateau above 0.05N is the AEC of the soil. In $(\text{NH}_4)_2\text{SO}_4$ systems the pattern is similar except that CEC values are consistently higher and no constant CEC value was found over the range of concentration employed. This is explained by concentration dependent ligand exchange of SO_4^{2-} for OH^- causing hydrolysis of Al^{3+} and an increase in CEC (Liu and Thomas,

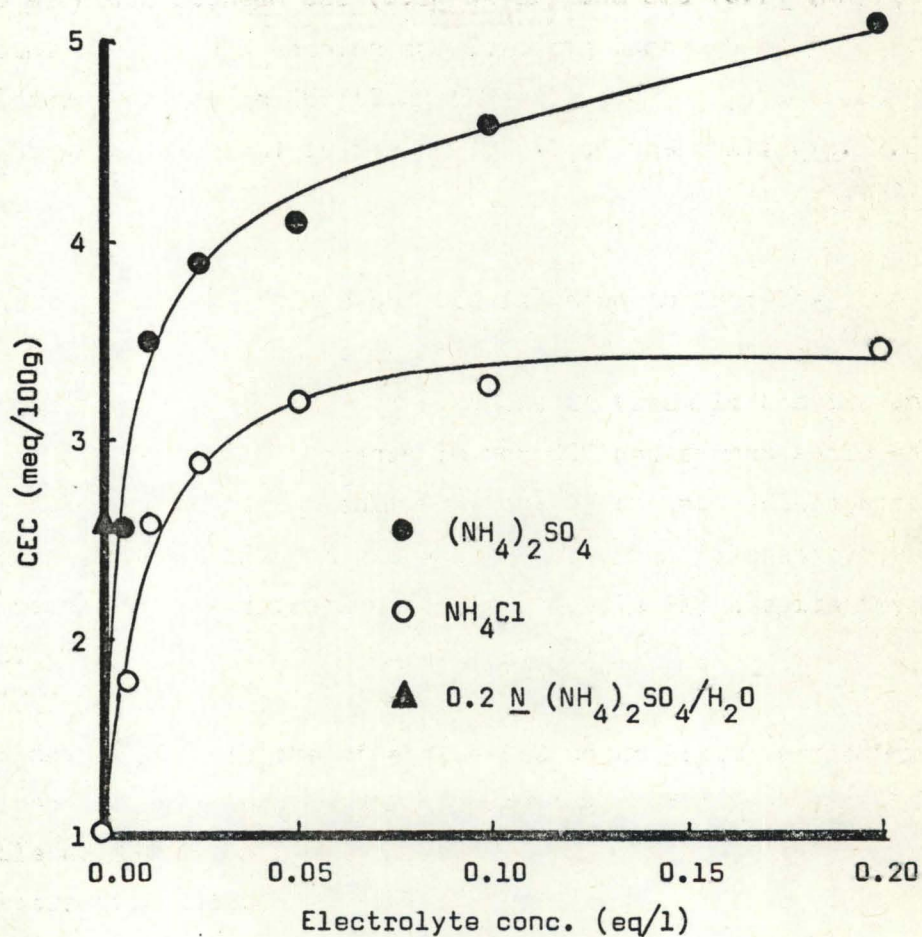


Fig.2 CEC of Farningham A subsoil (60-75cm) determined at varying concentrations of saturating electrolyte.

1961; paper 1). The difference between the curves represents the extent to which this reaction has taken place (1.6 meq/100g at 0.2N concentration). That SO_4^{2-} otherwise behaves similarly to Cl^- as an electrostatically exchangeable anion can be seen by the reduction in measured CEC at low concentration. In addition the difference of 1.6 meq/100g between CEC (0.2N NH_4Cl) and CEC (0.2N $(\text{NH}_4)_2\text{SO}_4$) was found by both H_2O washing and weighing techniques (Fig.2), and the difference between CEC (0.2N $(\text{NH}_4)_2\text{SO}_4$ /weighing) and CEC (0.2N $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ washing) is the AEC value of the soil, viz. 2.5 meq/100g.

Neutral salt or "field pH" CEC is known to increase with liming due to neutralisation and replacement of initially non-salt exchangeable "H" with salt exchangeable Ca (Bhumbla and McLean, 1965). In Fig. 3 the increase in net CEC and exchangeable cations with liming in the Hutton soil (0-15cm) is shown. Close agreement exists between net CEC and exchangeable cations (exchangeable bases after complete neutralisation of exchangeable Al) despite the increase in CEC.

Since net CEC is the effective CEC under field conditions, the difference between net CEC and exchangeable bases is a simple and reliable estimate of exchangeable Al (Fig.4); alternatively percentage base saturation calculated in terms of net CEC gives a realistic estimate of "effective" acidity.

DISCUSSION

Although the loss of the measured AEC and an equivalent amount of CEC on dilution (Tables 1 and 2; Fig.2) could be due to mechanisms such as removal of "imbibed salt" (e.g. in halloysite; Wada, 1959, quoted by Coleman and Thomas, 1967) or to hydrolysis of equivalent amounts of weak acid and weak basic sites, it seems more likely that the effect

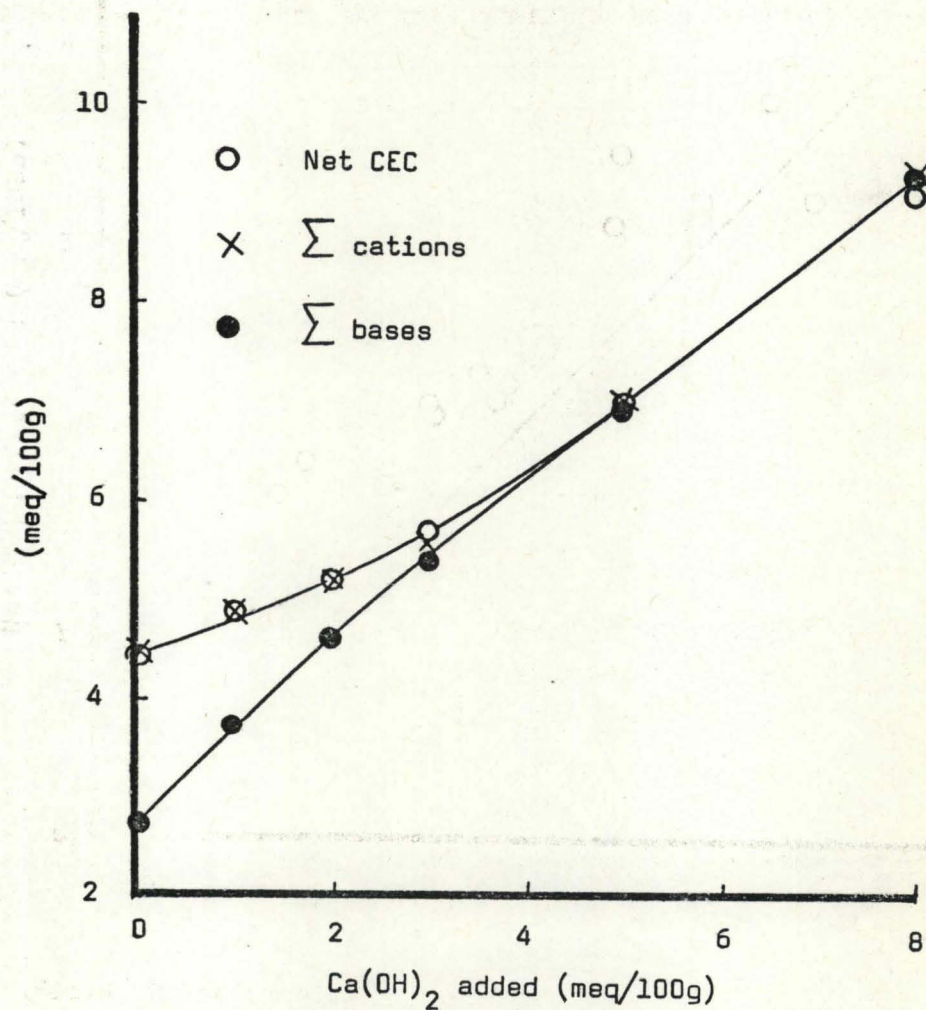


Fig.3 Variation in net CEC, exchangeable Al and exchangeable bases with increments of Ca(OH)_2 added to Hutton soil (0-15cm). The difference between the curves represents exchangeable Al.

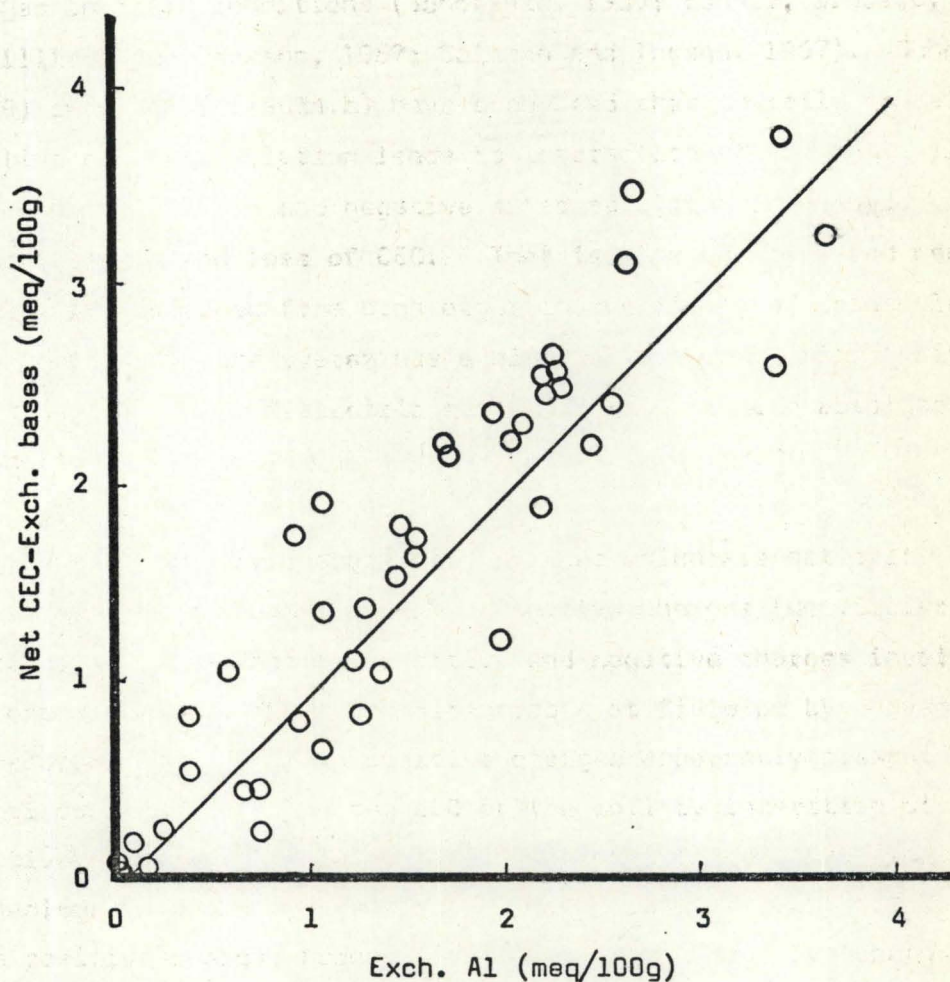


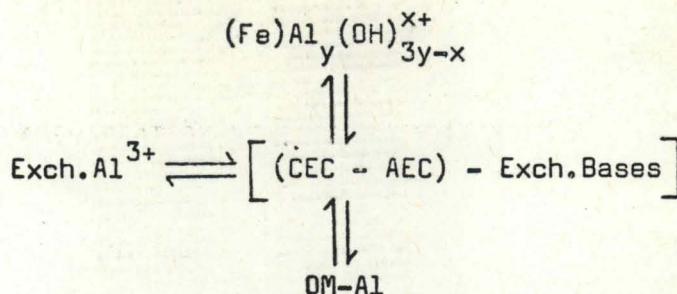
Fig.4 Relationship between exchangeable Al calculated by difference between net CEC and exchangeable bases and determined by the method of Skeen and Sumner (1967a,b) in eight Natal Oxisols, ($y = x + 0.08$; $r = 0.94^{***}$).

here is due to an interaction between positive and negative charges. If hydrolysis of weakly dissociated sites took place then such sites first became dissociated during the initial saturation with NH_4Cl (since net CEC $\equiv \sum$ exchangeable cations, Table 1); in contrast Fe and Al compounds in acid soils are widely held to exhibit positive charges in field conditions (Schofield, 1939; Sumner, 1963a,b; de Villiers and Jackson, 1967; Coleman and Thomas, 1967). Schofield (1939) and Sumner (1963a,b) have suggested that in soils containing positive charges, dilution leads to interaction of the double layers surrounding positive and negative sites resulting in mutual neutralisation and loss of CEC. That is, the positive and negative charges are screened from each other in conditions of double layer compression when the system has a high salt concentration (weighing technique) or a low dielectric constant (washing with absolute alcohol).

Thus positively charged sesquioxides which are not salt exchangeable can counter or block negative charges (de Villiers and Jackson, 1967) so that the positive and negative charges involved are not manifest and are not measureable at field pH by conventional procedures. In addition positive charges apparently present under normal conditions reduce the CEC of the soil by interaction with negative charges. The essential difference between the two mechanisms is probably a steric effect which physically prevents some positive charges from actually countering negative charges. Natal Oxisols are highly leached soils and it is clear from the agreement between exchangeable cations and net CEC (Table 1) that the natural soil solution is sufficiently dilute to allow complete interaction of positive and negative charges as in Fig. 2. Where positive charge equals negative charge the soil will be iso-electric and this was found to be the case for the Farmhill soil below a depth of 45cm. Sumner (1963a,b) has reported other such examples. Where the AEC is high the resultant net CEC and exchangeable cations (including exchangeable Al)

will be correspondingly low. The decrease in exchangeable Al with increasing depth in two soils (Farningham A, Table 2 and Farmhill) is attributed entirely to this effect. The increase in pH with depth in these two soils is not considered to be the cause of the decrease in exchangeable Al but is itself effected by the decrease in net CEC. In these soils pH (KCl) increased more rapidly than pH(H₂O) (e.g. Farningham A, Table 2); the increase in pH(KCl) to equal pH(H₂O) is attributed to a change in sign of the liquid junction potential (Coleman and Thomas, 1967) as the AEC increases to equal or exceed the CEC. In addition, Sumner (1963a) showed that under laboratory conditions positive charge decreases with increasing pH which is contrary to the apparent effect here. For the eight soils pH(KCl) was negatively correlated ($P = 0.05$) with exchangeable Al only below a depth of 15cm (the net CEC of surface soils is generally countered to a greater extent by basic cations than by Al (Table 1) and two soils (Farningham B, Table 2; and Balmoral) showed appreciable increases in exchangeable Al with depth without an accompanying decrease in pH.

This indicates that for Natal Oxisols under natural conditions pH plays a less prominent role in the occurrence of Al as an exchangeable cation than suggested by Pionke and Corey (1967). Indeed, any relationship between pH and exchangeable Al is probably not cause and effect but merely an alternative manifestation of a common property. Since Natal Oxisols contain large quantities of non-salt exchangeable Al (extractable with \underline{N} NH₄OAc-pH4; Table 1, Fig.1) which bears no apparent relationship to exchangeable Al (e.g. Farningham A, Table 2), an equilibrium relationship between the various forms of Al similar to that of Pionke and Corey (1967) but which is governed primarily by net CEC and exchangeable bases rather than by pH (or only secondarily by pH) is proposed as follows:



In the above diagram $(\text{Fe})\text{Al}_y(\text{OH})_{3y-x}^{x+}$ represents positively charged hydroxy Fe and Al polymers which can block CEC directly or neutralise it by double layer interaction. The hydroxy Al and organic matter complexed Al (OM-Al) exist in equilibrium with exchangeable Al depending on the resultant net CEC and on the amount of exchangeable bases present. That exchangeable bases influence this equilibrium is apparent since the large preponderance of non-exchangeable Al could easily shift the equilibrium to the left until the effective CEC was completely saturated with Al were the basic cations not sufficiently strongly absorbed to prevent this. The above equilibrium is consistent with the otherwise anomalous variation in exchangeable Al and hence lime requirement (papers 1 and 2) within a group of soils which are essentially similar as regards pH, organic matter, extractable Al, buffer capacity, CEC and other properties.

PAPER 4

AMELIORATION OF SUBSOIL ACIDITY
IN NATAL OXISOLS

Since incorporation of lime at depths greater than normal plough depth is both costly and undesirable due to exposure of infertile subsoil (paper 3), amelioration of subsoil acidity will depend on leaching of surface applied amendments. Although some authors indicate that subsoil liming does not increase yield substantially if the topsoil is adequately limed (Hourigan, et al, 1961; Estrada and Cummings, 1968) and that surface applied lime is as effective as lime incorporated into the plough layer (Abruna, Vicente-Chandler, and Pearson, 1964), others have found appreciable increases in yield resulting from deep placement of lime (Pohlman, 1946; Kehoe and Curnow, 1963). Liming subsurface horizons considerably increases root proliferation in the subsoil (Ragland and Coleman, 1959; Hourigan, et al, 1961; Kehoe and Curnow, 1963; Estrada and Cummings, 1968; unpublished data of the author) and it appears that benefits gained from deep placement of lime are largely ascribable to improved subsoil moisture utilisation (Haynes and Robbins, 1948; Rios and Pearson, 1964).

Although neutralisation of subsoil acidity, in particular the elimination of Al toxicity (papers 1 and 2) would account for improved root penetration in Natal Oxisols, Ca is known to be an essential factor in the root environment due to poor downward translocation by plants (Haynes and Robbins, 1948; Rios and Pearson, 1964; Howard and Adams, 1965). Data in paper 3 (and appendix 3) show that Natal Oxisols are generally low in exchangeable bases at depth in the profile; exchangeable Ca values < 0.1 meq/100g below a depth of 15 or 30cm are not uncommon. It therefore seems imperative to consider subsoil acidity in the amelioration of acid soils both

from the standpoint of toxic factors and low base status.

Although the downward movement of lime is enhanced by heavy dressings of acid forming nitrogenous fertilizers, the rate of movement is exceedingly slow (Pohlman, 1946; Brown, et al, 1957; Pearson, Abruna, and Vicente-Chandler, 1962; Abruna, et al, 1964; Adams, White, and Dawson, 1967). Unpublished data of the author (appendix 4b) show that after 14 years of cropping with maize 12 m.tons of dolomitic lime/ha (0-15cm) had little or no effect on exchangeable Ca and Al below a depth of 45cm in a typical Natal Oxisol. Reeve (1968) obtained similar results in micro-lysimeters. After extensive leaching with de-ionised water, Ca from heavily limed topsoil reached a maximum depth of 45cm. In soils treated with gypsum on the other hand, Ca rapidly moved through the entire profile. However, exchangeable Ca in gypsum treated soils increased largely at the expense of exchangeable Mg.

In most of the studies cited above, appreciable downward movement of lime was only obtained where extremely heavy dressings of lime had been applied; in Natal Oxisols, heavy liming could lead to a serious depression yield (paper 1). The object of this paper is to investigate the downward movement of Ca and the neutralisation of subsurface exchangeable Al at rates of amelioration comparable with the actual lime requirement of these soils (paper 2) and which are therefore likely to be acceptable in practice.

MATERIALS AND METHODS

For the purpose of this study, only one soil was used since Reeve (1968) showed that Natal Oxisols can be expected to behave similarly with respect to the leaching of soil ameliorants. The Clovelly series, a typical Natal Oxisol (studied by Reeve, 1968; papers 1, 2, and 3) contains approximately 2 meq/100g each of

exchangeable Al, Ca, and Mg, 3.3% oxidisable C, has a pH(KCl) of 4.1 and a CEC of 21 meq/100g at pH7 ($\text{N NH}_4\text{OAc}$) in the topsoil (0-15cm). The base status declines rapidly with increasing depth in the profile (exchangeable Ca = 0.5 meq/100g between 15 and 30cm depth and < 0.2 meq/100g below 30cm); exchangeable Al and pH remain essentially constant to a depth of 90cm (see appendix 3).

Seven sets of eight 100g subsamples of airdry Clovelly topsoil (0-15cm) were each treated with increments (0, 1, 2, 3, 5, 7, 9, 11 meq/100g) of either Ca(OH)_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; to three sets 1 meq N/100g (140 ppm) was added either as NH_4Cl or NaNO_3 and two sets were superimposed on 100g of untreated Clovelly subsoil (15-30cm) to simulate a profile. The samples were placed in 5cm diameter polythene leaching tubes, moistened to field capacity and incubated at 30°C for 10 weeks. With the exception of one set, all samples were leached with de-ionised H_2O (room temperature) at the rate of one pore volume per day (topsoil basis; 1 pore volume = 40ml H_2O = 2cm). The experimental treatments are listed in Table 1.

Table 1. Experimental treatments applied to sets of Clovelly topsoil treated with increments of lime or gypsum

Set No.	Leach	Ameliorant	N	Topsoil	Subsoil
A	no	Ca(OH)_2	no	yes	no
B	yes	Ca(OH)_2	no	yes	no
C	yes	Ca(OH)_2	NaNO_3	yes	no
D	yes	Ca(OH)_2	NH_4Cl	yes	no
E	yes	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	no	yes	no
F	yes	Ca(OH)_2	NH_4Cl	yes	yes
G	yes	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	no	yes	yes

Leachates were collected and analysed for Ca, Mg, and K by flame

photometry. When the amount of Ca in each pore volume displaced became < 0.02 meq/100g (< 0.05 meq/100g in the case of set E) the experiment was terminated, the soils air dried and analysed for exchangeable Ca, Mg, K, Na, NH_4 , and net CEC (samples were saturated with NH_4Cl , washed free of salt with H_2O and adsorbed NH_4 determined by Kjeldahl distillation; exchangeable NH_4 was displaced with 0.2N KNO_3 .) Exchangeable Al was taken as the difference between net CEC and total exchangeable bases (paper 3). Subsoils were analysed in the case of sets F and G. Nitrate was determined in leachates from sets B and D.

RESULTS

The rate of Ca removal dropped to the specified limits after six pore volumes of water had passed through treatments B, C and D and after 16 pore volumes had passed through treatment E. Leaching of both treatments F and G was terminated after 16 pore volumes of water had passed through the soil. Total Ca, Mg, and K leached from the limed soil are presented in Fig. 1 and from the gypsum treated soil in Fig. 2. K lost from individual treatments is not shown since the maximum K lost was < 0.05 meq/100g and < 0.12 meq/100g from lime and gypsum treated soil respectively. Although application of NaNO_3 and NH_4Cl increased the loss of bases from lime treated topsoil, the maximum amount leached (1.5 meq/100g) was far less than in the case of gypsum treated soil where total bases leached were equivalent to 80% of that applied. At low levels of ameliorant more Mg than Ca was removed supporting the earlier finding (Reeve, 1968) that in these soils Mg is considerably less strongly adsorbed than Ca. NaNO_3 and NH_4Cl increased the removal of Mg from limed soil but losses were nevertheless not appreciable. In the case of gypsum treated soil, however, serious losses of Mg occurred; more than half the native exchangeable Mg (1.7 meq/100g) being lost for gypsum applications above 3 meq/100g. Comparison of Figs. 1 and 3 shows that the greater loss

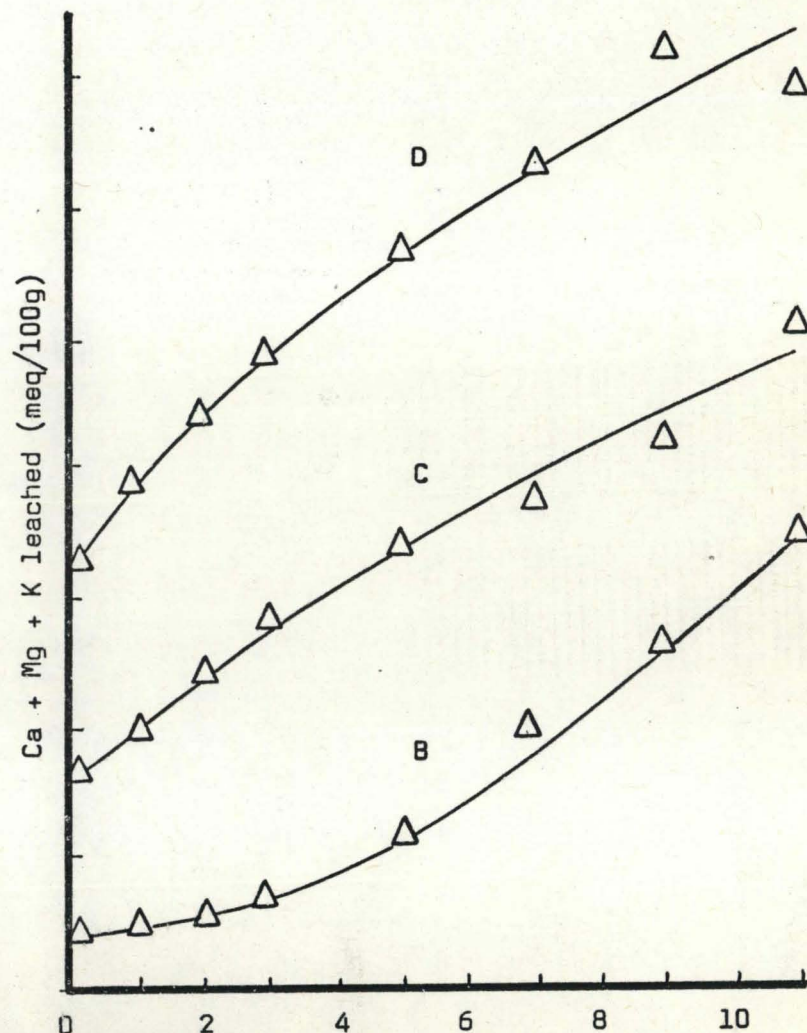
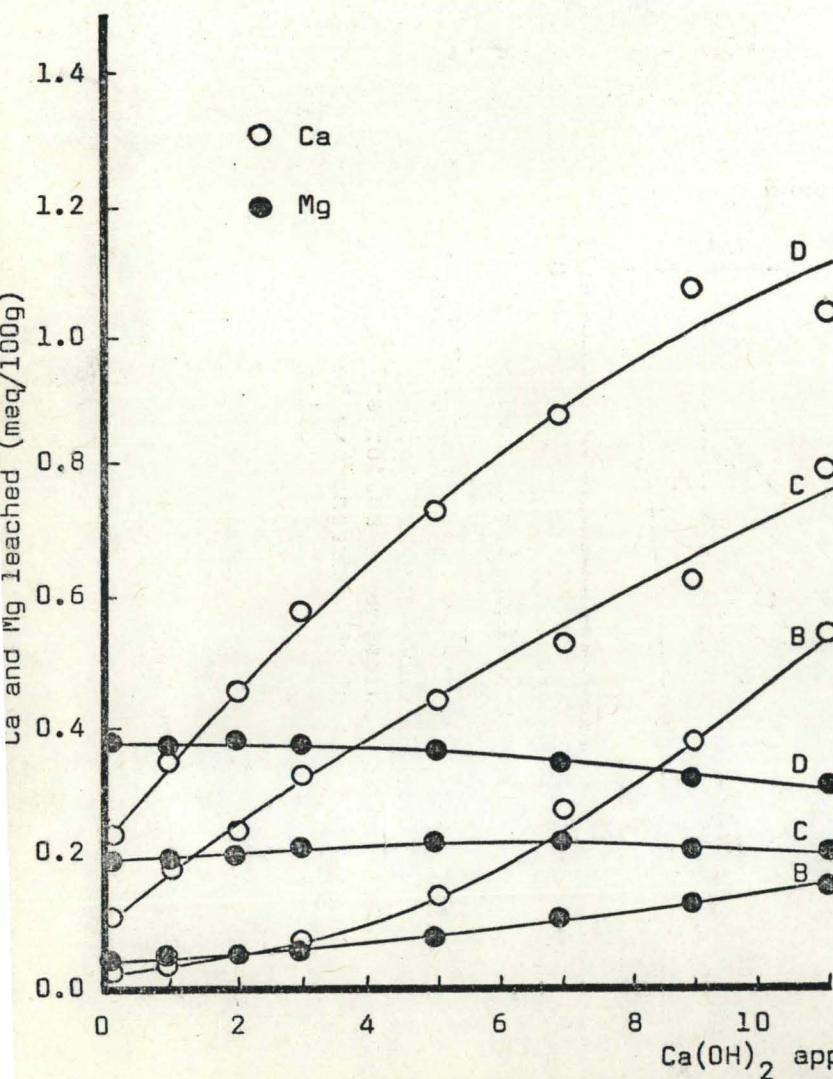


Fig.1 Total bases leached from Clovelly topsoil (0-15cm) treated with lime (set B), lime + NaNO_3 (set C) and lime + NH_4Cl (set D).

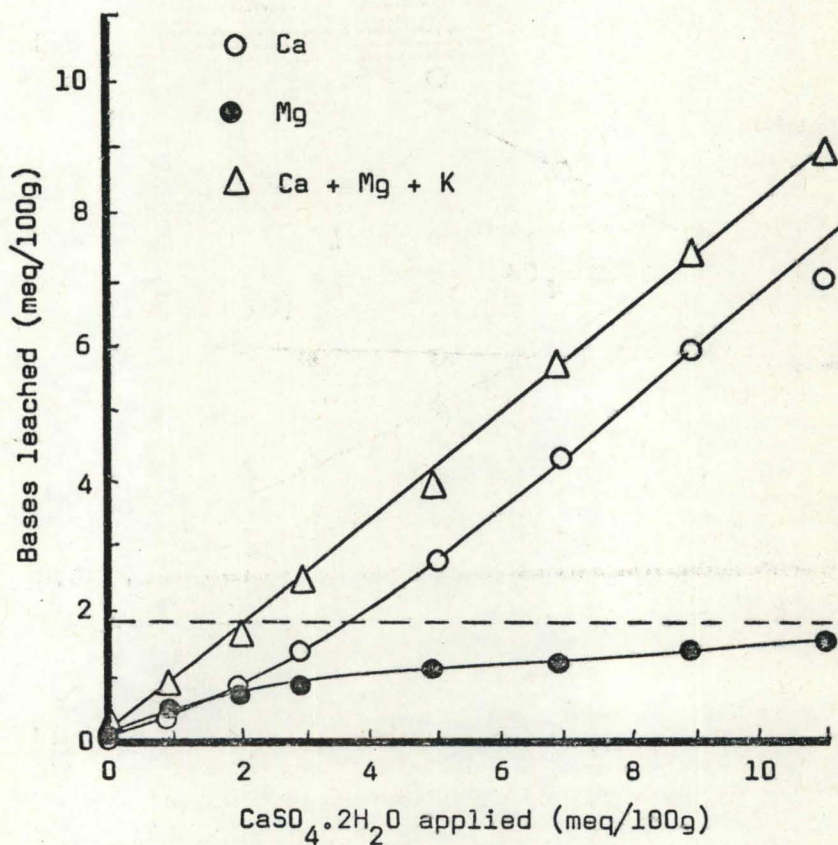


Fig.2 Bases leached from Clovelly topsoil (0-15cm) treated with gypsum (set E). The dotted line represents the level of exchangeable Mg in the untreated soil.

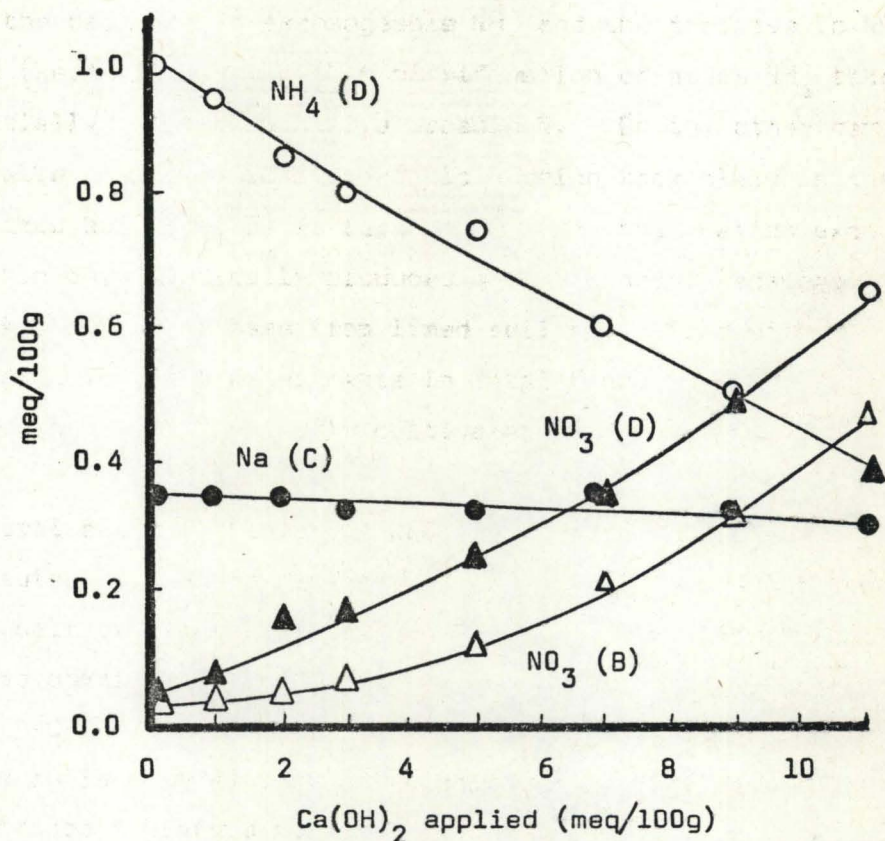


Fig.3. Nitrate leached (sets B and D) and exchangeable Na and NH₄ remaining in limed Clovelly topsoil (0-15cm) fertilized with NaNO₃ (set C) and NH₄Cl (set D) after leaching with de-ionised water. Soil not fertilized with N contained negligible amounts of Na and NH₄ after leaching.

of Ca, Mg, and K from N fertilized soil is adequately accounted for by the increase in exchangeable Na (set C) and largely by the increase in exchangeable NH_4 (set D). Nitrification increased with increased rate of liming as expected (Fig.3); the quantitative agreement between the decrease in exchangeable NH_4 and the increase in NO_3 produced (set D) indicates that nitrification of added NH_4 takes place preferentially to that of native organic N. On the other hand, the considerable nitrification of organic N which took place in the unfertilized soil (set B) is further evidence that cation exchange rather than physiologically produced acids is mostly responsible for the increased loss of base from limed soil fertilized with N. In support of this field experiments in Natal frequently show little or no crop response to N on newly cultivated soils.

Neutral salt or "field pH" CEC is known to increase with liming due to neutralisation or replacement of initially non-salt exchangeable "H" with salt exchangeable Ca (Bhumbla and McLean, 1965; paper 3). CEC values obtained at different levels of $\text{Ca}(\text{OH})_2$ are shown in Fig. 4 (set B). CEC values for the N fertilized soils (sets C and D) and unleached soils (set A) were not significantly different from those in Fig. 4 and are therefore not presented (appendix 4a). The increase in CEC accounts for the minimal movement of bases from limed soil. Exchangeable Al decreased to zero with increased rates of lime application as expected. In agreement with the findings in paper 2, the neutralisation of exchangeable Al is not a preferential reaction; the neutralisation of other forms of acidity leading to an increase in CEC takes place simultaneously. For gypsum treated soil on the other hand, the CEC remained unchanged, exchangeable Ca increasing largely at the expense of exchangeable Mg and to a lesser extent exchangeable Al. Although the decrease in exchangeable Al may be due in part to replacement by Ca and loss by leaching, gypsum has been shown to reduce exchangeable Al, probably by sulphate-induced Al polymerisation by ligand exchange for hydroxyl groups resulting in a "self liming"

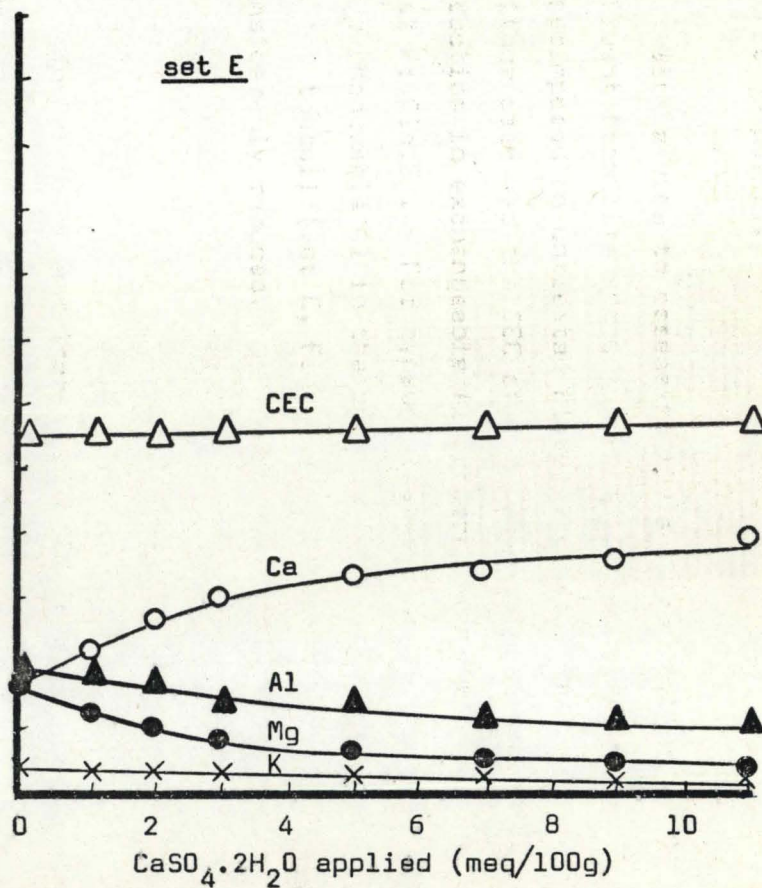
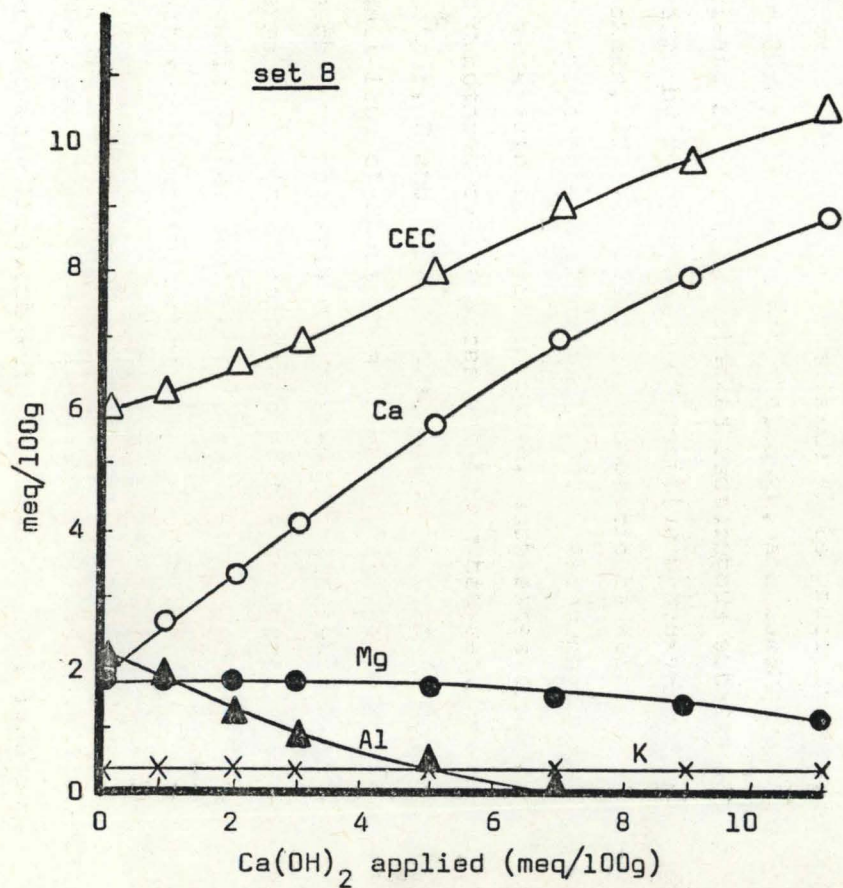


Fig.4 CEC and exchangeable cations in Clovelly topsoil (0-15cm) treated with lime and gypsum after leaching with water.

effect (paper 1).

With a view to assessing the acid neutralising capacity of effluent from lime and gypsum treated topsoil, sets D and E were superimposed on untreated Clovelly subsoil (sets F and G). In neither case was the CEC of the subsoil increased and only a small reduction in exchangeable Al occurred where the topsoil was limed (set F; Fig.5). For gypsum treated topsoil (set G) the reduction in exchangeable Al in the subsoil was comparable with that obtained in the topsoil (set E, Fig.3). Again, exchangeable Mg was considerably reduced.

DISCUSSION

The pH dependent increase in CEC in acid soils arises from (a) deprotonation of weak acid sites on organic matter or freeing of exchange sites as complexed Al is precipitated (Helling, Chesters, and Corey, 1964; McLean, Reicosky, and Lakshmanan, 1965); (b) release of initially blocked isomorphous substitutional negative charge by deprotonation of positive hydroxy alumina (de Villiers and Jackson, 1965); and (c) amphoteric behaviour of iron oxides also by deprotonation (Sumner, 1963). Although in general deprotonation of weak acid sites is involved, such sites are not easily hydrolysed as evidenced by the agreement found between CEC values of leached (sets B, C and D) and unleached soil (set A) (appendix 4a) and the small loss of bases from limed soil (Fig.1). Thus on liming, sites which were formerly not salt-exchangeable become so at least semi-permanently (that component of the pH dependent CEC which is due to organic matter would be slowly lost on decomposition of the organic matter). For this reason downward movement of bases from limed topsoil is largely dependent on fertilisation. Figs. 3, 4, and 5 show that added NH_4 is quantitatively adsorbed and that native exchangeable K is subject to little loss by leaching. Since K and

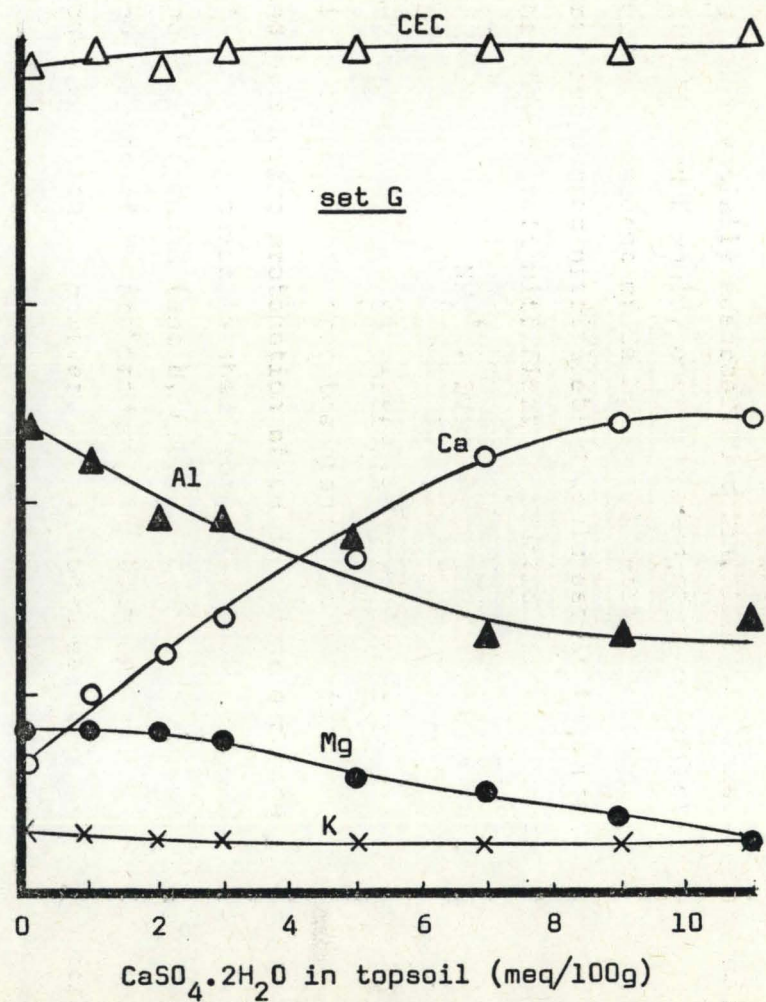
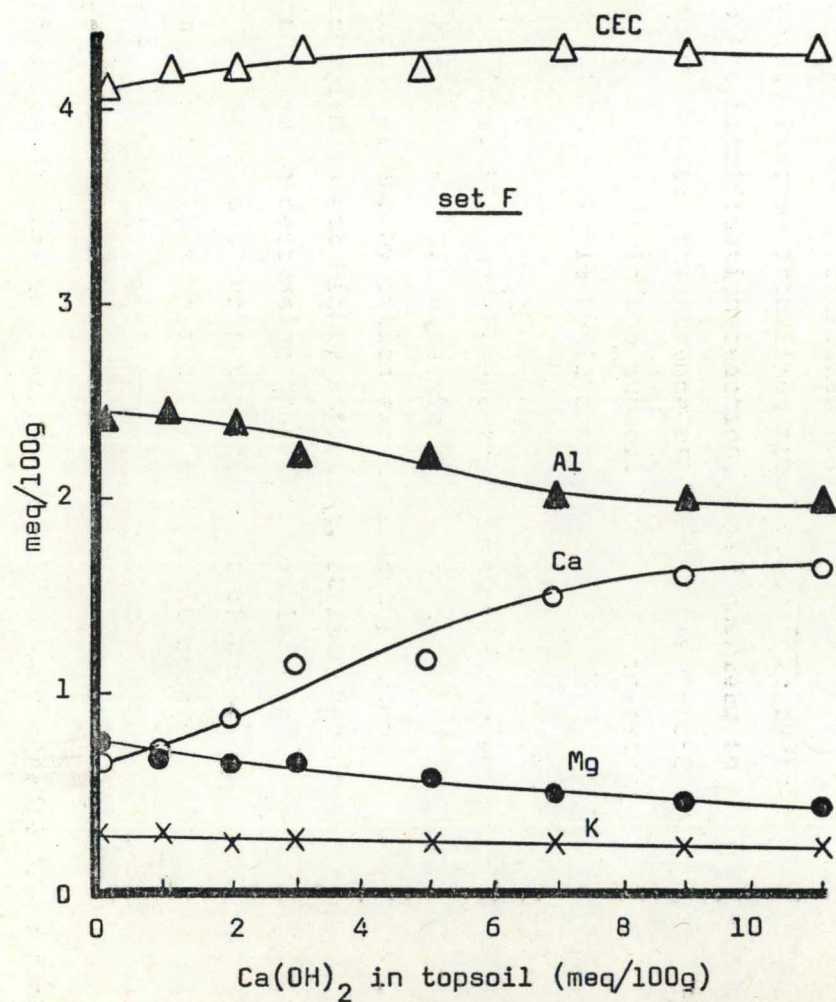
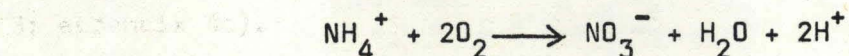


Fig.5 CEC and exchangeable cations in Clovelly subsoil (15-30cm) after leaching with effluent from ameliorated topsoil.

NH_4 have similar hydrated ionic radii, applied K is also likely to be preferentially adsorbed (Duthion, 1968). Thus heavy fertilization with NH_4 and K would, over a period of time, effect a considerable downward movement of Ca by simple cation exchange. In addition, acids produced during nitrification would assist this process. Assuming that the overall nitrification reaction is



the NH_4^+ ion should be particularly efficient in the removal of Ca from limed topsoil both from the standpoint of dissolving unreacted lime and by causing protonation of pH dependent exchange sites. Comparison of the total bases leached from unfertilized soil (set B, Fig.1) with the NO_3^- produced (set B, Fig.3) shows close agreement if two equivalents of H^+ are produced for each equivalent of NO_3^- as in the above equation. However, as mentioned earlier, physiologically produced acids are unable to account entirely for the increased loss of bases from N fertilized soil (Fig.1). From Fig. 4 it is clear that Ca leached from limed topsoil, whether by cation exchange or due to the nitrification reaction, moves downward in the form of a neutral salt; the absence of an increase in CEC or decrease in exchangeable Al in the subsoil indicates that the effluent from limed topsoil has little basic character.

Figs. 1, 2 and 5 show that gypsum is far superior to lime in increasing subsoil base status. Although the reduction of exchangeable Al either by cation exchange or the proposed "self liming" mechanism is not highly efficient, it is nevertheless more effective than lime in decreasing the exchangeable Al content of subsoils. It is interesting to note that movement of bases from gypsum treated topsoil was essentially complete within only 16 pore volumes of leaching (32cm of H_2O) which is considerably less than the annual precipitation in areas where Oxisols occur (ca.100cm). Since gypsum is not as effective as lime in decreasing topsoil exchangeable Al, a combination

of gypsum and dolomitic lime (to offset Mg loss caused by gypsum) should give better results than either alone. In support of this, the author has obtained a significant yield response of 'trudan' (Sorghum sudanense) in the field to 4 m.tons gypsum/ha in the presence of more than 6 m.tons dolomitic lime/ha on a member of the Farningham soil series (similar to the Farningham A studied in papers 1, 2, and 3; appendix 4c).

GENERAL DISCUSSION

Hitherto the use of lime in Natal has been largely restricted to an occasional arbitrary application seldom exceeding 2 m.tons/ha. That this approach has not been altogether unsatisfactory is explained by the relatively small lime requirements of many soils (paper 2) and the cumulative effects of successive applications due to small leaching losses (paper 4). However, the immediate need for increased productivity coupled with the greater acidification of soils by heavy fertilisation makes it imperative that the present hit or miss policy be replaced by a more quantitative assessment of soil acidity. It has been shown (papers 1 and 2) that the harmful effects of soil acidity in Natal Oxisols can largely be ascribed to Al toxicity and that lime requirements can be accurately assessed in terms of the amount of exchangeable Al present. The successful implementation of this policy depends on the assumption that undesirable effects associated with soil acidity, in a particular P fixation, are not significantly affected by lime in excess of that required to eliminate exchangeable Al and can be ignored in the assessment of lime requirement. According to the findings in papers 1 and 2 this assumption is valid; lime does not effect a significant reduction in P fixation. However, this is a conclusion based on pot experimentation and laboratory tests. It is axiomatic that chemical fertility tests are worth no more than the degree to which they are calibrated against actual plant growth in the field. The same could be said of pot trials. Nevertheless, although observed effects are often exaggerated in the glasshouse, this very sensitivity increases the value of pot experimentation as a diagnostic bio-assay of soil fertility. Regarded as such, pot experiments are an invaluable means of formulating a working model against which observed fertility patterns may be interpreted and further investigated. "New knowledge obtained through research comes mainly from the perspective inherent in the model and the theories it inspires" (Cline, 1961).

With regard to Al toxicity, experience in the field (e.g. appendix 4c) seldom shows responses to lime as spectacular as reported here. This is readily explained in terms of the high salt concentration in the undrained pots which would greatly increase the concentration of Al in the soil solution. For this reason "critical" Al values found in pot experiments are not expected to be directly applicable in the field. However, there seems no reason to doubt the applicability of lime requirements based on exchangeable Al in principle. In view of the inefficient reaction of lime with exchangeable Al (papers 2 and 4), coarse particle size, impurities, poor mixing in the field and the well known differences in Al tolerance between crops (Jackson, 1967), it is an impracticable and unnecessary refinement to attempt to lime to a critical value specific for the crop to be grown on a particular soil type. To aim at the elimination of exchangeable Al represents a satisfactory compromise; superfluous applications of lime would be minimal and overliming would be effectively avoided. In addition to the indications that excessive amounts of lime can depress yields (papers 1 and 2, appendix 4c), it warrants mention that heavy liming would be expected to greatly increase bacterial activity in the soil at the expense of organic matter (paper 4); van der Eyk, et al., (1969) emphasize the need to preserve a high organic matter content in Natal Oxisols in order to prevent structural deterioration and erosion. The production of high yielding crops with associated large residues is certainly the best insurance against organic matter depletion provided that the natural equilibria are not unduly prejudiced by treatments which are largely irrevocable.

Pot trials have been used to demonstrate P fixation as a growth limiting factor in principle. The marked growth response up to extremely high levels of P should not, however, be taken as evidence that good yields on Natal Oxisols are impossible without excessive P fertilization.

Unpublished data of E.R. Orchard* show that maize yields of the order of 8000kg/ha (grain) are possible with annual P applications of 94kg/ha (1:1 super/raw rock, broadcast). It is to be expected that reduced contact between fertilizer and soil should minimise loss by fixation; band placement of fertilizer is practised to some degree by most farmers in the region. Attempts to minimise P fixation by chemical treatment designed to block or neutralise P fixing sites have achieved little success in actually improving the supply of P to the plant. In some cases cognisance has not been taken of the physiological interference in P uptake caused by Al toxicity (Jackson, 1967) in interpreting apparent improved P availability. The author believes that the ultimate solution to the problem of P fixation will lie in the field of fertilizer technology, not in chemical amelioration of the soil.

The role of the H ion in soil acidity has caused considerable confusion in the past. Jenny (1961) remarks that although acid soils were known to be largely Al saturated at the beginning of the century, subsequent workers believed the base unsaturated cation exchange sites of acid soils to be countered by H ions. Contemporary workers are agreed that appreciable amounts of H cannot be extracted from soil with a neutral unbuffered salt unless the soil is first artificially saturated with H or unless free acids are present. In fact H saturated clays are known to change spontaneously to Al-clays (Coleman and Thomas, 1967). The situation may be expressed in quantitative terms when it is considered that the amount of H measured by the glass electrode at pH4.0 in a 1:1 soil/N KCl solution represents "exchangeable" H of the order of 0.01 meq/100g.

Current theory distinguishes between "exchange" acidity - that which can be displaced by a neutral unbuffered salt such as KCl and which

* Regional project No. NC 2(T).

is almost exclusively Al - and "titratable" acidity which is acidity neutralised by a buffered solution after exchangeable acidity has been removed. Titratable acidity therefore represents the difference between "total" and exchangeable acidity. The total acidity measured depends on the pH of the buffered extractant used - usually pH7.0 ($\text{N NH}_4\text{OAc}$) or 8.2 ($\text{BaCl}_2\text{-TEA}$). The titratable acidity is due to ionisation of tightly bound H ions from weak acid groups on organic matter and sesquioxides. In contributing to titratable acidity by losing a proton, such groups acquire a negative charge. Titratable acidity is therefore equivalent to pH dependent CEC (Pratt and Bair, 1962). Further confusion concerning the "exchangeability" of the H ion arises from incorrect usage of the above terms. Coleman and Thomas (1967) for example, define exchangeable and titratable acidity as above, but subsequently refer to "exchange" acidity as the difference between CEC measured with $\text{BaCl}_2\text{-TEA}$ (pH8.2) and basic metal cations!

Many soils contain clays extensively coated with positively charged Fe and Al hydrous oxides which reduce the negative charge carried by the clay (Coleman, et al., 1964); de Villiers and Jackson, 1967). When the pH is raised the sesquioxides lose protons and exchange sites on the clay are exposed. Coleman and Thomas (1967) point out that pH/percentage base saturation relationships depend on the proportion of the total acidity which is exchangeable. Where a high proportion of the total acidity is exchangeable, the pH will remain low as long as base saturation is incomplete, i.e. as long as exchangeable Al exists. In such cases a high percentage base saturation (ca. 80%, based on CEC at pH8.2) is required before the soil will attain a neutral pH. In soils containing sesquioxide coated clays and much organic matter, exchangeable Al is low due to the low effective CEC (at field pH) and the proportion of exchangeable acidity to total acidity is low. Here the percentage base saturation (CEC at pH8.2) required to reach a neutral pH is much lower (ca. 50%). Clearly Natal Oxisols fall into the latter category (paper 3; appendix 3).

Considered in this light, it is not surprising that lime requirements for the soils studied are high when based on buffer capacity to pH6.5 but are relatively low when based on exchangeable Al (paper 2). Any system which employs buffer capacity (or percentage base saturation) as a criterion for lime requirement is limited to groups of soils having similar exchange acidity/total acidity relationships. Where soils differing greatly in acidity characteristics must be catered for, exchange acidity provides the only common ground on which lime recommendations can be based.

APPENDIX 1

Sample localities of the soils studied

<u>Griffin</u>	<u>Nottingham Road</u> district - about one kilometer from the village on the Fort Nottingham road.
<u>Clovelly</u>	<u>Mooi River</u> district - about five kilometers north of the village turn east off the national highway onto the Middeldrust road - travel one kilometer from turnoff.
<u>Lidgetton</u>	<u>Lidgetton</u> district - about three kilometers east of the village on local district road.
<u>Farmhill</u>	<u>Howick</u> district - on Rietvlei road opposite entrance to farm "Triandra".
<u>Hutton</u>	<u>Himeville</u> district - on the farm "Hazeldene".
<u>Farningham A</u>	<u>Underberg</u> district - on the farm "Hlogoma".
<u>Farningham B</u>	<u>Darqle</u> district - on the farm "Selsley".
<u>Balmoral</u>	<u>Mooi River</u> district - about six kilometers past the Clovelly site on the Middeldrust road.

APPENDIX 2

Detailed results of pot experiment in paper 1

(a) Yield (g/pot; 20 ppm P applied)

Soil	Control	Lime			Gypsum			Silene		
	0*	L1*	L2	L3	G1*	G2	G3	S1*	S2	S3
Griffin	0.33	0.66	0.63	0.73	0.59	0.70	0.75	0.40	0.50	0.69
Clovelly	0.78	1.88	1.48	0.88	1.14	1.38	1.23	1.45	1.97	2.36
Lidgetton	0.52	0.94	1.04	0.80	0.72	0.81	0.95	0.76	1.18	1.05
Farmhill	0.81	0.94	1.08	1.06	1.06	1.46	1.28	1.10	0.92	1.15
Hutton	0.30	1.05	0.93	0.97	0.51	0.67	0.67	0.45	0.75	1.31
Farningham A	0.25	0.95	0.95	0.83	0.58	1.12	1.30	0.42	0.63	1.20
Farningham B	1.14	1.24	1.00	1.38	1.05	1.60	1.43	1.24	1.55	1.69
Balmoral	1.00	3.82	2.79	2.40	1.72	2.08	3.79	2.84	4.15	3.26

* level of ameliorant

(b) Yield (g/pot; 80 ppm P applied)

Soil	Control	Lime			Gypsum			Silene		
	0	L1	L2	L3	G1	G2	G3	S1	S2	S3
Griffin	0.35	1.85	1.84	2.00	1.44	1.90	2.09	0.46	0.94	1.75
Clovelly	2.66	10.42	7.85	7.38	6.97	5.25	6.73	9.95	9.86	9.26
Lidgetton	1.71	3.38	3.08	3.06	3.33	4.70	3.93	3.70	4.51	4.81
Farmhill	2.12	2.95	2.82	3.69	5.78	5.51	5.05	4.42	4.45	3.17
Hutton	0.34	3.75	6.72	4.83	0.76	1.88	1.29	0.77	2.54	4.80
Farningham A	0.25	6.64	5.26	4.07	1.15	5.41	7.80	0.97	2.63	6.34
Farningham B	4.66	5.56	4.50	4.21	5.56	4.88	5.12	5.90	6.12	5.34
Balmoral	9.50	13.35	11.71	9.53	12.29	13.00	11.22	13.00	14.08	14.41

App. 2

(c) pH(H₂O)

Soil	Control	Lime			Gypsum			Silene		
	0	L1	L2	L3	G1	G2	G3	S1	S2	S3
Griffin	4.25	4.81	5.30	5.73	4.41	4.65	4.63	4.45	4.72	4.78
Clovelly	4.69	5.10	5.60	6.20	4.60	4.52	4.50	4.85	4.92	5.03
Lidgetton	4.52	4.92	5.40	5.80	4.52	4.54	4.52	4.59	4.60	4.72
Farmhill	4.76	5.21	5.70	6.21	4.71	4.66	4.67	4.85	4.90	5.06
Hutton	4.28	4.80	5.40	5.85	4.42	4.35	4.43	4.43	4.59	4.70
Farningham A	4.25	4.78	5.32	5.85	4.36	4.50	4.68	4.28	4.50	4.60
Farningham B	4.72	5.15	5.62	5.95	4.78	4.89	4.76	4.82	4.90	5.02
Balmoral	4.73	5.05	5.55	6.10	4.70	4.65	4.60	4.80	4.98	5.00

(d) EAI (meq/100g)

Soil	Control	Lime			Gypsum			Silene		
	0	L1	L2	L3	G1	G2	G3	S1	S2	S3
Griffin	1.07	0.08	0.04	0.02	0.71	0.35	0.38	0.65	0.26	0.19
Clovelly	0.61	0.06	0.01	0.01	0.35	0.38	0.37	0.32	0.12	0.06
Lidgetton	0.78	0.07	0.01	0.01	0.39	0.32	0.30	0.41	0.21	0.12
Farmhill	0.18	0.02	0.02	0.01	0.12	0.08	0.08	0.09	0.04	0.03
Hutton	1.43	0.14	0.03	0.01	0.91	0.68	0.68	0.89	0.52	0.26
Farningham A	1.39	0.08	0.01	0.01	0.55	0.34	0.18	0.59	0.37	0.17
Farningham B	0.22	0.03	0.02	0.02	0.13	0.11	0.11	0.10	0.06	0.03
Balmoral	0.32	0.02	0.00	0.01	0.26	0.18	0.17	0.18	0.10	0.03

(e) Mn (ppm)

Soil	Control	Lime			Gypsum			Silene		
	0	L1	L2	L3	G1	G2	G3	S1	S2	S3
Griffin	7.9	0.0	0.0	0.0	9.8	9.9	11.9	5.6	5.4	2.6
Clovelly	5.2	0.0	0.0	0.0	7.5	8.4	6.5	3.4	2.5	1.7
Lidgetton	4.5	0.1	0.0	0.0	4.5	4.4	5.0	4.3	4.2	2.6
Farmhill	3.1	0.0	0.0	0.0	2.8	2.6	2.7	2.9	3.0	2.8
Hutton	4.8	0.0	0.0	0.0	7.0	8.5	8.4	4.3	4.2	4.0
Farningham A	9.1	0.1	0.0	0.0	9.3	9.3	9.2	8.4	6.7	4.5
Farningham B	6.1	0.0	0.0	0.0	5.2	6.3	6.2	4.1	2.8	2.6
Balmoral	9.8	0.2	0.0	0.0	11.5	17.3	20.0	7.8	6.2	2.3

APPENDIX 3

Detailed chemical properties of eight Natal Oxisols
(Determined as described in paper 3)

(a) Cation exchange properties (meq/100g)

Griffin										
Depth (cm)	Al	Ca	Mg	Na	K	Σ cations	CEC	AEC	net* CEC	net† CEC
0-15	1.46	2.00	1.36	0.19	0.91	5.9	7.7	1.6	6.1	6.0
15-30	1.69	0.27	0.54	0.17	0.32	3.0	6.3	2.5	3.8	3.5
30-45	1.07	0.11	0.29	0.13	0.13	1.7	4.8	3.3	1.5	1.3
45-60	0.91	0.09	0.27	0.11	0.13	1.5	4.2	2.9	1.3	1.4
60-75	1.28	0.09	0.31	0.13	0.13	1.9	4.7	3.2	1.5	1.5
75-90	1.21	0.09	0.35	0.11	0.14	1.9	4.6	2.3	2.3	1.8
Clovelly										
0-15	2.03	1.18	1.23	0.15	0.49	5.1	5.4	0.1	5.3	5.3
15-30	2.25	0.50	0.68	0.13	0.22	3.8	4.8	0.1	4.9	4.2
30-45	1.93	0.18	0.35	0.13	0.17	2.8	3.5	0.8	2.7	3.2
45-60	2.27	0.18	0.33	0.13	0.14	3.1	3.8	0.9	2.9	3.3
60-75	2.10	0.18	0.39	0.15	0.17	3.0	4.0	1.2	2.8	3.3
75-90	1.70	0.38	0.76	0.20	0.18	3.2	4.7	1.7	3.0	3.7
Lidgetton										
0-15	1.56	2.22	2.10	0.23	0.68	6.8	8.5	0.3	8.2	7.0
15-30	2.65	0.92	1.39	0.15	0.35	5.3	7.4	0.9	6.5	6.3
30-45	2.64	0.36	0.84	0.13	0.22	4.2	6.1	1.4	4.7	4.7
45-60	2.23	0.20	0.62	0.11	0.20	3.4	5.0	1.6	3.4	3.7
60-75	2.23	0.17	0.53	0.13	0.24	3.3	4.7	1.2	3.5	3.5
75-90	2.18	0.14	0.52	0.13	0.33	3.3	5.2	1.5	3.7	3.0
Farmhill										
0-15	0.17	1.70	1.36	0.20	0.86	4.3	6.9	1.6	5.3	4.2
15-30	0.10	0.44	0.64	0.14	0.39	1.7	5.4	2.7	2.7	1.8
30-45	0.00	0.22	0.30	0.10	0.24	0.9	3.8	3.3	0.5	0.5
45-60	0.00	0.22	0.29	0.10	0.20	0.8	3.3	3.1	0.2	0.0
60-75	0.00	0.13	0.21	0.10	0.12	0.6	3.4	3.4	0.0	0.0
75-90	0.00	0.13	0.21	0.08	0.10	0.5	3.1	3.4	-0.3	0.0

* CEC - AEC

† washed with water

App. 3

(a) Cation exchange properties (meq/100g)

Hutton										
Depth (cm)	Al	Ca	Mg	Na	K	Σ cations	CEC	AEC	net* CEC	net† CEC
0-15	3.42	0.20	0.41	0.12	0.52	4.7	5.5	1.0	4.5	5.0
15-30	2.22	0.10	0.17	0.10	0.32	2.9	4.3	1.8	2.5	3.2
30-45	2.54	0.10	0.14	0.10	0.27	3.2	4.8	1.8	3.0	3.0
45-60	2.44	0.00	0.14	0.11	0.35	3.0	5.2	2.2	3.0	2.8
60-75	3.40	0.00	0.15	0.12	0.35	4.0	5.9	2.3	3.6	3.2
75-90	3.67	0.00	0.17	0.10	0.37	4.3	6.0	2.0	4.0	3.9
Farningham A										
0-15	1.99	0.36	0.45	0.44	0.74	4.0	4.5	1.1	3.4	3.2
15-30	1.36	0.35	0.39	0.37	0.32	2.8	4.7	1.6	3.1	2.5
30-45	0.78	0.32	0.27	0.40	0.18	2.0	3.8	2.7	1.1	1.4
45-60	0.08	0.29	0.20	0.26	0.11	0.9	3.9	2.7	1.2	0.9
60-75	0.00	0.30	0.19	0.26	0.07	0.8	3.9	2.8	1.1	0.9
75-90	0.00	0.33	0.18	0.23	0.05	0.8	2.5	3.1	-0.6	0.7
Farningham B										
0-15	0.27	3.78	2.10	0.15	0.23	6.5	7.0	0.0	7.0	6.5
15-30	0.39	3.25	2.06	0.15	0.19	6.0	8.1	0.2	7.9	6.2
30-45	0.39	2.12	1.65	0.17	0.12	4.5	6.1	0.5	5.6	4.9
45-60	0.69	1.40	1.30	0.17	0.11	3.7	5.3	1.1	4.2	3.4
60-75	1.09	0.68	0.82	0.17	0.08	2.8	5.1	1.4	3.7	3.1
75-90	0.73	0.50	0.64	0.15	0.09	2.1	5.1	1.9	3.2	1.8
Balmoral										
0-15	0.59	1.51	1.44	0.12	0.25	3.9	5.3	0.5	4.8	4.4
15-30	0.91	1.32	1.52	0.12	0.16	4.0	5.9	0.5	5.4	4.9
30-45	1.07	0.93	1.32	0.12	0.11	3.6	5.2	0.8	4.9	4.4
45-60	1.53	0.56	0.70	0.12	0.09	3.0	4.6	0.7	3.9	3.1
60-75	1.47	0.42	0.39	0.12	0.07	2.5	4.9	1.5	3.4	2.8
75-90	1.30	0.09	0.29	0.12	0.21	2.0	4.6	2.1	2.5	2.1

App. 3

(b) CEC at pH7 (\underline{N} NH_4OAc ; meq/100g)

Soil	Depth (cm)					
	0-15	15-30	30-45	45-60	60-75	75-90
Griffin	39.2	37.1	28.3	27.3	24.7	18.0
Clovelly	21.1	18.6	16.0	15.0	15.0	16.0
Lidgetton	30.4	28.3	24.2	20.6	21.6	20.6
Farmhill	23.7	18.0	14.4	13.4	11.3	10.3
Hutton	26.8	23.2	22.6	21.6	21.1	21.1
Farningham A	23.0	18.0	17.4	17.0	18.3	17.7
Farningham B	33.5	35.0	31.4	29.4	27.8	28.4
Balmoral	14.3	16.1	15.6	13.8	13.8	13.3

(c) Organic matter content (%C)

Soil	Depth (cm)					
	0-15	15-30	30-45	45-60	60-75	75-90
Griffin	7.4	5.4	2.7	2.4	2.0	1.1
Clovelly	3.3	2.4	1.5	1.2	0.6	0.3
Lidgetton	4.7	4.0	2.5	1.7	1.3	1.2
Farmhill	4.8	2.9	1.4	1.2	0.7	0.4
Hutton	3.9	2.2	1.6	1.1	0.8	0.6
Farningham A	3.6	3.1	2.0	1.1	0.7	0.3
Farningham B	4.6	4.1	3.3	2.6	2.0	2.0
Balmoral	1.7	2.4	2.2	1.6	1.0	0.5

(d) Extractable Al* (\underline{N} $\text{NH}_4\text{OAc-pH}_4$; meq/100g)

Soil	Depth (cm)					
	0-15	15-30	30-45	45-60	60-75	75-90
Griffin	14.0	16.4	14.0	12.9	10.5	8.7
Clovelly	5.9	7.7	7.0	5.9	4.5	4.9
Lidgetton	7.0	10.5	10.5	8.7	8.7	8.0
Farmhill	6.3	6.2	4.6	4.2	4.3	4.3
Hutton	12.9	13.3	13.3	13.6	13.3	11.9
Farningham A	7.7	6.3	5.6	5.2	4.5	3.5
Farningham B	6.3	7.0	7.0	7.0	7.7	6.7
Balmoral	4.2	3.5	5.2	5.6	4.5	3.1

* 1:10 soil : solution ratio; single 2 min. shake

App. 3

(e) pH (KCl)

Soil	----- Depth (cm) -----					
	0-15	15-30	30-45	45-60	60-75	75-90
Griffin	4.3	4.4	4.5	4.5	4.5	4.4
Clovelly	4.1	4.2	4.3	4.2	4.2	4.2
Lidgetton	4.1	4.2	4.2	4.3	4.3	4.3
Farmhill	4.5	4.8	5.2	5.3	5.6	5.6
Hutton	4.4	4.5	4.5	4.5	4.4	4.3
Farningham A	4.3	4.4	4.5	4.8	5.0	5.4
Farningham B	4.5	4.5	4.5	4.6	4.5	4.6
Balmoral	4.3	4.3	4.3	4.3	4.3	4.4

(f) pH (H₂O)

Soil	----- Depth (cm) -----					
	0-15	15-30	30-45	45-60	60-75	75-90
Griffin	5.2	5.2	5.3	5.4	5.4	5.1
Clovelly	5.0	5.1	5.1	5.1	5.1	5.2
Lidgetton	5.1	5.1	5.1	5.1	5.2	5.1
Farmhill	5.4	5.4	5.5	5.5	5.8	6.0
Hutton	5.2	5.2	5.2	5.2	5.2	5.1
Farningham A	5.2	5.1	5.2	5.3	5.3	5.4
Farningham B	5.5	5.5	5.5	5.5	5.5	5.3
Balmoral	5.3	5.3	5.4	5.2	5.2	5.4

(g) CEC (field pH) of subsoils (60-75cm) determined by saturating with 0.2N NH₄Cl and correcting for entrained salts (a) by weighing and (b) by washing with absolute alcohol (meq/100g)

Soil	CEC (weighing)	CEC (alcohol washing)
Griffin	4.7	4.6
Clovelly	4.0	4.1
Lidgetton	4.7	5.1
Farmhill	3.4	3.1
Hutton	5.9	6.2
Farningham A	3.9	4.1
Farningham B	5.1	6.2
Balmoral	4.9	4.9
Means	4.6	4.8

APPENDIX 4

Miscellaneous data cited in paper 4

- (a) Net CEC values for Clovelly soil (0-15cm) treated with increments of $\text{Ca}(\text{OH})_2$ as described in paper 4.

$\text{Ca}(\text{OH})_2$ applied (meq/100g)	Set A	Set B	Set C	Set D	Means
0	5.6	5.7	5.9	5.8	5.8
1	6.0	6.1	6.3	6.1	6.1
2	6.4	6.5	6.7	6.5	6.5
3	6.9	6.9	7.1	6.8	6.9
5	7.7	8.3	8.1	7.9	8.0
7	8.7	9.2	9.2	8.8	9.0
9	9.3	9.9	10.0	9.5	9.7
11	10.0	10.5	10.7	10.7	10.5

- (b) EAI and exchangeable Ca values* (meq/100g) in the maize experiment[†] of Prof. E.R. Orchard at Thabamhlope (Farningham soil series; experiment planted in 1955, sampled in 1969; Regional project No. NC 1(T))

Depth (cm)	EAI			Ca		
	L0 [‡]	L1	L2	L0	L1	L2
0-15	0.95	0.41	0.07	1.15	2.68	4.40
15-30	0.52	0.21	0.08	0.80	2.00	2.61
30-45	0.14	0.11	0.06	1.09	1.52	1.44
45-60	0.21	0.29	0.17	0.90	0.96	0.97
60-75	0.35	0.29	0.34	0.75	0.79	0.70
75-90	0.35	0.33	0.35	0.70	0.76	0.67

* means of the control and L x P combinations at the high N and K treatment levels

† 3^4 factorial; annual dressings of 0, 20, and 40kg N; 0, 17.5, and 35kg P; 0, 50, and 100kg K/ha

‡ Dolomitic lime applied at the start and at five yearly intervals at rates of 0, 2, and 4 m.tons/ha

App. 4

(c) Results of field experiment on the farm "Lynton", near Underberg

Design

The experiment was a $2 \times 2 \times 2$ factorial, split for 4 sub-plot treatments, in 2 replications, on the Farningham soil series (see table). Whole plot treatments were:-

- 2 levels gypsum ($\frac{1}{2}$ and 4 m.tons/ha)
- 2 levels superphosphate ($\frac{1}{2}$ and 2 m.ton/ha; powder form)
- 2 depths of cultivation (15cm rotavation and ca. 30cm ploughing)

Sub-plot treatments were:-

- 4 levels dolomitic lime (0, 6, 12, 18 m.ton/ha).

In addition each plot received a standard dressing of 200kg/ha muriate of potash, 200kg/ha urea and 500kg/ha magnesium sulphate. Whole plot dimensions were 4.6m x 18.3m, sub-plots were 4.6m x 4.6m and net sub-plots harvested were 1.8m x 1.8m.

The lime, gypsum and ploughing treatments were applied on 7 Oct. 69, the remaining treatments were applied at planting on 16 Dec. 69. Fertilizers were broadcast and rotavated in to a depth of 15cm. 'Trudan' (*Sorghum sudanense*) was planted. The crop was reaped on 4 March 70 and the yields are expressed in tons green material per acre. (Analysis of the green material indicated that the moisture content on an oven dry basis was 78%.)

Results

(a) Depth of cultivation

The average yield obtained at the 15cm cultivation depth was 37.8 m.ton/ha and at 30cm was 39.2 m.ton/ha. The difference was not statistically significant. The object of the deep ploughing treatment was to effect a deep placement of lime in view of the relatively slow rate at which lime can be expected to move into the subsoil by normal leaching. A possible disadvantage of deep ploughing is that subsoil, low in nutrients, high in exchangeable Al and having a higher capacity to fix P, would be turned up to "dilute" the relatively more fertile topsoil. From the results obtained, such effects were not harmful. Since little more than two months elapsed between liming and planting it is possible that the effects of deep cultivation may be more apparent next season.

App. 4

(b) Effect of gypsum

The average yield obtained at the 500kg/ha level of gypsum was 36.8 m.ton/ha and at 4 m.ton/ha was 40.4 m.ton/ha, the increase being statistically significant at the 5% level. The object of the gypsum application was to increase the amount of Ca in the subsoil (see table) since gypsum can be expected to move downwards quite rapidly by leaching. Subject to confirmation by soil analysis, it appears that this effect was realised. The response to gypsum is not attributed to improved sulphate nutrition, since the low level of gypsum plus the superphosphate and magnesium sulphate applied are considered adequate to meet sulphate nutritional requirements.

(c) Effect of phosphate

The average yield obtained at the 500kg/ha level of supers was 34.4 m.ton/ha and at the 2 m.ton/ha level of supers was 42.6 m.ton/ha, the increase being statistically significant at the 1% level. Since this soil is considered to have a high capacity to fix P, growth response to P is expected. However, in contrast to pot experiment results, the magnitude of the response was relatively small indicating that P fixation effects are less serious in practice than is apparent in the greenhouse.

(d) Effect of lime

The average yields at the four levels of lime applied were 34.0, 39.4, 42.0, 38.6 m.tons/ha respectively. The increase in yield between 0 lime and 6 m.ton/ha was statistically significant at the 1% level and the decrease in yield between 12 and 18 m.tons lime/ha was significant at the 5% level. The difference between 6 and 12 m.tons/ha was not significant. Subject to confirmation by soil analysis the pattern of growth response was as expected, viz. that growth response took place only up to that level of lime (6 m.ton/ha) necessary to eliminate Al toxicity, followed by a depression in yield at very high levels of lime, probably due to induced trace element deficiencies. As in the case of P, the response to lime was less spectacular than was found in pot experiments. However, since the lime was applied only two months before planting it is possible that the effects will be more pronounced next season.

Analysis of soil from three sites within the experimental area before commencement of the experiment (meq/100g)

Depth (cm)	EAI*			Ca			Mg			K		
	A	B	C	A	B	C	A	B	C	A	B	C
0-15	1.4	1.2	0.8	0.7	0.8	1.8	0.8	0.8	1.4	0.7	1.1	0.9
15-30	1.1	1.3	1.2	0.3	0.4	0.6	0.5	0.4	0.7	0.5	0.7	0.4
30-45	1.1	1.2	1.1	0.1	0.0	0.2	0.3	0.1	0.4	0.2	0.4	0.2
45-60	1.2	1.5	1.6	0.3	0.0	0.1	0.4	0.1	0.3	0.1	0.3	0.2
60-75	1.2	1.8	1.4	0.1	0.0	0.1	0.2	0.0	0.3	0.1	0.2	0.2
75-90	1.2	1.5	1.3	0.0	0.0	0.1	0.4	0.0	0.4	0.1	0.1	0.1

* exchangeable Al index

ACKNOWLEDGEMENTS

The author gratefully acknowledges the helpful advice and criticisms of his supervisors, Prof. M.E. Sumner and Prof. E.R. Orchard, of the Department of Soil Science, University of Natal. The author also wishes to thank Mr. R. Ludorf, head of the department of Soil Science in the Natal Region for the opportunity to undertake this research, and the Department of Agricultural Technical Services for permission to submit the findings in the form of a thesis.

LITERATURE CITED

- Abruna, F., J. Vicente-Chandler, and R.W. Pearson. 1964. Effects of liming on yields and composition of heavily fertilized grasses and on soil properties under humid tropical conditions. *Soil Sci. Soc. Amer. Proc.* 28 : 657-661.
- Adams, F. and C.E. Evans. 1962. A rapid method for measuring lime requirement of Red-Yellow Podzolic soils. *Soil Sci. Soc. Amer. Proc.* 26 : 355-357.
- Adams F. and Z.F. Lund. 1966. Effect of chemical activity of soil solution aluminum on cotton root penetration of acid subsoils. *Soil Sci.* 101 : 193-198.
- Adams, F. and R.W. Pearson. 1967. Crop response to lime in the Southern United States and Puerto Rico. In Soil acidity and liming. *Agronomy* 12 : 161-206.
- Adams, W.E., A.W. White, and R.N. Dawson. 1967. Influence of lime sources and rates on "Coastal" Bermudagrass production, soil profile reaction, exchangeable Ca and Mg. *Agron. J.* 59 : 147-149.
- Awan, A.B. 1964. Effect of lime on availability of phosphate in Zamoro soils. *Soil Sci. Soc. Amer. Proc.* 28 : 672-673.
- Baker, D.E. and J.K. Hall. 1967. Measurements of phosphorus availability in acid soils of Pennsylvania. *Soil Sci. Soc. Amer. Proc.* 31 : 662-667.
- Beckwith, R.S. 1963. Chemical extraction of nutrients in soils and uptake by plants. *Agrochimica* 7 : 296-313.
- Bhumbla, D.R. and E.O. McLean. 1965. Aluminum in soils : VI Changes in pH dependent acidity, cation exchange capacity and extractable aluminum with additions of lime to acid surface soils. *Soil Sci. Soc. Amer. Proc.* 29 : 370-374.
- Brown, B.A., R.I. Munsell, R.F. Holt, and A.V. King. 1956. Soil reaction at various depths as influenced by time since application and amounts of limestone. *Soil Sci. Soc. Amer. Proc.* 20 : 518-522.
- Chang, M.L. and G.W. Thomas. 1963. A suggested mechanism for sulfate adsorption by soils. *Soil Sci. Soc. Amer. Proc.* 27 : 281-283.

- Cline, M.G. 1961. The changing model of soil. Soil Sci. Soc. Amer. Proc. 25 : 442-446.
- Coleman, N.T., G.W. Thomas, F.H. le Roux, and G. Bredel. 1964. Salt exchangeable and titratable acidity in bentonite-sesquioxide mixtures. Soil Sci. Soc. Amer. Proc. 28 : 35-37.
- Coleman, N.T. and G.W. Thomas. 1967. The basic chemistry of soil acidity. In Soil acidity and Liming. Agronomy 12 : 1-41.
- Coleman, N.T., S.B. Weed and R.J. McCracken. 1959. Cation exchange capacity and exchangeable cations in Piedmont soils of North Carolina. Soil Sci. Soc. Amer. Proc. 23 : 146-149.
- de Villiers, J.M. 1964. The genesis of some Natal soils. I. Clovelly, Kranskop and Balmoral series. S. Afr. J. Agric. Sci. 7 : 417-438.
- de Villiers, J.M. and M.L. Jackson. 1967. Cation exchange capacity variations with pH in soil clays. Soil Sci. Soc. Amer. Proc. 31 : 473-476.
- Deb, D.L. and N.P. Datta. 1967. Effect of associating anions on phosphate retention in soil : II under variable anion concentration. Plant and Soil 26 : 432-444.
- Duthion, C. 1968. Potassium in the soil. Potash Review, subject 4, suite 43.
- Estrada, J. and G.A. Cummings. 1968. Effects of lime and phosphorus treatments in specific horizons of acid soil on growth and chemical content of corn. Agron. J. 60 : 447-450.
- Fisher, T.R. 1969. Crop yields in relation to soil pH as modified by liming acid soils. Research Bulletin 947. Univ. of Missouri - Columbia College of Agric. Expt. Stn.
- Graven, E.H., O.J. Attoe, and D. Smith. 1965. Effect of flooding on manganese toxicity in Alfalfa. Soil Sci. Soc. Amer. Proc. 29 : 702-706.
- Haynes, J.L. and W.R. Robbins. 1948. Calcium and boron as essential factors in the root environment. J. Am. Soc. Agron. 40 : 795-803.
- Helling, C.S., G. Chesters, and R.B. Corey. 1964. Contribution of organic matter and clay to soil cation exchange capacity as affected by the pH of the saturating solution. Soil Sci. Soc. Amer. Proc. 28 : 517-520.

- Hourigan, W.R., R.E. Franklin, E.O. McLean, and D.R. Bhumbla. 1961. Growth and calcium uptake by plants as affected by rate and depth of liming. *Soil Sci. Soc. Amer. Proc.* 25 : 491-494.
- Howard, D.D. and F. Adams. 1965. Calcium requirement for penetration of subsoils by primary cotton roots. *Soil Sci. Soc. Amer. Proc.* 29 : 558-562.
- Hunter, A.S. 1965. Effects of silicate on uptake of phosphate from soils by four crops. *Soil Sci.* 100 : 391-396.
- Hsu, P.H. and C.I. Rich. 1960. Aluminum fixation in synthetic cation exchanger. *Soil Sci. Soc. Amer. Proc.* 24 : 21-25.
- Hsu, P.H. 1965. Fixation of phosphate by aluminum and iron in acidic soils. *Soil Sci.* 99 : 398-402.
- Jackson, W.A. 1967. Physiological effects of soil acidity. In Soil acidity and liming. *Agronomy* 12 : 43-124.
- Jenny, H. 1961. Reflections on the soil acidity merry-go-round. *Soil Sci. Soc. Amer. Proc.* 25 : 428-432.
- Kamprath, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. *Soil Sci. Soc. Amer. Proc.* 34 : 252-254.
- Keeney, D.R. and R.B. Corey. 1963. Factors affecting the lime requirements of Wisconsin soils. *Soil Sci. Soc. Amer. Proc.* 27 : 227-280.
- Kehoe, J.K. and B. Curnow. 1963. Root growth of subterranean clover on some acid sandy soils in Victoria. *Aust. J. Exp. Agric. and An. Hus.* 3 : 11-16.
- Kittrick, A.J. and M.L. Jackson. 1955. Common ion effect on phosphate solubility. *Soil Sci.* 79 : 415-421.
- Lin, C. and N.T. Coleman. 1960. The measurement of exchangeable Al in soils and clays. *Soil Sci. Soc. Amer. Proc.* 24 : 444-446.
- Liu, M. and G.W. Thomas. 1961. Nature of sulfate retention by acid soils. *Nature* 192 : 384.
- Mehlich, A. 1948. Determination of cation and anion exchange properties of soils. *Soil Sci.* 66 : 429-445.

- McLean, E.O., S.W. Dumford, and F. Coronel. 1966. A comparison of several methods of determining lime requirements of soils. Soil Sci. Soc. Amer. Proc. 30 : 26-30.
- McLean, E.O., W.R. Hourigan, H.E. Shoemaker, and D.R. Bhumbra. 1964. Aluminium in soils : V. Form of aluminum as a cause of soil acidity and a complication in its measurement. Soil Sci. 97 : 119-126.
- McLean, E.O., D.C. Reicosky, and C. Lakshmanan. 1965. Aluminum in soils : VII. Interrelationships of organic matter, liming, and extractable aluminum with "permanent charge" (KCl) and pH-dependent cation exchange capacity of surface soils. Soil Sci. Soc. Amer. Proc. 29 : 374-378.
- Moschler, W.W., G.D. Jones, and G.W. Thomas. 1960. Lime and soil acidity effects on alfalfa growth in a Red-Yellow podzolic soil. Soil Sci. Soc. Amer. Proc. 24 : 507-509.
- Nagarajah, S., A.M. Posner, and J.P. Quirk. 1968. Desorption of phosphate from kaolinite by citrate and bicarbonate. Soil Sci. Soc. Amer. Proc. 32 : 507-510.
- Okruszko, H., G.F. Warren, and G.E. Wilcox. 1962. Influence of calcium on phosphate availability in mulch soil. Soil Sci. Amer. Proc. 26 : 68-71.
- Pearson, R.W., F. Abruna, and J. Vicente-Chandler. 1962. Effect of lime and nitrogen applications on downward movement of Ca and Mg in two humid tropical soils of Puerto Rico. Soil Sci. 93 : 77-82.
- Peech, M. 1965. Lime requirement. In methods of soil analysis II. Agronomy 9 : 927-932.
- Pierre, W.H. and G.M. Browning. 1925. The temporary injurious effect of excessive liming of acid soils and its relation to the phosphate nutrition of plants. J. Amer. Soc. Agron. 27 : 742-759.
- Pionke, H.B. and R.B. Corey. 1967. Relations between acidic aluminum and soil pH, clay, and organic matter. Soil Sci. Soc. Amer. Proc. 31 : 749-752.
- Pohlman, G.G. 1946. Effect of liming different soil layers on yield of alfalfa and on root development and nodulation. Soil Sci. 62 : 255-266.

- Pratt, P.F. and F.L. Bair. 1961. A comparison of three reagents for the extraction of aluminum from soils. *Soil Sci.* 91 : 357-359.
- Pratt, P.F. and F.L. Bair. 1962. Cation-exchange properties of some acid soils of California. *Hilgardia* 33 : 689-705.
- Ragland, J.L. and N.T. Coleman. 1959. The effect of soil solution, aluminum and calcium on root growth. *Soil Sci. Soc. Amer. Proc.* 23 : 355-360.
- Raupach, M. and C.S. Piper. 1959. Interactions of silicate and phosphate in lateritic soil. *Aust. J. Agric. Res.* 10 : 818-831.
- Reeve, N.G. 1968. Amelioration of some acid Natal soils. M.Sc. Agric. dissertation, University of Natal.
- Rios, M.A. and R.W. Pearson. 1964. The effect of some chemical environmental factors on cotton root behaviour. *Soil Sci. Soc. Amer. Proc.* 28 : 232-235.
- Ross, G.J., K. Lawton, and B.G. Ellis. 1964. Lime requirement related to physical and chemical properties of nine Michigan soils. *Soil Sci. Soc. Amer. Proc.* 28 : 209-212.
- Schofield, R.K. 1939. The electric charges on clay particles. *Soils and Ferts.* 2 : 1-5.
- Shoemaker, H.E., E.O. McLean, and P.F. Pratt. 1961. Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. *Soil Sci. Soc. Amer. Proc.* 25 : 274-277.
- Shoop, G.J., C.R. Brooks, R.E. Blaser, and G.W. Thomas. 1961. Differential responses of grasses and legumes to liming and phosphorus fertilization. *Agron. J.* 53 : 111-115.
- Skeen, J.B. and M.E. Sumner. 1965. Measurement of exchangeable aluminum in acid soils. *Nature* 208 : 712.
- Skeen, J.B. and M.E. Sumner. 1967a. Exchangeable aluminum : I. The efficiency of various electrolytes for extracting aluminum from acid soils. *S. Afr. J. Agric. Sci.* 10 : 3-10.
- Skeen, J.B. and M.E. Sumner. 1967b. Exchangeable aluminum : II. The effect of concentration and pH value of the extractant on the extraction of aluminum from acid soils. *S. Afr. J. Agric. Sci.* 10 : 303-310.

- Smith, A.N. 1965. Aluminum and iron phosphates in soils. J. Aust. Inst. Ag. Res. 31 : 110-126.
- Sumner, M.E. 1963a. Effect of iron oxides on positive and negative charges in clays and soils. Clay Minerals Bulletin 5 : 218-226.
- Sumner, M.E. 1963b. Effect of alcohol washing and pH value of leaching solution on positive and negative charges in ferruginous soils. Nature 198 : 1018-1019.
- Taylor, A.W. 1961. Review of the effects of siliceous dressings on the nutrient status of soils. J. Agr. and Food Chem. 9 : 163-165.
- Taylor, A.W. and E.L. Gurney. 1965. Effect of lime on the phosphate potential and resin extractable phosphate in five acid soils. Soil Sci. Soc. Amer. Proc. 29 : 482-483.
- Thomas, G.W. 1960. Forms of aluminum in cation exchangers. Trans. 7th Int. Cong. Soil Sci. II : 364-369.
- van der Eyk, J.J., C.N. MacVickar, and J.M. de Villiers. 1969. Soils of the Tugela Basin. Town and Regional Planning Commission, Natal.
- Verster, E. and J.M. de Villiers. 1968. Criteria for the recognition of oxisols - a preliminary investigation. S. Afr. J. Agric. Sci. 11 : 1-8.
- Woodruff, G.M. 1948. Testing soils for lime requirement by means of a buffered solution and the glass electrode. Soil Sci. 66 : 53-63.