STUDIES OF ALUMINIUM AND PHOSPHORUS IN HILL SOILS

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DECLARATION

I hereby declare that this thesis has been composed by myself from the results of my own work.

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26/9/80.

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ABSTRACT

A study of the interrelationships between acidity, aluminium (Al) and phosphorus (P), and of their influence together with calcium (Ca) on ryegrass growth in hill soils has been conducted because limitations to pasture production include acidity, high levels of Al, low base saturation, and low P availability. Attention has been focused on the Acid Brown soils because of their potential productivity, and on soils derived from basalt because of their inherently high Al content.

Relationships between pH, NH_4OAc^- extractable-, KCL exchangeable- and $CaCl_2$ soluble-Al, and the chemical and biological availability of P, together with the modifying effects of added lime, gypsum, superphosphage, silicic acid and glucose, were investigated by laboratory and glasshouse techniques.

Soils of low pH (< 4) and high exchangeable-Al saturation ($> 70\%$) were associated with high levels of soluble-Al and low leves of Ca but the amounts of each form of Al were neither significantly correlated with pH, nor were significant correlations always maintained between the 3 forms of Al. Extractable-Al was significantly correlated with P-sorption which was inversely related to $CaCl_2$ soluble-P. However, plant growth was more closely related to extractable-P than to soluble-P, but extractable-P was not significantly correlated with any form of Al.

Herbage production and P-uptake were directly related to root weight which was significantly influenced by the concentration of soluble-Al : below 0.1×10^{-3} M soluble-Al had little influence on ryegrass growth or P-uptake , but between 0.1 and 0.3×10^{-3}M soluble-Al was associated with reduced Ca and P uptake, while above 0.3×10^{-3} M soluble-Al, root growth was almost totally inhibited. Possible mechanisms of Al interference with plant growth are discussed.

All soils gave significant responses in herbage production and P-uptake to added P, except where high levels of Al inhibited root growth : it was concluded that low P status was a serious limitation to pasture production on all these soils. It was further concluded that when Al was high, both lime and P were needed to raise pH, Ca and P-status, lower soluble-Al and P-sorption, to achieve satisfactory levels of improved herbage production.

CHAPTER 1.

REVIEW OF ACIDITY, ALUMINIUM AND PHOSPHORUS AND THEIR SIGNIFICANCE FOR PLANT GROWTH IN HILL SOILS

1.1. INTRODUCTION

Hill and upland areas represent 33% of the agricultural land in Great Britain but at present contribute less than 10% of the total production (JONES, 1978). However, it has been demonstrated (H.F.R.O., Jubilee Rep. 1979) that hill land improvement and its integration into improved systems of hill farming can significantly increase output. CUNNINGHAM (1976) discussed the potential of hill land and showed how pasture improvement and grazing management, with more efficient utilisation of herbage leading to higher intake of better quality feed at critical times in the annual nutritional cycle increased lambing percentages and reduced mortality rates. The need to realise the potential from hill land was stressed in the White Paper 'Food From Our Own Resources' (1975) which called for a 10% increase in lamb production. At the present time, however, the demand for lamb is less than was predicted, but with growing competition for hill land from forestry there is a greater need to increase agricultural production from a progressively declining acreage.

It is, therefore, important to examine the differences between current and potential production. Within the constraints imposed by climate many of the limitations to pasture production are dependent on the inherent characteristics of hill soils (MUNRO, 1967). Because the poor quality and low production from indigenous vegetation types are closely related to recognisable soil groups (FLOATE, 1978) it will be useful to consider some of the characteristics of hill soils.

1.1.1. HILL SOILS

Soils formed in upland environments are influenced by the nature of their parent material, as well as by climate and topography which contribute to and modify the processes of weathering and leaching (CROMPTON 1958 and 1960). The combination of relatively high rainfall which increases towards the west, the inverse relationship between altitude and temperature, and the high leaching but slow weathering rates, have given rise to distinct soil characteristics and distribution patterns (CROMPTON, 1958). Soils become progressively more acid with increased leaching and this, together with reduced biological activity at lower temperatures, allows the build up of organic matter. This may occur either within the soil profile or in the more extreme situations on the surface as peat, because of the excess of accumulation over decomposition. In these situations nutrients, especially phosphorus (P) are dominantly in organic forms which are not taken up by plant roots.

The sequence of soil formation begins with the weathering of minerals and the release of basic cations and aluminium (Al) from alumino-silicate minerals and clays. When the intensity of leaching exceeds the weathering rate bases are lost faster than they are released during weathering. In contrast Al accumulates and the development of acidity becomes self perpetuating : Al is hydrolysed and the concomitant release of H^+ ions accelerates the release of further Al from rock minerals. These Al ions with their high density of positive charge are more strongly adsorbed on to exchange sites than the basic ions so that in an environment where leaching is the dominant soil forming process the soil profile becomes more acidic and depleted of bases (CROMPTON, 1958). Furthermore, the increasing amounts of organic matter lead to an increase in the cation exchange capacity (CEC) which in the absence of basic cations results in progressive base unsaturation.

The extent of leaching has led to most hill soils being broadly classified within the podzol range (ROMANS, 1970). The pattern of increasing leaching and podzolisation, and the accumulation of organic matter with altitude results in the characteristic distribution of hill soil types. On the lower slopes, with above average temperatures, Brown Forest soils occur (FLOATE, 1977). These tend to be acid but a higher proportion of their nutrients are in forms available for plant growth than in the more highly organic soils at higher elevations. Brown forest soils exhibit a wide range of Al saturation and acidity depending on the degree of leaching and type of parent material. As a result of the slightly higher proportion of inorganic to organic forms of nutrient reserves in these soils compared with other types their indigenous vegetation is characteristically acid grassland which ranges from Agrostis/Fescue to Agrostis/Deschampsia swards on the more acid sites. This type of vegetation is more productive than that associated with more acidic, or more highly organic soils at higher altitude.

Further up the slope due to intensified leaching and the accumulation of a surface raw humus mat, the process of podzolization is more pronounced. Humic acids released from the breakdown of organic matter, attack the uppermost mineral horizon and combine with iron and aluminium to form soluble complexes which, together with bases, are leached down the profile either to form a B horizon (ROMANS, 1970) or, as in the case of basic cations to be lost from the profile. Two types, Iron and Humus Podzols are recognised which both support poor quality, low yielding vegetation dominated by Calluna, other ericaceous species, mat-forming grasses, sedges and mosses.

Above this zone, corresponding to approximately 200 m in the west and 600 m in the east, deep and extensive blanket peats have formed over large areas of rolling topography (FLOATE, 1978). These organic soils are strongly acidic, as result of severe leaching and the release of organic acids from the breakdown of organic matter, have high cation exchange capacities and contain the least amounts of available nutrients. The vegetation tends to be dominated by Eriophorum species, Sphagnum moss, Ericaceous species and Molinia or Deschampsia : production is very low.

Drainage has contributed to the formation of distinct soil types within this topographic sequence: Gleyed soils form where drainage is impeded. Noncalcareous gleys occur in the Brown Forest soil zone while peaty gleys typically occur amongst the podzols and peats. As a consequence of the highly reducing, anaerobic conditions, root penetration is restricted and plant growth is poor. These soils support low producing Molinia, Deschampsia, Juncus, Ericaceous species and mosses.

1.1.2. PRODUCTION

The permanent limitations to production in upland areas associated with climate and the short growing season restrict the utilisation of these soils to grazing systems of production. Thus, the main objective of land improvement is to increase the production of higher quality vegetation. It is apparent from the association between soil types and indigenous vegetation that soil properties exert a major influence on herbage production. FLOATE (1978) suggested that the limitations of strong acidity associated with high levels of Al, and low available nutrient status may be regarded as temporary since they can be overcome, while the more permanent limitations are not amenable to improvement. Main interest is therefore focused on the nature of chemical soil limitations and their relationships with requirements for land improvement.

NEWBOULD (1974, 1975) reviewed the techniques available for land improvement, which include fencing, cultivation, drainage, reseeding and the application of lime and fertilisers. HUNTER (1962) demonstrated the potential for increased production when he showed that average production (2-3,000 kg DM/ha/yr) was trebled by the use of lime and phosphate on reseeded pasture, which was further increased by nitrogen. The greatest interest centre on the Brown Forest soils where the production responses are likely to be greatest.

1.1.3. BROWN FOREST SOILS

RAGG et al. (1978) observed that the term Brown Forest Soil, used in Scotland for 25 years, included all brown mineral soils with free or imperfect drainage and merging horizons. The properties of these soils cover a wide spectrum partly due to the diversity of parent material but also to the consequences of leaching, which may range from only moderate in lowland areas to moderately severe in hill areas. When leaching is strongest the soils are acidic and dominated by Al with only small amounts of bases. Their high Al and also Fe contents make them strongly P fixing with low levels of soluble P which may restrict plant growth potential.

Two distinct groups of acid brown soils are recognised by the Soil Survey of England and Wales (AVERY, 1973): Brown Earths and Brown Podzolic soils. These groups, and the criteria for their definition, are similar to the distinctions between non podzolized and podzolized soils discussed by AVERY et al (1977) and RAGG et al. (1978). The distinctions have important consequences for plant growth since they include chemical properties. It is likely that the species-rich and species-poor grades of Agrostis-Fescue grassland described by ROGERS and KING (1972) correspond to the two groups.

Brown Podzolic soils differ from Brown Earths in having higher pyrophosphate extractable Fe and Al ratios, together with particular fluoride activity and the presence of integrated 2:1, 2:2 and smectite-like clay minerals in their surface horizons (LOVELAND and BULLOCK, 1976). Brown earths generally have a higher base content than Brown Podzolic soils but where leaching is strong they grade into the latter. Criteria for definition are generally difficult to apply in the field and when soils formed on a wide range of parent materials are included (RAGG et al., 1978). Because of these difficulties the soils used in this study are generally described as Acid Brown soils, but are more closely related to Brown Podzolic than to Brown Earth soils. It is important to recognise the significance of these two groups as they may exert different influences on plant growth.

The Acid Brown soils of hill areas often contain relatively large amounts of Al which may be detrimental for plant growth and smaller amounts of the major nutrients P and Ca in available forms than their more productive lowland counterparts. There is little published information concerning the specific interactions between acidity, Al and P supply in hill soils or on the effects of these on plant growth. The following sections, however, have been included to consider those aspects of the chemistry of acidity, Al and P in soils, of the physiology of plant growth and the effects of Ca and liming, which are relevant to understanding the limitations they might impose on herbage production in hill soils.

1.2. SOIL ALUMINIUM

Aluminium is the third most abundant element in the earth's crust, and is present mainly as alumino-silicate minerals in rocks and in various chemical forms in soil. The soil content varies both with the nature of the parent rock and also as a result of weathering and leaching processes. It is commonly abundant in the Acid Brown soils of the hills and upland.

Aluminium is generally found in 6-fold co-ordination with oxygen in the octahedral layer of many primary minerals, micas and feldspars, in secondary clay minerals, free sesquioxides and amorphous secondary weathering products. Typically it makes up 8.1, 8.2 and 2.5% of igneous, shale and sandstone rocks respectively and tends to occur in smaller quantities in soils with a predominance of sand while being more abundant where clays predominate (McLEAN, 1976).

1.2.1. WEATHERING AND THE RELEASE OF ALUMINIUM

In soil the weathering of minerals containing Al is strongly associated with the H^+ ion concentration in solution. As this increases and the pH falls to 4.0 or below, the hydronium ions formed cause the dissolution of Al ions from the edges of mineral surfaces. These Al ions form Werner-type complexes which can sequentially dissociate H^+ ions and thus behave as weak acids with a dissociation constant of 1.8×10^{-5} (McLEAN, 1976).

The dissociation of the aluminohexahydronium ion is both self-perpetuating through the production of H^+ ions encouraging further weathering and the release of more Al ions and, also self-limiting because of the build up of H^+ ions:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)5\ OH^{2+} + H^+$$

Some of the resulting Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ ions remain in solution, some may be adsorbed as monomers to the exchange sites and still others may be polymerized and also adsorbed on the surfaces of clay minerals while others are complexed by soil organic matter.

The enhanced release of Al^{3+} ions with decreasing pH means that in Acid Brown hill soils the concentration of Al in the soil solution may be high. In the lowland environment however where weathering is stronger and leaching is less intense there is less potential for the development of acidity and levels of soluble Al tend to be low.

1.2.2. FORMS OF SOIL Al

In most soils the greatest proportion of Al occurs in a relatively inert form in aluminosilicate minerals, with less than 1% extractable in sodium dithionite or other similar extractants (McLEAN, 1976). More readily soluble forms of Al include Al phosphates and the ionic forms Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ which exist primarily adsorbed to exchange sites or in solution together with some polymeric forms (BACHE and SHARP, 1976a). Al also occurs as the oxide (Al_2O_3) in both crystalline and amorphous form and as the hydroxide ($Al(OH)_3$).

PIONKE and COREY (1967) proposed a scheme relating the inorganic and organic forms of Al known to occur in soil to pH:-

$Al(OH)_3\ 3H_2O$ .... aluminium hydroxide or gibbsite

$\updownarrows$

$Aly\ (OH)_{3y-z}(H_2O)$ ...... polymerised nonexchangeable acidic Al; residing on or within the clay structure

$\updownarrows$

increasing pH

$\left[AlOH(H_2O)_5\right]^{2+}$ .... monohydroxyl monomer; principal ion in solution in equilibrium with aluminohexahydronium

$\updownarrows$

$Al(H_2O)_6^{3+}$ .... aluminohexyhydronium

$\swarrow\!\nearrow$ $\quad$ $\nwarrow\!\searrow$

Al-OM $\quad$ Al-X .... KCl exchangeable Al.

non-exchangeable
acidic Al
complexed by OM
(organic matter)

Non-exchangeable Al, some of which is complexed by organic matter through the formation of mono or multi-dentate chelates (CABRERA and TALIBUDEEN, 1977; ZUNINO and MARTIN, 1977), is extracted together with interlayer hydroxy Al, $Al(OH)_3$ gels and aluminophosphates using M NH_4OAc at pH 4.8 (PRATT and BAIR, 1961). McLEAN (1965) included these forms of Al under the general heading extractable Al, which also includes some exchangeable Al and the monomeric and polymeric species of Al in solution.

The amount of exchangeable Al (Al - X, in Pionke and Corey's scheme) which can hydrolyse and move into solution is related to the CEC of the soil (McLEAN, 1976). Cation exchange is a consequence of the negative electric charges on the colloidal clay and humus particles of the soil matrix (BACHE, 1976). Two components exist: permanent charge which is generated by partial isomorphous substitution within the lattices of clay-size layer silicates, and a variable pH-dependent charge which in mineral soils arises through the dissociation of hydroxyl groups from alumino silicate gels or the edges of layer silicates. Where the soil contains appreciable amounts of organic matter a major part of this variable charge arises with proton dissociation from carboxylic and phenolic groups.

The described forms of Al are to some extent an artefact of extraction and measurement techniques. The difficulties in precise determination of CEC and exchangeable Al pose one of the major problems to understanding reactions involving Al and in the next section both the nature of these forms and methods for their measurement will be considered.

Methods for determining CEC have been reviewed by COLEMAN and THOMAS (1967) and BACHE (1976). These differ in 1) the ion and its strength used to displace the exchangeable cations and 2) the pH of the solution used for displacement. Calculation of CEC assumes the charges of displaced cations are known. In acid soils dominated by Al, which can exhibit several hydrolysis states of different charge, such an assumption may not be justified. BACHE (1976) discussed these problems in detail and concluded that no single value for CEC could wholly describe the phenomena of cation exchange. He suggested however, that when the aim was to study soil reactions that might be influenced by CEC, it should be determined using a neutral salt solution at the natural pH of the soil.

Aluminium ions which are adsorbed at exchange sites and displaced by KCl leaching have been described as exchangeable (McLEAN, 1965). This term however, is not strictly accurate due to reactions which may occur during leaching. JACKSON (1960) found that treatment with neutral salt solutions could result in the hydrolysis of a certain proportion of Al which might then be precipitated within or on clay structures resulting in the misrepresentation of the amount of truly exchangeable Al ions. The effect of KCl on Al hydrolysis has been described by KISSEL et al. (1971) and SIVASUBRAMANIAN and TALIBUDEEN (1972) have dealt with the pH effect on the charge of the ionic species of Al occupying exchange sites. Because cation adsorption depends primarily on ionic charge the relative concentration of Al ions at the exchange surface will be different from that in the external solution with which they are in equilibrium. The order of surface enrichment follows, $Al^{3+} > Al\ OH^{2+} > H^+$, SIVASUBRAMANIAM and TALIBUDEEN (1972).

In the soil solution the relative proportion of particular hydrolysis species of Al is influenced primarily by pH since H^+ ions are one of the end products of hydrolysis reactions. PIONKE and COREY's scheme includes only the 2 major species which dominate the pH range 3.5 to 5.0 and excludes other species which also coexist with these two. The relationship between pH and the monomeric species of Al has been discussed by RAUPACH (1963a and b) and DALAL (1975). NEWMAN (unpub) and AVESTON (1965) described many polyhydroxy compounds of undefined composition and solubility in the pH range 4.5 to 6.0 and AVESTON proposed the following expression for the hydrolysis of Al^{3+}:-

$$pAl^{3+} + q\ H_2O = Alp\ (OH)\ q^{\ (3p\ -\ q)+} + q\ H^+.$$

Other formulae and structures have been given by HEM et al. (1973) BACHE and SHARP (1976a) described some of the polynuclear hydroxy Al ions occurring in acid soils and showed how their proportions increased above pH 4.8 and that they could be readily desorbed from soils by dilute salt solutions (10^{-2} M $CaCl_2$). The importance of these polymeric ions with respect to interactions between Al and other soil properties has yet to be examined and it must be stressed that although Al species with variable charge may exist in solution most techniques for measuring Al fail to distinguish between them.

It is well known that the concentration of ions in solution depends on the equilibrium between the ions in the solution phase and the ions on the exchange phase and that this in turn depends on the concentration and relative affinities for the exchange surface of the ions in solution. In soils where exchange reactions are dominated by sites with permanent negative charge the effects of changes in the concentration of other cations on the distribution of a particular ion between the exchange and solution phases can be predicted from the Ratio Law (SCHOFIELD, 1947). This law does not, however, strictly apply when soils such as many of the acid Brown hill soils have a significant component of pH dependent charge (BACHE and SHARP, 1976b). In order to describe the solubility of Al in such soils BACHE and SHARPE (1976b) formulated the Activity Ratio (A.R): $AR = (aCa + aMg)^3 / aAl)^2$; where a represents cation concentrations measured in a $10^{-2}MCaCl_2$.1:1 soil extract when certain conditions are met: (1) the salt concentration in the solution is low and (2) the analytically determined Al is equivalent to the true concentration of Al^{3+} rather than its hydrolysed forms. Earlier MISRA et al. (1974) had concluded that the concentration of Al in the soil extract could not be predicted from ion activity product considerations alone because of the effects of incongruent dissolution of Al hydroxy species but that it could be estimated if pH was taken into account.

Studies of reactions involving hydrolysis of Al in solution with respect to pH have mainly been conducted with simple systems and their applicability to soil reactions has yet to be tested on a wide range of soils. However, such experiments were outwith the objectives of this study.

1.2.3. ALUMINIUM AND SOIL ACIDITY

It is now accepted that acid mineral soils derive their acidic nature from the large amounts of Al saturated materials they contain (COULTER, 1969). JACKSON (1963) described acidity: 'as a soil system's proton yielding capacity in going from a given state to a reference state' and identified specific proton donors. These include monomeric aluminohexahydronium ions, polymeric Al adsorbed at edges of layered silicates and organic matter. The mechanism of Al hydrolysis is fairly well understood but the forms of Al and the reaction states involved are still being investigated. TURNER and CLARK (1966) proposed that pH was partially controlled by the solubility product of Al hydroxide (gibbsite) but consideration of all the component hydrolysis products of Al (BACHE, 1974 and DALAL 1975) refuted this for the pH range 4 to 6.3. BACHE (1974) showed that for some soils proton release from the hydrolysis of Al ions in solution accounted for pH and explained quantitatively the variation in pH with the ratio of Ca to Al on exchange sites. This study showed that the role of Al in determining pH could be modified by reactions between ions in the solution and exchange phases and suggested that other cations namely Ca may influence the role of Al in producing acidity in Acid Brown hill soils.

Two types of acidity are recognised: 1) exchangeable, (that which can be displaced using a neutral unbuffered salt) and 2) Titratible but non-displaceable, (that which consumes base when the soil itself is titrated following the removal of the exchangeable acidity component). Both types have been attributed to Al (KAILA, 1971 and CHERNOV, 1964) respectively.

In a survey of Finnish soils KAILA (1971) recorded significant correlations between Al soluble in oxalate (i.e. Al contributing to non-exchangeable acidity) and pH for clay soils ($r = -0.91^{***}$) but poorer correlations with silts and loams, and sands ($r = 0.66^{***}$, and -0.58^{***} respectively). She concluded that in these soils positively charged Al hydroxides were a more important source of non-exchangeable acidity than the Al blocking the interlayer spaces of 2:1 clay minerals, discussed by COLEMAN and THOMAS (1964).

1.2.4. INTERRELATIONSHIPS BETWEEN FORMS OF Al AND OTHER SOIL PROPERTIES

The concentration of soluble Al has been related to the percent saturation by Al of the CEC and EVANS and KAMPRATH (1970) found it greatly increased when this exceeded 60%. No quantitative relationship has been shown between pH and soluble Al (CLARK, 1966). WEAVER and BLOOM (1977) showed how aluminosilicates of variable composition contributed to the activity of Al in solution and it appears that several soil properties including CEC, Al saturation of the CEC and pH, together with parent material may need to be examined in order to understand the involvement of Al in soil chemical reactions.

1.2.5. REACTIONS BETWEEN ALUMINIUM AND PHOSPHORUS

The ability of Al, either in solution or adsorbed by exchange sites (WILD, 1953) or as amorphous or crystalline forms of the oxide and hydroxide (LOPEZ-HERNANDEZ and BURNHAM, 1974) to react with phosphate ions is a product of its charge density and resonant charge in the case of the latter forms. HSU (1964) suggested that in a special case of precipitation, chemical adsorption which essentially follows the solubility product principle, P is fixed by cations namely Al and Fe, while they remain constituents of soil minerals or sesquioxides as result of residual forces. HSU (1965) and BACHE and WILLIAMS (1971) also showed that while reactions between Al and phosphate ions in solution are governed by pH through its influence of the charged state of Al, adsorption of phosphate by amorphous hydroxides was independent of pH.

The 'reactivity' of Al is related to its ionization state, which is controlled by pH, and which varies in decreasing order from water soluble Al^{3+} > adsorbed (exchangeable) Al^{3+} or OH - Al monomers > OH - Al polymers > $Al(OH)_3$ with increasing pH SIVASUBRAMANIAM and TALIBUDEEN, 1972). These strongly positive ions show a high affinity toward anions and as a result of this exert many direct and indirect influences on plant growth. KHANNA and MAHAJAN (1971) showed that up to 90% of P fertiliser applied to acid soils could be precipitated by Al. HALSTEAD (1967) showed that regardless of whether or not acid soils had been limed, almost no Ca phosphate was recovered but instead phosphorus was recovered as Al or Fe phosphate. Although Al phosphates have been shown to be a good source of P for plants (TAYLOR et al., 1960) their solubility is depressed when the concentration of Al ions on the soil solution is high. Understanding of the processes of chemical and physical sorption, exchange, precipitation and the maturing of secondary reaction products is still far from complete. It is known that Acid Brown soils exhibit a range in pH and Al levels, are low in basic cations, have high P fixing ability and low P availability. Studies discussed here point to a relationship between low pH, high Al and low P availability but suggest that if hill soils are to be successfully amended for the growth of better pasture species, then an improved understanding of the interrelationships between these three properties is required, so that soil improvement techniques may be further developed.

1.3. SOIL PHOSPHORUS

Phosphorus is an essential plant nutrient which occurs naturally in soil but in very small quantities and usually less than 0.06% by weight. The only significant P containing primary minerals are the apatites. Because soil is the main source of nutrient P, with the exception of a very small input in rainfall, the level of P in the soil solution often imposes a serious limitation for plant growth.

The equilibrium between soluble and insoluble forms of P is established during pedogenesis and the two major influences on the level of soluble P are the nature of the soil parent material and the solubility of the secondary forms of P. The equilibrium P level is controlled through soil properties via the solubility product principle which itself is influenced by common ions, salt effects and exchange reactions. Removal of P from the system by plant roots or leaching, or its addition by mineralization or as fertiliser mean the soil P system is always dynamic and never truly reaches a steady state.

1.3.1. FORMS OF SOIL P

Up to 80% of the total P in hill soils occurs as organic P which is only slowly made available for plant growth by mineralization, a slow process in the hill environment because low temperatures and acidity restrict the activity of the micro-organisms (FLOATE, 1970). In most unimproved hill soils therefore plants may depend heavily on the small amount of inorganic P in equilibrium with Al and to a lesser extent Fe bound forms (BARBER, 1964). However, with soil improvement and reduced acidity the contribution of mineralized P from organic sources may become more important.

1.3.2. SOLUBLE P

The two most common forms of phosphate ion in solution under acid conditions are the di-basic orthophosphate ion ($H_2PO_4^-$) and the mono-basic orthosphosphate ion ($H\ PO_4^=$). Below pH 4.6 the di-basic $H_2PO_4^-$ ion is dominant but with increasing pH the proportion of the monobasic $H\ PO_4^=$ ion rises. Soluble complexes of P with hydroxy Al also occur (HSU, 1965, 1968, WHITE et al. 1976). It seems likely that in these Acid Brown hill soils a proportion of the P in solution may not be ionized but may exist in complex form with Al or hydroxypolymers of Al. If such complexes exist then they may influence the amounts of both Al and P in the soil solution, the way in which they take part in chemical reactions, and their uptake by roots and thus have important implications for plant growth.

1.3.3. FACTORS INFLUENCING THE CONCENTRATION OF P IN THE SOIL SOLUTION

Plant roots take up soluble ions and thus the concentration of phosphate ions maintained in the soil solution throughout the growing season is one of the critical factors influencing herbage production. KHASAWNEH (1971) described a number of factors that interact with each other to determine the functional relationship between the ionic status in the soil solution and nutrient uptake by plants:-

1) Intensity factor, viz the strength of the ion in the soil

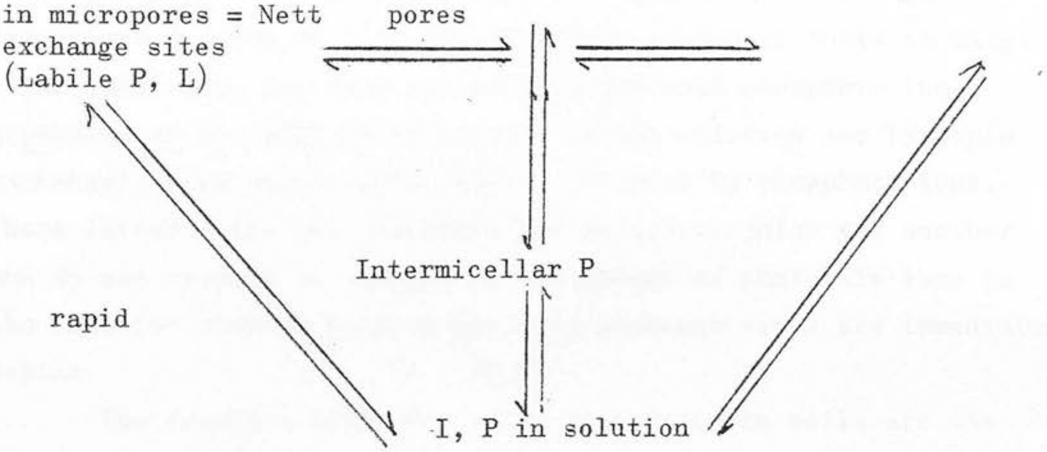
solution, its activity or potential.

2) Replenishment factor, which describes how the concentration of an ion is replenished when its concentration is depleted. This is influenced by 3 parameters; quantity (q), intensity (I) and buffering capacity (Pbc): q is a measure of the amount of nutrients in reserve and Pbc measures the resistance of the soil to changes in I, Pbc = $\Delta q / \Delta I$ (DALAL and HALLSWORTH, 1976).

Phosphate ions in the soil solution take part in many equilibria both within the liquid phase and also between the solid and liquid phases. The equilibrium between the 2 phases is heavily biased towards the solid so that I tends to be very low (LARSEN, 1967). The upper limit for I is set by the equilibrium between the solid and liquid phases and represents the balance between the solubility of readily soluble forms of P and the stable saturation level of nett exchange sites for P sorption on soil surfaces.

TALIBUDEEN (1957, 1958) described the equilibrium between the main fractions of P in the soil:-

<u>Labile inorganic P</u>	<u>Labile inorganic P</u>	<u>Stable inorganic P</u>
Rapidly exchangeable i.e. physically sorbed P. P held in external mineral surfaces and in micropores = Nett exchange sites (Labile P, L)	Slowly exchangeable Chemisorbed P. P held in the clay lattice and micropores	Very slowly exchangeable P in sub-surface, solid layer, e.g. apatite crystals.



LARSEN (1964) found that at very low levels of P in the soil solution all the P was labile but as I increased the solubility product of certain P compounds could be exceeded so that a crystalline phase was formed and P in the lattice was no longer able to freely enter into solution. HUFFMAN (1962) discussed the complexity of P equilibria in soil and suggested that the least soluble forms of P, phosphates of Ca, Al, and Fe governed I. More recently ERASHIDI and LARSEN (1978) reported that the constancy of the P potential measured following depletion of soil P by plant P uptake or by ion exchange resins, provided further evidence that I was controlled by the solubility of sparingly soluble phosphates.

However, JENSEN (1971) showed that the concentration of phosphate ions in the soil solution was seldom consistant with the presence of any known P compound, and work by CHAKRAVARTI and TALIBUDEEN (1962) and HINGSTON et al. (1967) supported this view. BACHE (1963) suggested that incongruent dissolution of P minerals or the presence of indefinable forms of P as result of adsorption might explain the inconsistencies of these observations and MATTINGLY (1975) indicated that adsorbed P may be as important as crystalline P in controlling I.

1.3.4. SORPTION OF PHOSPHATE IONS

Exchange reactions involve anions as well as cations due to the development of positively charged exchange sites which may attract the negatively charged anions. The capacity of the soil system for anion adsorption is related to the number of basic groups and pH (RUSSELL, 1973). BECKETT and WHITE (1964) recognised 2 types of site for phosphate exchange, 'nett exchange' sites which may, but need not necessarily hold phosphate ions, depending on the phosphate activity in the solution and 'isotopic exchange' sites which could only be occupied by phosphate ions. These latter sites only exchange one phosphate anion for another and do not respond to changes in the amount of phosphate ions in the solution whereas ions on the nett exchange sites are immediately labile.

The reactive sites for anion adsorption in soils are the Al-OH, Fe-OH groups which are present at the edges of clay minerals and on the surfaces of hydrous oxides (MOTT, 1970 cited by PARFITT, 1978). SCHOFIELD (1949) showed how Fe and Al could acquire positive charge by the transfer of hydronium ions to oxygen. Since the activation of these sites involves the transfer of protons the process of P sorption is almost totally pH dependent unlike cation exchange where the majority of charge is permanent.

The adsorption of phosphate ions is usually described as P fixation and the mechanisms by which this occurs are still not fully understood. Two separate approaches have figured in the interpretation of the mechanism of P sorption: one based upon theories of adsorption on surfaces of clay mineral and sesquioxides and the second postulating the formation of compounds by precipitation. Within these two not exclusive approaches, several theories abound and none singly adequately explain all the results observed. HSU (1965) HOLFORD (unpub Ph.D. thesis) and RAJAN (1975) identified 2 groups of sites where phosphate ions could be adsorbed simultaneously. They suggested that adsorption resulted from chemical reactions similar to those involved in the formation of discrete phases of Al or Fe phosphates. The 2 groups of sites have since been associated with 2 different energy levels (PARFITT, 1978 and ELLIS and TAYLOR, 1978). Using a range of phosphate levels in the bathing media in contact with the soil RYDEN et al. (1977) described a 3 stage sorption process. POSNER (pers. comm) however considers that the sorption process may in reality be considered as a continuum of energy levels.

RAJAN and FOX (1975) and PARFITT (1977) have endorsed the view put forward by KOLTHOFF (1936) and HINGSTON et al. (1967) that phosphate ions could exchange with OH^- ions by ligand exchange. KOLTHOFF recognised 3 positions on clays where this could occur:- 1) counter ions held extra to the lattice due to the unequal distribution of forces with the crystal, 2) lattice ions at the corners or edges, 3) the surface due to precipitation of hydrous Al oxides. Ligand exchange reactions involve competition with other anions for adsorption sites (RAJAN and FOX, 1975).

The competitive adsorption and desorption of organic acids and phosphate on artificially prepared clay minerals has been studied by NAGARAH et al. (1968, 1970). They found that phosphate adsorption was reduced considerably by polybasic acids, the effect being most marked with the Al surfaces. HASHIMOTO (1967) reported that additions of humates and nitrohumates were particularly effective in reducing P sorption in soils dominated by Al^{3+} and

Fe^{3+} ions and GESSA et al. (1978) showed how the formation of organo-mineral complexes was able to inactivate the pH dependent charge on clays. These results indicate that although phosphate is very strongly adsorbed by many soils it can be displaced by both inorganic and organic anions and that these may provide methods of increasing P availability. These concepts have formed the basis for many of the extraction procedures for 'available P'.

The adsorption of phosphate by ligand exchange however appears to rest on assumptions and data at variance with other published work. WHITE and TAYLOR (1977) who cite work by Breenwsma and Lyklema (1973) and Rajan et al (1975) to make the point that conclusions drawn from studies involving high concentrations of P may not be generally applicable to all sorption reactions. WHITE and TAYLOR also cite the work of Aslyng (1954) and Obihara and Russell (1972) who have examined the effect of ion concentration surface charge and pH on P sorption and shown that particularly with respect to pH the ligand exchange theory predicts contrasting results to those observed. WHITE and TAYLOR (1977) who examined the effect of varying levels of P concentration at different pHs concluded by stating how complex the mechanisms of P sorption are, but suggest that the affinity of the adsorption reaction is greatest between pH 4.8 and 5.2, decreasing above this pH. They indicate that the amphoteric properties of aluminium and its ability to form complexes with P, particularly around pH 5 confuses the interpretation of the results for sorption reactions.

It can be seen that as yet the evidence for and against different mechanisms for P sorption is still inconclusive and in view of the heterogeneity of the soil system more than one mechanism may be operational depending on the inherent soil properties.

Quantitative studies of P sorbing characteristics of different soils have used adsorption isotherms (PARFITT, 1978). The soil is equilibrated with different P concentrations and the amount of P sorbed by the soil is plotted against the concentration of P remaining in the soil solution. Mathematical formulae have been applied to describe the resulting isotherms and the usefulness of these, and their limitations have been discussed by BACHE and WILLIAMS (1971) and PARFITT (1978).

1.3.5. ADSORPTION SITES

The P fixing ability of clay minerals is based on their capacity for protonation, i.e. the accessibility of their octahedral groups and follows the order kaolinite $<$ montmorillinite $<$ vermiculite and illite. Thus the percentage of a particular clay mineral in a soil will influence its ability to sorb P. Work by ELLIS and TRUOG (1955) showed that Al is the main contributor to the ability of clays to sorb P and WILLIAMS et al. (1958) and SAUNDERS (1965) showed that for most soils extractable Al provided a better guide to P fixation than did extractable Fe.

Acid Brown soils contain large amounts of Al and lesser quantities of Fe and consequently their P fixing capacities are likely to be high. However, because the contribution by different forms of Al to P fixation appears to vary between soils the P fixing ability of each soil needs to be evaluated on its own merits along with the influence of other soil conditions such as pH on the process.

One of the main problems in identifying the particular soil components active in P fixation is concerned with the specificity of extracting reagents for particular soil components. Tamm's acid oxalate solution (TAMM , 1932) has been extensively used to extract Fe and Al from soils (PARFITT, 1978). This is thought to cause dissolution of amorphous Fe and Al compounds but it is also likely to include other forms of Al. PARFITT (1978) has discussed many more examples of the non-specificity of extractants, and concludes that the effects of Al and Fe are likely to be inseparable.

The respective activities of the different soil properties in P retention is likely to have important implications for the efficiency of P fertiliser. In strongly acid soils with high concentrations of both soluble Al and insoluble forms very little fertiliser P remains in solution and large amounts are recovered as Al phosphates (KHANNA and MAHAJAN, 1971; and TAYLOR et al. 1963). Since P fertiliser can be applied in several forms or together with other fertilisers, or amendments, such as lime, the influence of such amendments on the efficiency of P fertiliser needs to be examined.

1.3.6. AVAILABILITY OF SOIL P

The main influence on P availability in hill soils appears to be Al either when it occurs in soluble form, and can precipitate phosphate ions or depress the solubility of Al phosphates, or in insoluble forms, which as result of proton transfer provide sites for anion adsorption. This suggests that an improved understanding of the factors and reactions influencing P availability may only be gained from the simultaneous study of Al and pH together with the biological assessment of P available for plant growth.

The availability of P for plant uptake depends on the rate of desorption of P together with the rate of dissolution of readily soluble P. Because it represents the nett effects of many soil reactions and of uptake by plants, "available P" is a concept which is both difficult to define and measure. However, some chemical estimate of P is required so that an assessment may be made, of the influence of other soil properties on its supply for plant growth, in situations where plants growth studies are not feasible. The true value of any such chemical assessment of 'availability' does, however, depend on its correlation with P uptake by plants.

1.3.7. METHODS OF DETERMINING 'AVAILABLE P'

To obtain an estimate of the intensity of P in solution (I), its rate of replenishment and the size of the labile pool of P isotopic exchange techniques using the ^{32}P isotope have been used WILLIAMS and KNIGHT, 1963; and BECKETT and WHITE, 1964). Such methods however are rather time consuming precluding their use in routine analysis. Successive extractions of the soil with water or a dilute salt solution, either in a batch or continuous leaching process (FRIED and SHAPIRO, 1956; and GIBSON et al. 1976) comes nearer to obtaining a measure of the P supplying power without the long delay associated with growing plants. Anion exchange resins have also been used, (COOKE and LARSEN, 1966; HISLOP and COOKE, 1968) and WATERHOUSE and BILLE (1978) obtained results for nett plant P uptake which were closely correlated with the decrease in resin extractable P. ENWEZOR (1977) found that the amount of phosphate extracted in NH_4F, and thought to be associated with Al, was highly correlated with resin extractable P, and thus indicated its importance as a source of P for plant growth. However, the resin method itself has not been without criticism and BARROW and SHAW (1977) found that reproducibility between results was poor.

SCHOFIELD (1955) proposed an index of availability based on the potential of mono calcium phosphate(MCP) which describes the potential of P in solution, i.e. it accommodates into the value measured the effect of other ions on the distribution of P in solution. The main advantage of these methods compared to conventional extractions is that they accommodate the chemical effects of other soil properties on the apparent availability of P.

In conflict with the need to understand the factors controlling the P supplying power of the soil and its ability to maintain P supply against dilution factors, is the demand for a quick routine method to provide an assessment of soil P status for the prediction of fertiliser requirements. Extracting solutions such as Brays, Truog, Morgan and Olsens were developed to fulfill this latter demand. Essentially a known weight of soil is shaken with an extracting solution at a given soil:solution ratio. The amount of P measured in an aliquot of this solution after a specific time is that which is in equilibrium with the form of P dissolved by the extracting solution. The amount of P dissolved includes I and an unknown proportion of labile P. The problem with these methods is that; 1) they lack a kinetic factor, 2) extractants are generally not specific for particular forms of bound P and do not all dissolve the same forms of P equally, and 3) the relative supplying power of the soil is not indicated (LARSEN, 1973). Such problems may result in poor correlation between such estimates of "available P" and that P actually taken up by the plant. Results of this kind have been reported for hill soils (FLOATE and PIMPLASKER, 1976).

Apart from these uncertainties and those associated with defining 'available P' variations in the chemically determined value for 'available P' may occur due to experimental conditions affecting the kinetics of the reactions between extracting solution and soil P. These variables include the ratio of soil to solution, method and time of shaking and the temperatureand pH of the mixture while it is being shaken (BRELAND and SIERRA, 1962). The end result also is subject to considerable dilution error, the magnitude depending on the weight of sample and the sensitivity of the technique used to measure the extracted P. Similarly the plant P uptake standard against which chemical methods are compared may itself be susceptible to considerable variation depending on environmental conditions. If other soil properties are overriding the affect of P on plant growth then no method of determining 'available P' will provide a value which can be meaningfully correlated with plant P uptake.

FLOATE et al. (1980) have suggested that in order to interpret values of chemically determined 'available P' for hill soils information is also required concerning other soil properties which may interact with P and influence plant growth. Thus in this study it was sought to investigate the effect of other soil properties on the amounts of P extracted by various chemical procedures, and to compare these amounts with the actual amounts of P taken up by ryegrass.

1.4. ROLE OF ROOTS IN NUTRIENT UPTAKE

It is likely that some of the properties described in previous sections may contribute to herbage yield limitations in hill soils, and particularly to the reduced uptake of nutrients by roots. In this section the normal physiological functions of roots and the possible adverse effects of hill soils will be considered.

The movement of ions to and around root surfaces in the soil solutions occurs by diffusion and mass flow. Within the root two pathways are available for nutrient transfer, via the symplasm by cytoplasmic streaming from cell to cell and via the apoplasm, free space, which includes the space external to the plasmalemma of root cells. The important distinction between the two pathways is that entry into the symplasm involves the passage of ions across the plasmalemma, cell membrane. Ions can move relatively freely from the apoplasm to the symplasm in response to gradients of electro-chemical potential which may be effected by metabolism or the transfer of ions between cell organelles and also through active uptake mechanisms.

The free space system occupies about 10% of the root volume and is made up of non-cellular spaces between the cortical cells together with pores and intermicrofibullar spaces in the cellulose cell wall. It provides almost unrestricted passage to the root interior but is separated from the stele by the endodermis, a relatively impermeable barrier to the flow of water and solutes (CLARKSON and ROBARDS, 1974).

The structure and functions of the endodermis have been described in detail by CLARKSON and ROBARDS (1974) and RUSSELL and CLARKSON (1976). The barrier to the transfer of nutrients from the apoplasm to the stele comes into existence once the endodermis cells have entered their second state associated with the deposition of a continuous layer of suberin lamellae (casparian strip) between the plasmalemma and cell wall. However, in the region of newly initiated endodermal cells, just behind the root tip, the casparian strip is not complete. Because of this root tips play a very important role in ion transfer from the free space system to the stele and many of the ions which move via the apoplasm are dependent on this access route to the stele for their transfer to the shoots.

Cation and anion exchange sites exist in the free space. Negatively charged exchange sites arise from the many immobile carboxyl groups ($RCOO^-$) associated with pectin and other compounds in the middle lamellae and layers of cellulose. KIRKBY (1979) suggested that cation movement within the free space towards the stele is dependent on a large proportion of these sites being occupied by the particular cation so that a gradient can be established along which movement may occur by exchange diffusion.

A large proportion of ions absorbed into the symplasm do not however move into the free space system and are instead taken up at the epidermis or by root hairs which tend to be most abundant and active just behind the root tip. The detailed structure of the plasmalemma has still to be worked out. The most recent model put forward by SINGER (1972): the globular proteins were seen as being embedded in a liquid amphilic bilayer made up of $R\text{-}OH^-$, $R\text{-}NH_2^-$, $R\text{-}COO^-$ and phosphate groups attached to hydrocarbon chains (R) bonding between the lipids and globular proteins was envisaged through electrostatic H and hydrophobic bonds. The passage of water molecules and inorganic ions probably occurs via the channels provided by the globular proteins some of which extend through the membrane (WALKER, 1976).

Membrane integrity, the ability to influence the passive diffusion of ions across it, is now thought to arise from Ca^{2+} bridging between the phosphate groups on the phospholipids and the carboxylic groups on the globular proteins in the membrane (STEVENINCK, 1965). The frequency of this bridging, drawing the constituents together may control the size of the pores (HANDLEY et al. 1965). The importance of pore size and the distribution of Ca ions within the membrane on the selective nature of cation transport has been discussed by EPSTEIN (1961).

Movement of ions across the plasmalemma occurs as a result of both passive and active forces although even passive uptake relies on metabolism to create electrochemical potentials. Passive ion movement takes place until a dynamic state of electroneutrality is reached within the cell. It favours the movement of highly charged positive ions in high concentration in the apoplasm or soil solution. Active transport involves the expenditure of energy to move ions into the cell against the electrochemical potential. Various mechanisms have been put forward to explain active transport and the carrier concept discussed by HODGES (1973) and SUTCLIFFE and BAKER, (1974).appears to be preferred. The evidence suggests that active uptake is a more selective process than passive uptake implying less competition between ions in the case of active uptake.

Interference with nutrient uptake may result from any one of three processes being restricted i.e. metabolism, energy and protein synthesis, and the production of root tissue and it has been found that Al and or H are particularly likely to cause such interference.

1.5. ROLE OF PHOSPHORUS IN PLANT GROWTH

In the plant phosphate exists mainly as orthophosphate and to a lesser extent as pyrophosphate, but also occurs in organic compounds where orthophosphate is esterified with hydroxy groups of sugars and alcohols (BIELESKI, 1973). Proteins and other compounds containing P are essential components of biological membranes and protein turnover has been shown to accompany active nutrient uptake (SUTCLIFFE and COUNTER, 1962). The nucleotide triphosphates are involved in the synthesis of DNA and RNA, fundamental to the transfer of genetic information and protein synthesis, and as such are vital for growth (MENGEL and KIRKBY, 1978). However, one of the major functions of P is associated with the energy rich pyrophosphate bonds it forms since these provide energy to drive the endergonic processes in the plant such as assimilation.

1.5.1. P DEFICIENCY

The high requirement for P for growth means that in conditions of limited supply plants are small with restricted root systems. Deficiency symptoms include pinking and eventual necrosis of the foliage tips. In grasses tillering is reduced and leaf blades tend to be thin and dark green (HEWITT and SMITH, 1974). One or more of the following may cause P deficiency:- low levels of available P, inconsistency of P supply, inadequate root growth, immobilisation of P within the root and inhibition of metabolism. Most of these causes have been associated with high levels of soil Al.

The effects of soil Al, lowering the concentration of P in the soil solution by providing surfaces of P adsorption, or by its precipitation as aluminium phosphate have been discussed. In the plant also RORISON (1965) and CLARKSON (1965, 1967) have demonstrated the high affinity of Al for P. CLARKSON (1966) showed that Al ions adsorbed to cell walls in the free space were able to bind P with the result that its translocation to the shoots was markedly reduced. Further evidence of P precipitation has been provided by transmitting election microscope techniques. McCORMICK and BORDEN (1974) found scattered globules of Al bound P along the root epidermis and intercellular regions.

The affinity of the highly charged Al ions for negatively charged phosphate groups has also been demonstrated inside plant cells with more serious consequences for growth.

NAIDOO et al. (1978) using Xray microanalysis identified high concentrations of Al in the nucleus and other cell organelles. WOOLHOUSE (1969) suggested that the binding of Al to phosphate groups influenced the protein configuration of enzymes and as a result interfered with their activities. Polymerization of proteins through Al crosslinking increases the viscosity of cyloplasm and KLIMASHEVSKII and DEDOV (1975) found that cell elongation following mitosis was impaired by Al induced esterification of P in the membrane lipids. CLARKSON (1965) and SAMPSON et al. (1965) showed how mitosis itself is prevented by cross-linking between Al and the phosphate groups in the DNA helix which inhibits template formation and thus protein synthesis.

Inactivation of P by Al therefore causes serious disruption of metabolism and growth and seedlings are particulary vulnerable to the detrimental effects of Al - P interactions. RORISON (unpub) found that size of embryo P supply was strongly related to the susceptibility to Al toxicity shown by seedlings. In view of the nature of the interactions between P and Al it is possible that increasing the P supply by the addition of fertiliser, might offer some protection from Al toxicity. However, there is disagreement in the literature concerning the ameliorating effect of P on Al toxicity. HARTWELL and PEMBER (1918) found that the addition of large amounts of superphosphate reduced the detrimental effects of Al while MATSUMOTO and HIRASAWA (1979) showed that pre or post treatment with P gave no protection against Al toxicity. In view of the likely requirement for additional P in hill land improvement it would be useful to investigate whether or not added P influences the extent of Al toxicity.

1.5.2. UPTAKE OF P

Phosphate ions move through the soil by diffusion (VASEY and BARBER, 1963) and by some bulk mixing of soil water (FRIED and SHAPIRO, 1961). The rate of movement of P is slow and by demonstrating only small zones of depletion around roots it has been indicated that in order to exploit the P supply in an adequate volume of soil, plants require either a large diffuse root system or possibly symbiosis with mycorrhiza to enhance the surface are over which P can be absorbed (MUNNS, 1976).

P uptake occurs mainly via root hairs and the outer cortical cells, directly into the symplasm. Maximum P uptake occurs over the region with most numerous root hairs, behind the tip and corresponding to the area where cell elongation is complete. This means that P uptake by the apical meristems of axial and lateral roots is more than double that from the most actively absorbing regions of differentiated root (CLARKSON and SANDERSON, 1970). Thus the P sorbing power of roots is greatly reduced by the restriction of lateral roots to short stubs which hardly protrude from the epidermis and which may be due to toxic levels of Al (FOY et al. 1978).

P uptake is an active process enabling roots to absorb P from very dilute solutions (DREW and NYE, 1970), and generally the P content of root cells is between 100 and 1000 fold higher than the concentration of phosphate ions in the soil solution. Mechanisms for P uptake are still being investigated (HODGES, 1973, BIELESKI, 1973) and the influence of other cations and anions is disputed. However, it is generally thought that occupation of a high proportion of sites in the free space by Ca^{2+} ions enhances P uptake (ROBSON et al. 1970) whereas occupation by Al ions reduces P uptake (WHITE, 1977).

pH has been shown to influence P uptake. HENDRIX (1967) found that at acid pHs far more P was absorbed which he explained by the 'preference' of roots to absorb nutrients in their most oxidised states and at the lower pH a higher proportion of P occurred. as $H_2PO_4^-$ (HAGEN and HOPKINS, 1955). However, by reason of its greater solubility at low pH, Al is also likely to have a more active influence over P availability and may counteract this effect. The interactions between pH, P supply, and Al in hill soils therefore requires study with a view to minimising the potentially deleterious effects of acidity and high Al levels.

1.6. ROLE OF CALCIUM IN PLANT GROWTH

The detailed functions of calcium (Ca) in plant growth have been discussed in an excellent review by FOY (1974) and only the most relevant aspects are discussed here. The role of Ca in membrane integrity has been covered (1.4.) and STEVENINCK (1965) found no other cation to be as effective. Calcium is also important for giving structure to plant cells again through its attribute of binding, cross linking pectins in the cell wall (RASMUSSEN, 1966). A few enzymes have been shown to require Ca^{2+} as a cofactor (JONES and LUNT, 1967) while BURSTROM (1968) identified a specific requirement for Ca in cell division; when Ca levels were deficient spindles failed to develop. The Ca requirements of different plants have been discussed by LONERAGAN and SNOWBALL (1968) and LONERAGAN et al. (1970).

1.6.1. CAUSES AND CONSEQUENCES OF Ca DEFICIENCY

There are several causes of Ca deficiency but it rarely arises as a direct consequence of low levels of soil Ca but rather when the proportion of Ca to other cations such as Al or Mg in the soil solution is low (WALLACE et al. 1966, LUND, 1970 and FOY, 1974). Most calcium is transported via the apoplasm and is largely transferred to the stele at the root tips where the endodermis is incompletely formed (RUSSELL and CLARKSON, 1976). CLARKSON (1974) showed that a large proportion of the Ca in the apoplasm was firmly bound and movement of Ca toward the stele was dependent on a large proportion of the exchange sites being occupied by Ca. However, when the concentration of ions such as Al is high, as might be expected on hill soils, these trivalent ions can displace the divalent Ca from the exchange sites and thus reduce the flow of Ca to the shoots (SHONE, 1966). In the pH range 4.5 to 5.0 when Al is hydrolysed to the $Al(OH)_2^+$ ion the movement of Ca into the free space was found to be almost totally inhibited due to the repulsion of like charges as these built up around the epidermis and the peripheral layers of the cortex (CLARKSON and SANDERSON, 1969; MOORE, 1974).

A reduction in the concentration of Ca in the apoplasm has been shown to have serious consequences for plant growth. Movement of Ca ions across the plasmalemma is greatly reduced so that there is insufficient Ca available for the maintenance of membrane integrity. The consequences of this are that membranes become leaky with the resultant loss of ions from the cell interior and also as result of their increased permeability they present less of a barrier to the passive diffusion of large hydrated ions such as $Al^{3+} \times H_2O$. Since many physiological processes are highly susceptible to Al toxicity e.g.nucleotide synthesis and some enzyme functions (FOY et al., 1978) this breakdown of membrane integrity is usually devastating for the normal functioning of the cell units. Thus by reducing the uptake of Ca by direct antagonism Al can increase the extent of its toxicity. FOY (1974) considered that in acid soils below pH 5.5, Al/Ca antagonism was probably the most important influence on Ca uptake.

Membrane integrity would appear to be a crucial factor in the control of the disruptive effects of Al on cell division and metabolism. However, Al is not the only detrimental influence; below pH 4.4, when the H ion concentration is high,H ions may exchange for Ca ions in the membrane with consequences similar to those observed in the absence of Ca (MOORE, 1974). This effect was reduced by increasing the level of Ca in the bathing soil solution although the actual concentration needed appears to vary for the individual plant species and circumstances (LANCE and PEARSON, 1969; HALL, 1972). CLARKSON (pers. comm.) indicated that the concentration would usually need to exceed 10×10^{-3} M Ca. However, most of these observations have been made for nutrient solution work and concentration ratios and pH effects need verifying in the soil.

These observations suggest that the extent of Al toxicity increases with the lowering of pH. This is because; 1) the solubility of Al is increased and this may depress the level of P in solution; 2) membrane integrity is reduced facilitating movement of Al ions across the plasmalemma and 3) growth is limited by the restricted uptake of Ca.

All the observations reported indicate that the effects of Al, pH and Ca on plant growth are inter-related and suggest that in order to improve hill soil conditions for plant growth, where low pH, low levels of Ca and high levels of Al prevail, amendments must be added to the soil which deal with all three factors simultaneously: experimental confirmation is required.

1.7. INFLUENCE OF AL ON PLANT GROWTH

Although trace amounts of aluminium have been shown to stimulate growth in some species (tea, rice, FOY et al. 1968; and *Deschampsia flexuosa*, HACKETT,1962), in acid soils its significance for plant growth is usually associated with its toxic effects of which many have been mentioned with reference to interference with growth and nutrient uptake (1.4, 1.5). The root cap which protects the root tip from physical damage is freely permeable to Al ions and as observed for Ca ions access to the shoots is via the root tip (HENNING, 1975). It has been suggested, McCORMICK and BORDEN (1974) that Al ions may be relatively mobile in the apoplasm but that entry to the symplasm is impeded because of the high charge and large size of the hydrated Al ion. When the concentration of Al builds up in the apoplasm however, some ions may diffuse across the plasmalemma and the rate of movement is increased by the loss of membrane integrity (CLARKSON, 1966).

Movement of Al across the plasmalemma is enhanced when it is in a chelated form possibly because such complexes have no charge or much lower charge, and as such are non-toxic (DeKOCK and MITCHELL, 1957). WHITE (1977) found that Al could be taken up in a chelated non-toxic state as Al hydroxy phosphate. WHITE (1977) suggested that not only was the Al/P complex non-toxic it might also be beneficial, providing a reserve of P in the cell vacuole, the significance of this however has still to be demonstrated. The mobility of Al chelates and also their stability's are still under investigation although BARTLETT and RIEGO (1972) suggested that in many instances translocation via the stele was hindered by the ligand part of the complex.

The evidence presented suggests that the adverse effects of Al occur mainly in the unprotected root tip with far reaching repercussions due to contribution of the root tip to growth and nutrient uptake. The effects of Al appear to be relatively non-specific due to the affinity of its high charge density for phosphate ions. Other polyvalent ions have been shown to produce similar effects to Al (CLARKSON and SANDERSON, 1971) but the reason Al stands out is because it may occur naturally in high concentrations in acid soils (1.2.)

1.8. LIME

Soil acidity and its related effects, which include the increased solubility of Al, Fe and Mn have long been known to restrict herbage production and methods to counteract its effects, such as the applications of marl or lime are not a recent innovation. Acidity develops most quickly in strongly leached soils which,as a consequence of high leaching, also have low contents of exchangeable bases. In soils where the inherent Al content is high, or where its release through chemical weathering is relatively rapid, such as in the Acid Brown, and particularly in the Brown Podzolic soils, the need to correct acidity is greatest. An understanding of the development of soil acidity and of the changes involved when lime is added is required for greater precision in the use of corrective treatment and for a better understanding of the effects lime amendments might have on the interactions between Al and P and between Al and Ca.

1.8.1. LIME REQUIREMENTS OF SOILS

In the past the lime requirement (LR) of soils has been calculated from the amount of lime required to overcome undesirable properties associated with acidity and soil Al. Since there are many such properties of differing importance in different soils many methods for determining LR are currently in use and there are several review papers dealing with their respective merits (COLEMAN and THOMAS, 1967; YUAN, 1974; McLEAN, 1977).

Some of the complex interactions which contribute to the LR, reactions of a physical nature, reactions between organic and inorganic colloids, moisture status and the level of Al, Mn and P, have been discussed by PEARSON and ADAMS, (1967). PIONKE et al. (1968) described the usefulness of certain properties for assessing LR in order of priority: pH dependent cation exchange sites on OM,* non-exchangeable Al (which contributes to the buffering capacity of the soil with respect to the addition of bases), exchangeable Al, and pH dependent sites on clays. However, REEVE and SUMNER (1970) found no relationship between

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* OM = organic matter

LR and exchangeable Al, CEC, clay content or pH in oxisols but showed that OM provided the major source of buffering capacity and that LR was correlated with the % carbon content. In the hill situation where the soils contain larger amounts of organic matter FLOATE (1978) found that LR was related to the CEC and exchangeable acidity, so that as OM content increased so did CEC and the LR despite the decreasing contribution of exchangeable Al to the total exchange acidity.

The large number of soil properties that have been used to assess LR indicates the need to first identify the main parameters which are influencing acidity in the soils to be studied. Once these have been established and their interactive effects considered the parameters then need to be evaluated with respect to their influence on plant growth and in particular for the plants which are to be grown in hill soils. Different plant species exhibit a range of tolerance to acidity (VOSE and RANDALL, 1962 (ryegrass); VOSE, 1963, HACKETT 1964, 1965 (<u>Deschampsia flexuosa</u>); CLARKSON, 1966 (<u>Agrostis sp</u>); CHAMURA, 1967 (Italian ryegrass); PALAZZO and DUELL, 1974 (American strains of ryegrass)).

1.8.2. EFFECTS OF LIMING

When lime is added to soil there is an input of Ca and carbonate ions which initiate a sequence of reactions:-

$$CaCO_3 + H_2O \longrightarrow Ca^{2+} + HCO_3^- + OH^-$$

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3 \downarrow$$

The production of OH^- ions is the rate determining step and these are removed by precipitation with monomeric exchangeable Al ions which have been displaced from exchange sites by Ca ions released as lime dissolves. As the reaction proceeds and the pH begins to rise more Al ions are precipitated and hydroxy species of Al formed. These reactions proceed very slowly where soils show a strong affinity for intermediary products. The extent of the increase in pH caused by liming therefore appears to be related to the quantity of exchangeable Al which in turn is related to the CEC of the soil, and its percent saturation by Al.

As a result of the rise in pH the addition of lime influences many soil properties. A reduction in the level of both exchangeable and soluble Al has been demonstrated by EVANS and KAMPRATH (1970), MACLEAN et al. (1972) and RYAN and SMILLIE (1975). These workers have found that above pH 5.0 - 5.2 soluble Al is hardly measurable and above pH 5.4 exchangeable Al is reduced to trace amounts. Reductions in the levels of these 2 forms of Al have been associated with improved plant growth, and especially root growth, in some circumstances.

Plant response to lime appears to be governed by the extent of tolerance of the plant species to low pH or to the high levels of active Al associated with low pH. EVANS and KAMPRATH (1970) found that corn only responded to liming when Al saturation of the CEC exceeded 65%, which was accompanied by a concentration of 0.13×10^{-3}M Al in the soil solution, while with soya beans there was a response when the concentration of Al exceeded 0.07×10^{-3}M. These lime responses were not predictable from levels of exchangeable Al or pH. HELYAR and ANDERSON (1970) reported that in the pH range 4.2 to 4.6, when percent Al saturation was between 25 and 50%, and soluble Al concentration was approximately 0.01×10^{-3}M, ryegrass did not respond to lime but phalaris and lucerne exhibited Al toxicity symptoms. It would seem that despite the amount of work done on lime responses such effects are not always predictable and require study with the appropriate soil and species to be grown. The present state of knowledge of hill soils and the tolerance of more productive species to Al is inadequate to determine when liming is crucial to the success of introduced species.

As well as reducing the level of Al, and thus its toxic effects, lime also increases the Ca content of the soil which can itself counteract the effect of Al and acidity (1.6, 1.7). Three fractions of Ca are recognised in soil, viz. non-exchangeable, exchangeable - and soluble - Ca, non-exchangeable forms include minerals such as Ca felspars, amphiboles, phosphates and carbonates. The latter two forms however are generally absent in Acid Brown hill soils as they are highly unstable at the low pHs of these soils. Generally the native Ca content of these soils is low due to the high rate of leaching and the immediately available Ca reserve is that which is exchangeable (KIRKBY, 1979). Thus the input of Ca as lime appears to greatly improve the availability of Ca to plants not only because it increases the amount of Ca per se, but also because it reduces the proportion of Al and acidity.

Although the benefits of liming soils containing high concentrations of soluble Al are without doubt (MUNNS, 1965), due to improved root growth increasing the biological availability of P the effect on the chemical availability of P is debateable. Where P uptake is impaired because levels of Al are restricting root growth, or P translocation is reduced as a result of its fixation by Al in the root the addition of lime may increase yields (JUSTE, 1964). However, in species which did not respond to lime, HELYAR and ANDERSON (1970) recorded lower P contents and a reduction of the level of P in the soil solution. ENWEZOR (1977) also recorded a negative interaction between lime and P uptake when the pH exceeded 4.7.

Evidence for and against the increased chemical availability of P effected by liming has been presented by AMARASIRI and OLSEN (1973). They concluded that the evidence was inconclusive when the same chemical methods gave contrasting results for different soils (ASLYNG, 1954). The decreases in both soluble and labile P which resulted in minimum values between pH 6 and 7 have been explained for soils where there is a high content of Al and Fe through the fixation of P by newly precipitated hydroxides (WILD 1953, and COLEMAN et al. 1960). HALSTEAD (1967) found that irrespective of liming or soil pH more than 50% of added P was recovered from Al-P fractions and KAMPRATH and FOY (1971) reported that P fertiliser added to limed soils was precipitated as a compound having the overall composition of variscite. RIEMSDIJK et al. (1975) found that above pH 5.5. Al hydroxy polymers formed which both blocked cation exchange sites and adsorbed phosphate ions.

The increases measured in the concentration of P in solution after liming have been attributed to the hydrolysis of strengite and variscite releasing phosphate ions (LINDSAY and MORENO, 1960 and McLEAN, 1976). Also the concentration of both Al and Fe ions are lowered by liming so that the likelihood of their reacting with phosphate ions is reduced. However, it is generally accepted that P adsorption by the precipitated Al/Fe hydroxides would more than compensate for the lowering of soluble Al/Fe ions which can react with P.

There are also contrasting views with regard to the effects of lime on the P sorption maxima. BACHE (1963) showed that the energy of P sorption by Al hydroxide decreased with increasing pH confirming the observation by HSU and RENNIE (1962) that at low pH P sorption increased because surface OH^- groups were held with less intensity. WOODRUFF and KAMPRATH (1965) found for three soils with high Al saturation that the P sorption maximum decreased with liming but when Al saturation was lower the P sorption maxima was not changed by liming. This latter observation is in contrast to other reports and indicates that in order to determine the effect of lime on P fixation by Al compounds in hill soils both chemical and biological data will be required. KAMPRATH and FOY (1971) expressed the opinion that several standpoints need to be considered in order to understand the effect of lime on P fixation; namely the neutralization of exchangeable Al and the effect of increasing Ca saturation.

Other more general benefits of lime which may or may not enhance herbage production are those involving micro-organisms. The activities of N fixing organisms are highly sensitive to soil pH and Ca levels (ALLISON, 1966; LOWTHER and LONERAGAN, 1968; HELYAR and ANDERSON, 1971). Also breakdown and mineralization of organic matter has been found to increase with increasing pH. RYAN and SMILLIE (1975) attributed increases in Morgan, Truog and resin extractable P as result of liming, to increased mineralization although KAILA (1961) found no positive evidence for this view. BARBER and LOUGHMAN (1967) found that when P was in low supply micro-organisms were more efficient competitors for P than plant roots and thus could deprive them of P.

Although the need to lime soil to reduce the effects of Al toxicity seems unquestionable the role of lime in soils where the effects of Al are not pronounced is less substantiated. The evidence suggests that in order to establish liming needs for hill soils the range of hill soil properties contributing to acidity and their low P availability need identifying and the changes due to lime recorded. Then, a better understanding of situations where lime is required, will be available. The experiments to be described in this study have been designed to include these objectives.

1.9. OBJECTIVES OF THE STUDY

Acid Brown soils have been found to have the most potential for improvement but published data is lacking for the ranges of some of their soil properties, including pH, exchangeable Al, available P and proportion of Al to base saturation. Such properties are likely to influence herbage production from these soils and therefore it is important to quantify not only their effects on plant growth but also the plant response to added lime and P fertiliser.

In this study the limits to herbage production set by the inherent Al content of the soil will be examined in relation to its influence on acidity and the availability of P and Ca. Experiments described in this study have been designed to survey and quantify the range in soil properties so as to examine the effects of particular treatments on typical soils and to assess the relative importance of acidity, Al and phosphorus supply, and to understand the mechanisms by which these processes operate. The data on the apparent effects of soil on plant responses are discussed in relation to measured soil properties and criteria are sought for the identification of kind and degree of limitation to plant growth. The requirements of particular soils for improved pasture production are discussed in relation to the relative importance of inherent limitations, and to the mechanisms by which these limitations restrict plant growth under certain circumstances.

CHAPTER 2

MATERIALS AND METHODS

2.1. GENERAL PRINCIPLES

A survey of some properties of selected Acid Brown hill soils was undertaken initially with the view to selecting suitable soils for further study and to evaluating suitable methods of analysis. Objectives often determine the method of choice as different methods may be only suitable for purposes of classification, general soil description, the understanding of soil genesis, and the interpretation of related properties rather than predicting plant growth requirements and responses. BACHE (priv. commun.) commented on the dilemma of choosing between methods suitable for the investigation of relationships between soil exchange properties and the proportion of various ions in solution, and those most suitable for the determination of ionic concentrations which are more appropriate to plant growth requirements. Consequently, both in the initial survey and at the outset of the various experiments described in chapters 3 to 12, other methods were examined as well as those reported in the text which only includes those methods whose results have been used for the interpretation of data.

In order to describe inter-relationships between two soil components it would seem logical to measure the effect on one component both before and after the removal of the other. Such an approach was used by CHU and SHERMAN (1952), WILLIAMS (1957) and BROMFIELD (1967) in attempts to quantify the effect of sesquioxides on P sorption. However, the removal of sesquioxides usually involve the use of highly acidic oxidizing agents which may also influence other soil properties so that any subsequent change in the extent of P sorption could not necessarily be attributed to removal alone. In view of the heterogeneity of the soil system with its many interdependent components it is rarely possible to achieve the removal of a single component without affecting others.

However, provided the side effects just described are appreciated, the attempted removal of one constituent does provide a technique for examining its influence on other soil properties and plant growth. The usefulness of this approach was examined in an experiment (Chapter 7) where the soil was leached with M KCl in an attempt to remove and thereby assess the influence of exchangeable Al on plant growth.

Experimentation has included the chemical measurement of nutrients, and of other soil properties associated with Al and acidity, which may influence laboratory estimates of nutrient 'availability'. Such measurements have been compared with 'biological availability' assessed by the growth of ryegrass in pot experiments in the glasshouse.

Pot experiments under standard glasshouse conditions provide a technique for examining the effects of interactions between applied treatments and soil properties in the absence of other environmental influences. As such these experiments are of value in the interpretation of possible mechanisms by which these interactions operate. However, the quantitative results cannot necessarily be extrapolated to predict field effects. Reasons for this are the special conditions of pot experiments which include:- limited rooting depth and volume, more nearly optimum temperatures and moisture conditions, complete mixing of soil with additives, drainage without leaching loss and absence of indigenous competitors. Also when grown in pots the competitive effects of indigenous species are absent and this is a very important adverse factor operating to reduce 'potential' yields in the hill environment (NEWBOULD, pers. commun.).

2.2. SOILS

2.2.1. LOCATION

The soils used for experimental purposes (Table 2.1.) were collected from a number of sites on several different parent materials to include a representative range of Acid Brown soils from those Brown Earths of low Al content and higher pH to the more acidic Brown Podzolic soils having higher Al content. The soils are numbered 1 to 25 and their sample locations in Scotland are shown in Figure 2.1. (soil 5 came from North Wales).

Table 2.1. Soils used in Laboratory and Glasshouse Experiments

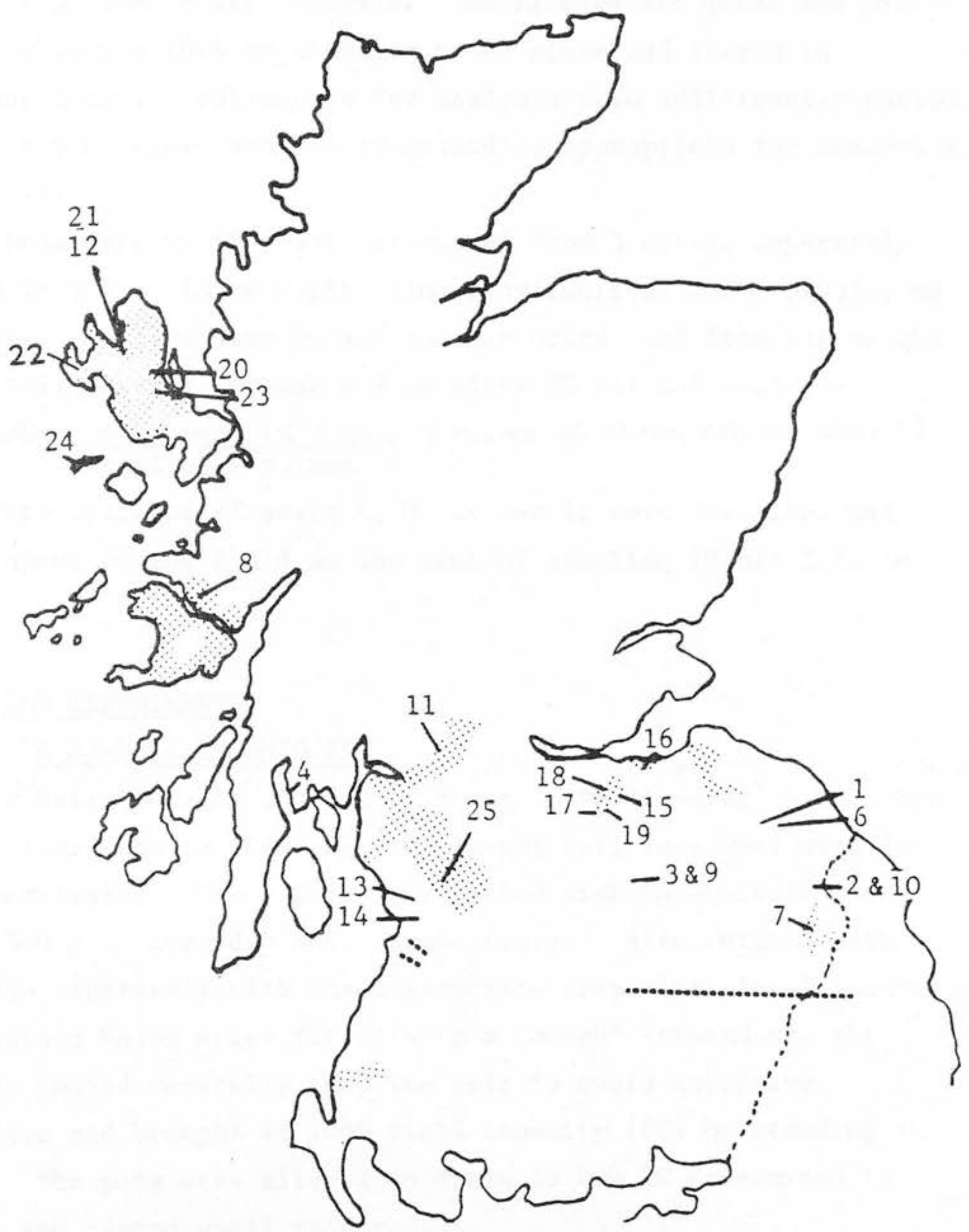
Soil Number	Location	Depth cm	Soil Series	Parent Material	Sampled by*	Chapter
1	Minchmoor A	0–10	Minchmoor	Greywacke	1	3
2	Sourhope 1	0–10	Sourhope	Andesite	1	3
3	Stanhope	0–10	Linhope	Greywacke	1	3
4	Lephinmore	0–10	Fungarth	Highland Schist	2	4
5	Llansannan	0–15	Hiraethog	Shale/Slate	1	3
6	Minchmoor B	30–40	Minchmoor	Greywacke	1	3
7	Carter Bar	0–5	Darleith	Basalt	1	3
8	Fiunary Forest	0–15	Darleith	Basalt	3	3
9	Stanhope Glen	0–10	Linhope	Greywacke	2	3,4,5,6
10	Sourhope 2	0–10	Sourhope	Andesite	2	4
11/11a	Carron Forest	0–5	Darleith	Basalt	2	4,5,6,7, 8,9,10
12	Bay, Skye	0–5	Darleith	Basalt	4	9
13	Carrick Hills	0–5	Darleith	Basalt	2	9
14	Carrick Hills (L)	0–5	Darleith	Basalt	2	9
15	Corstonhill	0–10	Darleith	Basalt	5	11
16	Mons Hill	0–10	Darleith	Basalt	5	11
17	Harperlg Res'r	0–10	Darleith	Basalt	5	11
18	Riccarton	0–10	Darleith	Basalt	5	11
19	Tarbrax	0–10	Darleith	Basalt	5	11
20	Glenvaragill(Skye)	0–15	Darleith	Basalt	4	12
21	Bay (Skye)	0–15	Darleith	Basalt	4	12
22	Osdale (Skye)	0–15	Darleith	Basalt	4	12
23	Woodend (Skye)	0–5	Darleith	Basalt	4	12
24	Canna	0–15		Basalt	4	12
25	Carrick	0–15	Darleith	Basalt	4	12

Legend:

A - A horizon; B = B horizon, 1 and 2 refer to different locations

* - 1 Dr M J S Floate, HFRO); 2 Author; 3 Aberdeen University Soil Science Department; 4 Soil Survey of Scotland; 5 Edinburgh School of Agriculture

Fig 2.1 Locations of soil samples
(with the exception of soil 5 from North Wales).



2.2.2. SAMPLING PROCEDURE

After removal of the superficial organic litter layer the top 5 or 10 cm of mineral soil was sampled in different quantities for pot experiments and analysis. Soils were air dried and passed through a coarse (6.4 mm diameter mesh) sieve and stored in polythene sacks. Subsamples for analysis were additionally passed through a 2 mm sieve and finely ground as appropriate for analytical techniques.

Bulk density (BD) was determined from 5 cores, separately sampled to a 5 or 10 cm depth using a cylindrical corer of 37.7 mm diameter. Samples were bulked and air dried, and from the weight of dry soil passing through a 2 mm sieve BD was calculated:-

$$BD = \frac{\text{wt of soil } (< 2 \text{ mm})}{\text{total core volume}}$$ (volume of stones not considered)

The profiles of soils 4, 9, 10 and 11 were described and photographed in the field at the time of sampling (Table 2.1A to 2.4A).

2.3. POT EXPERIMENTS

2.3.1. GLASSHOUSE TECHNIQUES

Plastic pots of 2 sizes (7.5 and 10 cm diameter) with glass fibre filter pads in the bases to prevent soil loss were used for pot experiments. These pots were filled with an equivalent of 100 or 300 g of oven dry soil respectively. After mixing each replicate separately with the appropriate treatments for 5 minutes in a Kenwood Major mixer fitted with a 'dough' attachment, the soil was packed carefully into the pots to avoid excessive compaction and brought to 100% field capacity (FC) by standing in water. The pots were allowed to drain to 60% FC determined by weight, and stored until required.

The top 1 cm of soil was scraped to the edge of each pot and 0.12 or 0.20 g of perennial ryegrass seed was sprinkled over the soil in 7.5 and 10 cm pots respectively; finally the soil was replaced over the seed. Lolium perenne (S24) was chosen as the test plant not only because of its importance in improved hill pastures, but also because it is not excessively sensitive to aluminium, and it avoids the difficulties of interpretation associated with clover and its attendant microbial requirements.

Pots were transferred to the glasshouse and the replicates arranged in randomized blocks. Until germination was completed (approximately 7 days) the pots were covered with polythene to minimise water loss. During the growth period water was given daily into the saucers in which the pots stood and weights were checked weekly to maintain 60% FC. At the end of the second and every subsequent fortnight, applications of NH_4NO_3 were given to eliminate possible N limitations on plant growth. The amounts of N applied are detailed for individual experiments together with treatments and greenhouse conditions in the Methods section and/or appendix for each experiment.

Regular notes were made for germination (percent), colour and state of herbage growth, and harvest cuts were taken after 28 or 40 days as detailed for individual experiments. When a single harvest was taken, herbage was cut to soil level but when sequential cuts were taken 1 cm of stubble was left for regrowth, and this was either analysed separately or included with the root.

2.3.2. PREPARATION OF PLANT MATERIAL

The herbage was wiped with tissue paper, and the cut ends were brushed over with a fine paint brush to remove any soil contamination. The cut grass was dried for 24 hours at 80°C in brown paper bags, weighed, and milled in a Moulinex coffee grinder in preparation for analysis.

Roots and attached stubble were separated from the dry soil. RUSSELL and ADAMS (1954) recommended soaking the soil and roots in 15% w/v lead acetate solution before washing to prevent the loss of water soluble P. This procedure was tested in a preliminary experiment. The results of a comparison between pre-soaked and washed roots (Table 2.1A) showed that there was no significant difference in P content but that the Ca content was 30% lower in the lead acetate pre-soaked samples. This was possibly due to the displacement of adsorbed Ca^{2+} in the root free space by the more strongly adsorbed Pb ion. RUSSELL and ADAMS (1954) estimated loss of P by measuring the concentration of P in the washing solution, but here the P contents of the actual roots was compared, and it is possible that some loss of P occurred from both presoaked and washed samples. However, in view of the likelihood of Pb interference with the cation content of the root which was also required Russell and Adam's method was not used.

Roots were washed clean on a sieve using a fast jet of tap water, dried at 80°C for 48 hours, weighed and cut up. (The roots were too fibrous to be milled.) Stubble was removed from the roots before weighing and both these were weighed, cut up or milled and analysed separately. In later experiments when there was evidence to show that the mineral content of the root and stubble were similar these were combined.

2.3.3. PLANT ANALYSIS

The milled herbage was either wet digested using the PARKINSON and ALLEN (sulphuric acid/peroxide) procedure (1975) or made into discs for analysis by X-ray fluorescence spectrometry (Note 2.2A). This latter method was used when Al determinations were required (all root and some herbage analyses) as facilities for measuring Al by atomic absorption were not available. Other elements, Ca, Mg, K, Fe and Mn were measured in the digest by atomic absorption while P was measured by auto-colorimetry (Section 2.4.1.6).

2.4. SOIL ANALYSIS

Analyses were conducted on subsamples of the bulk soil used for pot experiments, soil samples from pots which had been treated and stored but not planted and also from some pots in which ryegrass had been grown. Results are given per 100 g of oven dry soil. Actual analyses were done on soil which had been air dried for at least 2 weeks unless stated otherwise.

2.4.1. PHOSPHORUS

2.4.1.1. TOTAL P

0.200 g of finely ground oven dry soil was weighed into 50 ml Kjeldahl flasks and digested in 6.4 ml of a solution containing 350 ml of 30% w/v H_2O_2 + 0.21 g Se powder + 7 g $Li SO_4 . H_2O$ + 210 ml 98% H_2SO_4 (PARKINSON and ALLEN, 1975). After 2½ hours the digest was transferred to a 50 ml volumetric flask and made up to volume with deionized water. Blank digests, used to prepare standard solutions, were similarly prepared. P in this and the following extracts was determined by autocolorimetry (Section 2.4.1.6).

2.4.1.2. ORGANIC P

One pair of 1.0 g samples of finely ground soil were weighed into pyrex crucibles and ignited at 550°C in a muffle furnace for 1 hour. Then, together with a second pair of non-ignited samples these were shaken with 50 ml of 5×10^{-1}M H_2SO_4 for 1 hour at 21° ± 2° C and filtered (SAUNDERS and WILLIAMS, 1955). Inorganic P in solution was measured as described below (Section 2.4.1.6) and organic P was calculated as by difference:-

Organic P = Inorganic P in ignited sample - inorganic P in
non-ignited sample.

2.4.1.3. EXTRACTABLE P

a) Morgan:- 2.0 g of soil was shaken with 25 ml M NH_4OAC, buffered to pH 4.5 for 1 hour at 21° C ± 2° C and filtered (HENDE et al. 1951).

b) Truog: 2.0 g of soil was shaken with 100 ml 10^{-3} M H_2SO_4 buffered to pH 3 with $(NH_4)_2SO_4$, for 30 min. at 21° C ± 1° C (TRUOG, 1930).

2.4.1.4. RESIN EXCHANGEABLE P

2.00 g of finely ground soil (< 30 mesh) was shaken with 6 ml of pretreated resin suspension (amberlite IRA 410 strongly basic > 25 mesh) in 50 ml deionized water for 18 hours. The resin beads were separated by washing and sieving from the soil and P was leached from the beads in columns using 25 ml M HCI (FLOATE and PIMPLASKAR, 1976). SIBBESIN (1978) suggested enclosure of the beads within nylon mesh bags in order to expedite separation but when this was tested the recovery of added P was incomplete.

2.4.1.5. P SORPTION INDEX (PSI)

2.50 g of finely ground soil was shaken with 50 ml of

2×10^{-2} M KCl containing a known weight of KH_2PO_4 for 18 hours at 21^{0} C $\pm$ 1^{0} C and a drop of chloroform, centrifuged at 5,000 rpm for 20 min. and filtered (BACHE and WILLIAMS, 1971). For some of the soils a concentration of 75 mg/L of P was used, but soils derived from basalt required 150 mg/L in order to detect measurable amounts of P in the final equilibrium solution.

P concentrations in the filtrates were compared with standards from 0 to 60 mg/L of P in 2×10^{-2} M KCl. PSI was calculated as follows:-

$$\mathrm{PSI} = \frac{\text{mg P sorbed/100 g soil}}{\mathrm{Log}C}$$

where C is the final concentration of the equilibrium solution in mgP/L.

2.4.1.6. P IN SOLUTION

The P in solution was measured using continuous flow analysis with $SnCl_2$ as the reducing agent for the formation of the blue, phosphomolybdate complex at pH 3.0. The colorimeter was set at a wavelength of 700 nm. A modified less acidic ammonium molybdate solution was developed for the measurement of P in the sulphuric acid/peroxide digests (IRONSIDE, unpub.). Standards were made up in blank solutions of the appropriate extractant and these were used for the construction of standard curves against which the unknown values were compared. Calculations are described in 2.3A.

2.4.2. ALUMINIUM

2.4.2.1. EXTRACTABLE Al

The concentration of Al was determined in the NH_4OAC (MORGAN) extract prepared for P (Section 2.4.1.3.).

2.4.2.2. EXCHANGEABLE Al

2.50 g samples were weighed into cellulose extraction thimbles which fitted into polythene tubes set up for automatic leaching with M KCl where the flow rate was controlled by a peristaltic pump. These were sealed at the top with rubber bungs enclosing an inflow tube while at the outlet a piece of narrow gauge (transmission) tubing led the outflow into 250 ml volumetric flasks.

The system was primed with M KCl, so that the soil column was covered by a 2 cm deep head of KCl, before automatic leaching was started. Leaching was stopped after 250 ml had been collected, approximately 7 hours (35 ml/hr). The apparatus was designed so that 18 leaching columns could be run simultaneously. The method was adapted from that described by BACHE (1976). Al in solution was determined colorimetrically as described in Section 2.4.2.4.

2.4.2.3. SOLUBLE Al

5.0 g of soil was shaken with 25 ml of 10^{-3} M $CaCl_2$ for 1 hour at 21° C $\pm$ 1° C and filtered. This method was based on the procedure described by HOYT and WEBBER (1974).

2.4.2.4. Al IN SOLUTION

The Al in solution was determined colorimetrically using continuous flow analysis with Alizarin Red S as the coloured complexing agent in a solution of mercapto acetic acid, glacial acetic acid and sodium acetate buffered to pH 4.2. A 490 mm filter was used. The method was developed by LANCASTER and BALASUBRUMANIAN (1974) and was adapted for continuous flow analysis by EVANS (unpub.). Standards were made up in blanks of the appropriate solutions.

2.4.3. OTHER ANALYSES

2.4.3.1. EXCHANGEABLE ACIDITY

Two 50 ml aliquots of the M KCl leachate from the procedure 2.4.2.2. above, were titrated with 1×10^{-1} M NaOH to pH 8.0 using the pH meter. 10 ml of M NaF were added to complex the Al ions and finally the pH was brought back to pH 8.0 by titration with 1×10^{-1} M HCl. Exchangeable acidity was calculated from the volume of NaOH used in the first stage of the titration and acidity due to exchangeable Al was calculated from the volume of HCl used in the second stage (McLEAN, 1965).

2.4.3.2. CATION EXCHANGE CAPACITY (CEC)

Using the procedure described for exchangeable Al (Section 2.4.2.2.) M KCl at the natural pH of the soil (BACHE, 1976) was used to displace exchangeable cations. Excess KCl was washed from the column using 40% isopropanol and K^+ ions were displaced using a second stage leaching with 250 ml M NH_4Cl. Finally CEC was calculated either from a) the K^+ concentration determined by atomic absorption in the NH_4Cl leachate, of b) from the sum of exchangeable Al + Ca + Mg. The latter two cations were determined by atomic absorption.

2.4.3.3. EXTRACTABLE Mn

5.0 g of soil was shaken with 25 ml M NH_4OAc (buffered at pH 7) continuously for 30 min. then intermittently for 8 hours at $21^{o}C \pm 1^{o}$ C (ADAMS, 1965).

2.4.3.4. EXTRACTABLE K

This was measured by flame emission spectroscopy in the Morgan extract (Section 2.4.1.3.).

2.4.3.5. EXTRACTABLE Fe

1.50 g of soil was shaken with 200 ml Tamm's acid ammonium oxalate at pH 3.3 for 1 hour at 21^{o} C $\pm$ 2^{o} C and filtered: then 2 x 25 ml aliquots were boiled with a 1:1 mixture of concentrated HNO_3 and H_2SO_4 to destroy any organic matter (TAMM, 1932). Fe in solution was measured colorimetrically using sulphonated bathophenanthroline (QUARMBY & GRIMSHAW 1967) by continuous flow analysis as developed by IRONSIDE (unpub.).

2.4.3.6. ORGANIC CARBON

0.25 g of finely ground soil was digested in 25 ml of 0.07 M $K_2Cr_2O_7$ for 1 hour under reflux. The excess dichromate in the digest was titrated against standard $FeSO_4$ acidified with phosphoric acid using diphenylamine indicator with a little $BaSO_4$ to provide a background milky colour (TINSLEY, 1950).

2.4.3.7. pH

25 ml of 10^{-2} M $CaCl_2$ was added to 5.0 g of soil and stirred periodically for 1 hour. The pH was read by inserting an Intek sealed reference combination electrode with a KCl/AgCl gel into the

soil/solution paste, based on method by SCHOFIELD and TAYLOR (1955).

2.4.3.8. SOLUBLE NUTRIENTS - P, Ca, Mg, K, Fe and Mn

These were determined in the same extract in which soluble Al was determined. 10^{-2} M $CaCl_2$ was suggested as a medium for measuring soil phosphate potentials by SCHOFIELD (1955) and ion activities (BACHE and SHARP, 1976b). Because of the inherently low levels of Ca in hill soils a more dilute (10^{-3} M) $CaCl_2$ solution was used here.

2.4.3.9. MOLAR CONCENTRATION RATIO (M.C.R.)

BACHE and SHARP (1976b) suggested that the Activity Ratio provided the most appropriate assessment of the solubility and reactivity of Al in relation to plant growth, where its activity was likely to be influenced by the presence of divalent ions in solution. However, its calculation depends on a knowledge of the appropriate selectivity coefficients and for the present purposes an approximation referred to here as Molar Concentration Ratio (MCR) has been used. MCR has been calculated from the concentrations of Ca, Mg and Al in the 10^{-3} M $CaCl_2$ extract.

$$\text{MCR} = \frac{\left([\text{Ca}] + [\text{Mg}]\right)^3}{[\text{Al}]^2}$$

where concentrations are expressed in Moles/litre and the excess Ca over the initial 10^{-3} M concentration was used. Ratios were not calculated when Ca concentrations were less than 10^{-3} M.

2.4.3.10. DETERMINATION OF Ca, Mg, K, Fe and Mn IN SOLUTION

Ca, Mg, K, and Fe were measured by atomic absorption in a IL 251 Atomic Absorption Spectrophotometer. Both solutions and standards were diluted (x 100) with 0.1% $LaCl_3$ which is a releasing agent. Mn was also measured by this method but in this case 0.1% $SnCl_2$ was added to both standards and solutions to ensure that all the Mn was in the same oxidation state.

2.4.3.11. MECHANICAL ANALYSIS

The modified Bouyoucos hydrometer method described by FLOATE (1965) was employed but due to the high OM content of some samples, results were sometimes not reproducible with incomplete assessment of all size fractions.

2.5. STATISTICAL ANALYSIS

Analysis of Variance, students t test and regression analysis of the data were carried out according to the methods of SNEDECOR and COCHRAN (1967) using the VARANAL, TE TEST and MULTREG programmes (provided by ROGERS, unpub.) on the Edinburgh Multi Access Computer System. The probability levels for statistical differences between values are denoted in the text by asterisks * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$. Regression analysis and correlation coefficients have been examined for linear relationships only. Correlation coefficients have been used to evaluate the inter-relationships amongst different soil properties, and between these and plant growth.

Diagrammatic representation of the results includes RICHARD'S (1941) interaction figures, (see also HEATH 1970). Two way interaction tables were compiled to accompany analysis of variance, see YATES (1937).

CHAPTER 3

PRELIMINARY SURVEY OF Al AND P IN HILL SOILS

3.1. INTRODUCTION AND OBJECTIVES

A preliminary survey of selected properties of some typical hill soils was made using samples already available and by collecting some additional samples to extend the range. The sampling locations and parent materials of eight soils are listed in Table 2.1. The specific objectives were to:-

1. Examine the suitability of different soils and methods for further studies of Al and P.
2. Determine the ranges in amounts of forms of Al and P, and of some other soil properties in typically acid and predominantly mineral hill soils.
3. Investigate relationships between Al and P, and examine their relationships with other soil properties.

3.2. EXPERIMENTAL

3.2.1. TECHNIQUES

To accomplish these objectives the following analyses of general properties were undertaken: percentage clay, Tamms Fe, organic carbon, pH, exchangeable acidity, exchangeable Ca and Mg, together with measurements of some different forms of Al and P viz: extractable Al (NH_4OAc), exchangeable Al (KCl), total P, organic P resin exchangeable P, Morgan-extractable P (NH_4OAc) and Truog extractable P by the methods described in Chapter 2.

The P sorption characteristics of the soils were also examined using different concentrations of added P to accommodate the range in sorbing abilities of the soils, similar to those used by BACHE and WILLIAMS (1971). The P sorption index (PSI) was calculated from $x/\log c$ where c is the Molar concentration of P remaining after equilibration following the addition of 126 ppm P and x is the amount of P sorbed by 100 g of soil. The method was as follows:- 5.0 g air dry, finely ground soil was shaken for 18 hours with 100 ml 2×10^{-2} M KCl containing 0, 40, 80, or 126 ppm P (0, 26, 55 or 80 μmolP/g soil) and two drops of chloroform to inhibit microbial activity. The suspension was centrifuged at 5,000 r.p.m. for 20 minutes and filtered and finally the concentration (C) of P was determined in the filtrate. The amount of P extracted in 2 x 10^{-2} M KCl is described here as salt soluble P. Results were plotted as sorption isotherms.

3.2.2. CHOICE OF METHODS

Some of the effects of Ca and Mg saturation of the CEC on reactions involving Al were discussed in Chapter 1, together with a few of the problems associated with measurement of CEC. In this survey the concentration of those ions most likely to be predominant (Al, Ca and Mg) in acid mineral soils were measured (BACHE and SHARP, 1976b). CEC was determined at the natural pH of each soil by displacing the K^+ ions (used in the initial soil leaching to determine exchangeable Al and other cations) with M NH_4Cl. Results are also given for the sum of exchangeable cations by the KCl leaching and also the values for Al determined colorimetrically and by titration (McLEAN, 1965) and the difference between them are given in Table 3.1.

The amount of exchangeable Al determined by titration was calculated from the amount of alkali (0.1 M NaOH) required to neutralize the acidity due to Al and was therefore calculated as base equivalents and so did not presume the valency of Al. In the colorimetric procedure the determination of Al was made at pH 4.4 when it was assumed for the conversion of the measured Al concentration to equivalents that all the Al in the KCl solution is Al^{3+}. It can be seen from Table 3.1. that the titration method for Al gave higher values for Al than did the colorimetric method; this type of discrepancy was also observed by DEWAN and RICH (1970). DALAL (1975) has, however, shown that although the predominant species of Al below pH 4.5 is Al^{3+}, small amounts of $Al(OH)^{2+}$ and $Al(OH)_2^+$ may also occur. It is possible, therefore, that one explanation for the differences shown in columns B and C (Table 3.1) between the two methods of determining the amount of Al in the KCl leachate maybe the proportion of hydroxy - Al species present under the conditions of the colorimetric method (DEWAN and RICH, 1970). In the titration

Table 3.1. Acidity, Al and Cation exchange characteristics of hill soils showing the variation in results calculated by different procedures (meq/100 g)

Soil	A	B		C
	Exch. acidity	Exch. Al		% difference between T&C
		Titration(T)	Coloration(C)	
1	10.8	5.9	5.8	2
2	11.8	9.7	8.4	13
3	11.1	7.6	7.3	4
4	3.4	3.0	2.3	23
5	18.9	14.5	12.3	15
6	11.1	9.9	8.6	13
7	15.6	13.6	13.2	3
8	5.0	4.4	3.8	14

Soil	D	E	F	
	(Al+Mg+Ca)	CEC (K in MNH_4Cl)	$\frac{\text{Al}}{{}^{*}\text{Al+Ca+Mg}} \times 100$	
1	6.5	8.8	89%	
2	12.2	13.5	69%	
3	8.7	10.1	84%	
4	3.9	5.3	59%	
5	13.7	13.9	90%	
6	8.9	8.2	97%	
7	14.3	14.5	92%	
8	6.0	11.1	63%	

* Al by coloration

procedure, however, all Al would be converted to $Al(OH)_3$. A possible alternative explanation for the observation that many of the values for the colorimetric method are lower than the values by titration is that some of the Al in polymeric form or as hydroxy species may not react with alizarin red in the time available for colour development although these species may react with the alkali in the titration method (BACHE, pers. comm.). However, since one of the main objectives of this study was to compare the relative amounts of Al in exchangeable, extractable and soluble forms it was decided to use the colorimetric values for exchangeable Al so as to be consistent with the values obtained for extractable and soluble forms.

CEC (Column E, Table 3.1), determined from the concentration of K ions displaced by NH_4Cl was greater than the sum of Al, Ca and Mg ions displaced by KCl for all 8 soils. The difference, which in most cases was not large was probably due to other cations (e.g. K, Na, Mn and Fe). However, JAMES et al. (1979) found that the difference between CEC and Σ (Al+ Mg+Ca) in a soil from Fiunary (similar to soil 8) could not be accounted for by other cations. It seems likely that the value for CEC in this soil was erroneously high possibly because the washing of excess KCl from the soil after the first stage of leaching was incomplete.

A further comparison of the results given in Table 3.1. shows that inclusion of the values for exchangeable acidity, which includes exchangeable H^+, causes the values for (exchangeable - Al + Ca + Mg + H) to exceed the CEC. A possible reason for this disagreement found for soils, 1, 3, 5, 6 and 7 is that some Al was in mono- or divalent states which required less K^+ for displacement. It has also been observed (THOMAS, 1960 and BACHE, pers. comm.) that in some soils non-exchangeable Al may be removed by KCl leaching which could result in excessively high values for apparent CEC by summation.

Thus a number of problems confound the accurate determination of CEC, which may be particularly acute when this is attempted at the natural pH of the soil, although BACHE (1976) observed that this condition should be fulfilled when the aim is to study soil reactions, such as those of Al, which may themselves be influenced by CEC. Therefore, since in these soils Ca and to a lesser extent Mg are likely to be the major ions influencing the exchange reactions involving Al (BACHE, 1974; BACHE and SHARP, 1976b) further attempts to measure CEC have not been pursued. Instead the ratio Al: Al + Ca + Mg (column F, Table 3.1) given in percent and hereafter referred to as percent Al saturation has been used to describe Al in relation to the other exchangeable cations.

3.3. RESULTS AND DISCUSSION

3.3.1. GENERAL PROPERTIES

In common with most hill soils the clay content was less than 25%. Unlike the more peaty soils, these acid mineral soils which included the A horizons from two peaty podzols (Minchmoor A(1) and Llansannan (5)) generally contained less than 10% carbon (Table 3.2.). The relatively low carbon values for these two soils was probably due to the fact the A horizons were sampled below the A_0 horizons which held most organic matter in the form of a peaty surface. All eight soils were acid ranging in pH from 3.1 to 4.5 ($CaCl_2$) and most had correspondingly high levels of exchangeable acidity ($>$ 10 meq/100 g) except soils 4 and 8 which were the least acidic (Table 3.2.). For the most of the soils, with the exception of Minchmoor A(1), Stanhope (3) and Llansannan (5) more than 75% of the exchangeable acidity was attributed to Al. This is in agreement with the concensus of work on soil acidity given in Chapter 2. As might also be expected from the literature there was an inverse relationship between pH and exchangeable acidity ($r = 0 -.650^{NS}$) and it can be seen (Figure 3.1a) that above pH 5 ($CaCl_2$) the amount of exchangeable acidity was very low.

The highest values for exchangeable acidity and other cations tended to occur in the soils with high clay contents (e.g. 5 and 7 Table 3.2), although the opposite was not always true. BACHE (1976) reported that permanent negative charge was due largely to the presence of colloidal clays as suggested here. In general the content of exchangeable bases was low in these soils (except in soil 2 (Sourhope), where the Mg level was unusually high) and was consistent with the degree of leaching associated with their

Fig 3.1 Relationship between pH and(a) exchangeable acidity(b) Al saturation (%) and(c) exchangeable and extractable-Al.

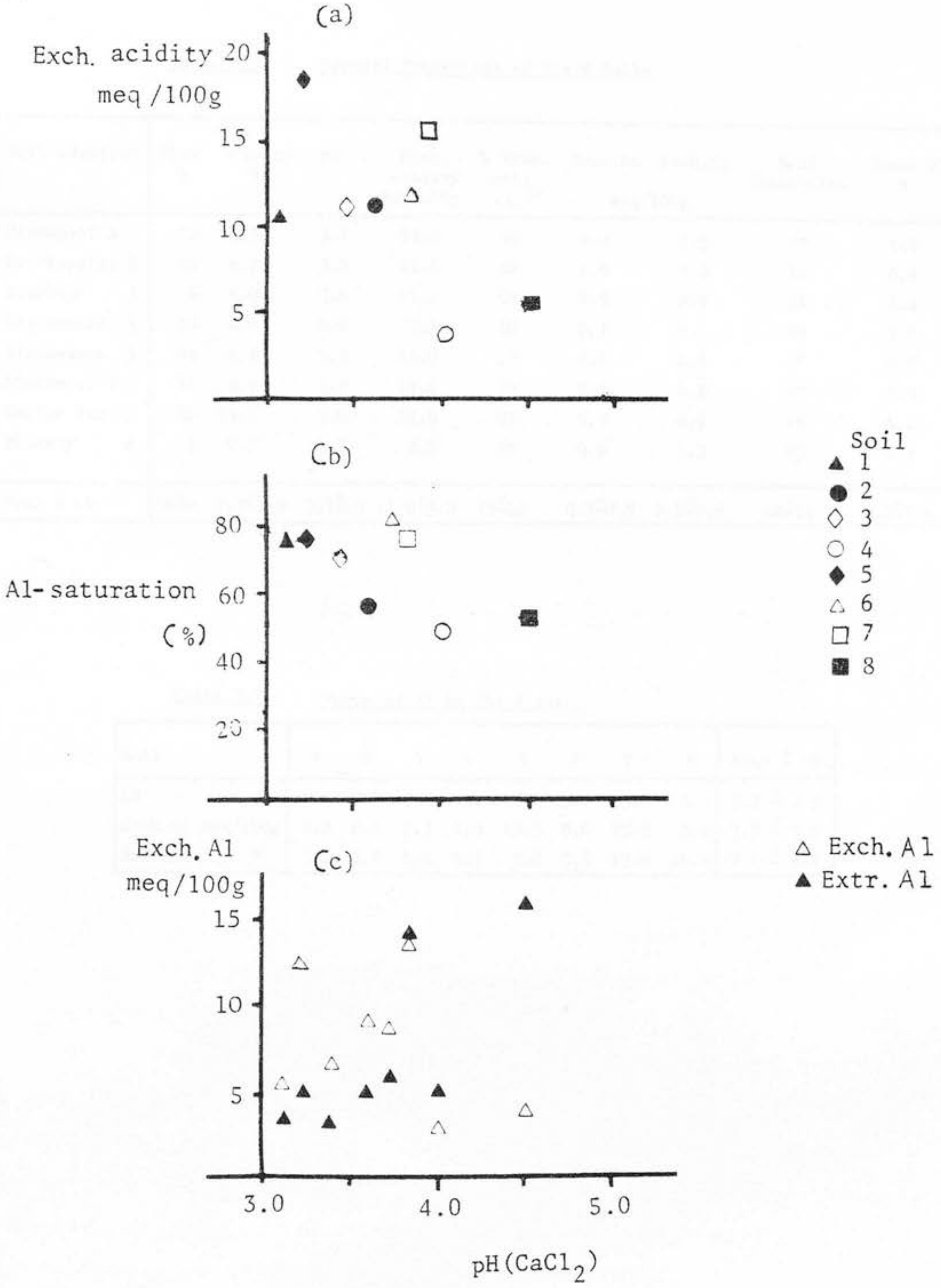


Table 3.2. General Properties of the 8 Soils

Soil identity	Clay %	Carbon %	pH	Exch. acidity meq/100g	% Exch. acid Al.$^{3+}$	Exch.Ca	Exch.Mg	% Al Saturation	Tamms Fe %
						meq/100g			
Minchmoor A 1	16	3.9	3.1	10.8	55	0.2	0.5	89	1.6
Sourhope(a) 2	11	8.7	3.6	11.8	82	1.6	2.2	69	0.8
Stanhope 3	6	9.8	3.4	11.1	68	0.5	0.9	84	1.2
Lephinmore 4	16	4.9	4.0	3.4	88	0.7	0.9	59	0.9
Llansannan 5	24	8.3	3.2	18.9	77	0.8	0.6	90	0.5
Minchmoor B 6	11	2.9	3.7	11.1	89	0.1	0.2	97	3.3
Carter bar 7	21	13.2	3.8	15.6	87	0.5	0.6	92	4.1
Fiunary 8	9	9.6	4.5	5.0	85	0.9	1.3	63	4.5
Mean ± SD	14±6	7.7±3.5	3.7±.4	11.0±5.2	79±12	0.7±0.5	0.9±0.6	80±14	2.1±1.6

Table 3.3. Forms of Al in the 8 soils

Soil	1	2	3	4	5	6	7	8	Mean ± SD.
pH	3.1	3.6	3.4	4.0	3.2	3.7	3.8	4.5	3.7 ± 0.5
Exch.Al meq/100g	5.8	8.4	7.3	2.3	12.3	8.6	13.2	3.8	7.7 ± 3.8
Extr.Al " "	3.2	5.0	2.9	5.0	5.0	5.5	13.8	16.0	7.1 ± 5.0

development (1.1.1).

Because of the relationship between exchangeable acidity and exchangeable Al, the inter-relationships between the two forms of Al will be examined before the other effects of pH are considered.

3.3.2. SOIL ALUMINIUM

Amounts of exchangeable Al ranged from 2.3 to 13.2 meq/100 g (Table 3.3) where the smallest amounts occurred in soils from Lephinmore and **Fiunary**, (4 and 8) which were also the soils of highest pH, while the largest amounts of exchangeable Al occurred in soils from Llansannan and Carter Bar (5 and 7). These observations are in agreement with the generalisations presented in Chapter 1.

Amounts of extractable Al ranged from 2.9 meq/100 g to 16.0 meq/100 g with the lowest amounts from Minchmoor A and Stanhope (1 and 3) and the highest amounts from Carter Bar and **Fiunary** (soils 7 and 8) (Table 3.3). It may be noted that these soils with the least amounts of Al were formed on sedimentary rocks while the high Al soils were developed on basalt.

Mean values for extractable and exchangeable Al were similar at around 7 meq/100 g (Table 3.3) but whereas exchangeable Al was inversely correlated with pH ($r = -0.440^{NS}$) the amount of extractable Al increased with pH ($r = 0.761^{*}$) (Fig. 3.1c). For these eight soils it maybe seen that below pH 3.8 ($CaCl_2$) the amount of exchangeable Al was relatively higher than extractable Al while above this pH the amount of extractable Al exceeded that for exchangeable Al: consequently the relationship between the 2 forms of Al was poor ($r = 0.076^{NS}$).

The increase in exchangeable Al with decreasing pH (which was not significant as the relationship accounted for only 19% of the variation) may be a real effect as the conditions of measurement reflect the natural soil pH. As pH increases smaller amounts of Al usually occur in an exchangeable state (Chapter 1). The higher amounts of extractable Al with increasing pH are more difficult to explain but may be related to the conditions of extraction and/

or nature of parent material. Ammonium acetate reagent is buffered at pH 4.5 and is therefore more or less independent of soil pH and BACHE and SHARP (1976) found that dissocaition of HoAc molecules could dissolve the more insoluble forms of Al including those present at higher pH. It is likely that the relationship between pH and extractable Al is accidental and that the values for extractable Al really reflect the higher Al content of soils developed on basalt. It is also possible that the higher extractable Al contents from soils 7 and 8 are associated with the higher organic carbon content of these soils in a similar association to that observed by WILLIAMS et al. (1958), although for the group of soils described here the overall correlation coefficient for the relationship between organic carbon and extractable Al was not significant ($r = 0.215$).

It has already been observed that in most of the soils exchangeable Al, or more precisely the hydrolysis of exchangeable Al, has contributed to exchangeable acidity and only in the peaty podzols Minchmoor A and Llansannan (soils 1 and 5) did H^+ ions significantly contribute to the measured acidity. There was no obvious relationship between pH and the amount of exchangeable acidity but pH was almost significantly and inversely related to percent Al saturation at the 5% level of significance ($r = -0.638$). This relationship suggests a tendency for pH to increase as the relative amount of exchangeable base cations increases and Al occupies a decreasing proportion of cation exchange sites (Fig. 3.1b).

3.3.3. SOIL PHOSPHORUS

Amounts of total P were very variable ranging from 41 to 556 mg/100g (Table 3.4). The largest proportion of this total P occurred in organic form in most of the soils, and in general in hill soils this form of P has been found to contribute only very slowly to the inorganic pool of P available to plants (Chapter 1). More than 75% of the P in the two peaty podzols (2 and 5) and an average of 60% in all soils was organically bound. Since the inorganic pool of P is more likely to provide P for plant growth this has been examined in more detail.

Table 3.4. Forms of P in the 8 soils

Soil :-	1	2	3	4	5	6	7	8	Mean ± SD
Total P mg/100g	69	177	290	80	41	76	278	556	196 ± 175
Organic P "	45	165	187	34	31	37	99	297	112 ± 97
Inorganic P (Tot P-Org.P)	24	12	103	46	10	39	179	259	84 ± 91
% Organic P	65	93	65	42	77	49	36	53	60 ± 19

Amounts of inorganic P were very low in the podzol soils 2 and 5 (10 and 12 mg/100 g respectively) and high (> 170 mg/100g) in soils 7 and 8 developed on basalt (Table 3.4.) LARSEN (1967) explained some of the differences in the inorganic P fraction on the basis of parent material: in general igneous rocks (e.g. basalts) have a higher apatite content than the sedimentary rocks (Chapter 1). Other possible reasons for these differences include the degree of P sorption which may influence the extent of P loss from the soil. The amounts of P in various reagents which have been used to assess the availability of P which may reflect this ability to adsorb P will next be examined.

The 'availability' of the inorganic P fraction was assessed by several methods and the results are given in Table 3.5. The amount of P extracted by the different reagents was found to vary considerably with the largest amounts being extracted in the Truog reagent and the smallest amounts in Morgan's solution (ammonium acetate). However, even using Truog's reagent the percentage of the total inorganic P in 'available' form was found to be very low (mean 11.6%) especially in the subsoil (6) and the soils formed on basalt (7 and 8).

The largest amounts of P were extracted from soil 3 (Stanhope) and this soil had consistently higher amounts of P by all four methods while soil 6 (the subsoil) was consistent in having the least amounts. The ranking order for decreasing amount of P (left to right) is given in Table 3.6.

Table 3.5. Amounts of 'Available P' extracted in Four Reagents

Soil :-	1	2	3	4	5	6	7	8	Mean ± SD
Resin extractable P mg/100g	0.87	6.10	12.90	1.64	0.9	Tr	0.12	Tr	2.82 ± 4.5
0.02 MKCl Soluble P	0.67	1.86	4.87	1.50	0.87	Tr	Tr	Tr	1.22 ± 1.6
Truog P (0.001 M H_2SO_4)	2.7	1.3	37.5	5.5	1.7	1.0	5.0	1.5	7.02 ± 12.4
Extractable P (NH_4OA_c)	0.16	0.64	2.50	0.27	0.06	Tr	0.26	0.06	0.49 ± 0.8
Extractable P as % of total inorgan. P.	11	11	36	12	17	2	3	0.6	11.6 ± 11

Table 3.6. Ranking order for the soils based on the amount of 'available P' extracted by 4 methods

Resin exchangeable P	$3>2>4>5>1>7>8=6$
0.02 M KCL soluble P	$3>2>4>5>1>7=8=6$
Truog P	$3>7>4>1>5>8>2>6$
Extractable P	$3>2>4>7>1>5=8>6$

The order for P availability by the resin method was in good agreement with that for KCl salt soluble method and both indicated larger amounts of 'available' P in soils 3, 2, 4, and 5 than in soils 6 (the subsoil) and 7 and 8 (derived from basalt). The ranking orders for ammonium acetate and Truog extractable P were also similar but differed from the order described above. These two acid extractants removed relatively large amounts of P from one of the soils on basalt (7) (Table 3.5).

Table 3.7. Correlation coefficients describing the Relationships between the different values for P

	Org.P	Inorg.P	Resin-P	KCl-P	Truog-P	Extractable-P
Total P mg/100g	0.94***	0.93**	0.12	0.14	0.20	0.20
Organic P mg/100g		0.73*	0.30	0.21	0.27	0.34
Inorganic P mg/100g			-0.13	-0.20	0.10	-0.20
Resin P				0.96***	0.88**	0.97***
KCl-P					0.89**	0.95***
Truog P						0.96***

$P < 0.05$ $r \geq 0.71$*, $P < 0.01$ $r \geq 0.83$**, $P < 0.001$ $r \geq 0.93$***.

The relationships between the amounts of P extracted by the four methods, and their relationships with total, inorganic and organic P were tested by reference to their correlation coefficients (Table 3.7). There were highly significant positive correlations between inorganic, organic and total P which were not surprising in view of the high relative proportions, of these fractions of the total. The amounts of 'available' P on the other hand represented only very small proportions of the amounts of total P and the poor correlations between these values and those for total P were also not unexpected. However, the amounts determined by the four methods all correlated significantly with each other despite the different amounts of P they extracted and the ordering of relative 'availability' being different between methods. The results provided no basis for assessing which methods might best predict the amount of P plants can utilise, but it is worth noting that the results for salt soluble - and resin extractable - P were closely related, and that the most acid reagent (TRUOG pH 3) extracted the most P.

The negative correlation coefficients for the relationships of resin -P, salt soluble P and extractable P with inorganic P, together with the observation that the relative availability of P was lower on the soils developed on basalt suggested that P retention might be higher in these soils. This was investigated by plotting P sorption isotherms (Fig. 3.2.).

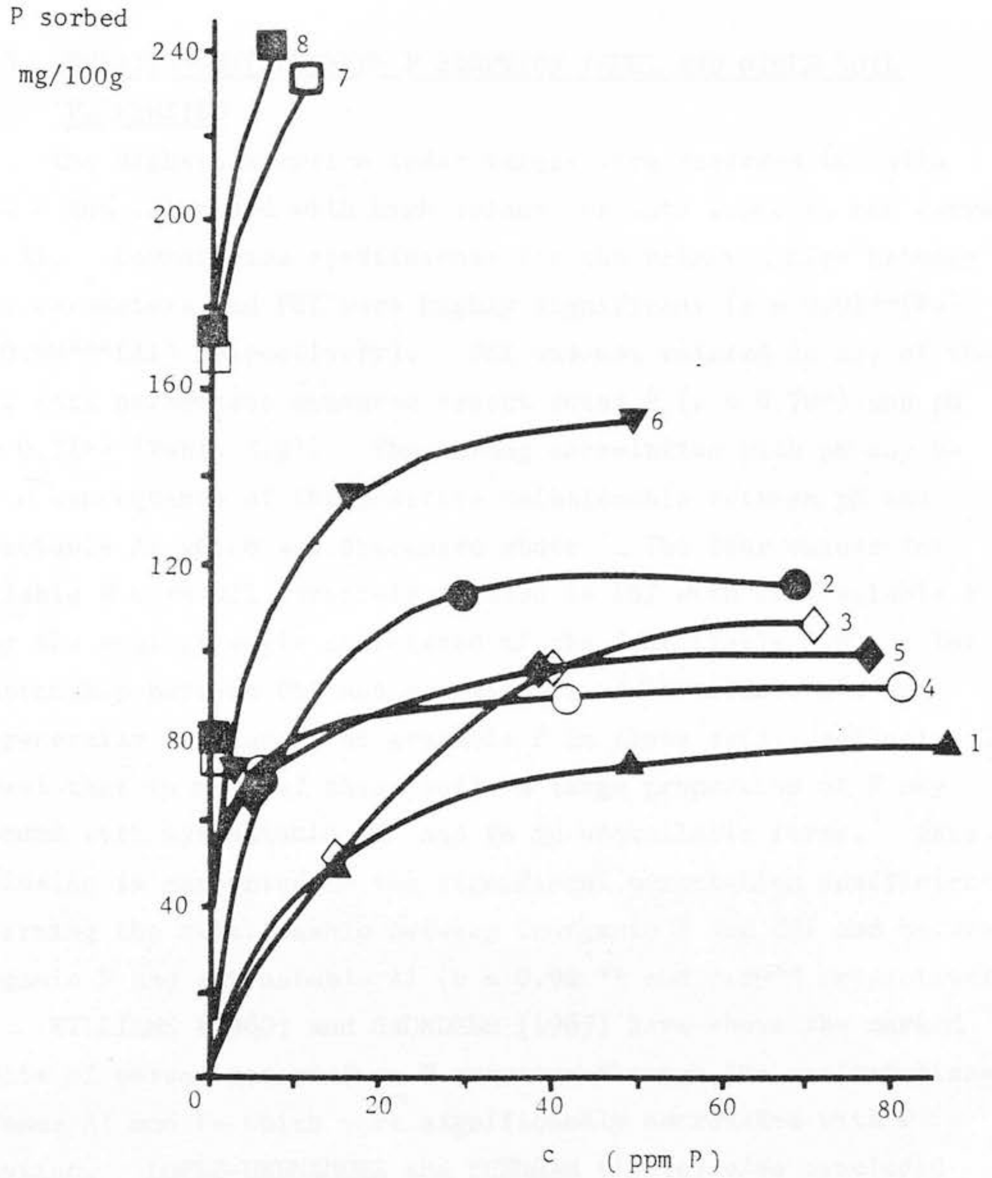
3.3.4. PHOSPHORUS SORPTION

Soils 1 to 5 gave rather similar sorption curves while soil 6 (the subsoil from soil 1) exhibited a higher sorption ability. The greatest adsorption of added P was measured for soils 7 and 8, both derived from basalt and containing large amounts of Tamms Fe and extractable Al (Tables 3.2 and 3.3). Soils 1 and 3 adsorbed the least P at the lowest level of P addition, equivalent to 80 mgP/100 g soil. This suggests that lower levels of P addition are needed on these two soils, than on the other soils, to make P available for plant growth.

Further consideration of the isotherms shows that the soils on basalt (7 and 8) have similar and strong sorption properties, indicating that large amounts of P have to be added before measurable amounts of P can be detected in the equilibrium solution. Compared with the other soils, 7 and 8 appear to have many more sites on which phosphate can be adsorbed and the whole group can be arranged in order of increasing P sorption:- $1 < 4 < 2 < 3 < 5 < 6 \ll 7 < 8$.
Some workers have used the shape of the isotherms to describe the type of sites and the energy involved in sorption reactions, PARFITT (1978), but as mentioned in Chapter 1 (1.3.4) opinions differ as to how they may be intepreted. No attempt has been made here to interpret reaction mechanisms from the shape of the isotherms.

The sorption index, PSI, has been calculated from the addition of 80 μ molP/g soil. This amount of P is higher than that recommended by BACHE and WILLIAMS (1971) but was necessary because of the large amounts of P adsorbed by some of these soils, and the

Fig 3.2 Relationship between P sorption and the equilibrium P concentration (c).



need to obtain sufficient P in the final equilibrium solution for accurate determination. These values (Table 3.8) provide a quantitative expression for the order of sorption described above.

Table 3.8. PSI values for the 8 soils

Soil	1	2	3	4	5	6	7	8	Mean ± SD
PSI	27	29	31	27	35	48	92	105	49 ± 31

3.3.5. RELATIONSHIP BETWEEN P SORPTION INDEX AND OTHER SOIL PROPERTIES

The highest sorption index values were recorded in soils 7 and 8 and coincided with high values for both Tamms Fe and extractable Al. Correlation coefficients for the relationships between these parameters and PSI were highly significant ($r = 0.91^{**}$(Fe) and 0.98^{***}(Al) respectively). PSI was not related to any of the other soil parameters measured except total P ($r = 0.78^{*}$) and pH ($r = 0.71^{*}$) (Table 3.9). The strong correlation with pH may be only a consequence of the positive relationship between pH and extractable Al which was discussed above. The four values for available P were all inversely related to PSI with salt soluble P being the most strongly correlated of the four (Table 3.9). The relationship between PSI and assessments of 'available P', and the generally low levels of available P in these soils, collectively suggest that in most of these soils a large proportion of P may be bound with extractable Al and Fe in unavailable forms. This conclusion is supported by the significant correlation coefficients confirming the relationship between inorganic P and PSI and between inorganic P and extractable Al ($r = 0.92^{**}$ and 0.89^{**} respectively).

WILLIAMS (1960) and SAUNDERS (1965) have shown the marked effects of parent material on P sorption through the contributions of Tamms Al and Fe which were significantly correlated with P retention. LOPEZ-HERNANDEZ and BURNHAM (1974a) also concluded that free iron oxides together with extractable Al were the most important soil factors affecting P retention in temperate acid soils explaining 85% of the variation in PSI and that these two properties were closely related. In these eight soils parent

	Clay	% C	pH	Tot.P	Org.P	An.P	KClP	Tr.P	Extr.P	PSI	Extr.Al	Ex.Al	Ex.Ca	Ex.Mg	Ex.Acid
% clay															
% C	-.24														
pH	-.43	.22													
Total P	-.442	.611	.701												
Org. P	-.637	.381	.573	.943											
Anion P	-.47	.29	-.3	.124	.306										
KCl P	-.43	.44	-.12	.147	.214	.902									
Truog P	-.52	.23	-.16	.273	.275	.897	.888								
Extr. P	.22	-.02	-.24	.341	.347	.97	.95	.96							
P.S.I.	0	.545	.706	.783	.555	0.424	0.522	0.144	-0.300						
Extr. Al meq/ 100g	.07	.215	.762	.766	.549	0.25	-.06	-.11	-0.14	.979					
Ex. Al "	.472	.39	-.440	-.189	-.26	-0.01	-.14	-.18	-0.08	.130	.076				
Ex. Ca "	-.08	.38	.13	.16	.40	.29	.20	-.07	.10	-.012	- 07	.11			
Ex. Mg "	-.35	.32	.21	.26	.56	.42	.31	.07	.24	-.021	-.01	-.15	.983		
Ex. Acid "	.561	.20	-.650	.04	-.39	.07	-.03	-.07	.41	-.076	-.27	.952	.05	-.19	
Tamms Fe %	.005	.28	.64	.608	.413	-.45	-.57	-.25	-.31	.914	.852	-.03	-.38	-.29	-.29

Significance

$r \geqslant .707$	$r \geqslant .834$	$r \geqslant .920$
*	**	***
P = 0.05	0.01	0.001

Table 3.9. Correlation Matrix (8 observations) for selected properties of the 8 soils

material has also played a major role in P retention. Soils 1 to 5 which included soils formed on greywacke, andesite, Highland schist and shale (Table 2.1) had similar levels of extractable Al and Tamms Fe and also similar PSIs ($<$ 40). Soil 6, the subsoil, had intermediate levels of these 3 properties, between those of 1 to 5 and soils 7 and 8, developed on basalt rich in Fe and Al and strongly P sorbing.

Both WILLIAMS (1960) and SAUNDERS (1965) suggested that organic matter content might influence P sorption through its association with Al although LOPEZ-HERNANDEZ and BURNHAM (1974a) found that this explained very little of the variation in PSI. For these eight soils neither extractable Al nor Tamms Fe were correlated with percent C content, but the correlation coefficient ($r = 0.545$) for the relationship between percent C and PSI was positive (Table 3.9) suggesting that the association of Al with percent C might be related to an increase in P retention. This was in contrast to the results of GHOSHAL and CHAKRAVARTI (1967) who found that humic acids depressed P adsorption by the various forms of Al through their chelation properties.

3.4. CONCLUSIONS:

In this survey of eight hill soils derived from a variety of parent materials wide ranges have been recorded for all the properties described. Several soils have been exceptional in a few of the parameters measured. The soils developed on basalt (7 and 8) contained large amounts of total P due to the high P content of their parent material and possibly due to their high P fixing ability associated with their high extractable Al and Tamms Fe content. The Fuinary soil (8) had a much higher pH and lower percent Al saturation than the Carter Bar soil (7) which also had a high level of exchangeable acidity highlighting the range in properties displayed even by soils grouped within the same soil series.

Apart from the Stanhope soil (3) all the soils were very low in 'available' P and the abnormally high value for this soil (which cannot be accounted for by parent material) suggests that it may have had some past history of P fertiliser use. Despite quite high values for total P in some of the soils, most appears to be in unavailable forms, organically bound or tightly bound by Al and Fe. The inorganic P fractions were correlated with extractable Al, which, together with Tamms Fe accounted for most of the variation in PSI but the very high proportion of variation in PSI accounted for by extractable Al alone suggests that this can be used to assess the P fixing ability of mineral hill soils. From data presented so far however no conclusions can be reached concerning the superiority of any one of the four methods for assessing the amount of 'available' P and plant growth assays will be required to evaluate the amounts of P available in the biological sense. There was, however, a good correlation between the dilute salt extractant and the resin method for determining the chemical availability of inorganic P.

Although percent clay was measured for the purposes of this survey none of the other properties which have been related to either P availability or acidity were very strongly related to this parameter and so percent clay was not determined in subsequent experiments. The strong associations between Al and acidity and P availability support the observations described in Chapter 1 and indicate that most of the acidity in these mineral hill soils is due to exchangeable Al.

Parent material has been shown to have a major influence on soil properties relevant to the subject of this study so that with the small number of samples and several different parent materials it has not been possible to comment on the mechanisms by which Al influences P fixation availability and soil acidity. The next stage in understanding how the different properties interact to influence plant growth is to select soils with a range of Al content and use these in a pot experiment with certain treatments applied. The most common method of improving P availability and overcoming acidity is by the addition of P fertiliser and lime. The experiments which are described in ensuing chapters have been designed to examine the effect of inherent soil properties and of changes in pH and P levels on the interactions between Al and P on plant growth and on the chemical and biological availability of both native and added P.

CHAPTER 4

POT EXPERIMENT TO EXAMINE THE EFFECTS OF ADDED P AND Ca ON RYEGRASS GROWTH IN DIFFERENT SOILS

4.1. INTRODUCTION AND OBJECTIVES

An experiment is described using four soils chosen to represent a range in soil Al to investigate the relationships between soil aluminium, soil phosphorus and P uptake during plant growth. The specific objectives in this experiment were as follows:-

1. To investigate the relationships between forms of Al, and the chemical and biological availability of native and added P.
2. To determine the effects of lime on forms of soil Al.
3. To assess the influence of the different forms of soil Al on the growth of ryegrass herbage and roots.
4. To distinguish those plant growth effects due to lime induced pH changes in soil from the direct effects of added calcium.

4.2. EXPERIMENTAL

4.2.1. SOILS

From the information on the initial survey of hill soils (Chapter 3) four soils, Lephinmore (4), Stanhope Glen (9), Sourhope, (10) and Carron Forest (11) were chosen for this pot experiment, and of these only soil 4 was common to that study. Different sites were chosen at Stanhope because of the abnormally high P content, and at Sourhope because the original site was limed. The Carron Forest site was chosen to represent freely drained soils developed on basalt of the Darleith series, with no known history of lime or P addition. Profile descriptions and photographs of these soils are given in the appendix (2.5A to 2.8A). Full details of the measured chemical properties are given in the appendix (Table 4.1A), while some general properties of the four soils are given in Table 4.1.

pH was low in all the soils and percent Al saturation ranged from 48% in soil 9 to 89% in soil 11. Total P was high in soil 11 ($>$ 200 mg/100 g), intermediate in soil 10 and lower in soils 4 and 9 ($<$ 100 mg/100 g) but extractable P comprised very small proportions of the total in all these soils.

Table 4.1. Some Properties of Soils 4, 9, 10 and 11 describing their acidity, aluminium, calcium and P status

Soil	pH ($CaCl_2$)	Exch. Al (meq/100g)	Al.Sat^n %	Extr. Al (meq/100g)	Sol. Al (meq/100g)	Exch. Ca (meq/100g)	Total P (mg/100g)	Extr. P (mg/100g)	Sol. P (mg/100g)	PSI
4	4.2	3.3	56	4.0	0.02	1.92	75	0.19	0.03	44
9	4.2	3.5	48	3.5	0.02	2.60	81	0.21	0.06	27
10	3.5	9.1	80	5.6	0.12	1.16	118	0.49	0.05	46
11	3.9	16.3	89	20.3	0.53	0.39	214	0.33	Trace	168

4.2.2. TECHNIQUES

Using these soils the effects of adding lime, superphosphate and gypsum, combined in a 2^3 factorial design, were tested by growing Lolium perenne (S24) in a pot experiment in the glasshouse and by chemical analysis of the treated soils.

Table 4.2. Lime (L), Superphosphate (P) and Gypsum (G) treatments applied to soils 4, 9, 10 and 11 in the pot experiment

Treatment	Amounts applied g/pot
1. L_o P_o G_o	L_1 = 1.0 g $CaCO_3$ (20 meq Ca)
2. L_1 P_o G_o	(≡ 1250 kg ha)
3. L_o P_o G_1	
4. L_1 P_o G_1	P_1 = 0.72 g superphosphate (71 mg/P, 8 meq Ca) (≡ 80 kg P/ha)
5. L_o P_1 G_o	
6. L_1 P_1 G_o	G_1 = 1.72 g Gypsum (20 meq/Ca)
7. L_o P_1 G_1	
8. L_1 P_1 G_1	

General descriptions of techniques are given in Chapter 2 while the treatments applied are listed in Table 4.2. Four replicates of each treatment were seeded with ryegrass following a 3 month storage period for equilibration between treatments and soils. A fifth replicate was retained for analysis to assess the treatment effects on the following soil properties:-

pH, extractable - exchangeable - and soluble - Al, extractable - and soluble P, exchangeable - and soluble Ca, soluble Mg and PSI.

Experimental details, glasshouse conditions and harvest dates are given in Table 4.2A. Following the third harvest roots and stubble were separated from the soil and prepared for analysis as described in Chapter 2. Extractable P was measured in the separated soil. The data are presented in diagram form but the mean values are given in tables in the appendix, with statistical analysis where appropriate (4.2A to 4.12A).

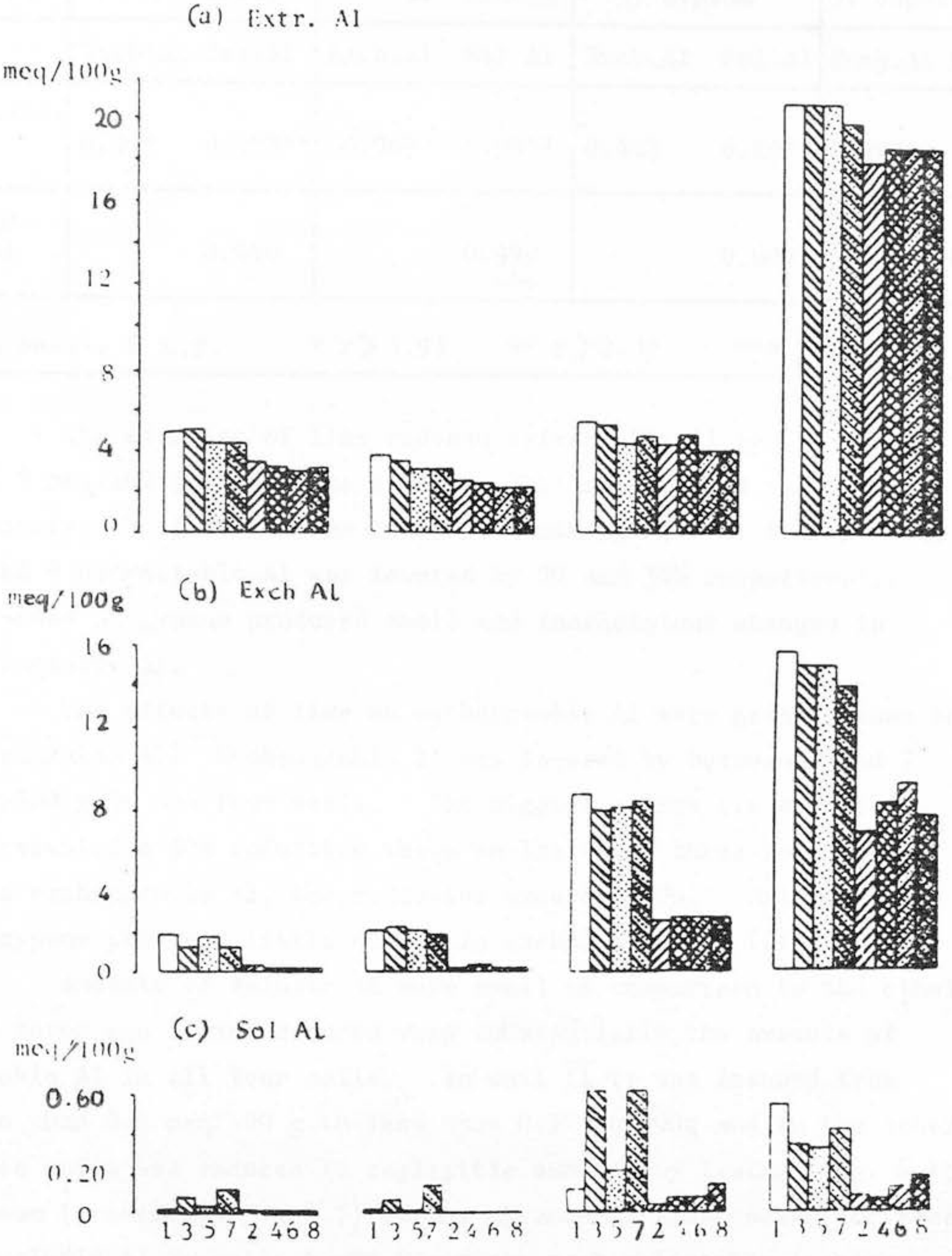
4.3. RESULTS

4.3.1. SOIL ALUMINIUM

Three forms of Al: extractable (NH_4OA_C) exchangeable (KCl) and soluble ($CaCl_2$) were examined and as a result of inherent differences between the four soils there were wide ranges in their respective amounts: extractable Al ranged from 3.5 to 20 meq/100 g, exchangeable Al from 3 to 16 meq/100 g and soluble Al from 0.02 to 0.5 meq/100g (Table 4.1). The largest amounts of all three forms of Al were measured in the Caron Forest soil (11) developed on basalt while the smallest amounts occurred in soils 4 and 9. The amounts of these 3 forms of Al in the four untreated soils and in the same soils treated with lime, gypsum and P are illustrated in Figures 4.1 a, b and c and the correlation coefficients for the relationships between the three forms are given in Table 4.3. In the untreated soils the amounts of all three forms of Al were positively correlated ($r > 0.9$) and the correlation coefficient for the relationship between the amounts of soluble and extractable Al was highly significant ($r = 0.993^{**}$).

As well as this variation between soils, there were also differences brought about by treatment (Fig. 4.1 a, b, and c). An examination of paired treatments, with and without added P, shows that superphosphate addition had only a small influence on the amounts of soil Al although it did modify the relationships between the three forms (Table 4.3): soluble Al was found to be less strongly correlated with extractable Al because soluble Al was proportionately more influenced by the addition of superphosphate than was extractable Al (Fig. 4.1 a and c).

Fig 4.1 Changes in the amounts of (a) Extractable Al (b) Exchangeable Al and (c) Soluble Al in soils 4, 9, 10 & 11 treated with lime, gypsum and superphosphate.



Footnote: Throughout this Chapter each treatment is identified by the appropriate Treatment number, as well as by the shading code

Lime ▨ Superphosphate ░ Gypsum ▧

Table 4.3. Correlation coefficients for the relationship between the 3 forms of Al in the 4 soils for different treatments

Treatment	1. Untreated		2. Lime		3. Gypsum		5. Superphosphate	
	Exch.Al	Sol.Al	Exch.Al	Sol.Al	Exch.Al	Sol.Al	Exch.Al	Sol.Al
Extractable Al	0.903	0.993**	0.969*	0.969*	0.903	0.228	.897	.792
Exchange-able Al		0.946		0.999 ***		0.607		0.977*

(4 soils, 2 d..f. * $r > 0.95$ ** $r > 0.99$ *** $r > 0.999$

The addition of lime reduced extractable Al by between 2 and 3 meq/100 g in all the soils. This represented only a small proportional effect in the soils containing most Al but in soils 4 and 9 extractable Al was lowered by 29 and 34% respectively. Ca added as gypsum produced small and inconsistent changes in extractable Al.

The effects of lime on exchangeable Al were greater than for extractable Al. Exchangeable Al was lowered by between 1 and 7 meq/100 g in the four soils. The biggest change (in soil 11) represented a 50% reduction while in the other three soils, with less exchangeable Al, the reduction exceeded 50%. Calcium added as gypsum produced little change in exchangeable Al (Fig. 4.1b).

Amounts of soluble Al were small in comparison to the other two forms and liming reduced very substantially the amounts of soluble Al in all four soils. In soil 11 it was lowered from more than 0.5 meq/100 g to less than 0.1 meq/100g and in the other three soils was reduced to negligible amounts by liming (Fig. 4.1c). Gypsum (treatments 3 and 7) in the absence of lime caused increases in soluble Al in soils 4 and 9 and the most noticeable increase (from 0.1 to 0.6 meq/100 g) was measured in soil 10. Such increases were not recorded in soil 11.

The effects of lime and gypsum on each of the three forms of Al modified the inter-relationships described for the untreated soils (Table 4.3). In the lime treated soils all three forms of Al were more significantly correlated with each other. As gypsum only influenced soluble Al, to any great extent, only the relationships between this form of Al and extractable and exchangeable were affected and the correlation coefficients were lower (Table 4.3).

4.3.2. SOIL pH ($CaCl_2$)

Soil pH was influenced more by lime than any other treatment (Fig. 4.2a). The addition of 1.0 g of lime to soils 4 and 9 increased pH by one unit while the corresponding increases in soils 10 and 11 were 0.5 and 0.4 units respectively. It was observed that these smaller incremental responses to lime occurred in the soils with much larger exchangeable Al contents (Fig. 4.1b). The gypsum and superphosphate produced only minor changes in soil pH (not exceeding 0.2 pH units) and did not interact with the dominant effect of lime (Fig. 4.2a).

4.3.3. PHOSPHORUS SORPTION INDEX

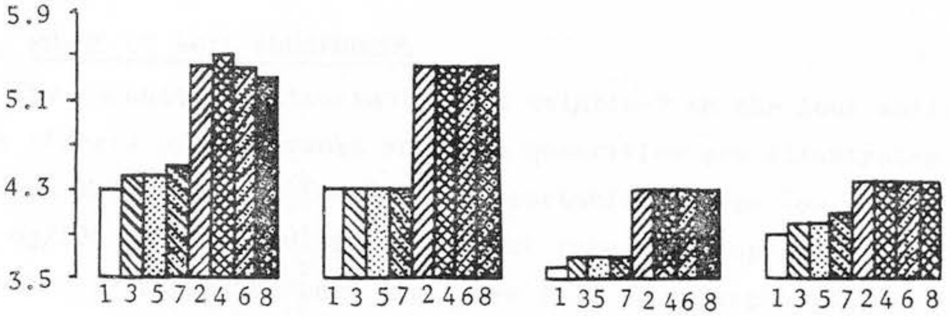
It was shown in Chapter 3 that high levels of extractable Al were strongly associated with high values for PSI. Within this group of 4 soils (4, 9, 10, 11) PSI was very significantly correlated with extractable Al (Table 4.4) and was therefore also correlated with other forms of soil Al as a result of the interrelationships described in Section 4.3.1. Where, however, treatments produced differential changes in the three forms of Al particularly those due to gypsum and superphosphate, the correlation coefficients between PSI and both soluble and exchangeable Al were lowered (Table 4.4).

Table 4.4 Relationships between PSI and forms of Al for different treatments

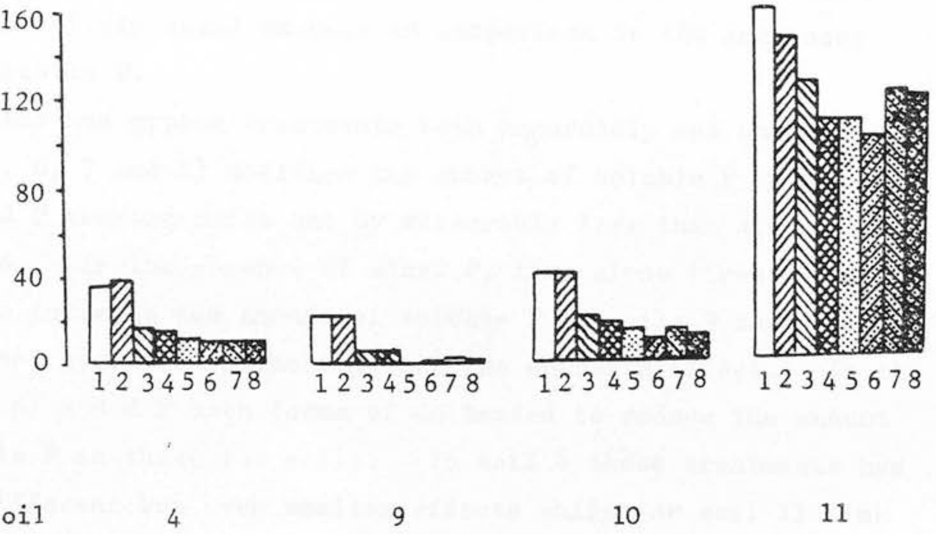
Treatment / Soil property	1. Untreated	2. Lime	3. Gypsum	5. Superphosphate
Extr. -Al	0.999***	0.997**	0.999***	0.971*
Exch. -Al	0.911	0.968	0.911	0.911
Sol. -Al	0.993**	0.965*	0.822	0.815

Fig 4.2 Changes in(a) pH and(b) P sorption index in soils 4, 9, 10 & 11 treated with superphosphate, lime and gypsum.

(a) pH$(CaCl_2)$



(b) PSI



The addition of superphosphate brought about large decreases in PSI, from 36 to 12, from 22 to 6, from 40 to 14, and from 168 to 102 in soils 4, 9, 10 and 11 respectively. Calcium as gypsum, but not as lime, lowered PSI by almost as much as did superphosphate in soils 4, 9 and 10 while in soil 11 the addition of lime and gypsum (treatments 2, 3 and also 4 when added together) progressively reduced PSI by almost as much as did superphosphate on that soil (Fig. 4.2b).

4.3.4. FORMS OF SOIL PHOSPHORUS

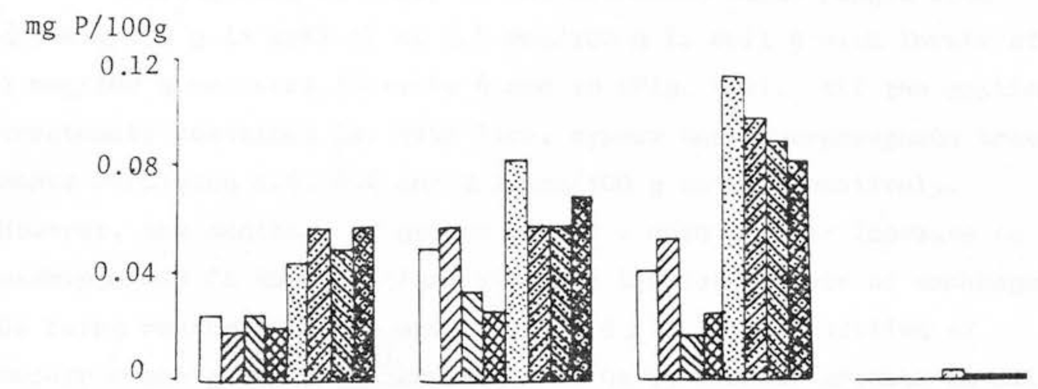
The amounts of extractable- and soluble-P in the four soils and the effects of treatments on these quantities are illustrated in Figures 4.3a and b. Levels of extractable- P were low (0.2 to 0.5 mg/100 g) in those treatments not receiving superphosphate (1-4) but were increased more than five fold by superphosphate (treatments 5-8) in all the soils. The increase in extractable-P was especially large in soil 9. Neither lime nor gypsum significantly influenced the amounts of extractable-P in the presence or absence of added P.

Amounts of soluble P in the non-P treated soils were extremely low and were much smaller than the amounts of extractable P, ranging from trace levels in soil 11 to 0.06 mg/100 g in soil 9. The addition of superphosphate increased the level of soluble P but by relatively small amounts in comparison to the increases in extractable P.

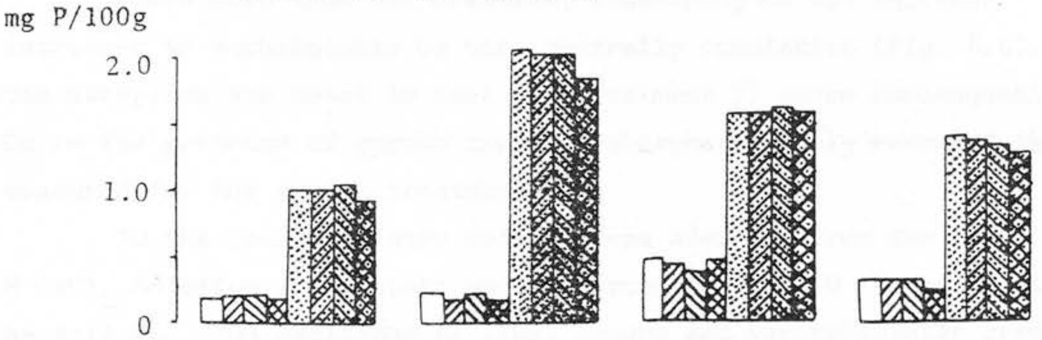
Lime and gypsum treatments both separately and combined (2, 3, 4, 6, 7 and 8) modified the amount of soluble P in both non-P and P treated soils but by measurably less than did superphosphate. In the absence of added P, lime alone (treatment 2) tended to increase the amount of soluble P in soils 9 and 10 while calcium as gypsum (treatment 3) had the opposite effect. In the presence of added P both forms of Ca tended to reduce the amount of soluble P in these two soils. In soil 4 these treatments had rather different but even smaller effects while for soil 11 lime and gypsum had no appreciable effect on the very small amounts of soluble P.

Fig 4.3 Changes in the amounts of (a) Soluble P (b) Extractable P prior to growth and (c) Extractable P post growth in soils 4, 9, 10 & 11 treated with superphosphate, lime and gypsum.

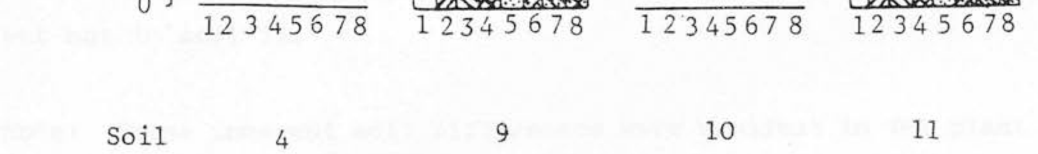
(a) Sol.P (pre growth)



(b) Extr.P (pre-growth)



(c) Extr.P (post-growth)



As a proportion of extractable P, soluble P ranged from less than 1% in soil 11 to almost 30% in soil 9 and this range was further modified by treatments. There was consequently no relationship between the two forms of P in these four soils.

4.3.5. FORMS OF SOIL CALCIUM

Exchangeable Ca (KCl) in the untreated soils ranged from 0.4 meq/100 g in soil 11 to 5.4 meq/100 g in soil 9 with levels of 3 meq/100 g measured in soils 4 and 10 (Fig. 4.4). All the applied treatments contained Ca, with lime, gypsum and superphosphate treatments supplying 6.6, 6.6 and 2.7 meq/100 g soil respectively. However, the addition of gypsum caused a much greater increase in exchangeable Ca than did lime with the largest amounts of exchangeable Ca being measured in the order $10 > 4 > 9 > 11$. The addition of superphosphate increased exchangeable Ca by similar amounts in all four soils (Fig. 4.4).

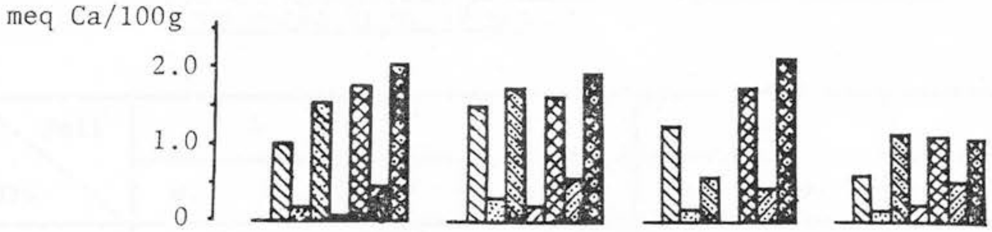
Where more than one treatment containing Ca was included increases in exchangeable Ca were generally cumulative (Fig. 4.4). One exception was noted in soil 10 (treatment 7) where exchangeable Ca in the presence of gypsum and superphosphate barely exceeded that measured for the gypsum treatment (3).

In the four untreated soils Ca was adsorbed from the 10^{-3} M $CaCl_2$ solution in greatest amounts from soil $11 > 10 > 4$ and least by soil 9. The additions of lime, gypsum and superphosphate produced similar increases in soluble Ca in three of the soils (4, 9 and 10). As observed with exchangeable Ca, gypsum increased soluble Ca by far more than did lime which increased soluble Ca by less than did superphosphate (Fig. 4.4). The increases in soluble Ca were smallest in soil 11 and here the increase due to lime exceeded that due to superphosphate. The tendency for cumulative increases in soluble Ca when gypsum was added with superphosphate, lime or both (treatments 7, 4 and 8 respectively, Fig. 4.4) was observed in soils 4, 9 and 10, but not in soil 11.

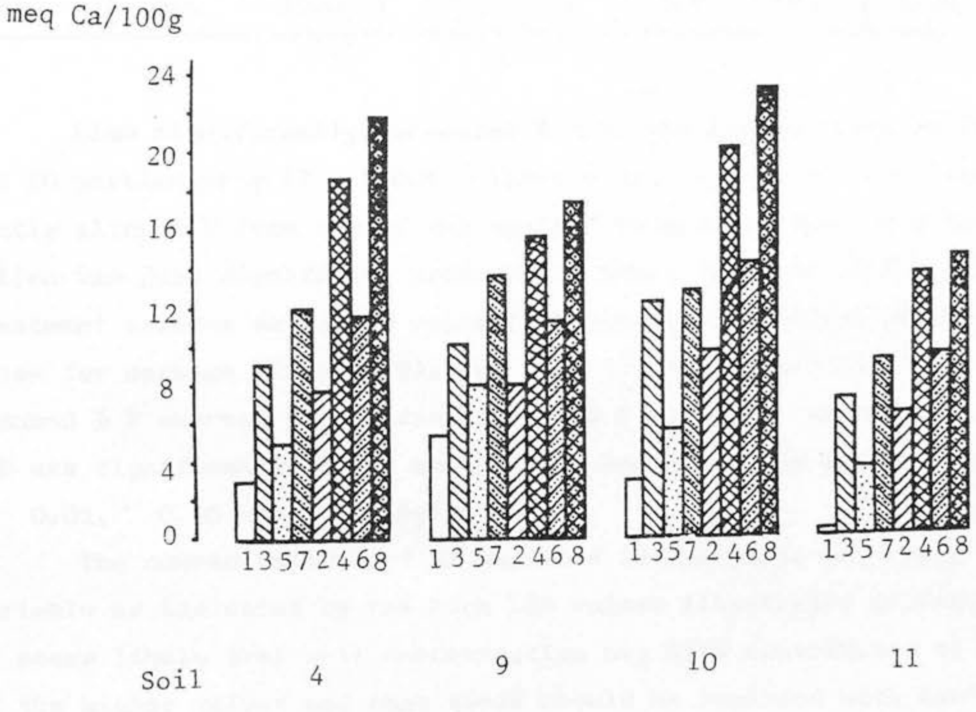
Note: These inherent soil differences were manifest in the plant data and because of the individual response of ryegrass, growing on soil 11, to superphosphate the ensuing data was analysed separately for individual soils.

Fig 4.4 Changes in the amounts of (a) Soluble Ca and (b) Exchangeable Ca in soils 4, 9, 10 & 11 treated with lime, gypsum and superphosphate.

(a) Sol. Ca



(b) Exch. Ca



4.3.6. CONCENTRATIONS OF P, Al AND Ca IN ROOTS AND HERBAGE

In the absence of superphosphate, P concentrations in the herbage and the roots were low, less than 0.11% (Fig. 4.5a and b) and not significantly affected by lime or gypsum. Because of the very large main effect with superphosphate the effects of lime and gypsum were only considered in the presence of added P (treatments 5 - 8). Generally, herbage P levels exceeded those in the root, and P contents were highest from soils 9 and 10 and lowest from soil 11.

Table 4.5. Effects of lime and gypsum in the presence of superphosphate on % P levels in herbage and roots from soils 4, 9, 10 and 11

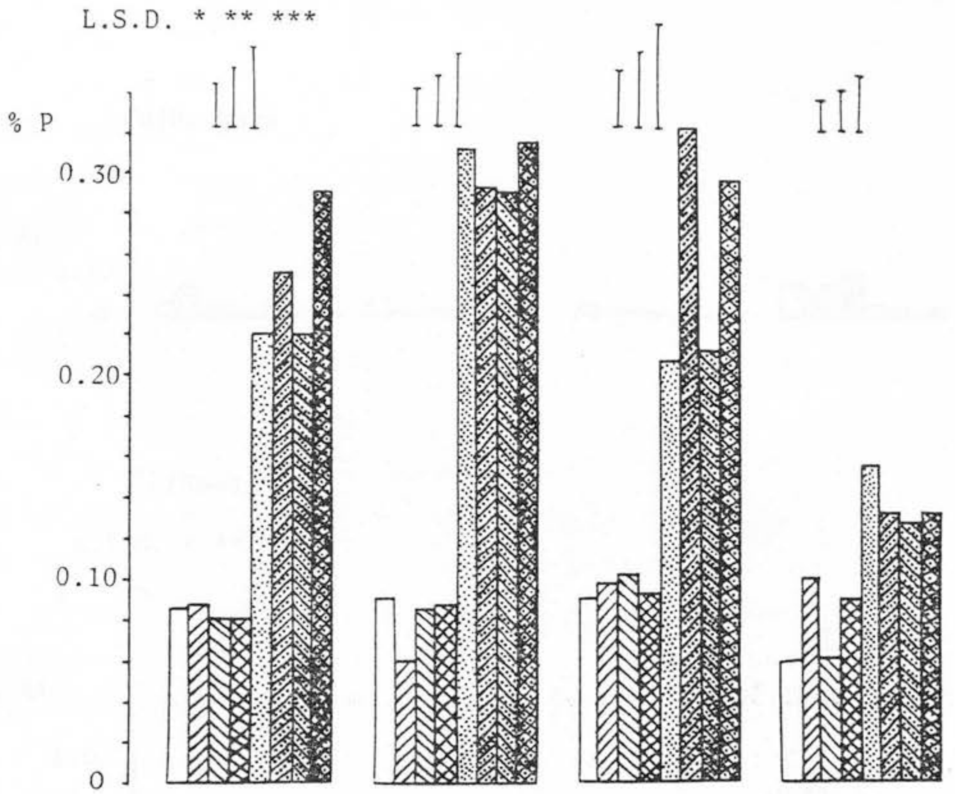
Soil	4		9		10		11	
Tr.	H.	R.	H.	R.	H.	R.	H.	R.
L	+0.05***	-0.01NS	0 NS	-0.1NS	+0.10***	-0.03*	+0.01NS	-0.04**
G	+0.02 NS	+0.01NS	0 NS	+0.1NS	-0.01NS	+0.04**	-0.01NS	0
L x G	+0.02 NS	0 NS	+0.02*	+0.02*	-0.01NS	-0.03*	-0.01NS	-0.03*
SE	0.01	0.006	0.008	0.007	0.013	0.01	0.008	0.009
CV%	8.4	10.6	5.3	7.9	9.8	12.0	11.4	11.9

Lime significantly increased % P in the herbage from soils 4 and 10 particularly (P = 0.001) (Table 4.5). Gypsum did not significantly alter % P from any of the soils. On soil 9, the L x G interaction was just significant producing a small increase in % P. Treatment effects on Root P concentrations did not always resemble those for herbage (Table 4.5). On soil 10 lime significantly (P = 0.005) reduced % P whereas gypsum increased the P content. On soil 11, also, % P was significantly lower on the lime and lime plus gypsum treatments (P 0.01, 0.05 respectively).

The concentrations of Al measured in the roots were very variable as indicated by the high LSD values illustrated in Fig. 4.6b. It seems likely that soil contamination may have contributed to some of the higher values and that these should be regarded with caution. However, in view of the high levels of soluble Al in the unlimed soil the high levels of Al in the roots from soil 11 may be a real effect.

Fig 4.5 % P content of Ryegrass (a) Herbage and (b) Roots from soils 4, 9, 10 & 11 treated with superphosphate, lime and gypsum.

(a) Herbage



(b) Root

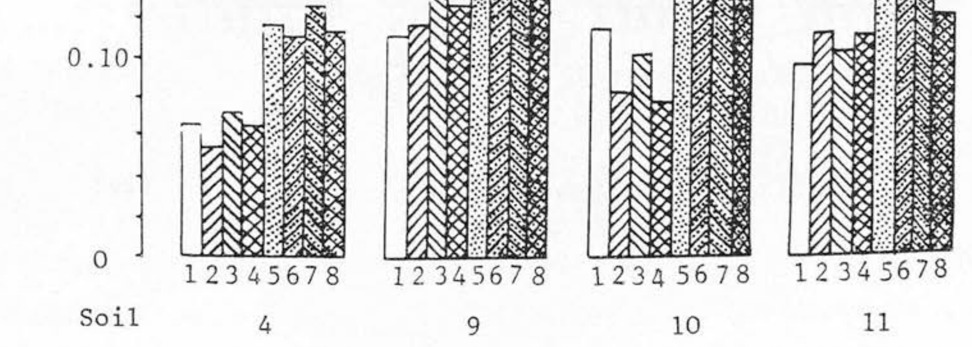
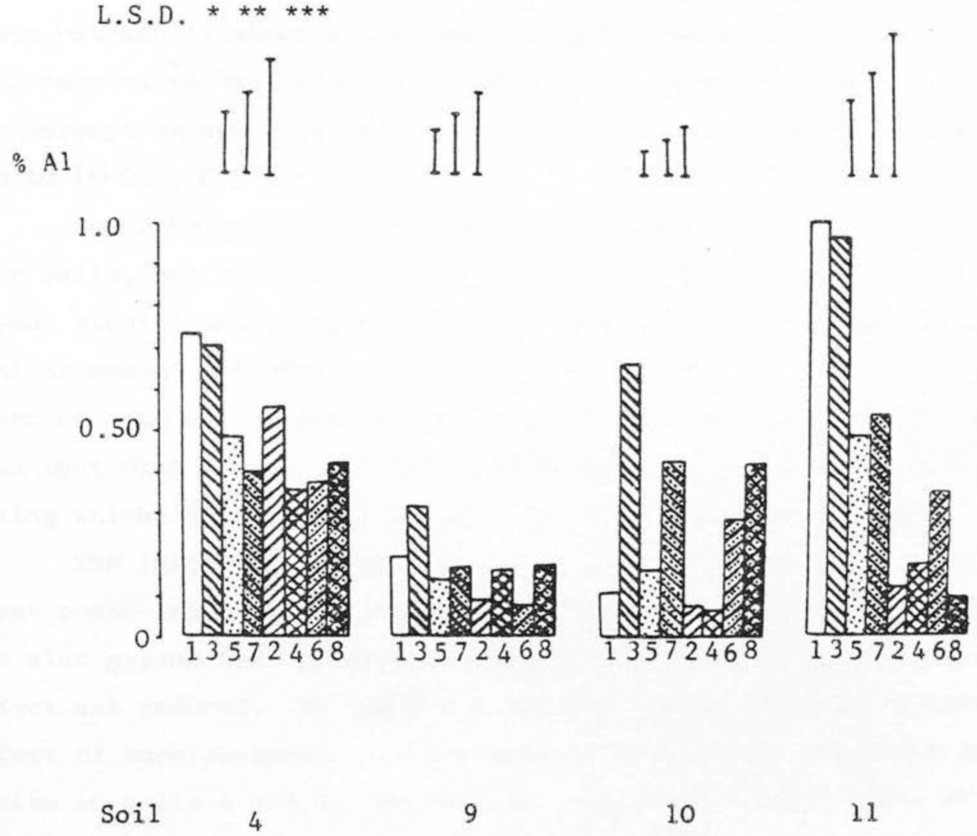


Fig 4.6 % Al content of Ryegrass(a) Herbage and(b) Roots from soils 4, 9, 10 & 11 treated with lime, gypsum and superphosphate.

(a)Herbage

(b)Root



It is interesting to note that in general higher levels of Al were recorded in association with elevated levels of soluble Al in the presence of gypsum and in the absence of lime on all four soils.

Herbage Al contents were approximately ten times lower than in the roots but again variability among replicates was high (Table 4.8A) (Fig. 4.6a).

Each of the main treatments, lime, gypsum and superphosphate contain Ca, with superphosphate providing one third the amount of Ca as each of the other two treatments. Also, while lime and gypsum had only minor influences on herbage and root growth, superphosphate substantially increased growth, with a consequent dilution effect on nutrient concentrations.

Herbage Ca levels on soils 4 and 9 were similar, between 0.6 and 2.6 % depending on the treatment. Concentrations were only slightly below this on soil 11, but the dilution effect was very significantly smaller than on soils 4 or 9. % Ca levels and their range between treatments was both low and restricted on soil 10. With respect to the roots, % Ca levels were generally below those in the herbage except from soil 9, and were particularly low on soils 4 and 10 (∼ 0.4, 0.5 % respectively).

Superphosphate caused significant reductions in % Ca on all four soils, but had least effect on soil 10 (Table 4.5). In contrast, gypsum significantly increased Ca concentrations on all the soils, by similar amounts (0.28%). On soils 4 and 9 lime increased % Ca by twice as much as had gypsum, while on soil 10 the increase was less than that with gypsum, and not significant. Conversely, on soil 11 liming which significantly enhanced growth decreased Ca levels.

The large main effects may partly reflect the large significant first order interactions (Table 4.5). Because superphosphate and lime, and also gypsum had opposing effects in combination their interactive effect was reduced. In the P x G interaction the negative dilution effect of superphosphate was dominant as it was with the P x L interaction on soils 4 and 9. On soil 11, despite the enhancement of growth by the P x L interaction, the % Ca level was increased. The L x G interaction was only important on soil 11, with the negative influence of lime overruling. These first order interactions may be seen from Fig. 4.7 (after RICHARDS 1941) by drawing in by eye the quadrilaterals joining together the midpoints, designated a, b, c on

Fig. 4.7. Interaction diagrams illustrating a 2^3 experiment using lime, gypsum and superphosphate on % Ca levels in herbage and roots from soils 4, 9, 10 and 11.

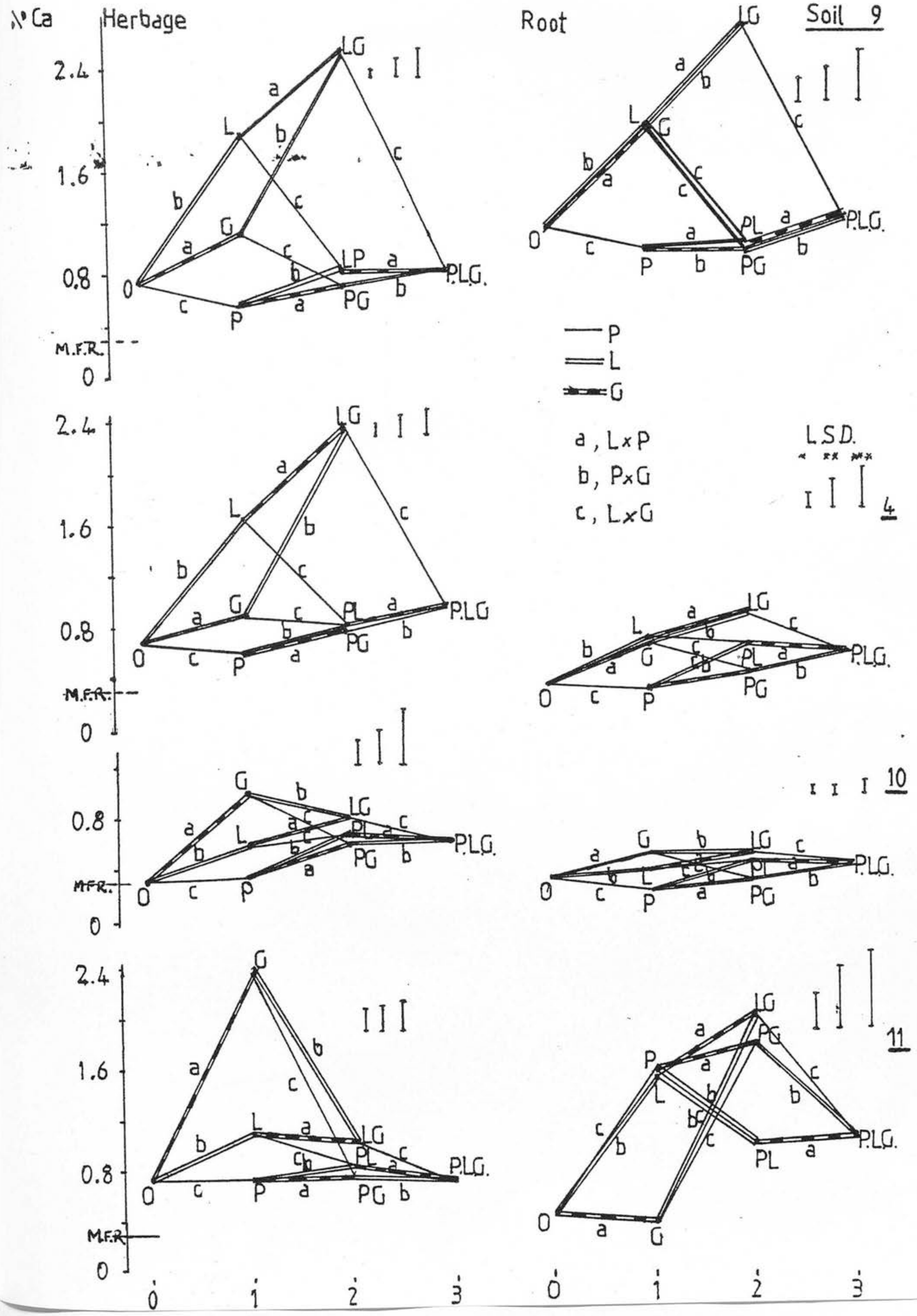


Table 4.6. Effects of Treatment on % Ca levels in the herbage and roots from soils 4, 9, 10 and 11

HERBAGE

Tr. \ Soil	4	9	10	11
P	-0.52***	-0.83***	-0.16*	-0.42***
G	+0.30***	+0.31***	+0.25***	+0.25***
L	+0.60***	+0.71***	+0.11 NS	-0.17***
P x G	-0.16*	-0.20***	-0.18*	-0.22***
P x L	-0.46***	-0.56***	+0.08 NS	+0.19***
L x G	+0.12 NS	-0.03 NS	-0.11*	-0.38***
P x G x L	-0.16 NS	-0.06 NS	-0.02 NS	-0.16**
SED	0.09	0.05	0.11	0.06

ROOTS

Tr. \ Soil	4	9	10	11
P	+0.08*	-0.85***	-0.08***	+0.28**
G	+0.14***	+0.46***	-0.05***	+0.16*
L	+0.25***	+0.47***	-0.05***	+0.36***
P x G	-0.10*	-0.32***	-0.06**	+0.01 NS
P x L	-0.02 NS	-0.31***	+0.05**	-0.82***
L x G	+0.01 NS	+0.04 NS	-0.04 NS	+0.09 NS
P x G x L	0 NS	-0.01 NS	+0.01 NS	-0.10 NS
SED	0.07	0.10	0.02	0.15

Table 4.7. Effects of lime and gypsum in the presence of superphosphate on P uptake by herbage and roots growing in soils 4, 9, 10 and 11 (mg P/pot)

Tr. \ Soil	4		9		10		11	
	H	R	H	R	H	R	H	R
G	+2.07***	+0.16	-0.39	-0.11	-0.45	-0.78	-0.19	-0.41***
L	+2.84***	-0.11	-2.53***	+0.47	+6.56***	1.28**	+4.72***	+2.43***
G x L	+0.30	-0.16	+2.09***	+0.51	+1.19	+0.99	-0.17	-0.43**
SE	0.49	0.34	0.30	0.34	0.84	0.37	0.15	0.08
CV%	6.3	20.7	3.5	12.3	10.8	23.1	7.1	8.6

the pied, solid and open lines, respectively. For example, joining the a's gives the interactive effect of lime and P, since gypsum remains 'constant'. The degree of interaction is inferred from the departure of the quadrilateral from a parallelogram.

Treatment effects on % Ca levels in the roots were not markedly different from those reported for herbage although there were exceptions; on soil 4 superphosphate increased % Ca ($P < 0.05$) and on soil 10 lime reduced the Ca concentration ($P < 0.001$). This latter response probably partly reflects the significant enhancement of growth due to lime (see appendix Table 4.11A). On soil 11, the P x G and L x G interactions produced opposite effects to those described for the herbage, increasing, though not significantly, % Ca.

4.3.7. PLANT GROWTH AND P UPTAKE

Observations made of plant growth are given in Table 4.8. Germination was not affected by either inherent soil differences or treatments. Red-tinged leaf tips, possibly symptomatic of P deficiency were first observed on ryegrass growing on soil 11 and plant growth, generally poor on this soil, was much improved by the combined treatment of lime and superphosphate. These differences in growth are shown in the photographs (Fig. 4.8a and b) taken before the first harvest. The marked response of ryegrass to superphosphate on all soils except soil 11, together with the more nearly similar response to superphosphate on all soils when lime, phosphate and gypsum were applied together, is illustrated in these photographs.

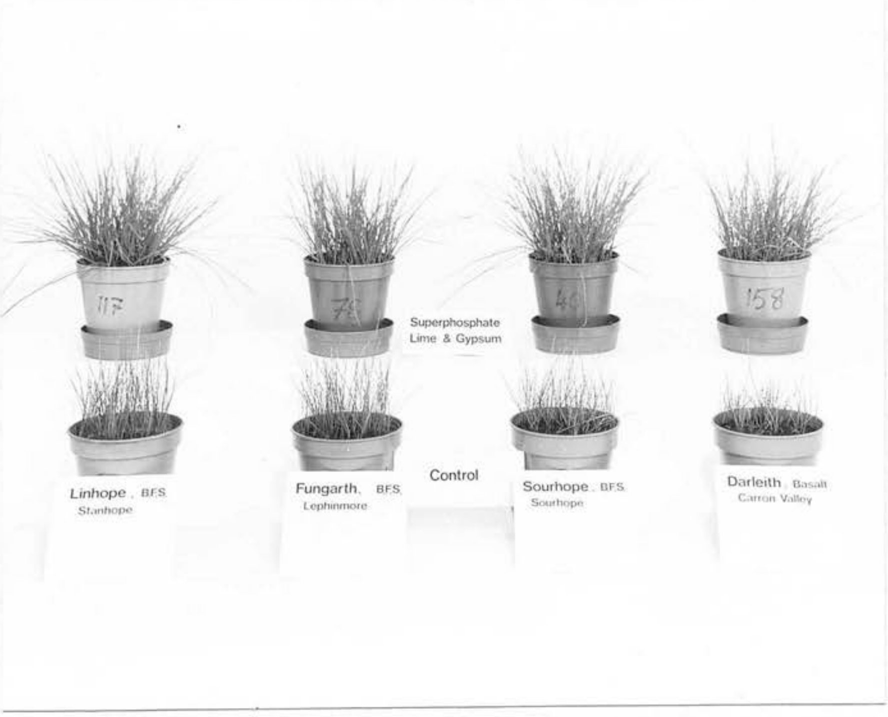
Quantitative effects of treatment and soils on the growth of ryegrass were recorded as dry matter (DM) production and P uptake (Table 4.9A to 4.12A). Plant P uptake was calculated from the weight of herbage DM and its P content at each of three harvests, and from root and stubble DM and P content after the final harvest is shown in Fig. 4.9. P uptake was not of any real significance in the absence of added P and the response to superphosphate dominated that of the other treatments, lime and gypsum. Their effects therefore are discussed for the P treatments (5 - 8) only. The effects of inherent soil differences are exemplified in Fig. 4.9 with P uptake on soil 11 in response to superphosphate treatments only half the amounts on soils 4, 9 and 10.

Table 4.8. Summary of weekly observations on growth of ryegrass on Soils 4, 9, 10, 11 in the pot experiment

Soil	4	9	10	11
Germination (per 100 seeds ± SEM)	82 ± 4	84 ± 3	83 ± 3	80 ± 5
Herbage appearance	Green and healthy, large response to P, good tillering, response to gypsum P deficiency on P_o treatments	Green healthy leaf blade 0.5 mm, good tillering and large response to P. P deficiency on P_o treatments.	1st fortnight herbage all treatments lush, positive response to lime at 6 wks, by 10 wks gypsum treatment (3) chlorotic and dying back.	Growth poor except with lime. Leaf blades thin, dark green, chlorotic tips curled and dried up by 3rd harvest on L_o treatment symptoms similar to those for Ca deficiency
1st sign of P deficiency symptoms	3rd week	3rd week	4th week	2nd week
Root Morphology	Dense, fibrous, healthy for all treatments.	White, fleshy, diffusely branched, healthy all treatments.	Dense, fibrous and healthy except in G_1 treatments (3 and 7)	Rudimentary and brown cast on the L_o treatments, diffuse and healthy on the L_1 treatments

Fig. 4.8. The effect of lime and gypsum on the response to superphospate of ryegrass growing in soils 9 (Linhope), 4 (Fungarth), 10 (Sourhope) and 11 (Darleith)

(photographed 28 days following germination)



On soil 4 significant increases in herbage P uptake were recovered from lime, and gypsum treatments (Table 4.7) although their combined effect was not significant. In contrast, on soil 9 lime alone significantly lowered P uptake but the interaction L x G significantly increased P uptake. For soils 10 and 11 there were significant enhancements in P uptake from lime.

Treatment responses by the roots were less marked but again on soils 10 and 11 there were significant increases from liming. The L x G interaction however lowered P uptake on soil 11.

4.4. DISCUSSION AND INTERPRETATION

4.4.1. RELATIONSHIPS BETWEEN FORMS OF Al AND P

The choice of soils included a wide range in soil Al content, and the applied treatments lime and gypsum brought about further changes in the three forms of Al, while superphosphate increased both forms of soil P. These inherent and induced ranges in both Al and P allow an examination of the relationships between extractable-, exchangeable- and soluble Al, and extractable- and soluble P. Amounts of each form of Al and P in the untreated soils are given in Table 4.1 and the correlation coefficients for their inter-relationships are given in the first column of Table 4.9. In the untreated soils the small amounts of soluble P tended to decrease as all forms of Al increased whereas extractable P was not related to any form of Al.

Table 4.9. Correlation coefficients for the relationships between forms of Al and P for different treatments

Property	1.Untreated		2. Lime		3. Gypsum		5. Super-phosphate	
Treatment	Extr.P	Sol.P	Extr.P	Sol.P	Extr.P	Sol.P	Extr.P	Sol.P
Extr. Al	0.69	-0.90	0.23	-0.91	0.41	-0.97*	-0.15	-0.85
Exch. Al	0.56	-0.72	0.46	-0.82	0.18	-0.90	-0.02	-0.47
Sol. Al	0.26	-0.85	0.44	-0.84	0.87	-0.30	-0.22	-0.61
PSI	0.15	-0.91	0.24	-0.93	0.43	-0.92	-0.21	-0.79

* r > 0.95 ** r > 0.99 *** r > 0.999,
significance, P = 0.05, 0.01, 0.001 respectively

For the treated soils it was found that all three forms of Al were significantly reduced by lime (treatments 2, 4, 6 and 8), that soluble Al was appreciably increased by gypsum but that none of the three forms was changed to any great extent by superphosphate (treatments 5, 6, 7 and 8) (Fig. 4.1a,b and c). In contrast both forms of P were significantly increased by superphosphate addition and the amounts of soluble P were slightly changed by the additions of lime and gypsum (Fig. 4.3a,b). Although lime lowered the amounts of soluble Al more than exchangeable Al, and exchangeable Al more than extractable Al, the magnitude of the change in each of the forms was similar in all four soils. The relationship between these three forms of Al and both forms of P were therefore broadly similar to those described for the untreated soils (Table 4.9 columns 1 and 2).

The large increases in soluble Al in soil 10 and to a lesser extent in soils 4 and 9 brought about by the addition of gypsum which effected only minor changes in amounts of soluble P resulted in their being no relationship between soluble Al and soluble P. However, since gypsum had little effect on exchangeable and extractable Al, the inverse relationships between soluble P and these forms of Al was unaltered (Table 4.9 column 3). The relationship between soluble Al and extractable P however was improved by the addition of gypsum but in general treatments did not improve the poor relationships between extractable P and the three forms of Al calculated for the untreated soils (Table 4.9).

In the superphosphate treatments both forms of P tended to decrease as all 3 forms of Al were increased but because of the differential effects between soils the forms of Al were less well correlated with forms of P than in the untreated soils (Table 4.9 columns 1 and 4).

When all the results were considered, for the eight treatments and four soils, soluble P was shown to be inversely correlated with extractable and soluble Al but not with exchangeable Al ($r = -0.71^{***}$, -0.420^{*} & 0.09 (NS) respectively). Al could influence the amounts of extractable and soluble P through its effects on P sorption (3.3.5). For this reason an examination has been made of the relationship between the two forms of P, sorption index and the three forms of Al.

In the untreated soils, soluble P was found to decrease with increasing PSI and PSI in turn increased with increasing extractable Al (Table 4.4 column 1, Table 4.9 column 1). Exchangeable and soluble Al may only be related to PSI through their relationships with extractable Al and it was noted that the correlation coefficients (r) for their relationships with soluble P were smaller than those between extractable Al and soluble P. No corresponding relationships were noted between extractable P, and PSI or any form of soil Al.

Addition of P as superphosphate markedly increased soluble P and reduced PSI, but had little effect on extractable Al. It seems likely that this reduction in PSI resulted from the sorption of P on sites provided by extractable Al without necessarily changing the amount of extractable Al. Small changes in exchangeable and soluble Al together with large changes in PSI and soluble P as a result of P treatment meant that the values of r for the relationships between these forms of Al with extractable Al (Table 4.3), PSI (Table 4.4) and soluble P (Table 4.9) were lower than for the untreated soils.

Lime has been shown to incur small changes in both PSI and soluble P although in view of the larger effects on soil Al it might have been expected to have a greater effect on PSI. Lime, however, has been shown to have differential effects on the various forms of soil Al, with least effect on extractable Al which was most significantly correlated with PSI. This possibly explains the observed small changes in PSI and soluble P brought about by liming.

Gypsum as an alternative source of Ca produced quite different effects from those of lime. It caused a lowering in PSI almost equal to that effected by the addition of P but did not influence extractable nor increase soluble P as would be expected from the previously established correlations between PSI, extractable Al, and soluble P. The lowering of PSI by gypsum could be due to the displacement of Al by Ca and the consequent reduction in the affinity of the sorbing surfaces for P. The observed increase in soluble Al in soils 4, 9 and 10 when gypsum was added, may provide some evidence for this effect.

It was also observed that soluble P in soils 9 and especially 10, was lowered by the addition of gypsum. This was contrary to what would have been predicted from the previously described effect of gypsum on PSI and the strong correlation between PSI and soluble P. However, the increase in soluble Al with addition of gypsum may have precipitated the phosphate ions thus explaining the fall in soluble P. An inverse relationship was established between soluble Al and soluble P ($r = -0.46^*$), although it only explained 20% of the variation in the overall level of soluble P in the four soils.

4.4.2. PLANT GROWTH AND P SUPPLY

Differences in biological availability indicated by P uptake appeared to be attributable to both soil and treatment effects (Fig. 4.9), but these were not necessarily reflected in values for extractable or soluble P (Fig. 4.3).

The relationships between plant P uptake and soluble- and extractable P are illustrated in Figs 4.10 and 4.11 respectively. In the absence of added P (open symbols) P uptake was invariably low (not exceeding 2 mg/pot) and for the untreated soils was significantly correlated with soluble- but not with extractable P (r = 0.991** and 0.093 respecively). When all the non-P treatments, including those with lime and gypsum, were examined there was a relatively wide range in soluble P from trace amounts to 0.07 mg/100 g but a much smaller range in amounts of extractable P, from 0.19 to 0.50 mg/100 g). The amounts of extractable P were less than, but more nearly similar to amounts of P taken up during plant growth (0.34 to 2.11 mg/pot) compared with the values of soluble P.

Soluble P measured prior to the commencement of growth represented the intensity of P supply (I) at that time. In order to provide for the continuing requirement of P by ryegrass this would need to be replenished at a rate at least commensurate with those requirements otherwise growth of roots and herbage would be checked together with the plants ability to exploit the P reserves in the soil. Effective utilisation of soil P requires plant roots to explore a high proportion of the soil volume because a) diffusion of P in the soil solution is very slow and roots can only withdraw P from within approximately 1 mm of this surface (VASEY and BARBER 1963) and b) the rate at which labile P comes into solution may be slow in these soils.

P deficiency symptoms were observed after 2-3 weeks on the non-P treated soils and for these treatments, P uptake was not related to the initial level of soluble P which ranged considerably more than did P uptake (Fig. 4.10). This suggests that either plant P uptake is not related to that amount of soluble P or that the amount of soluble P measured prior to growth was quickly used up but not maintained. The amounts of extractable P in each individual soil, however, were all low and quite similar as were values for P uptake except for some low uptake values in soil 11 and 10 (Fig. 4.11).

Addition of superphosphate (74 mgP/pot) enriched total P in soils 4, 9, 10 and 11 by 33, 38, 21 and 10% respectively and hardly increased levels of soluble P although levels of extractable P were increased by between 3 fold in soil 10 and nearly 10 fold in soil 11. This increase more nearly reflected the magnitude of increase in plant P uptake. The lack of relationship between soluble P and P uptake in some soils is illustrated in Figure 4.10. The addition of superphosphate, which produced only a small change in the level of soluble P in soil 11 resulted in P uptake values in excess of 10 mg/pot on some treatments. This was only slightly less than plant P uptake from soil 10 where the level of soluble P was more than 20 times higher.

Extractable P not only includes (I) but may also include some measure of a soil's capacity to maintain that intensity. Determinations of extractable P after the period of plant growth (Fig. 4.3c), showed that this form of P was depleted by between 1.5 and 3 mg/pot on soils 9 and 11 when plants had removed between 10 to 25 mg/pot. In the absence of added P however (treatments 1-4) where P uptake amounted to between 0.5 and 2 mg/pot there was no detectable depletion in extractable P. In all instances the depletion of this form of soil P accounted for only a small proportion of the amount of P removed by plant growth.

In general, the amounts of extractable P and the changes resulting from the addition of superphosphate more closely reflected P uptake than did soluble P except that extractable P did not indicate the changes which lime and gypsum brought about in P uptake. It appears that in general the treatments including both lime and P (6 and 8) allowed greater P uptake while treatments with P but excluding lime (5 and 7) imposed limitations on the plants' ability to take up P.

Evidence for this reduced ability to exploit the 'available' P was most clearly demonstrated in soils 10 and 11 (treatments 5 and 7) where it was associated with poorly developed root systems. These two soils have been shown to have much higher amounts of exchangeable Al than either soils 4 or 9 and in the presence of gypsum (treatments 3 and 7, Figure 4.10) were associated with high levels of soluble Al, which is known to influence root growth (Chapter 1,1.7). The implications of these high levels of Al for plant growth and espcially root development and P uptake will now be discussed.

Fig 4.9 Total P uptake by Ryegrass growing in soils 4, 9, 10 & 11 treated with superphosphate, lime and gypsum.

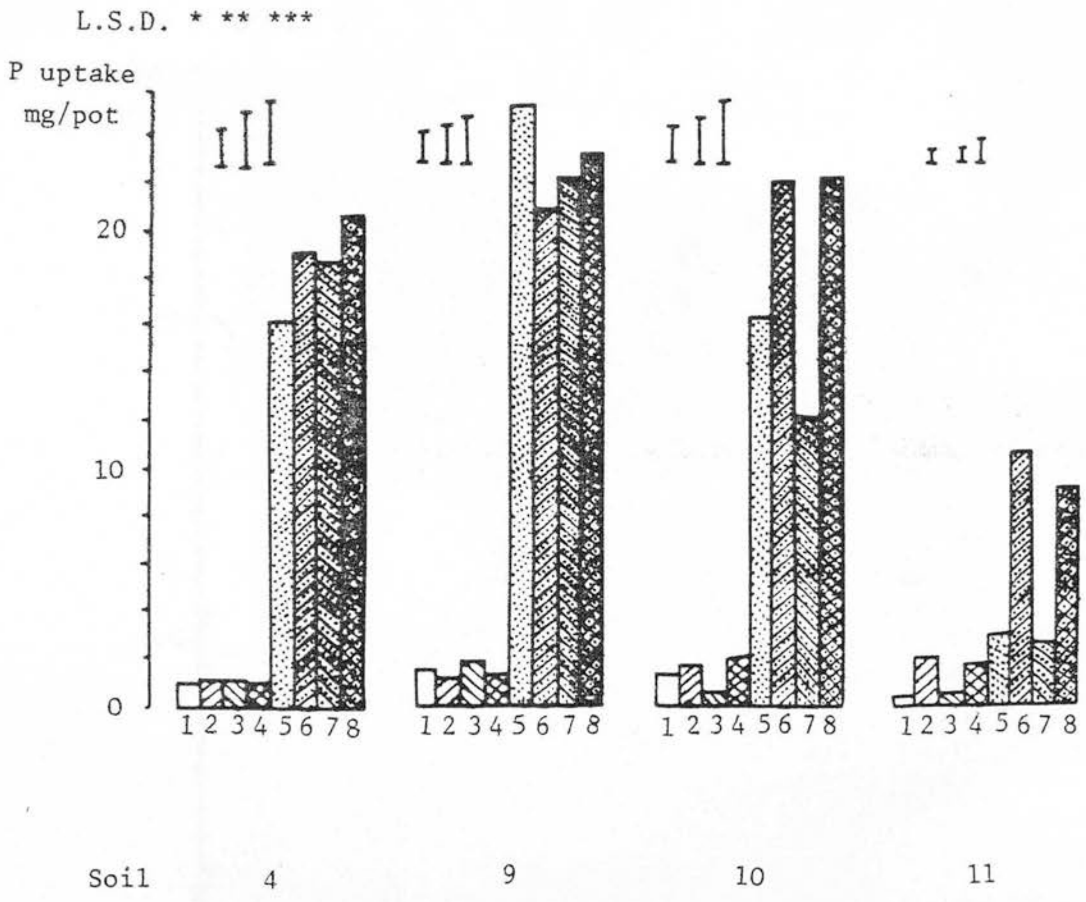


Fig 4.10 Relationship between P uptake by Ryegrass and Soluble P in soils with and without added P (closed and open symbols respectively).

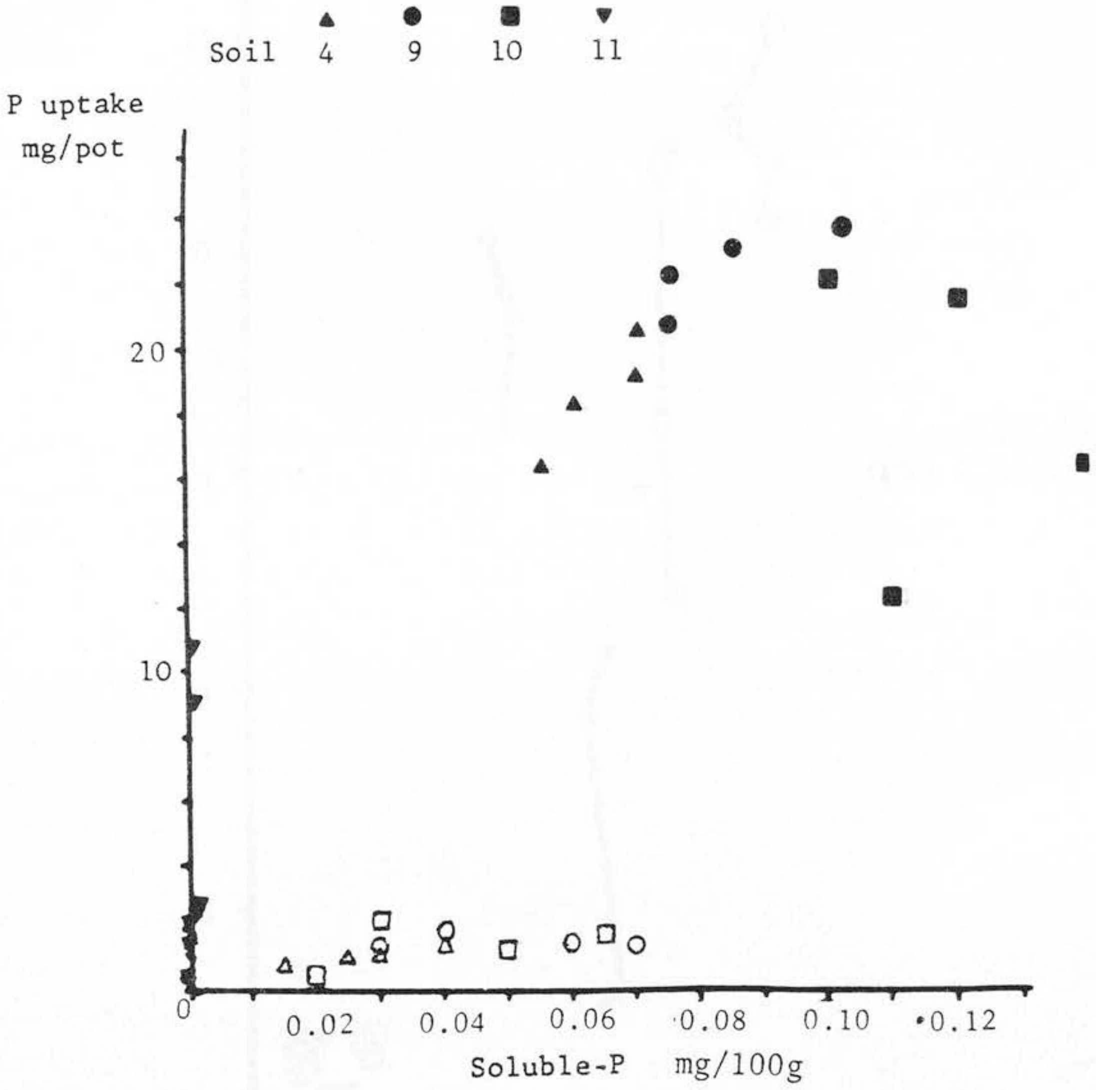
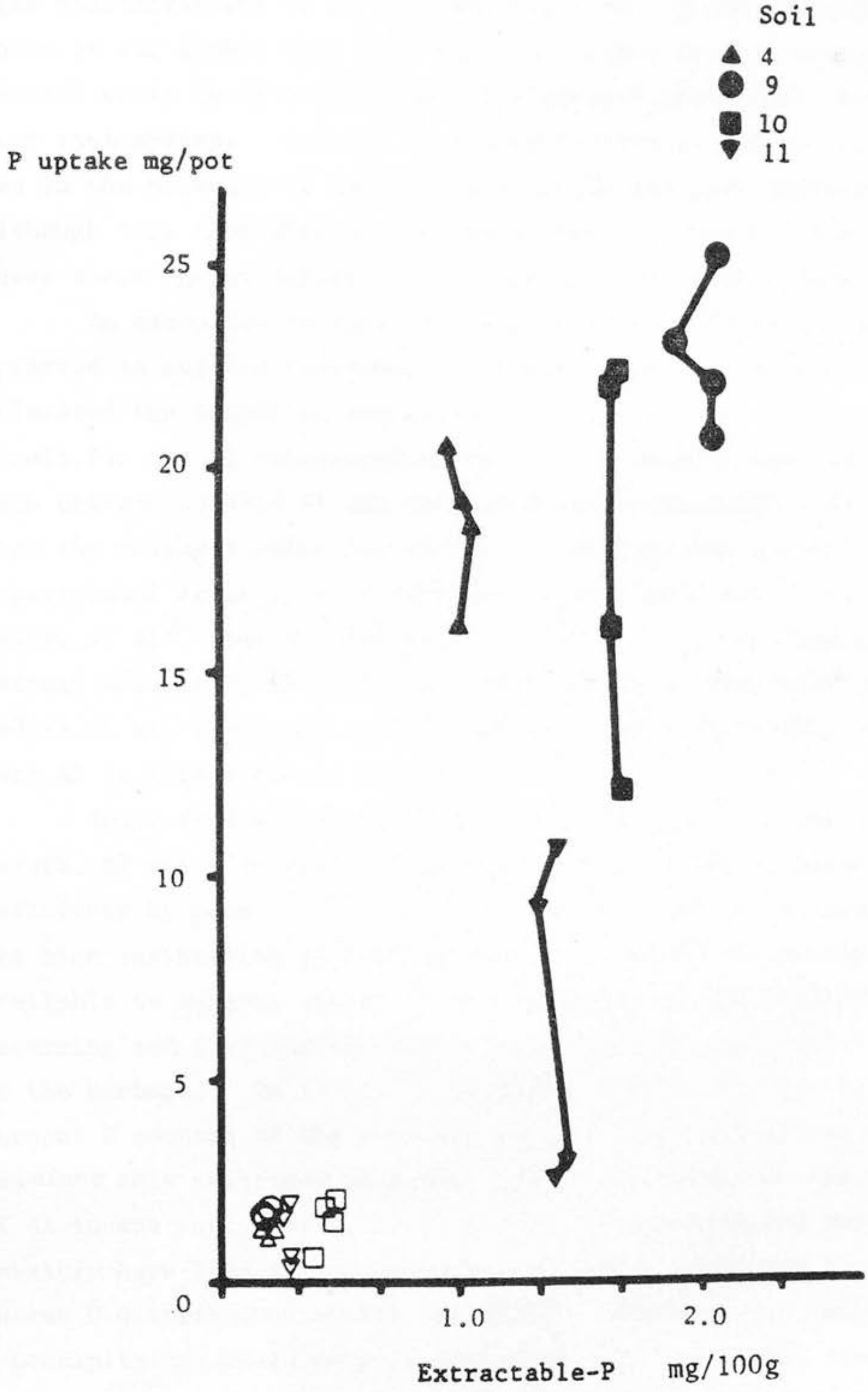


Fig 4.11 Relationship between P uptake by Ryegrass and Extractable P in soils with and without added P (closed and open symbols respectively).



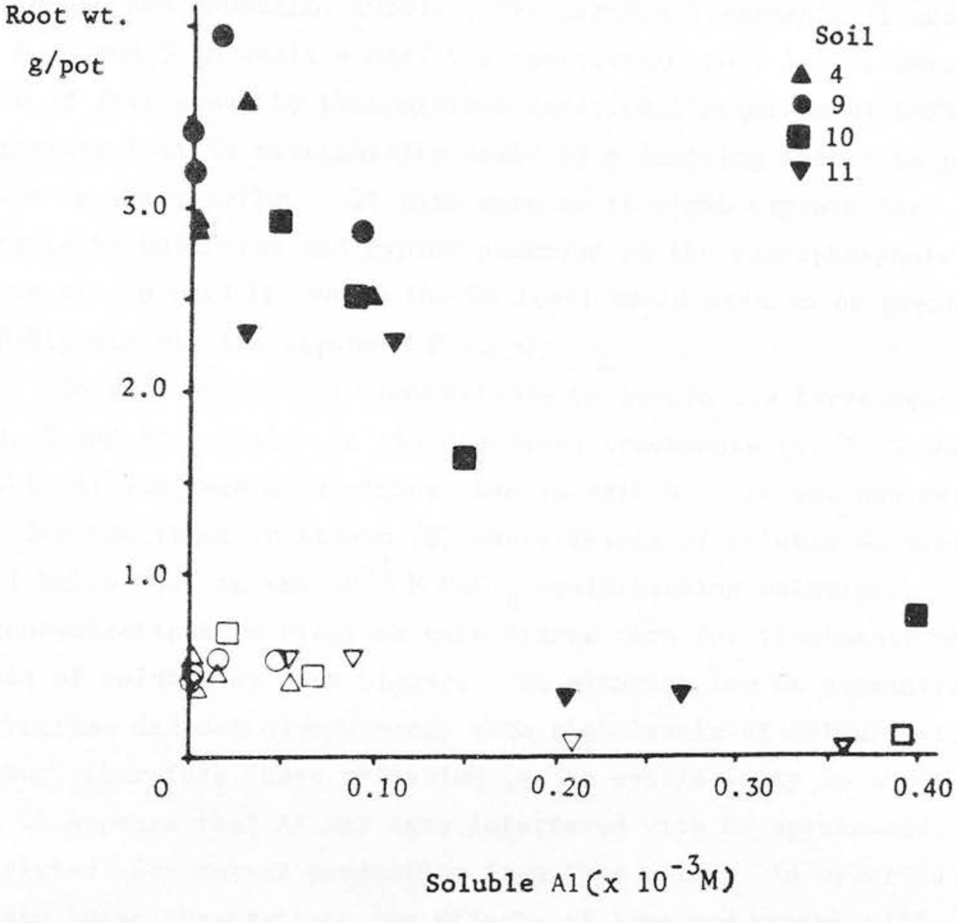
4.4.3. EFFECTS OF Al ON PLANT GROWTH

The inverse relationship between root weight and the concentration of soluble Al ($r = -0.743^{***}$) is shown in Figure 4.12. Root growth in most instances appeared to be severely restricted when concentrations of Al exceeded 0.2×10^{-3} M and in soil 11 where it was double this (0.4×10^{-3}M) only a few rudimentary lateral roots could be distinguished amongst the meagre, brown, cast root system. Between Al concentrations of 0.1 to 0.2×10^{-3}M and in the presence of added P root growth was much improved although less than when Al concentrations were below 0.1×10^{-3} M where there was no apparent influence of Al on root growth.

An exception to these Al concentration effects on root growth occurred in soil 10 (treatment 7) where ryegrass seemed to have tolerated the higher Al concentration (Fig. 4.12). This particular result for the Al concentration was also anomalous when the relationship between soluble Al and soluble P was considered. This suggests that the measured value for Al may be too high due possibly to experimental error or alternatively to the value for Al not consisting solely of Al^{3+} ions but possibly also including some complexed or hydroxy species of Al. Soluble Al/P complexes have been identified (WHITE et al. 1976) and work by BARTLETT and RIEGO (1972) suggested that Al in this state is not toxic.

Apart from affecting P uptake through its influence on root growth, Al may also restrict herbage growth through induced P deficiency by means of fixation of P in the roots. Because of the high variability in root Al levels no conclusive evidence is available to suggest whether P precipitation in the root by Al was occurring and reducing the amount of P available for translocation to the herbage. On soil 10 (treatment 7, Fig. 4.5a and b) the percent P content of the root was greater than that in the herbage and since this coincided with high levels of soluble Al the levels of Al in the root free space were likely to be high and may possibly have lead to P precipitation, thus accounting for the uneven P distribution within the plant. However, confirmation of P precipitation based only on percent P contents is not very satisfactory as P content is also influenced by the amount of P available for uptake by plants, the intensity of P, the size of

Fig 4.12 Relationship between Root weight and the concentration of Soluble Al in soils with and without added P (closed and open symbols respectively).



the root sorbing capacity and the amount of growth made.

Al has also been shown to affect plant growth by interfering with Ca uptake; by way of competition for exchange sites in the root free space which effectively interferes with Ca movement to the stele (SHONE, 1966). Therefore, in order to establish whether Al has influenced growth, via its effect on Ca uptake in any of these soils the amounts of Ca in the soil and plant will next be examined.

4.4.4. CALCIUM IN RELATION TO PLANT GROWTH

Calcium levels of around 0.3% in tissue are needed by ryegrass in order to sustain its metabolic functions and concentrations in excess of this are required for the production of new tissue (LONERAGAN and SNOWBALL, 1968). For certain treatments, (1 and 5, and 1, 2 and 5 on soils 4 and 10 respectively), root levels were below or just equal to this minimum functional requirement (MFR) suggesting that Ca availability could be a limiting factor to plant growth in these soils. If this were so it might explain the response to both lime and gypsum observed on the superphosphate treatments on soil 4; where the Ca level would need to be greater to fully exploit the improved P supply.

On soil 10 not only were soluble Ca levels low (treatments 1, 2, 5 and 6) but also in the non-limed treatments (1, 3, 5 and 7) soluble Al was generally higher than in soil 4. It was observed that for the limed treatment (2) where levels of soluble Ca were still below that in the 10^{-3} M $CaCl_2$ equilibrating solution, Ca concentrations in ryegrass were higher than for treatments where levels of soluble Ca were higher. So although low Ca concentrations in ryegrass did not always occur with high levels of soluble Al, and may, therefore, have reflected low Ca availability in this soil it appears that Al may have interfered with Ca uptake and restricted dry matter production from this soil. In order to explain these observations the effects of lime and gypsum will now be discussed in relation to their effects on soil Al and Ca and interactions between them.

4.4.5. EFFECTS OF LIME AND GYPSUM ON Al and Ca

In general the values of both exchangeable and soluble Al fell into two treatment categories, limed and non-limed. The addition of lime has a profound effect on soil pH (Fig. 4.2a) which in turn influences the solubility of Al (Chapter 1, 1.2) so that when pH is high these forms of Al are low. In soils 4 and 9 the pH was considerably higher than in soils 10 and 11 and inherent differences in Al content and/or CEC appeared to influence the pH 'response' to lime in these sites. The addition of lime increased pH to 5.3 in soils 4 and 9 but in soils 10 and 11 it was only raised to 4.3 (equivalent to the pH of the unlimed soils, 4 and 9). Amounts of exchangeable and soluble Al were much lower in soils 4 and 9 than in 10 and 11, and the change due to lime reduced exchangeable and soluble Al to even smaller amounts in 4 and 9.

In contrast gypsum additions had virtually no effect on either pH or levels of exchangeable Al but caused increases in soluble Al in all soils except 11 and greatly increased levels of exchangeable and to a lesser extent soluble Ca.

For the untreated soils high levels of soluble Al were only recorded in soil 11. The distinguishing properties of this soil compared to soil 10 were that the amount of exchangeable Al and also percent saturation by Al were higher (Table 4.1) but these properties in themselves offer no clear reason for the different levels of soluble ions measured between the soils. The results suggest that a more detailed study of exchange reactions involving Al and the effects of Ca as lime or gypsum on Al are needed to explain the observations but this was beyond the scope of this study.

4.4.6. EFFECTS OF Ca/Al INTERACTIONS ON PLANT GROWTH AND P UPTAKE

The addition of Ca as lime or gypsum, mainly because of its influence on soil Al is known to have wide reaching effects on plant growth (Chapter 1, 1.6). The reactions which occur in the soil to attain an equilibrium between adsorbed and exchangeable ions and those in solution are related to the chemical activity, bonding strength, relative amounts of the ions and the size and nature of the CEC (Chapter 1). However, uptake of nutrients by plant roots is related to the relative concentrations of the respective ions in solution (KIRKBY and MENGEL, 1978).

Fig 4.13 Changes in the Log. Molar Concentration Ratios for soils 4, 9, 10 & 11 treatment with lime, superphosphate and gypsum.

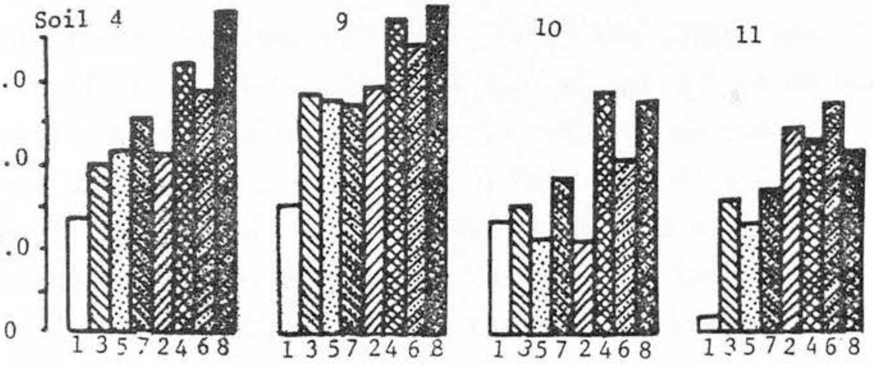
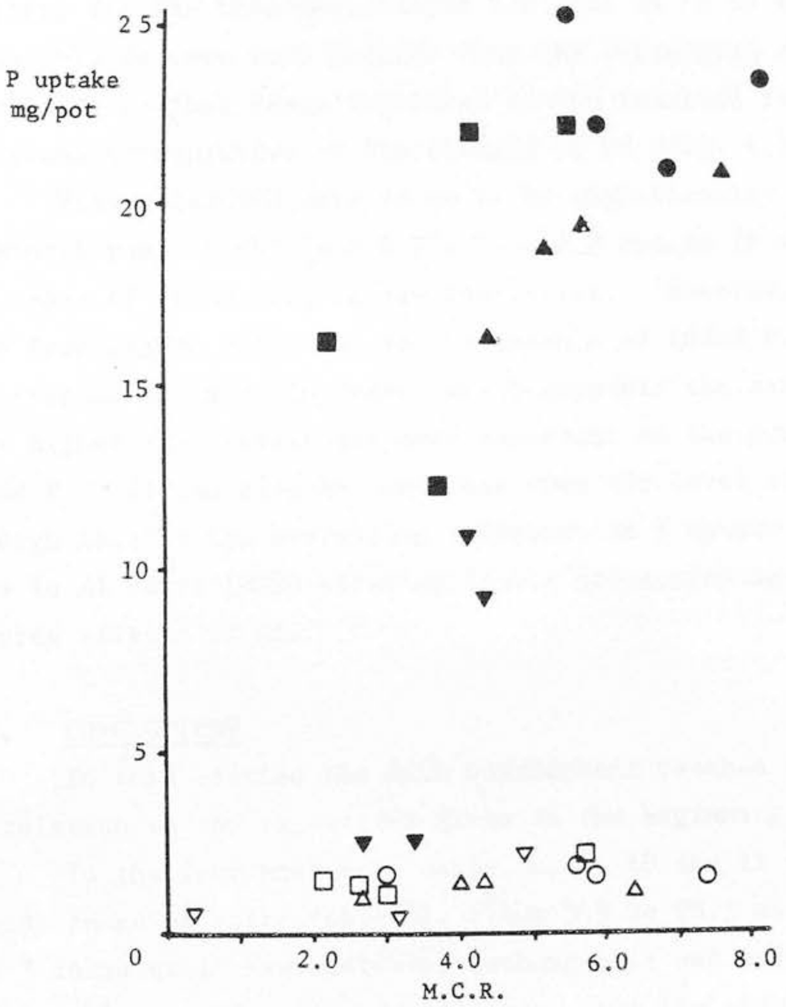


Fig 4.14 Relationship between P uptake by Ryegrass and the Log. Molar Concentration Ratio in soils with and without added P (closed and open symbols respectively).



BACHE and SHARP (1976b) have described the effect on exchange reactions on the solubility of ions in the soil solution using the Activity Ratio (AR) (Chapter 1, 1.2). However the wide range in pH, Ca and Al levels resulting from both inherent soil differences and treatment effects together with the lack of the appropriate selectivity coefficients, have precluded the calculation of AR here. As an alternative method of integrating soil effects on ion concentrations and examining the effect of the ratio of soluble bases(Ca + Mg) to soluble Al ions on plant growth the ratio of the concentrations of these ions in 10^{-3} M $CaCl_2$ was calculated (see Chapter 2) and has been designated the Molar Concentration Ratio (MCR).

MCR values for the untreated soils were high and similar except in soil 11 where the ratio was very low (Fig. 4.13). However, for the treatments which included Ca (2 to 8) the increases in soluble Ca were much greater than the associated changes in soluble Al so that large increases in MCR resulted from the additions irrespective of the changes in Al (Fig. 4.13.).

Values for MCR were shown to be significantly correlated with both root weight (r = 0.701**) and P uptake (r = 0.654*) for the range of treatments on the four soils. However, it can be seen from Figure 4.14 that in the absence of added P, P uptake did not respond to these increases which supports the earlier observations that higher base levels are more important in the presence of added P. It can also be seen that when the level of soluble Al is high this is the overriding influence on P uptake with the high base to Al ratio (MCR) offering little protection against the adverse effects of Al.

4.5. CONCLUSIONS

In this section the main conclusions reached are summarised in relation to the objectives given at the beginning of this chapter.

1. In the four untreated soils, 4, 9, 10 and 11 which spanned a wide range of extractable Al, (from 3.5 to 20.3 meq/100 g) all 3 forms of Al (extractable, exchangeable and soluble) were shown to be significantly correlated. For the eight soils examined in the previous chapter no corresponding correlation

could be established and it seems that more soils need to be examined to find out what inherent properties influence this relationship. The strong relationship between extractable Al and P sorption index was confirmed for this further group of soils. Sorption index was also found to be inversely correlated with soluble P and because of the inter-relationships between the three forms of Al, soluble P tended to decrease with increasing amounts of all forms of Al. There was however no similar relationship between extractable P and either PSI or any form of Al.

Although soluble P may be regarded as a measure of the intensity of P supply for plant growth the concentration of soluble P gave little indication of the amount of P actually taken up during plant growth especially on the high P fixing soil (11) where soluble P was very low. In the absence of added P, soluble P, extractable P and P uptake were all very low. The treatments, lime, gypsum and superphosphate did not influence all the soil properties equally and depending on the amounts of Al or Ca present initially, the size of the effects differed between the soils. Lime decreased all forms of soil Al but had least effect on extractable Al and little effect on soil P or PSI while superphosphate increased soil P, especially extractable P and reduced PSI but had little effect on soil Al. Gypsum had the least effect of all, although it did lower PSI and in some instances caused increases in soluble Al. The addition of superphosphate produced relatively small increases in soluble P, but without exception caused large increases in extractable P which were in most cases associated with large increases in P uptake. However, on soil 11 (formed on basalt) where the concentration of soluble Al was high, ryegrass only responded to added P in the presence of lime which also reduced the concentration of soluble Al.

Measurements of root growth, plant composition, lime induced changes in pH, soil Al and Ca and the molar concentration ratio have suggested some relationships between these factors and plant growth. However, further examination of the nature of the interactions between Al and plant growth is required before possible causal relationships can be described.

2. The single rate of lime addition used in this experiment lowered the amounts of all three forms of Al but had proportionally different effect on each form so that the correlation coefficients describing their inter-relationships were lowered. The magnitude of change was influenced by inherent soil properties and by the form in which Al occurred. In general the greatest proportional changes occurred in soils 4 and 9 in which the unit response in pH was also greatest. In soils 10 and 11 where the native Al levels were much higher the unit response in pH was least but the changes in absolute amounts of extractable-, exchangeable- and soluble Al were largest, and as a consequence the effects on plant growth were most evident. In order to understand these differential effects of lime in the different soils further work is required, using incremental additions of lime, or soils of contrasting Al status.

3. Extractable Al appeared to have little direct effect on plant growth but was inversely related to soluble P through its effect in P sorption. However P uptake and plant growth in general was rarely correlated with the amount of soluble P. Exchangeable Al was more closely and inversely related to plant growth particularly in instances where initial high levels were significantly reduced by lime and P uptake was correspondingly increased. This effect was most clearly demonstrated in the basalt soil (11) where plant growth was especially poor even when P was added, unless lime was also included.

Soluble Al was related to plant growth through its influence on root development and it is suggested that exchangeable Al may not influence plant growth directly but only indirectly by acting as a reservoir for soluble Al. However, the relationship between exchangeable and soluble Al needs to be investigated further with respect to effects of other soil properties.

When the concentration of soluble Al was very high (0.4×10^{-3} M) root growth was almost totally inhibited and even at concentrations between 0.1 and 0.2×10^{-3}M root growth appeared to be impaired: at concentrations below 0.1×10^{-3}M Al did not appear to influence root growth. The mechanisms by which Al brought about inhibition of root growth could not be elucidated from these results although interference with metabolism and mitosis may be involved. The molar concentration ratio, $([\mathrm{Ca} + \mathrm{Mg}]^3 : [\mathrm{Al}]^2)$ gave a significant correlation with both root growth and P uptake and it is possible that some of the interference with growth may have been due to Al/Ca interactions in the roots and soil.

Although germination 'per se' was not influenced by soil Al the early appearance of symptoms associated with Al toxicity indicated that the early stages of plant growth were very sensitive to Al. This observation suggested that further investigation of the influence of Al on both seedling root development and on root growth in more mature plants might be justified. In view of the deleterious effects of soil acidity and Al on the growth of ryegrass methods of lowering the amounts of active Al need to be investigated if pasture improvement is to be successful on hill soils.

4. Calcium as gypsum (calcium sulphate) did not bring about the pH changes and associated effects on Al which were attributed to lime. Gypsum brought about much larger increases in exchangeable and soluble Ca than did lime and in some instances the addition of gypsum was accompanied by increases in soluble Al with detrimental consequences for root growth and P uptake. It was not possible to distinguish between the effects of the naturally low levels of Ca on plant growth from possible Al/Ca antagonism but it appears that adding Ca without increasing pH does not overcome the adverse effects of soluble Al.

SUMMARY

These hill soils were found to be very deficient in available P and supplementary P was required for significantly increased yields. Ryegrass however, only responded to added P when the concentration of Al was below 0.2×10^{-3} M in 10^{-3} M $CaCl_2$ and adverse effects of Al were still observed down to 0.1×10^{-3} M. The data also indicated that the inherently low Ca availability may be limiting the higher production made possible by the addition of P and that this situation could be aggravated by Al.

CHAPTER 5

POT EXPERIMENT TO EXAMINE THE EFFECT OF GLUCOSE ADDITION ON P UPTAKE BY RYEGRASS

5.1. INTRODUCTION AND OBJECTIVES

In this experiment glucose was added to two of the soils included in the previous experiment to provide an additional energy source for micro-organisms. The objectives were as follows:-

1. Test, by assessing P uptake by ryegrass, whether the addition of glucose, through its influence on microbial activity, can influence the supply of phosphorus for plant growth.
2. Examine the interactions of acidity, and lime induced pH changes, on any energy related changes in the supply of P for uptake by ryegrass.

5.2. EXPERIMENTAL

This pot experiment was run concurrently with the one described in the previous chapter so that glasshouse conditions and procedures were as detailed in Table 4.2A. The two soils used were 9 and 11 (Table 4.1A) and the treatments only differed from that experiment in two respects (1) glucose (4.5 g/pot was substituted for gypsum and (2) only 25% of the amount of superphosphate (≡ 20 kg/ha) was used (Table 5.1). The pots were arranged in 3 randomised blocks in the glasshouse. A fourth replicate was kept for the analysis of Truog extractable P, carbon and pH. Following the 3rd harvest after the roots had been removed pH and Truog P were measured on the soils.

Table 5.1. Glucose (GL) superphosphate (P) and lime (L) treatments applied to soils 9 and 11

$GL_o\ P_o\ L_o$	1	$L_1 = 1.0$ g $CaCO_3$
$GL_1\ P_o\ L_o$	2	≡ 1250 kg/ha (20 meq Ca/pot)
$GL_o\ P_o\ L_1$	3	
$GL_1\ P_o\ L_1$	4	$P_1 = 0.18$ g superphosphate
$GL_o\ P_1\ L_o$	5	≡ 20 kg P/ha (17.83 mg P/pot)
$GL_1\ P_1\ L_o$	6	
$GL_o\ P_1\ L_1$	7	$GL_1 = 4.5$ g glucose/pot
$GL_1\ P_1\ L_1$	8	1.5% w/v (1.8 g C/pot)

Because of the contrasting treatment effects on the 2 soils the respective data have been analysed separately using the methods of YATES (1937). Data, analysis of variance and two way interaction tables are in the appendix (5.1A to 5.3A).

5.3 RESULTS

5.3.1. VISUAL OBSERVATIONS

All pots treated with glucose became covered with fungal mycelium after two weeks, suggesting no apparent effect of soil pH or soil P status.

P deficiency symptoms were observed on some plants growing in soil 9 after two weeks and were most pronounced in the glucose treatments and those with no additional P. The symptoms were less noticeable in the latter weeks. On soil 11, ryegrass grew poorly in the absence of lime.

5.3.2. DRY MATTER PRODUCTION AND P UPTAKE

Root and herbage weights were treated together because of the similarity in treatment response. DM and P uptake were significantly correlated (r = 0.99***, 0.93*** on soils 9 and 11 respectively) and treatment effects are discussed for P uptake (see Figure 5.1).

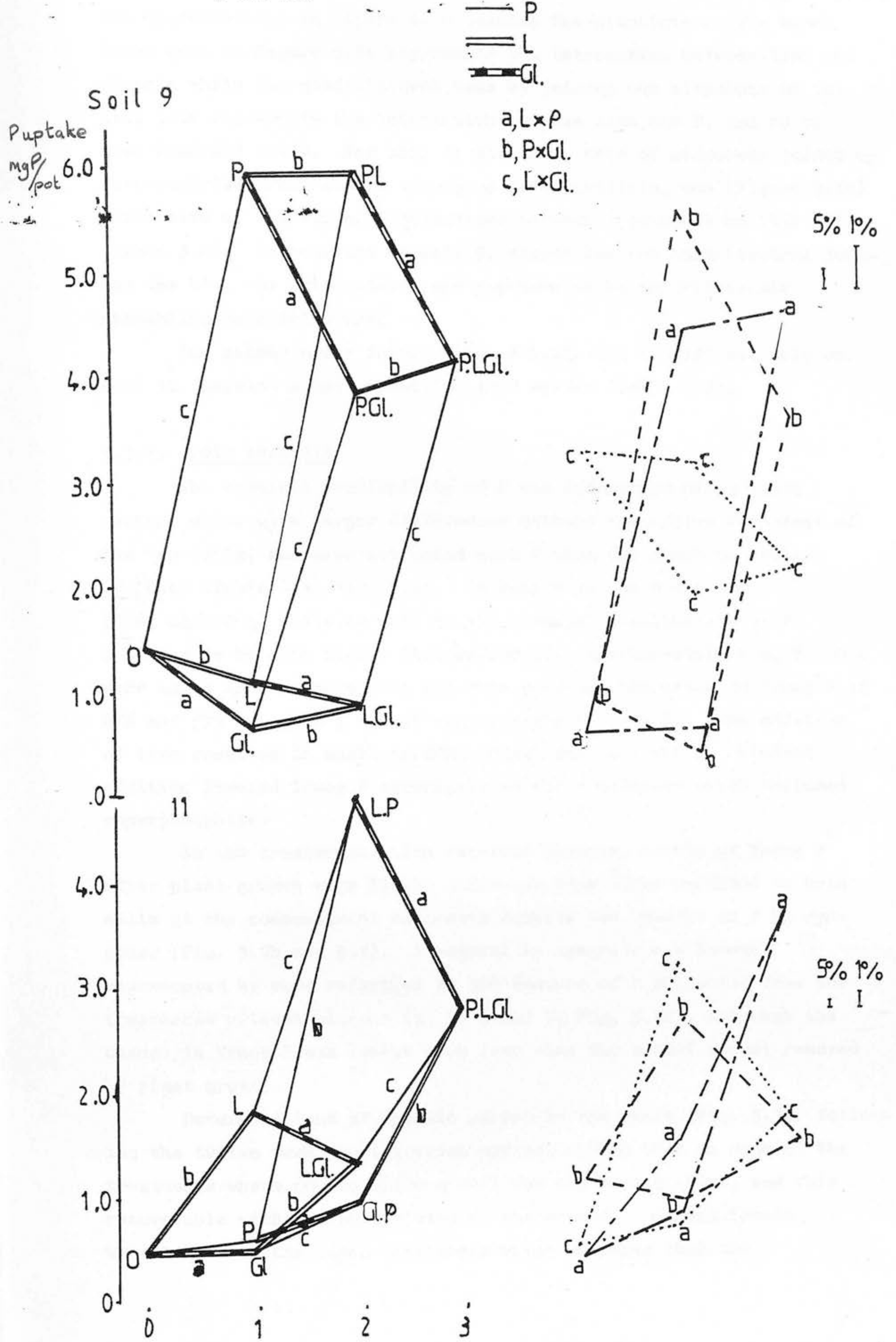
On soil 11 all treatments produced significant responses. Lime and superphosphate increased P uptake, glucose reduced P uptake (Table 5.2). On soil 9, P uptake exceeded that on soil 11 (mean P uptake 3.09 compared with 1.62 mg/100 g) and only superphosphate had a significant effect, increasing P uptake.

Table 5.2. Treatment Effects on Total P Uptake (mg P pot) on Soils 9 and 11

	9	11
O	-	-
P	+ 3.93***	+ 1.19***
L	0	+ 2.02***
Gl	- 1.28***	- 0.59***
P.L	+ 0.01	+ 0.88***
P.Gl	- 0.73***	+ 0.35***
L.Gl	+ 0.24	- 0.85***
P.L.Gl	- 0.05	- 0.27***
SED	0.183	0.033
CV%	7.24	3.64

Significance P 0.05*, P 0.01**, P 0.001***

Fig. 5.1. Interaction diagrams illustrating a 2^3 experiment using lime, superphosphate and glucose on P uptake from soils 9 and 11.



The effects of first order interactions are shown by Figure 5.1b. The quadrilateral in Figure 5.1b joining the midpoints on the black lines seen in Figure 5.1a represents the interaction between lime and glucose while the quadrilateral made by joining the midpoints on the pied line represents the interaction between lime and P, and so on (see RICHARDS 1941). For soil 11 all three sets of midpoints joined up form quadrilaterals widely diverging from parallelograms (Figure 5.1b) indicative of the strong interactions between treatments on this soil (Table 5.2). In contrast on soil 9, except for the quadrilateral joining the b's, the interactions are represented by quadrilaterals resembling parallelograms.

The second order interaction, P.L.Gl, was significant only on soil 11, causing a nett reduction in P uptake (Table 5.2).

5.3.3. SOIL ANALYSIS

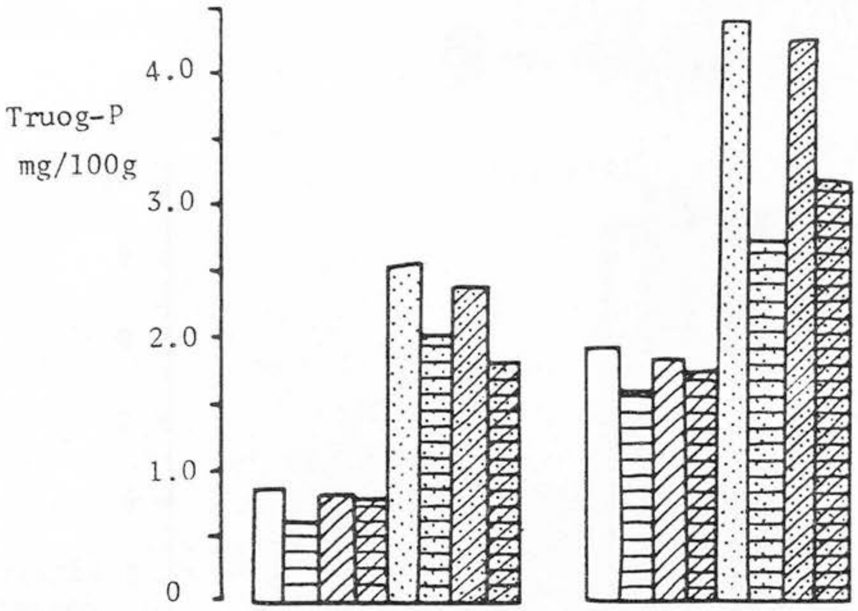
The chemical availability of P was determined using Truog reagent which gave larger differences between the native P content of the two soils, and also extracted more P than did ammonium acetate (NH_4OAc) (Table 4.1; Fig. 5.2). In soil 9 native P was low (0.85 mg/100 g) while in soil 11 the chemical availability of P appeared to be much higher (4.4 mg/100 g). Approximately 6 mg P/100 g were added as superphosphate and this produced increases in Truog P of 67% and 57% in soils 9 and 11 respectively (Fig. 5.2). The addition of lime resulted in small ($<$ 10%) reductions in Truog P. Glucose addition lowered Truog P especially in the treatments which included superphosphate.

In the treatments which received glucose, levels of Truog P after plant growth were little different from those recorded in both soils at the commencement of growth despite the removal of P by ryegrass (Fig. 5.2b and 5.1). P removal by ryegrass was however represented by some reduction in the amounts of P extracted from the treatments without glucose (1, 3, 5 and 7; Fig. 5.2b), although the change in Truog P was always much less than the actual amount removed by plant growth.

Determinations of organic carbon in the soils (Fig. 5.3), following the twelve week equilibration period, showed that in none of the treatments where 600 mg C/100 g soil was added as glucose, was this recoverable with the sensitivity of the method. Carbon levels were lowest in the limed treatments which suggests that the

Fig 5.2 Changes in the levels of Truog P extracted from soils 9 and 11 treated with glucose, lime and superphosphate (a) pre and (b) post plant growth.

(a) pre growth



(b) post growth

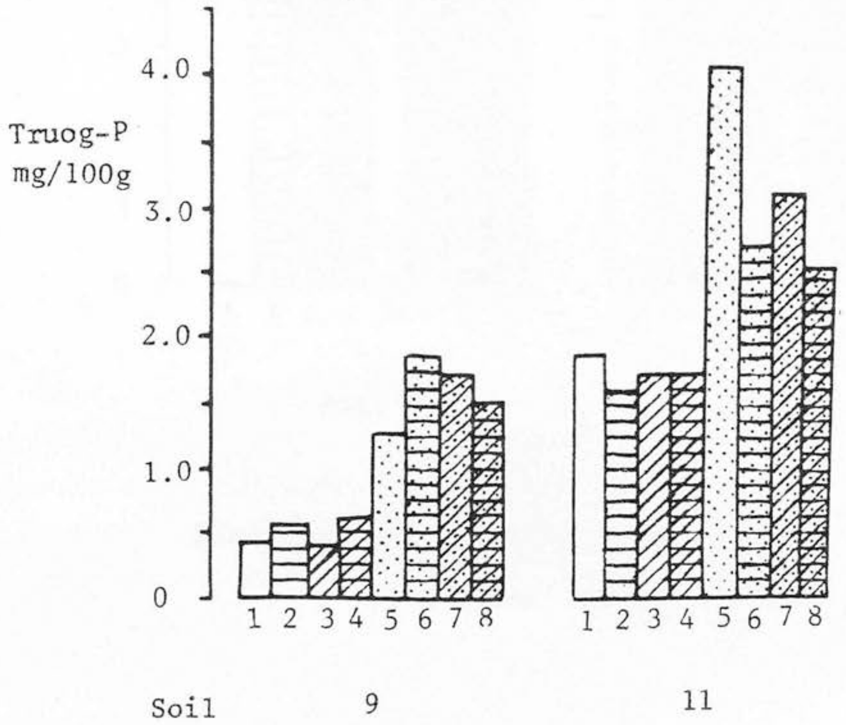
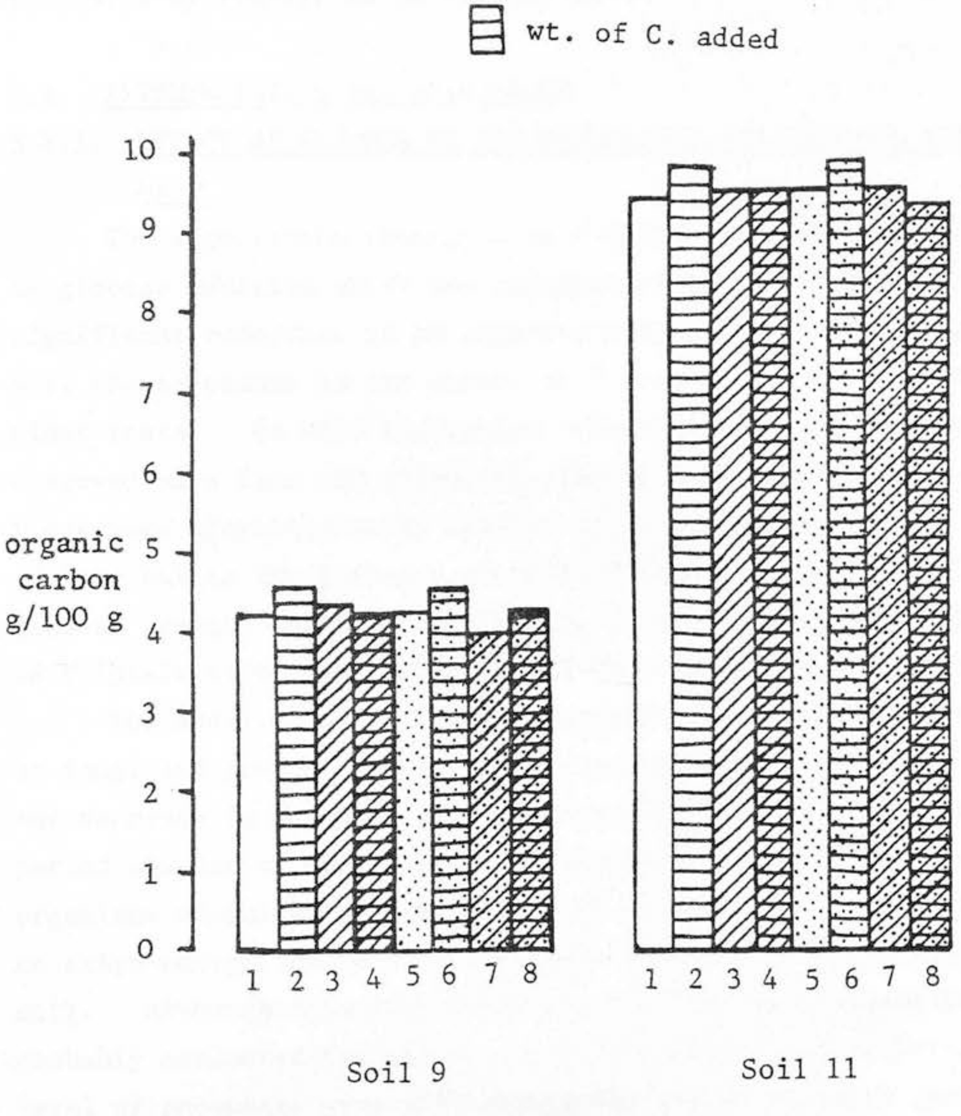


Fig 5.3 Changes in the organic carbon content of soils 9 and 11 treated with glucose, lime and superphosphate.



Footnote: 4.5 g/pot glucose added.

(1.8 g/pot carbon added)

correction of the high acidity of these soils (pH 4.4 and 3.9 in 9 and 11 respectively) may have influenced the activity of 'decomposer' organisms in these soils. However, direct measurements of their activity, such as monitoring O_2 and CO_2 fluxes were not made. pH was not influenced by glucose or P addition but was increased by liming, as in chapter 4.

5.4. INTERPRETATION AND DISCUSSION

5.4.1. EFFECT OF GLUCOSE ON THE BIOLOGICAL AND CHEMICAL AVAILABILITY OF P

The significant reduction in P uptake on soil 9 attributed to glucose addition which was accompanied by only a small and non-significant reduction in DM suggests that its main effect in this soil was to reduce in the amount of P available for uptake by plant roots. On soil 11 similar effects of glucose were only observed when lime was added (treatments 4 and 8, Fig. 5.1b) and these were proportionately smaller than on soil 9. In the absence of lime but in the presence of added P on soil 11 the addition of glucose brought about an increase in P uptake which was reflected in P uptake values far more than in DM values.

The addition of glucose was associated with enhanced growth of fungi and probably other micro-organisms. It is likely that the decrease in Truog P observed after the 3 month equilibration period was due to microbiological processes in which the micro-organisms assimilated both the native and applied P using glucose as an extra energy source to the organic matter already present in soil. Although this immobilisation of P by micro-organisms probably accounted for the decrease in P uptake, by reducing the level of phosphate available during the period of plant growth it appears that this effect may be only transitory because the similarity in Truog P following plant growth with that initially present suggests that P was also being mineralised and returned to the inorganic pool. BIRCH (1964) found that the addition of a readily metabolisable source of energy brought about large increases in the microbial population. The consequent immobilisation of P was followed by its release due to dephosphorylation and cell lysis when the energy source had been used up.

In this experiment on soil 9, where there was no confounding influence of high levels of Al influencing root growth and thus P uptake, there was a significant correlation between the amount of Truog P in the eight treatments measured before plant growth and P uptake (r = 0.99***). The correlation between P uptake and Truog P measured after growth however was poor (r = 0.53 NS). This suggests that if P was released from its immobilised form release occurred too late for it to be utilised during the three month period of plant growth; or that the amount released was only sufficient to replace the P removed by ryegrass. There was no visual sign nor evidence from the sequential harvests, that P was more available in the latter period of the experiment.

In an incubation experiment GHOSHAL and JANSSON (1975) measured changes in the amount of acetic acid extractable P from a soil with P added, alone, and with 0.5% glucose. They found that in the P alone treatment approximately 66% was fixed by the soil after 4 days while in the P + glucose treatment the amount of acetic acid extractable P was reduced to just below the amount of P in the control. They did not aportion the change in extractable P to processes of fixation or immobilisation but showed that the period of reduction in extractable P (25 days) in the treatment including glucose was followed by a steady increase in extractable P. Because similar observations were not made in the absence of glucose they concluded that a large proportion of the added P had been immobilised but was slowly being returned to the inorganic pool.

GHOSHAL and JANSSON (1975) also monitored changes in pH and organic carbon and found that the addition of glucose was associated with the immediate liberation of many organic acids, a rapid change in pH, and a consequent increase in fungal growth. STRUTHERS and SIELING (1950) found that organic acids (e.g. citric acid) which were exuded by micro-organisms could form stable complexes with Fe and Al over the pH range 4 to 5 and thereby reduce P retention in the soils. MULLER et al. (1977) showed that citric acid was able to decrease the sorption of P by the soil from KH_2PO_4 solution while DATTA and SRIVASTRA (1963) found that when the content of organic carbon was high the affinity of sesquioxides surfaces for phosphate ions was reduced. These data suggest that both the availability of P and the plants ability to exploit soil P might be higher either where Al was complexed by organic acids or where the affinity of electro positive Al surfaces for P was reduced as a result of adsorption of organic acids.

In soil 9 where the capacity of the soil to fix P, the extractable Al content, and the concentration of soluble Al were all low (chapter 4) no increase in P availability attributable to glucose addition was demonstrated, and throughout the experiment in this soil more P appeared to be immobilised than was released. On soil 11 though, there was some evidence of enhanced P uptake with glucose treatment (6), which appears to be due to increased levels of P in solution since root growth did not increase. Possible explanations for this are that P fixation was being reduced by organic acids produced by the micro-organisms or that soluble Al was complexed and was thus unable to precipitate the phosphate. It is, however, unlikely that such complexing would lead to an improvement in root growth as the level of soluble Al would need to be very significantly reduced for this (from 0.4 to $< 0.15 \times 10^{-3}$ M)(Chapter 1).

5.4.2. EFFECT OF ACIDITY ON P SUPPLY

In the presence of lime as also recorded by LARSEN (1967) the breakdown of organic carbon was much greater irrespective of whether P had been added or not. It was suggested (cited by LARSEN, 1967) that this stimulatory effect of lime may not necessarily be due to increased pH but rather to the change in the Ca:Mg ratio associated with the addition of lime. The apparent lack of stimulation accompanying the addition of superphosphate may be due to the fact that the availability of P was not the main factor limiting the growth of these micro-organisms. Although they must have had a high requirement for P in the assimilation of new tissue and to produce energy , ATP, to utilise the glucose. On the basis of this it might have been expected to record greater depression of P uptake on the limed treatments. In fact, the opposite was true for soil 9 when lime and glucose were added together the nett reduction in P uptake was slightly less than when either were added separately (Fig. 5.1). A possible explanation is that the apparent reduction in the level of soluble P accompanying liming was diminished by the addition of glucose and although more P was used by the micro-organisms the nett effect was that slightly more P became available in the limed treatments.

In soil 11 where both lime and glucose individually enhanced P uptake their combined effect was not additive (treatments 4 and 8). In fact the effects of glucose together with lime were more similar to the effect of glucose on soil 9 suggesting that glucose is only effective in enhancing P uptake when the soil Al content is high. MULLER et al. (1977) found that although complexants could be shown to decrease P sorption in the laboratory, pot experiments with maize failed to demonstrate increased utilisation of P by the plants. DALTON et al. (1952) however did show enhanced P uptake in the presence of organic matter (starch).

5.5. CONCLUSIONS

The results from this experiment suggest that the addition of glucose to an acid soil with high levels of extractable and soluble Al may enhance P uptake possibly by the formation of complexes between Al and metabolites resulting from enhanced fungal activity. Where soil Al levels were not so high the addition of glucose apparently reduced P uptake through P immobilisation. The difference between P uptake by ryegrass and that apparently available, extracted in Truog reagent, was greater than with MORGAN reagent (ammonium acetate) used in the previous experiment. In view of the good relationship between Morgan extractable P and P uptake shown in chapter 4 and because of the lower discrepancy between Morgan extractable P and P uptake this method was adopted for subsequent experiments.

CHAPTER 6

EFFECTS OF LIME ON SELECTED SOIL PROPERTIES AND PLANT GROWTH

6.1. INTRODUCTION AND OBJECTIVES

The study of four soils of contrasting Al status described in Chapter 4 showed that lime addition had profound effects on the amounts of Al in the soil. However, only one level of lime was used and the pH response differed between soils. In the experiment described here increments of lime were applied to two soils of widely differing Al status (9 and 11a). The properties of soil 9 were given in Tables 4.1, 4.1A but soil 11a was from a second collection made at the same site as soil 11 in the autumn of 1977: it had a slightly lower pH and higher Al content than the original soil 11. The specific objectives of these experiments were as follows:-

1. Examine the effects of incremental additions of lime on pH and its relationship with extractable, exchangeable and soluble Al.
2. Examine the effects of lime on the chemical and biological availability of P.
3. Examine the influence of duration of the equilibration period on the effect of lime on pH and soil Al.

6.2. EXPERIMENTAL

Incremental additions of 100 mg$CaCO_3$ were applied to 100 g of soil in 7 steps upto the equivalent of 3,000 kg lime/ha (Table 6.1.). Preliminary work showed that these amounts raised the pH to about 7 which adequately covers the pH range encountered in upland agriculture.

Table 6.1. Incremental lime treatments applied to soils 9 and 11a

Treatment :-	0	1	2	3	5	8	10	15
Wt $CaCO_3$ (g/100 g soil)	0	0.1	0.2	0.3	0.5	0.8	1.0	1.5
$CaCO_3$ (meqCa/100 g soil)	0	2.1	4.2	6.3	10.6	15	21.2	31.8
$CaCO_3$ (approx. equiv. kg/ha)	0	200	400	600	1000	1600	2000	3000

6.2.1. PHASE I

7.5 cm diameter pots containing the equivalent of 100 g air dry soil, mixed with the appropriate increments of lime for both soils were made up, in quadruplicate. All 4 replicates were thoroughly wetted and kept at 60% FC in the store for 1 month. 7 days prior to sampling 1 set of replicates was brought to and maintained at 100% FC. A sample of this wet soil was removed, and placed over a Buchner funnel attached to a vacuum pump, from which 5 ml of the soil solution were extracted under pressure for the determination of P and Al. The soil remaining in the pots was air dried, sieved and used for the determination of pH, exchangeable- and extractable-Al, extractable-P, exchangeable acidity, PSI and % carbon by the methods described in Chapter 2.

6.2.2. PHASE II

The 3 remaining replicates were kept at 60% FC for a further 5 months before being bulked and a 20 g subsample removed for soil analysis which included - pH, PSI, exchangeable acidity, extractable- and exchangeable-Al. The suction method was not used for Phase II to measure Al and P. Amounts of soluble P, Al, Ca, Mg, K, Fe and Mn were measured in 10^{-3}M $CaCl_2$, so that the results could be expressed in terms of a given amount of soil.

The bulked soil was divided into 3 lots and replaced in the pots. 30 seeds of ryegrass (S24) were sown in each pot. The pots were transferred to the glasshouse and arranged randomly in 3 blocks. Lighting was supplemented using overhead lamps providing between 60 and 70 watts m^{-2} for 16 hours a day. In order to reduce any variation due to uneven lighting or heat emitted from the lamps, pots were moved round weekly. NH_4NO_3 equivalent to a total of 90 kg N/ha was applied in solution at intervals over the 30 day growing period, taken from germination. A single harvest was taken down to soil level. Because of the small amounts of plant material, bulked replicates were prepared for herbage and root analysis. P, Ca, Mg, Mn and Fe were determined on the herbage and additionally K and Al were measured in the roots, by the methods described in Chapter 2.

The results of the analyses for soil and plant material are given in Tables 6.1A to 6.3A. As the replicates for the plant material were bulked, statistical analysis of the data was not possible. The main features of the results are described in the next section.

6.3. RESULTS : PHASES I AND II

6.3.1. SOIL ANALYSIS

In the absence of lime the pH of both soils 9 and 11a was low (3.8 and 3.2 respectively) and, as observed in Chapter 4 the lower pH of soil 11a was associated with larger amounts of exchangeable acidity and exchangeable Al.

With increasing lime additions both soils showed increases in pH, but the incremental response on soil 11a was less than on soil 9 (Fig. 6.1a). The largest additions of lime raised the pH of soils 9 and 11a to 6.9 and 6.6 respectively. As pH increased so both exchangeable acidity and exchangeable Al decreased (Fig. 6.1a). Because the rate of decrease in exchangeable acidity was greater for soil 11a than soil 9, the values tended to converge with increasing additions of lime. When soil pH had been increased to around 5.5, requiring 5 and 10 increments of lime in soils 9 and 11a respectively, exchangeable acidity was lowered to values $<$ 1 meq/100 g. Exchangeable Al accounted for more than 90% of the exchangeable acidity in both soils and was correspondingly lowered by lime additions. Its value fell to below 1 meq/100 g at a lower pH requiring less lime than exchangeable acidity to reduce its value (Fig. 6.1a). The fall in both exchangeable acidity and exchangeable Al was more pronounced in soil 11a than soil 9 until the level of lime brought the pH of soil 11a upto that measured initially for soil 9. Above that pH the rate of change per unit of pH was similar in both soils.

Comparison of Figures 6.1a and 6.1b for equilibration periods of 1 and 6 months respectively shows that the duration of contact between lime and soil had no appreciable influence on the effects of lime on the measured properties.

The duration of contact between the soil and lime also had little appreciable effect on extractable Al (Fig. 6.2a and b). This was lowered in both soils, as it was for these soils in Chapter 4, but here the incremental changes due to lime can be examined. As more lime was added to soil 11a the effect was

Fig 6.1 Changes in the amounts of Exchangeable acidity, Exchangeable Al and pH in soils 9 and 11a after (a) 1 month and (b) 6 months equilibration with different levels of lime

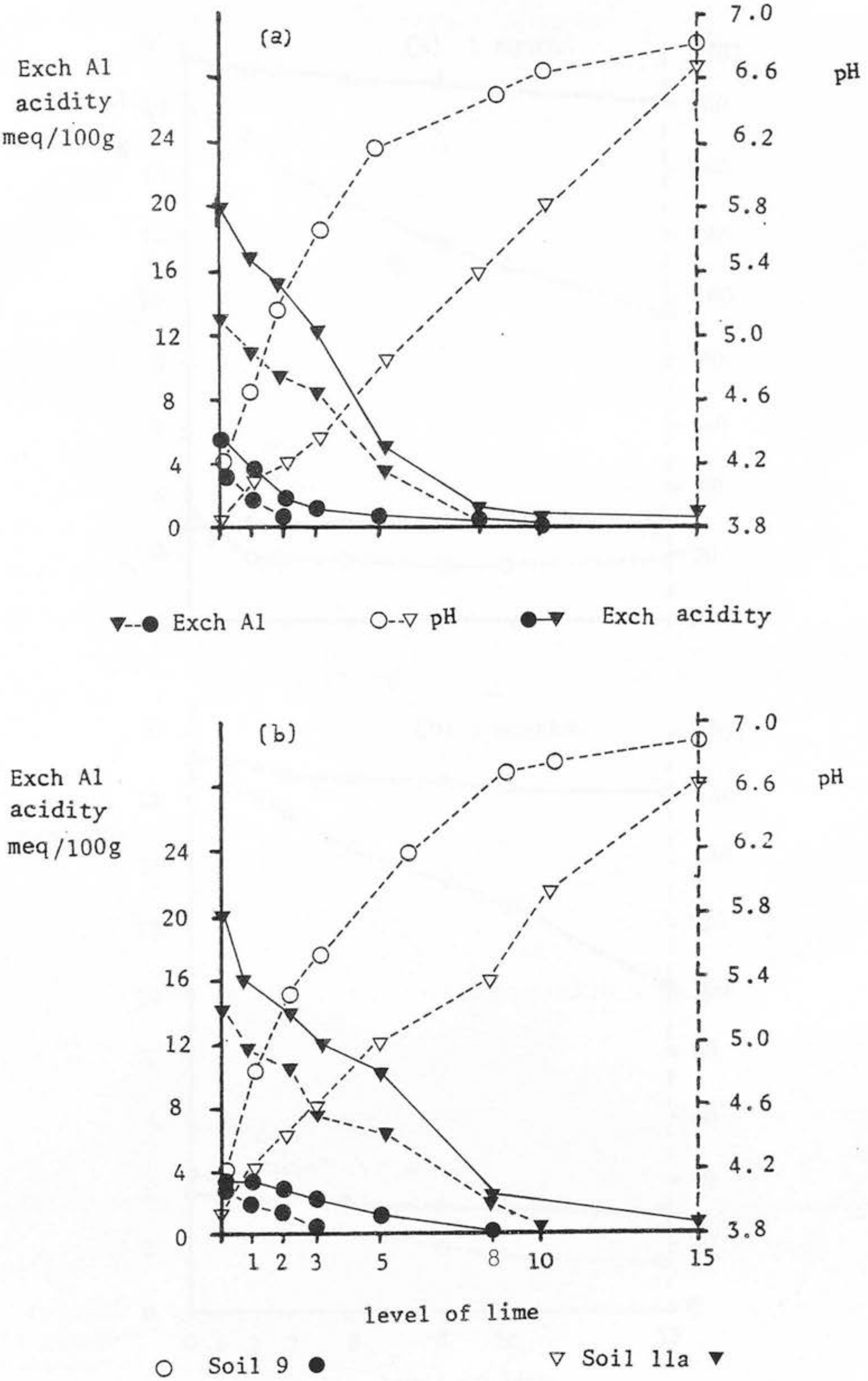
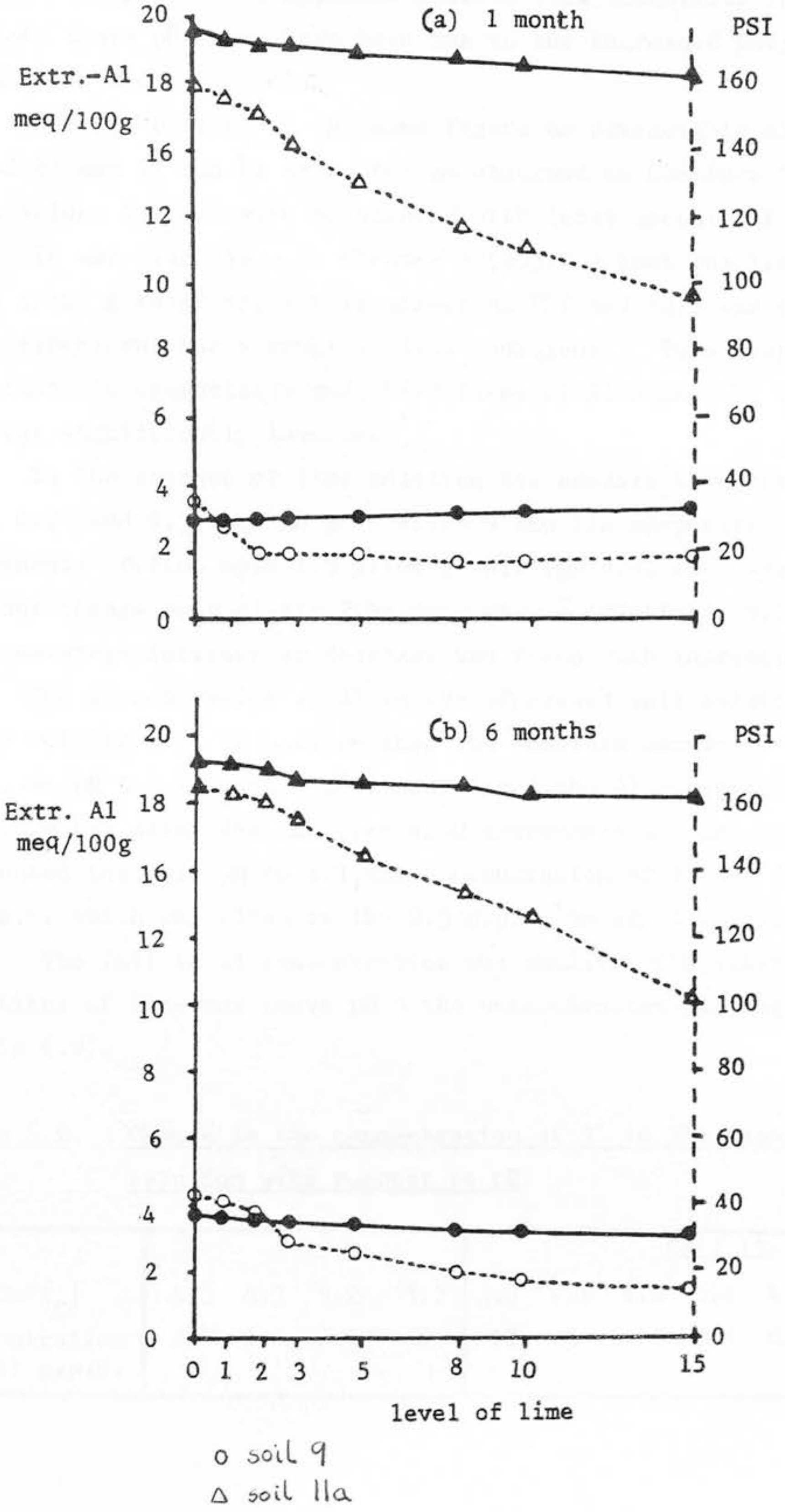


Fig 6.2 Changes in the amounts of Extractable Al and PSI in soils 9 and 11a after (a) 1 month and (b) 6 months equilibration with different levels of lime



similar but less pronounced than for exchangeable Al. In contrast in soil 9 extractable Al was lowered by 50% (but only 2 meq/100 g) with the first 2 increments of lime, but thereafter showed no further change. This apparent reduction in solubility in ammonium acetate above pH 5 may have been due to the increased polymerization of Al hydroxide.

PSI was plotted on the same figure as extractable Al (Fig. 6.2 a and b) and it can be seen that as observed in Chapters 3 and 4, high values for PSI were associated with large amounts of extractable Al. It was also shown in Chapter 4 (4.3.3.) that one lime treatment (0.3 g/100 g soil) had little effect on PSI and this was confirmed in this experiment for a range of lime additions. Thus despite the reduction in extractable and other forms of Al caused by liming PSI was not significantly lowered.

In the absence of lime addition the amounts of extractable P were 0.22 and 0.34 mg/100 g in soils 9 and 11a respectively and increments of lime upto 1.5 g/100 g soil (pH 6.9, 6.6 respectively) did not change extractable P by more than ± 10% (Table 6.1A). No consistent increase or decrease was found with increasing pH.

The concentration of Al in the expressed soil solution appeared to be related more to soil pH than the absolute amount of lime added. Thus, at pH 3.8 in soil 11a(without lime) the Al concentration was 17 p.p.m but after the addition of 2 increments of lime, which increased the soil pH to 4.1, the concentration of Al had fallen to 3 p.p.m. which was close to the 2.5 p.p.m. measured in soil 9 at pH 4.2. The fall in Al concentration was smaller with subsequent additions of lime but above pH 5 the concentration was negligible (Table 6.2).

Table 6.2. Change in the concentration of Al in the expressed soil solution with respect to pH.

	Soil 9				Soil 11a					
pH ($CaCl_2$)	4.2	4.7	5.2	5.2	3.8	4.1	4.2	4.4	4.9	4.9
concentration of Al p.p.m.	2.5	1.0	0.5	0	17	3	1.0	0.5	0.2	0

Fig 6.3 Changes in the amounts of (a) Soluble Al and Mn (b) Soluble Ca & Mg and (c) Soluble K in soils 9 & 11a after 6 months equilibration with different levels of lime.

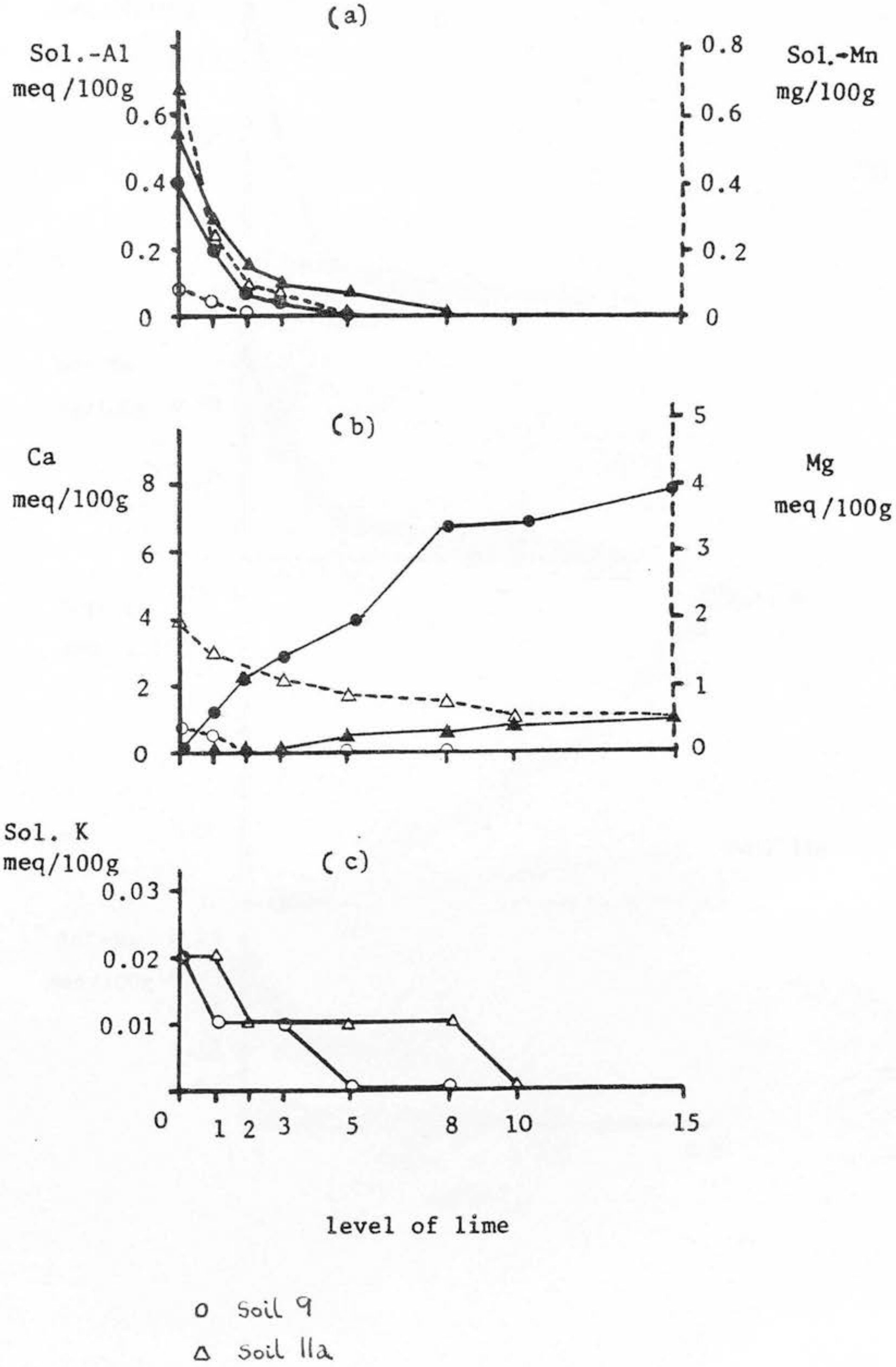
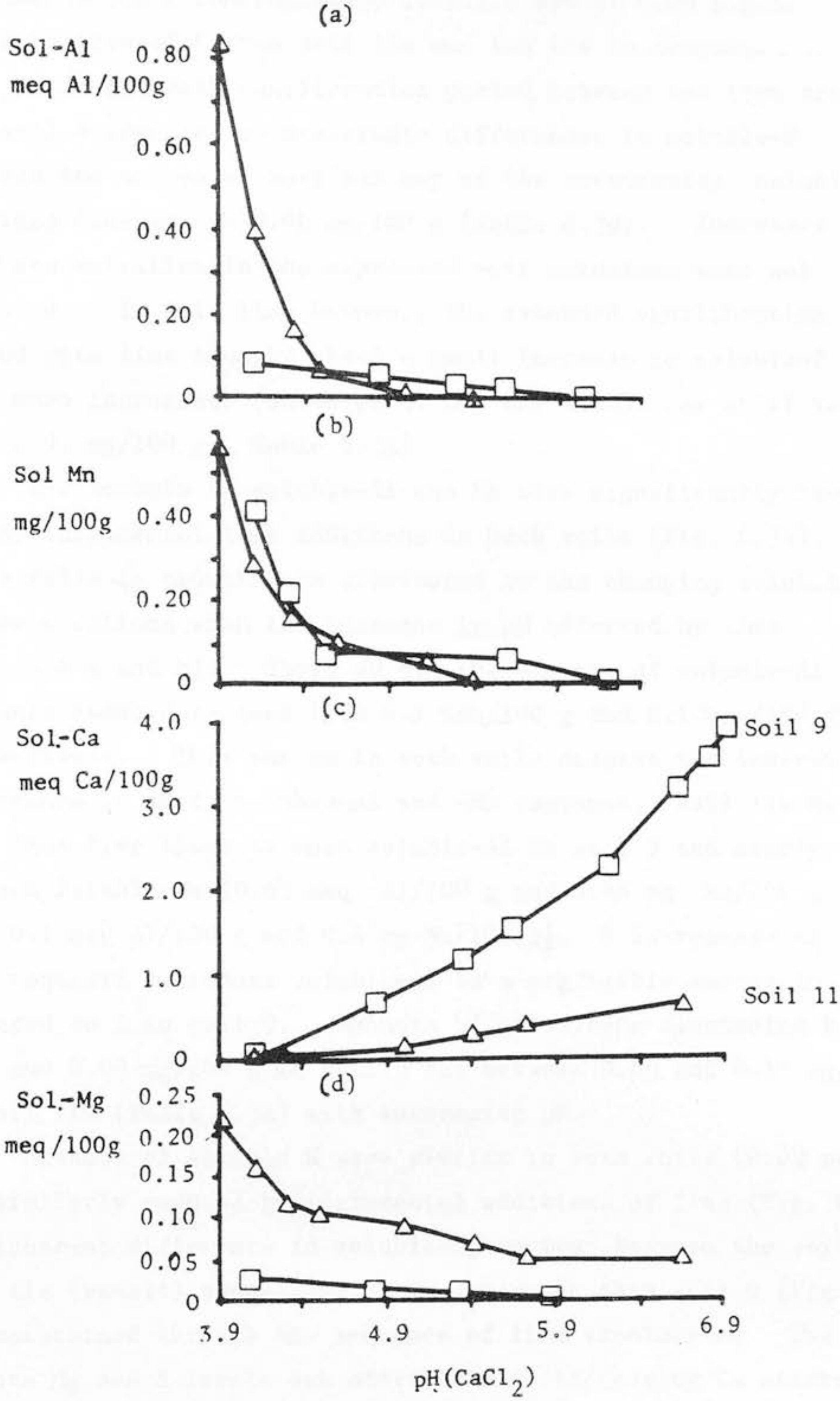


Fig. 6.4 Relationships between the amounts of (a) Al, (b) Mn, (c) Ca, and (d) Mg soluble in 10^{-3} M $CaCl_2$ solution, and pH in soils 9 and 11a.



The concentration of P in the soil solution expressed from soil 9 increased from 0.05 p.p.m. in the untreated soil to 0.07 p.p.m. with the first five increments of lime. With subsequent increments the P concentration levelled out at 0.09 p.p.m. The concentration of P from soil 11a was too low to measure.

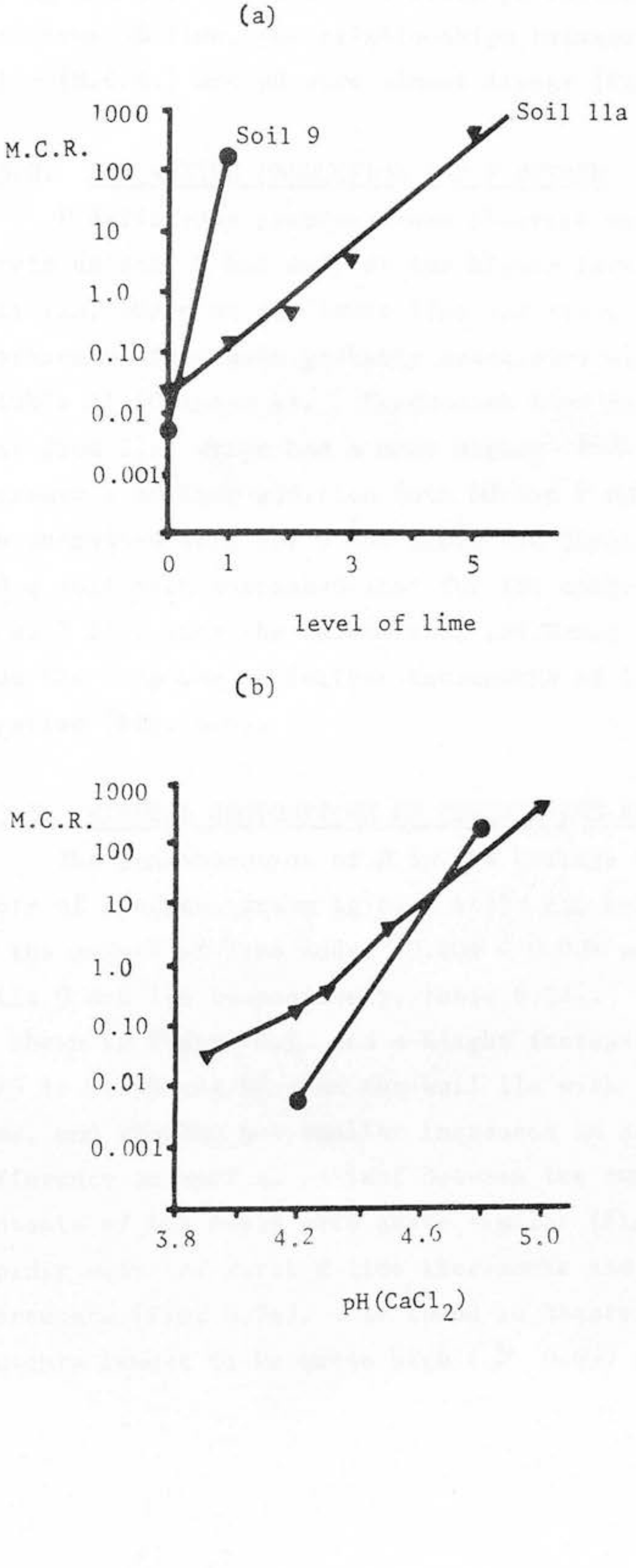
The six month equilibration period between the lime treatments and soil 9 produced no measurable differences in soluble-P between the untreated soil and any of the treatments; soluble-P remained constant at 0.02 mg/100 g (Table 6.3A). Increases in P concentration in the expressed soil solutions were not detected. In soil 11a, however, the extended equilibration period with lime brought about a small increase in soluble-P with 8 or more increments (above pH 5) but the amount was still very low (0.01 mg/100 g; Table 6.3A).

The amounts of soluble-Al and Mn were significantly lowered by the incremental lime additions in both soils (Fig. 6.3a). These falls in amounts are attributed to the changing solubilities of these cations with the increase in pH effected by lime (Fig. 6.4 a and b). Above pH 4.4 the amounts of soluble-Al and -Mn were reduced to less than 0.1 meq/100 g and 0.1 mg /100 g respectively. This was so in both soils despite the inherent difference in their soluble-Al and -Mn contents; soil 11a had more than five times as much soluble-Al as soil 9 and nearly twice as much soluble-Mn (0.55 meq Al/100 g and 0.68 mg Mn/100 g compared with 0.1 meq Al/100 g and 0.4 mg Mn/100 g). 8 increments of lime were required to reduce soluble-Al to a negligible amount in soil 11a compared to 2 in soil 9. Amounts of soluble-Fe fluctuated between 0.06 and 0.09 mg/100 g in soil 9 and between 0.06 and 0.16 mg/100 g in soil 11a (Table 6.3A) with increasing pH.

Amounts of soluble K were similar in both soils (0.02 meq/100 g) and similarly reduced by incremental additions of lime (Fig. 6.3). The inherent difference in soluble-Mg content between the soils, with 11a (basalt) containing 7 times more Mg than soil 9 (Fig. 6.3) was maintained through the sequence of lime treatments. The fall in both Mg and K levels was attributed to increasing Ca saturation of exchange sites and a change in the affinity of exchange surfaces for these ions, rather than to the lowering of their solubilities with increasing pH (THOMAS and COLEMAN, 1959).

Both untreated soils adsorbed Ca from the 10^{-3} M $CaCl_2$ solution, but soil 11a adsorbed 9 ppm Ca compared to the loss of only 2 ppm to soil 9. Increases in soluble Ca per

Fig 6.5 Relationships between the Molar Concentration Ratio and (a) the level of lime addition and (b) pH in soils 9 & 11a.



unit rise in pH were greatest in soil 9. The rise in amount of soluble Ca increased above pH 5.6 in this soil and above 5.0 in soil 11a corresponding to the pHs at which the concentrations of Al were negligible. (Fig. 6.4). Comparison of this data with those of KAMPRATH and FOY (1971) suggest that this may coincide with Ca saturation of the CEC exceeding 70%. As a result of these changes in the levels of Ca, Mg and Al, and with increasing pH associated with the incremental additions of lime, the relationships between the Molar Concentration Ratio (M.C.R.) and pH were almost linear (Fig. 6.5b).

6.3.2. DRY MATTER PRODUCTION AND P UPTAKE

P deficiency symptoms were observed on all lime treatment levels on soil 9 but only at the higher levels of lime addition on soil 11a, where at the lower lime additions there was a marked improvement in growth probably associated with the reduction in soluble Al (Chapter 4). Production from soil 9 always exceeded that from 11a, which had a much higher PSI. At the lower increments of lime addition both DM and P uptake were less than on the untreated soil for 9 but where the application exceeded 1.0 g/100 g soil both surpassed that for the untreated soil. Similarly on soil 11a, once the deleterious influence of Al had been overcome the response to further increments of lime was small or even negative (Fig. 6.6).

6.3.3. MINERAL COMPOSITION OF HERBAGE AND ROOTS

The concentration of P in the herbage was higher than in the roots of ryegrass grown in both soils and neither were influenced by the amount of lime added (0.20% ± 0.02% and 0.14% ± 0.03% on soils 9 and 11a respectively, Table 6.3A). Root P content is is shown in Figure 6.7 and a slight increase in % P content from 0.15 to 0.19% can be seen for soil 11a with increasing levels of lime, and similar but smaller increases in soil 9. Despite the difference in soil Al content between the two soils the % P contents of the roots were quite similar (Fig. 6.7a) and decreased rapidly with the first 2 lime increments and more slowly with further increments (Fig. 6.7a). As found in Chapter 4 (4.3.6) root Al contents tended to be quite high ($>$ 0.4%) regardless of the

Fig 6.6 Dry Matter and P Uptake as Influenced by a range of lime addition to soils 9 & 11a.

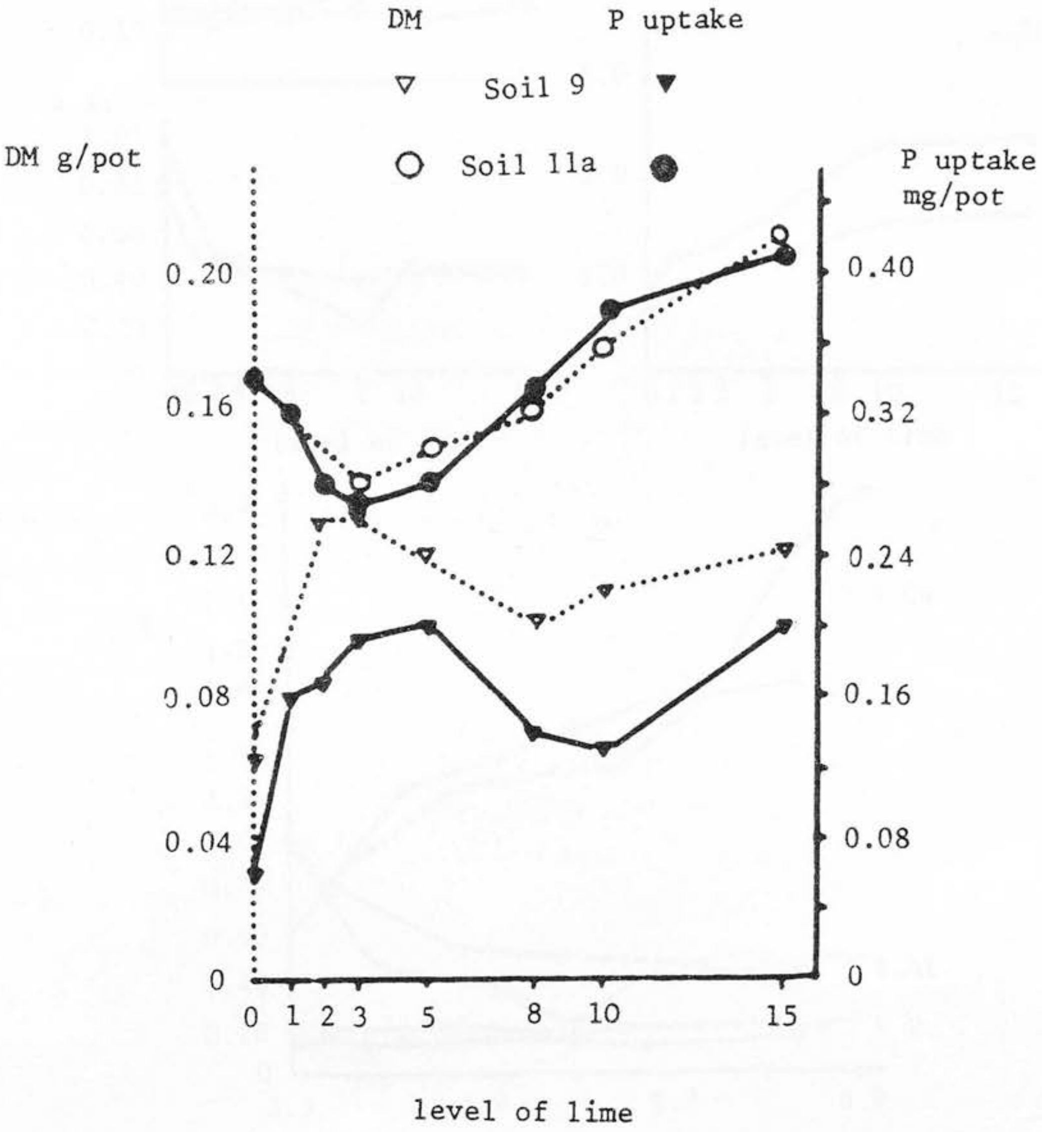
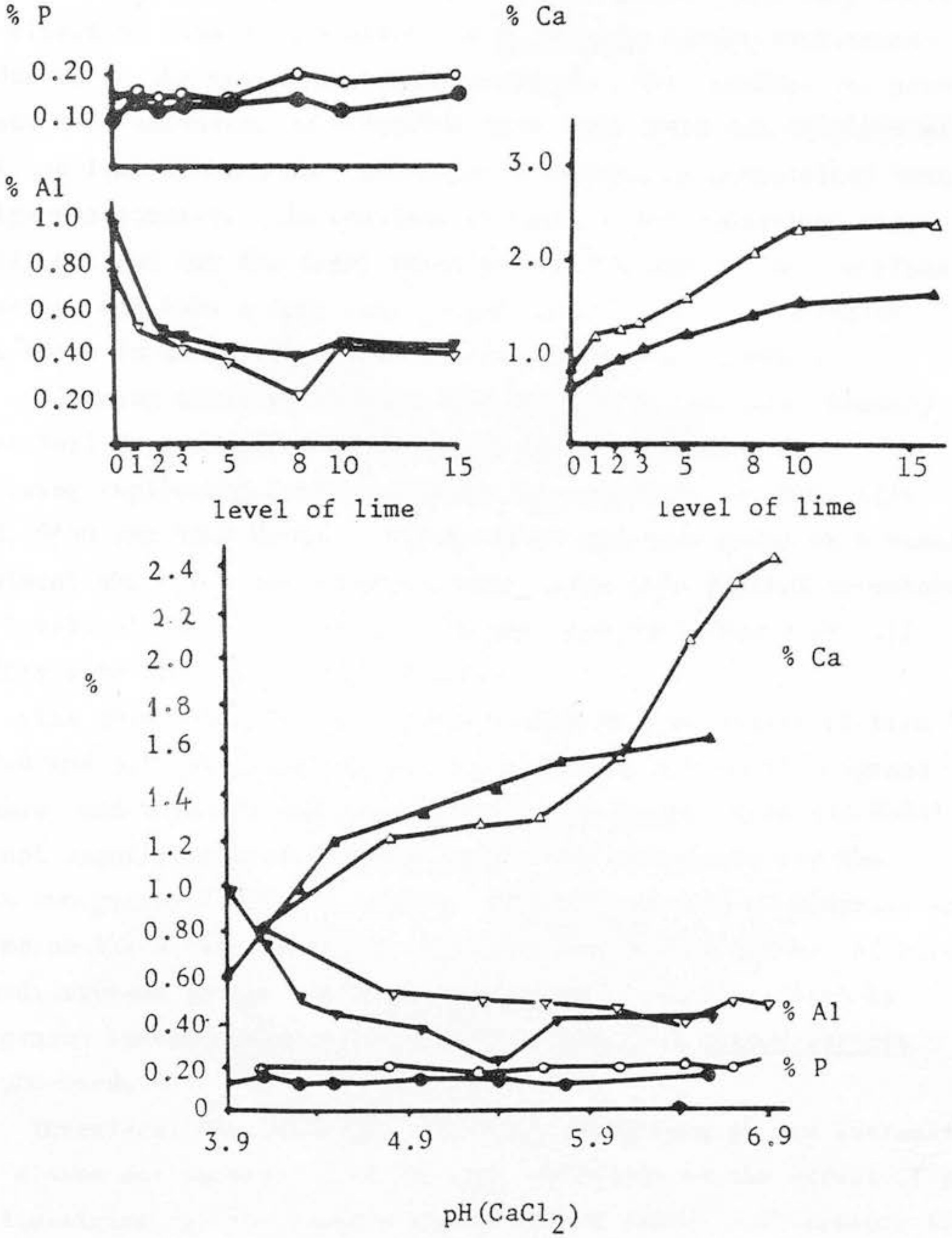


Fig 6.7 Mineral Content (% P, % Al, % Ca) of Ryegrass roots as influenced by (a) lime additions and (b) pH in soil 9 (open symbols) and soil 11a (closed symbols).



concentration of soluble Al in the soil. The concentrations of Ca in the roots from soil 9 were higher than from soil 11a and the difference between the root Ca contents for the two soils was accentuated with the treatments.

6.4. OBSERVATIONS ON THE EFFECTS OF LIME IN A FIELD EXPERIMENT

The results presented so far in this thesis have only reflected the effect of lime on the growth of L. perenne in pot experiments conducted in the greenhouse where conditions were optimal for growth: plants were harvested on a regular basis and there was complete mixing of soil and lime without any influence of subsoil or competition from indigenous species. In contrast to this, field conditions are rarely optimum and the lime, which is usually applied as a surface dressing, can take a long time to penetrate the soil especially when there is an organic layer present on the soil surface.

A liming trial was established in 1975 at the site, Stanhope, where soil 3 was sampled (HFRO Annual Report, 1976). The following replicated lime treatments were applied: 0, 625, 1250, 1875, 2500 and 5000 kg/ha. N.P.K. dressings were given as a basal treatment and twice yearly applications were also applied to maintain the levels of these nutrients to ensure that the effects of soil acidity were the dominating influence.

The 2500 and 5000 kg/ha applications of lime raised pH from 4.5 to 5.0 and 5.5 (in water) respectively and the growth of ryegrass (Gremie and Caprice) and clover (Trifolium repens hiua and S184) was not significantly different between any treatments for the first two years. However, after 4 years the growth of ryegrass and clover on the 0 lime treatment was very poor and in patches of bare ground, exposed by the death of these plants, recolonization by indigenous species particularly mosses, Carex species and Nardus stricta was observed.

Therefore, one important attribute of raising pH and increasing base status not apparent from the pot experiment is the effect of pH on maintaining species composition of a sown sward. It appears that keeping the pH above 5 improves the competitive abilities of ryegrass and clover against indigenous species. ROBERTSON and NICHOLSON (1961) and CROMACK ET AL.(1970) also observed this effect of lime on the composition of species rich grassland, including L. perenne with Agrostis and Fescue which were not associated with increases in DM production.

6.5. DISCUSSION

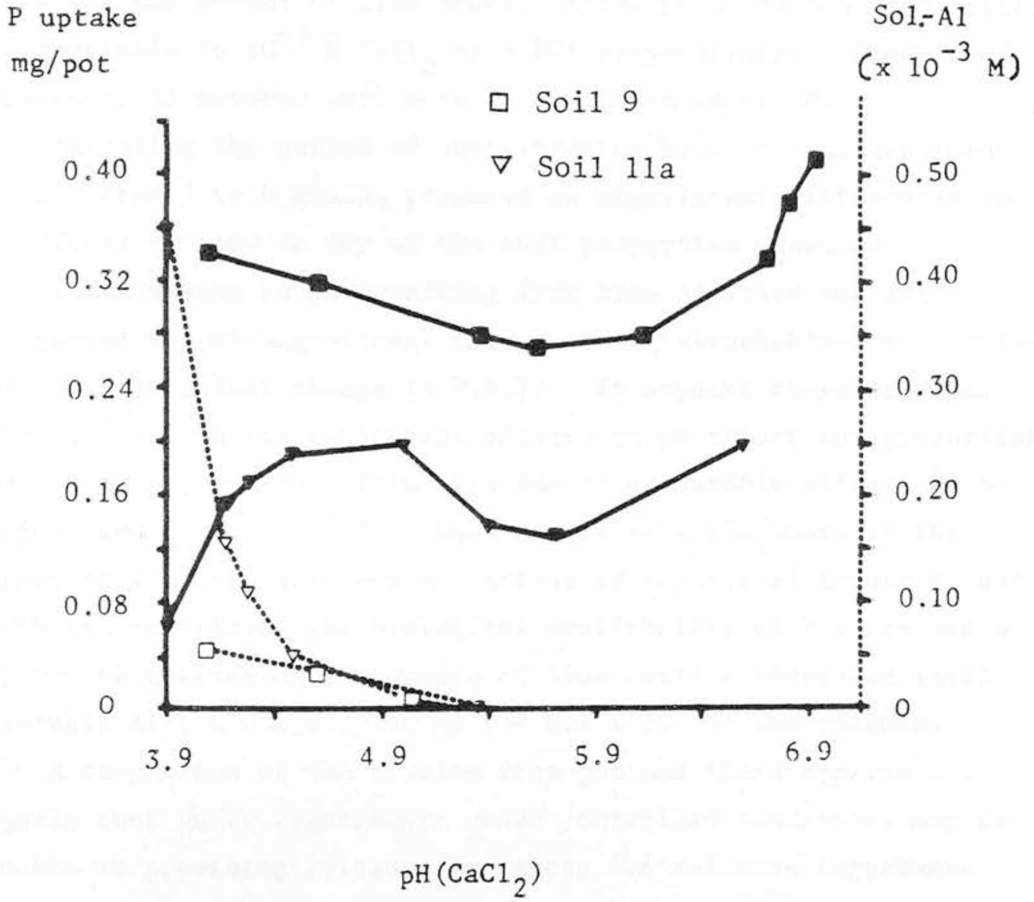
The reduction in level of extractable Al caused by liming was not associated with a fall in PSI (see also 4.3.3.). This lack of change (5% only) in PSI with increasing pH was also shown by BACHE and WILLIAMS (1971) who found that at pH 6.3 PSI was only 3% lower than at a more acid pH. This suggests that Al hydroxides formed at higher pH have a high affinity for P and compensate for the absence of actual P precipitation by soluble Al.

Increases in soluble P were not apparent in soil 9 and only very small in soil 11a as the pH exceeded 6 whereas in both soils increases in P uptake were observed suggesting that P is more readily available as the pH approaches 7. A possible explanation for this, consistent with the absence of appreciable change in PSI, is that as pH approaches neutrality the energy of P sorption decreases so that phosphate ions are more readily desorbed (BACHE, 1964). It is also possible P release from organic sources by mineralization was enhanced above pH 6.

In soil 11a the beneficial effect of lime, increasing the biological availability of P through reducing the level of soluble Al, was again demonstrated. A significant inverse relationship was shown between soluble Al and root weight (r = 0.998***) (Fig. 6.8). However, once the adverse influence of Al on root growth was overcome or in soils where it was not demonstrated, such as 9 the benefits of lime with respect to increased P uptake were only apparent at a pH well above that necessary for good growth, even in the field. It seems therefore that lime/P interactions were not responsible for the pH requirement shown for ryegrass in the field on soils relatively low in Al.

The reason for the pH requirement of 5 to sustain ryegrass in the field, against competition from indigenous species was not apparent from the effects of Al either. The data suggest that levels of soluble Al are not likely to be influencing root growth above pH 4.5 and the poor correlation with the molar concentration ratio (r = 0.445 NS) tends to eliminate base status too. In

Fig. 6.8 Relationships between P uptake (closed symbols) and concentration of soluble Al (open symbols), and pH in soils 9 and 11a.



the absence of any meaningful explanations at this time the problem will be returned to in the general discussion when all the data is available.

6.6. CONCLUSIONS

The addition of lime to soils 9 and 11a, representing soils of low and high Al content, showed that the incremental increases in pH was greatest when exchangeable Al was lowest. Both exchangeable and soluble Al were reduced by liming and the quantitative effects were more closely related to the resultant incremental change in pH than to the amount of lime added: above pH 5 and 5.4 very little Al was soluble in 10^{-3} M $CaCl_2$ or M KCl respectively. Amounts of extractable Al however were much less influenced by pH.

Extending the period of equilibration between lime treatment and soil from 1 to 6 months produced no significant differences in the effects of lime on any of the soil properties measured.

The increase in pH resulting from lime addition was not accompanied by any significant increases in extractable- or soluble-P or any significant change in P.S.I. It appears therefore that although lime and its consequent effects on pH affect the proportion of Al in each particular form this has no measurable effect on the chemical availability of P. However, in soil 11a, where in the absence of lime the high concentrations of soluble Al impaired root growth and restricted the biological availability of P, there was a response to increasing increments of lime until a threshold level of soluble Al ($<$ 0.1 meq/100 g) ($\sim$ 0.1 x 10^{-3}M) was reached.

A comparison of the results from pot and field experiments suggests that while experiments under controlled conditions may be valuable in providing evidence to assess the relative importance of soil factors for plant growth, the responses under these conditions do not represent the full benefits of lime application in the field. The significance of lime for the competitive ability of introduced, more palatable, productive grasses against indigenous grasses cannot be assessed under controlled conditions and is not obvious from the type of pot experiment described here.

CHAPTER 7

COMPARISON OF THE EFFECTS OF LOWERING SOIL Al BY LEACHING AND BY LIMING ON PLANT GROWTH

7.1. INTRODUCTION AND OBJECTIVES

At the time this experiment was planned all the results from chapter 4 were not available and those that were suggested that exchangeable Al was a major influence on plant growth. The need to measure soluble Al only became apparent much later in the analysis when it was found that neither values for extractable- nor exchangeable-Al were able to explain some of the results for plant growth. By the time the importance of soluble Al was established soil from this experiment had been used up so that the results of experiments described in this chapter have only been considered with respect to exchangeable-Al. It was however established that exchangeable-Al falls with increasing pH (chapters 1, 3 and 4), and the positive correlation between exchangeable- and soluble Al established in chapter 4 (section 4.3.1.) suggested that the former might influence plant growth indirectly by acting as a reservoir for soluble Al. Methods for improving plant growth may therefore include ways of reducing amounts of exchangeable-Al and an alternative approach to using lime might be to remove Al by leaching as in the method for determining exchangeable cations. In the experiment described here both these approaches were adopted and their consequences were assessed by measuring the resultant changes in soil properties and plant growth.

The objective of this experiment was to compare the effects of leaching and liming on exchangeable Al, pH and plant growth.

7.2. EXPERIMENTAL

Soil 11 was used for this experiment because of its high content of exchangeable Al (Table 4.1). 1 Kg of air dry, sieved soil was leached in five 200 g batches at a rate of 100 ml/hr using 5 litres of M KCl per batch. The batches of soil were then washed through with deionized water until all excess KCl had been removed, air-dried and the batches thoroughly mixed together.

(The silver nitrate test was used to indicate that all excess KCl had been washed out of each batch).

Four replicates of each of the treatments described in Table 7.1 were made up (Chapter 2) and 100 g of treated soil was added to each 7.5 cm pot. The soil was moistened to approximately 60% FC and left for 1 week to equilibrate. Four of the treatments (A to D) were given 187 mgP/100 g as KH_2PO_4 (compared with 25 mgP/100 g as superphosphate in chapter 4) but no P was added to Treatment E. Treatments A and B were made up from non-leached soil with lime (3 times as much as used in chapter 4) added to B (Table 7.1). Treatments C and D were similarly prepared with and without lime, but using leached soil.

Table 7.1. Description of the treatments and composition of of Nutrient Solution

Treatment		KH_2PO_2	Lime
A	Non leached	0.82 g	–
B	"	"	1.0 g
C	Leached	"	–
D	"	"	1.0 g
E	"	–	–
Nutrient Solution		**Amount added/100 g soil**	
2.0 g/l	$Mg(NO_3)_2$	5 meq Mg	
3.2 g/l	NH_4NO_3	245 mg N	
0.9 g/l	KH_2PO_4	0.6 meq K	
0.5 g/l	$MgSO_4$	22 mg S	
0.5 g/l	$CaSO_4 \cdot 2H_2O$	0.6 meq Ca	
0.12 g/l	ferric citrate		

After one week one replicate was air dried for the determination of pH, PSI, extractable- and exchangeable-Al, and extractable-P and-K by methods described in chapter 2. The 3 remaining replicates of each treatment were sown with 0.12 g of *L.perenne* (S24) and transferred to the glasshouse. In order to replace some of the nutrients removed in the leaching procedure these pots received 2 ml of nutrient solution (Table 7.1) per day until the 1st harvest and thereafter 5 ml NH_4NO_3 per week. Additional moisture was provided daily in the form of a fine spray. Five harvests, cut at 1 cm height, were taken at 28 day intervals. Herbage and roots were prepared for analysis (chapter 2) and % P, % K, % Al, % Ca and % Mg were determined.

Treatment differences for root and herbage DM production and P uptake were assessed statistically using the Students t test. There was only sufficient material for single analyses on the bulked replicates to be determined.

7.3. RESULTS

7.3.1. SOIL ANALYSIS

Analysis of the soil before and after leaching with KCl showed that exchangeable- and extractable-Al and PSI were decreased while extractable K and pH were increased by the leaching procedure. This treatment had no appreciable effect on extractable P (Table 7.2.).

Table 7.2. Effects of leaching with KCl on selected soil properties

Treatment	pH	Exch.Al meq/100g	Extr.Al meq/100g	PSI	Extr.K meq/100g	Extr.P mg/100g
Before leaching	3.8	16.0	15.3	158	0.4	0.26
After leaching	4.5	9.8	10.4	99	13.8	0.27

The mixing of lime with the leached soil (treatment D) caused a further increase of 1.1 units in pH from 4.5 to 5.6 which was only 0.1 of a pH unit greater than the response in the non-leached soil where the pH was raised by 1.0 units from 3.8 to 4.8 (Table 7.3). The addition of lime to the non-leached soil reduced exchangeable Al by 9 meq from 16 to 7 meq/100 g. In the leached soil liming reduced exchangeable Al by 8 meq/100 g to 1 meq/100 g soil. Thus in both situations lime increased pH and lowered exchangeable Al by similar amounts despite the initial differences between the non-leached and leached soils. Liming produced little change in the amount of extractable Al in the non-leached soil but reduced it from 6.4 to 4.7 meq/100 g in the leached soil.

Table 7.3. Effects of leaching, lime and P treatment on selected soil properties

Treatment	pH	Exch.Al meq/100g	Extr. Al meq/100g	PSI	Extr. K meq/100g	Extr. P mg/100g
A Non-leached +P	3.8	16.0	13.8	103	0.5	3.2
B Non-leached +P + lime	4.8	7.0	13.7	129	0.6	3.6
C Leached + P	4.5	9.4	6.4	82	13.0	3.3
D Leached + P + lime	5.6	1.0	4.7	109	12.7	3.5
E Leached (without P)	4.5	9.8	10.4	99	13.8	0.3

The addition of KH_2PO_4 reduced PSI by 36% in the non-leached soil (treatment A) but only by 18% where it was included with lime (treatment B). In the leached soil, where leaching had already reduced PSI, P addition (treatment C) reduced PSI by a further 33%. Lime, however, (treatment D) reduced this P induced fall in PSI (Table 7.3.). The addition of P increased extractable P values from 0.26 to a similar amount, (approximately 3.4 mg/100g) in all four P treatments. On the leached soil the addition of P also reduced the amount of extractable Al. (Table 7.3).

7.3.2. PLANT GROWTH

Plants in the leached soil(treatment C and E) grew very badly showing symptoms of Ca deficiency (i.e. marginal chlorosis of the leaf blades with tips folding and dying back) and were dead by the first harvest. Ryegrass growing on the other treatments (A, B and D) exhibited no deficiency symptoms and leaf blades were a 'healthy' green colour.

Table 7.4. Effect of leaching and lime treatments on herbage and root DM and P uptake

Treatment	Herbage g/pot	Root g/pot	Total P Uptake mg/pot
A	6.2	1.1	32
B	7.7	1.9	48
C	0.1	0.1	ND
D	8.4	1.4	47
E	0.2	0.1	ND[+]

+ ND : not determined (insufficient growth)

Herbage production from treatment D (leached plus lime) was significantly greater than from treatments C and E, or A and B ($P < 0.001$ and 0.05 respectively)(Table 7.4). Root weight however was highest on treatment B (non-leached plus lime) and was significantly ($P < 0.001$) higher than on A or D. Both root and herbage weights were very low on treatments C and E as a result of the early death of the plants. Total P uptake was not significantly different between leached and non-leached lime treatments (B and D) suggesting that it was not influenced by leaching. P uptake on the non-limed, non-leached treatment (A) was significantly ($P < 0.001$) less than on the limed treatments (B and D).

7.3.3. MINERAL COMPOSITION OF HERBAGE AND ROOTS

The P contents of the herbage from both limed treatments (B and D) were high and similar (0.53 and 0.55% respectively) (Table 7.5) but from the non-leached, non-limed treatment (A) P content (0.47%) was slightly lower. There was virtually no difference in P content between the leached treatments C and E despite the large addition of P in treatment C. K concentrations were exceptionally high in the herbage from these leached treatments ($> 6.5\%$) but when lime was included (treatment D) the K content was only marginally higher than from the non-leached treatments (A and B).

Table 7.5. Effect of leaching and lime treatments on mineral composition of ryegrass herbage (mean of 5 harvest cuts)

Treatment	% P	% K	% Al	% Ca	% Mg	K/Ca
A Non-leached	0.47	3.75	0.030	0.32	0.11	12
B Non-leached +L	0.53	4.32	0.015	0.95	0.07	4
C Leached*	0.22	8.0	0.050	0.17	0.09	47
D Leached +L	0.55	4.97	0.015	0.86	0.07	5
E Leached (without P)*	0.23	6.8	0.040	0.07	0.11	96

* only 1 harvest

Herbage Al content was twice as high (> 0.03%) from the non-limed treatments (A, C and E) as on the treatments (B and D) to which lime was applied (Table 7.5). Ca levels were high (> 0.8%) where lime was included (treatments B and D), lower (0.32%) in the absence of lime (A) and well below the minimum functional requirement for herbage at 0.17 and 0.07% from both leached and unlimed treatments C and E respectively. Mg levels were more similar amongst the five treatments but were smallest where lime was included (B and D). As a result of the very low Ca levels and high K contents the K/Ca ratios were exceptionally high for treatments C and E (47 and 96 respectively).

Table 7.6. Effect of leaching and lime treatments on mineral composition of ryegrass roots

Treatment	% P	% K	% Al	% Ca	% Mg	K/Ca
A	0.26	0.16	0.69	0.13	0.10	1
B	0.18	0.13	0.67	0.67	0.10	0.3
C	Not determined					
D	0.19	0.43	0.43	0.45	0.08	1
E	Not determined					

The mineral composition of the roots is given in Table 7.6. but no data for treatments C or E are available because there was insufficient material for analysis. The content of P in the roots was lower than in the herbage, and was lower on the limed treatments (0.19%), than on the unlimed treatments (0.26%). Root K levels were considerably below herbage levels and were highest on the leached soil (treatment D). By contrast root Al levels were, as found in chapter 4, some ten times greater than herbage levels. The Al concentration was approximately 30% lower from the leached soil, even when lime was mixed with the non-leached soil. Ca contents were low on the non-limed treatment (A) (0.13%). On the limed treatments (B and D) they were much higher 0.67% and 0.43% respectively. Root Mg levels were similar to those measured in the herbage but because of the low K contents K/Ca ratios were very much lower than for the herbage.

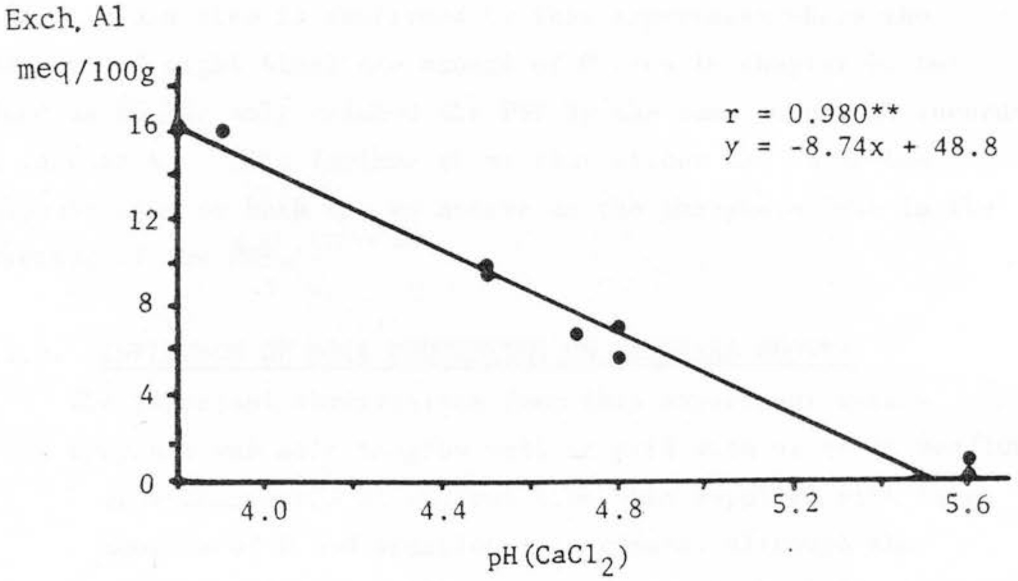
7.4. DISCUSSION

7.4.1. EFFECTS OF LIME AND LEACHING ON SELECTED SOIL PROPERTIES

Both leaching and liming brought about large reductions of similar magnitude in levels of exchangeable-Al and for both methods these reductions were accompanied by a rise in pH. There was a highly significant inverse linear relationship between pH and exchangeable-Al ($r = 0.995^{***}$) (Fig. 7.1). It may be seen from this that above pH 5.6 ($CaCl_2$) the amount of exchangeable-Al was very low. This pH dependent reduction in Al is in good agreement with the data of LOWE (unpub.) and that discussed by COLEMAN and THOMAS (1967) who showed that above about pH 5.5 the amount of exchangeable Al is negligible.

Leaching reduced extractable-Al by 32% whereas this form of Al was little affected by lime. This fall in the amount of extractable Al supports work reported in chapter 3(3.2.2.) that KCl leaching removes more than just exchangeable-Al. The large addition of P as KH_2PO_4 also reduced the level of extractable-Al suggesting that reactions between Al and P reduce the solubility of Al in ammonium acetate.

An important difference between leaching and liming procedures is that the former removes Al from the soil whereas the latter only changes its state and solubility. The significance of this was reflected in the significant decrease in PSI in the leaching treatments, also observed by COLEMAN ET AL. (1960). The likely conversion of exchangeable Al^{3+} ions to $Al(OH)_x^{(3-x)+}$ polymers, Fig 7.1 Relationship between Exchangeable Al and pH in soil 11a.



which are not readily exchangeable but sorb P strongly, by liming confirms earlier suggestions (sections 4.4 and 6.5) that in soils high in exchangeable Al increasing pH increases the soils affinity for P.

7.4.2. EFFECT OF ADDED P ON PSI

It was suggested in section 4.4. that the reduction in PSI concomitant with the addition of superphosphate, which contains Ca, phosphate and sulphate ions, may not have been due solely to the adsorption of phosphate ions reducing the number of available sites. This view is confirmed by this experiment where the addition of eight times the amount of P used in chapter 4, but added as KH_2PO_4 only reduced the PSI by the same amount as recorded in chapter 4. This further shows that either the Ca or the sulphate ions or both are as active as the phosphate ions in the lowering of the PSI.

7.4.3. INFLUENCE OF SOIL PROPERTIES ON RYEGRASS GROWTH

The important observations from this experiment were:-

1) ryegrass was able to grow well in soil with up to 16 meq/100 g of exchangeable Al without lime when supplied with large amounts of P and additional nutrients, although the addition of lime still gave responses in both DM production and P uptake.

2) in the presence of lower levels of exchangeable-Al, as on the leached treatments, lime was required to increase the levels of Ca and overcome the acute Ca deficiency caused by saturating the soil with K. It seems that saturation of the exchange sites with K in the leaching procedure (Table 7.3) not only removed a proportion of the already small amount of exchangeable Ca (Table 4.3) but also created high levels of soluble K which may have interfered with the uptake of Ca through the well documented phenomena of K/Ca antagonism (MENGEL and KIRKBY, 1978). The imbalance between Ca and K uptake indicated by the very high K/Ca ratios on the leached treatments (C and E) was suggestive of severe physiological disorder in

these plants quite capable of causing their death. (DEKOCK, 1964).

7.5. CONCLUSIONS

An attempt was made to compare two techniques for lowering the amount of exchangeable Al in a soil of inherently high Al status. Leaching with KCl lowered Al by 39% but resulted in a very wide K/Ca ratio in the soil with consequent K/Ca antagonistic effects on plant growth. These could be overcome by the application of lime but in its absence plants died within a month. This confounding effect precluded the direct comparison of the effects of the two techniques on plant growth. However, chemical analysis of the soil showed that exchangeable- and extractable-Al and PSI were reduced by leaching while pH increased providing further evidence of the importance of Al in P fixation and of the relationship between exchangeable-Al and pH.

The main difference between leaching and liming was that the former removed Al from the soil and thus reduced PSI while liming slightly increased the affinity of Al for P. The results suggested that the addition of sufficiently large amounts of P might at least partially overcome the adverse effects associated with Al and led to the experiment described in chapter 9.

CHAPTER 8

INVESTIGATION OF THE EFFECTS OF SILICIC ACID ON SOIL Al AND THE CONSEQUENCES FOR PLANT GROWTH

8.1. INTRODUCTION AND OBJECTIVES

In this experiment a further attempt was made to reduce soil Al by means other than the addition of lime using a method based on the observations of PEASLEE and FRINK (1969). These workers found that additions of silicic acid (H_2SiO_3) to soil increased the amount of P soluble in 10^{-2} M $CaCl_2$ and lowered the concentrations of Mn and Al in tomato plants (Lycopersicum esculentum) suggesting that silicic acid had reduced the level of Al in the soil. In this experiment 2 levels of silicic acid were added to soil 11a, both with and without lime and superphosphate, so that both soil effects and plant growth responses could be studied. The specific objectives were:-

1. Examine the effects of adding silicic acid to soil on the amounts of exchangeable- and soluble- Al and on other related properties.
2. Determine whether plant growth is affected by the direct or indirect effects of silicic acid addition.

8.2. EXPERIMENTAL

Silicic acid, lime and P treatments (Table 8.1.) were mixed with soil 11a (described in Table 9.1A) individually to give 4 replicates of each treatment, as described in chapter 2. Two levels of silicic acid were used (0.17 and 0.33% by weight) while levels of lime and superphosphate additions were as used in chapter 4 (Table 4.2.). 300 g of air dry soil were used in 10 cm pots (see chapter 2) and the treatments were equilibrated at 60% FC for 6 weeks. After this period soil samples ($\sim$ 10g) were taken from all 48 pots using a cork borer. This soil was used for determinations of pH, PSI, exchangeable- and soluble-Al, exchangeable- and soluble-Ca and soluble-K, -Mn and -Fe (chapter 2), pH was measured in the filtrate from the 10^{-3} M $CaCl_2$ extract and not in 10^{-2}M $CaCl_2$.

Table 8.1. Silicic acid, lime and P treatments applied to soil 11a

Treatment		Amounts added
$L_o\ P_o\ Si_o$	1	L_1 = 1.0 g $CaCo_3$/pot ≡ 1250 kg/ha P_1 = 0.723 g superphosphate/pot 71 mgP/pot ≡ 80 kgP/ha Si_1 = 0.5 g silicic acid/pot = 0.17% w/w Si_2 = 1.0 silicic acid/pot = 0.33% w/w
$L_o\ P_o\ Si_1$	2	
$L_o\ P_o\ Si_2$	3	
$L_1\ P_o\ Si_o$	4	
$L_1\ P_o\ Si_1$	5	
$L_1\ P_o\ Si_2$	6	
$L_o\ P_1\ Si_o$	7	
$L_o\ P_1\ Si_1$	8	
$L_o\ P_1\ Si_2$	9	
$L_1\ P_1\ Si_o$	10	
$L_1\ P_1\ Si_1$	11	
$L_1\ P_1\ Si_2$	12	

All 48 pots were sown with 0.20 g of L. perenne (S24), transferred to the glasshouse and arranged in 4 randomized blocks. A single application of NH_4NO_3 (≡ 30 kg/ha) was given after 2 weeks. The plants were watered daily and brought back to 60% FC at the end of each week. Temperatures in the glasshouse ranged between 20 and 30°C during the day with night temperatures between 15 and 20°C. After 28 days a single harvest was taken at soil level.

As a result of the very poor growth on treatments 1 to 3 (Table 8.1) the 4 replicates were bulked and single determinations of P, Ca, K, Mn, and Fe made on the herbage, with P, Ca, Al, K and Si measured for the roots. Replicates from treatments 4 to 12 were individually analysed. Differences between treatments were tested statistically by analysis of variance when 4 replicates were available. The results of these analyses for the soil and plant material are given in the appendix (Tables 8.1A to 8.3A) and are presented graphically in the text.

8.3. RESULTS

8.3.1. PLANT GROWTH

In the absence of lime symptoms of Al toxicity were observed, resembling those described in chapter 4 (section 4.3.7).

Because of the poor growth in the absence of added P consideration of the effects of lime and silicic acid were restricted to the + P treatments (7 to 12). Total P uptake is discussed, other features of plant growth (Fig. 8.1) exhibited similar responses.

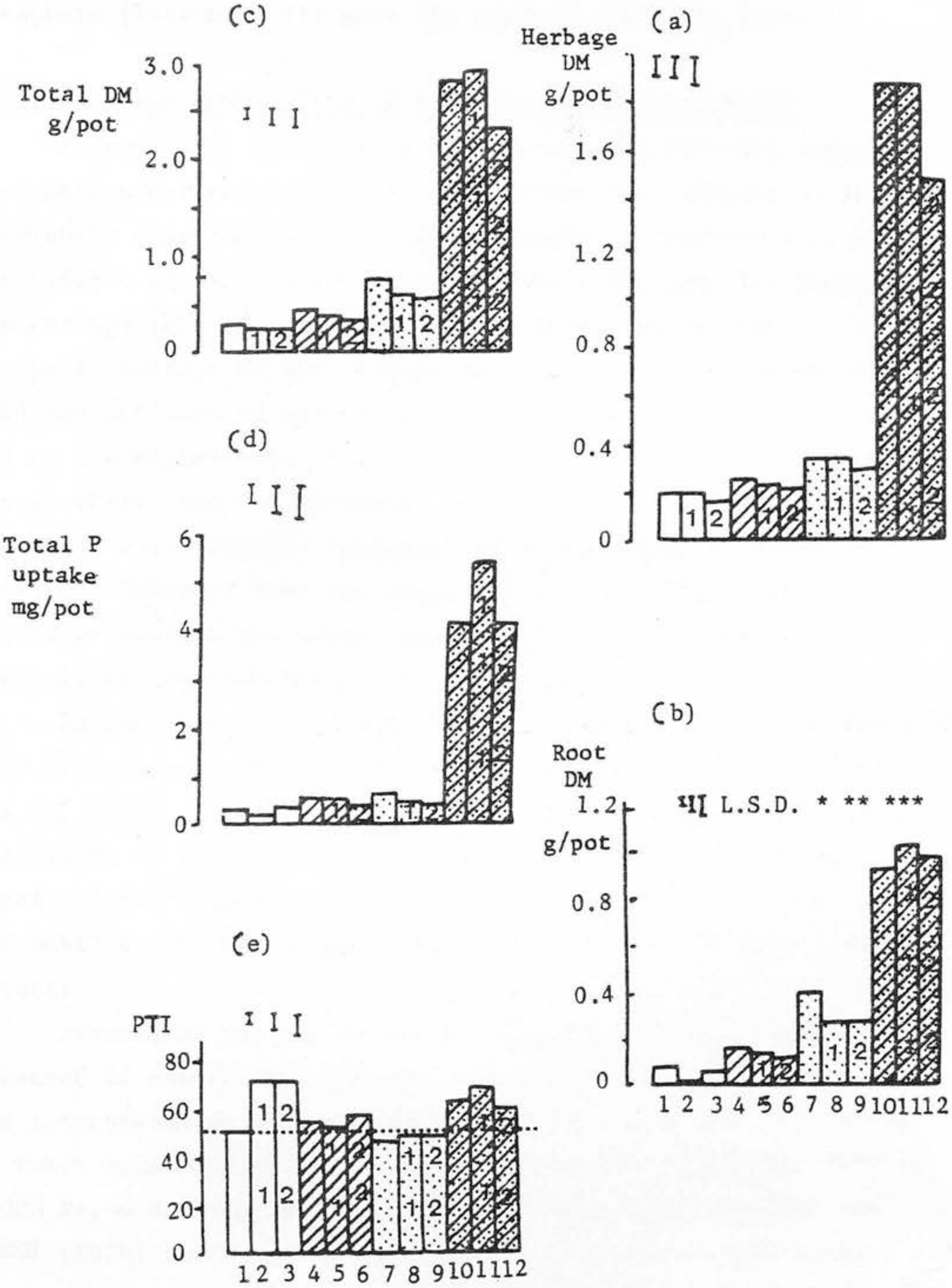
Table 8.2. Mean effects of lime and silicic acid in the presence of superphosphate on P uptake (mg P/pot)

L	+ 3.96***	SED = 0.11	CV = 11.2%
Si_1	+ 0.43**	SED = 0.14	
Si_2	- 0.03		
L x Si_1	+ 0.43*	SED = 0.20	
L x Si_2	+ 0.08		

Both lime and silicic acid (level 1) separately and together significantly ($P < 0.001$, < 0.01, < 0.05 respectively) increased P uptake. However the effect of silicic acid was minimal in proportion to that of lime. Silicic Acid (level 2) had no significant effect on P uptake, either alone or with lime, in the presence of superphosphate.

The P transport index (Fig. 8.1e) indicates the concentration of P in the herbage with respect to the root. In the control (treatment 1) P was equally distributed but in the presence of silicic acid (treatments 2 and 3) P was highest in the herbage. Neither lime nor superphosphate/

Fig 8.1 Effects of silicic acid, lime and superphosphate treatments on (a) DM tops (b) DM roots (c) Total DM (d) Total P uptake and (e) P transport index.



Footnote: Treatment symbols as for chapter 4 excepting silicic acid denoted:-

$1 = Si_1$ and $2 = Si_2$

(treatments 4 and 7) greatly influenced the distribution of P, but when they were added together more P was found in the herbage. The inclusion of silicic acid at the lower rate with lime and phosphate (treatment 11) gave the highest transport index.

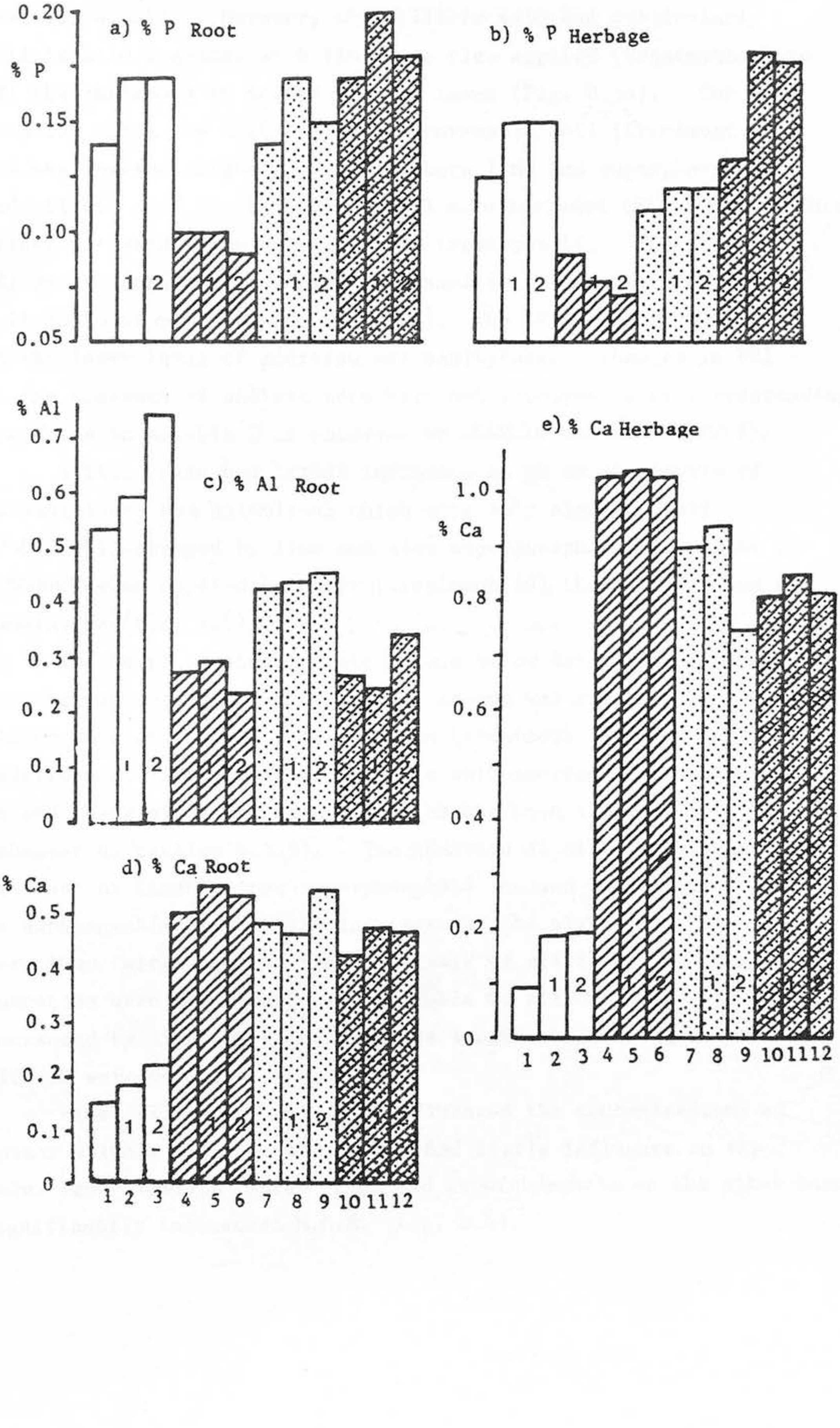
8.3.2. MINERAL COMPOSITION OF RYEGRASS ROOTS AND HERBAGE

Essentially, the effects associated with lime and superphosphate additions on mineral composition were similar to those previously described for soil 11 in chapter 4 (section 4.3.6). The effects of silicic acid were generally the same for roots and herbage (Fig. 8.2) and may be summarised as follows:- i) the P contents of the herbage tended to be higher where silicic acid was included except on the limed treatments (5 and 6): ii) at the higher rate of addition root Al contents were increased except where lime was included: (iii) concentrations of Ca in the roots were slightly increased by silicic acid at both levels. However, when the small effects of silicic acid on dry matter production are taken into account these changes in mineral composition are probably of no significance.

In the absence of added lime or superphosphate (treatments 1 to 3) Ca concentrations in both roots and herbage were very low ($<$ 0.2%), below the minimum functional requirement and suggestive of acute Ca deficiency. Concentrations of K were about 4 times higher in the herbage than in the roots, indicating the mobility of this element, but there were no apparent treatment effects.

Amounts of Si, Mg, Fe and Mn in plant materials were also measured to ensure that abnormal concentrations did not confound the interpretation of the results. Their concentrations, given in Table 8.2A were within the ranges, 0.006 to 0.012% Mn, 0.01 to 0.02% Fe, $\sim$ 0.20% Mg given by BUTLER ET AL. (1962) and REAY and MARSH (1976) for ryegrass growing in less adverse conditions. There were no significant effects attributable to the applied treatments and it was concluded these elements have not influenced the results.

Fig 8.2 Effects of silicic acid, lime and superphosphate treatments on the mineral content of herbage and roots.



8.3.3. SOIL PROPERTIES

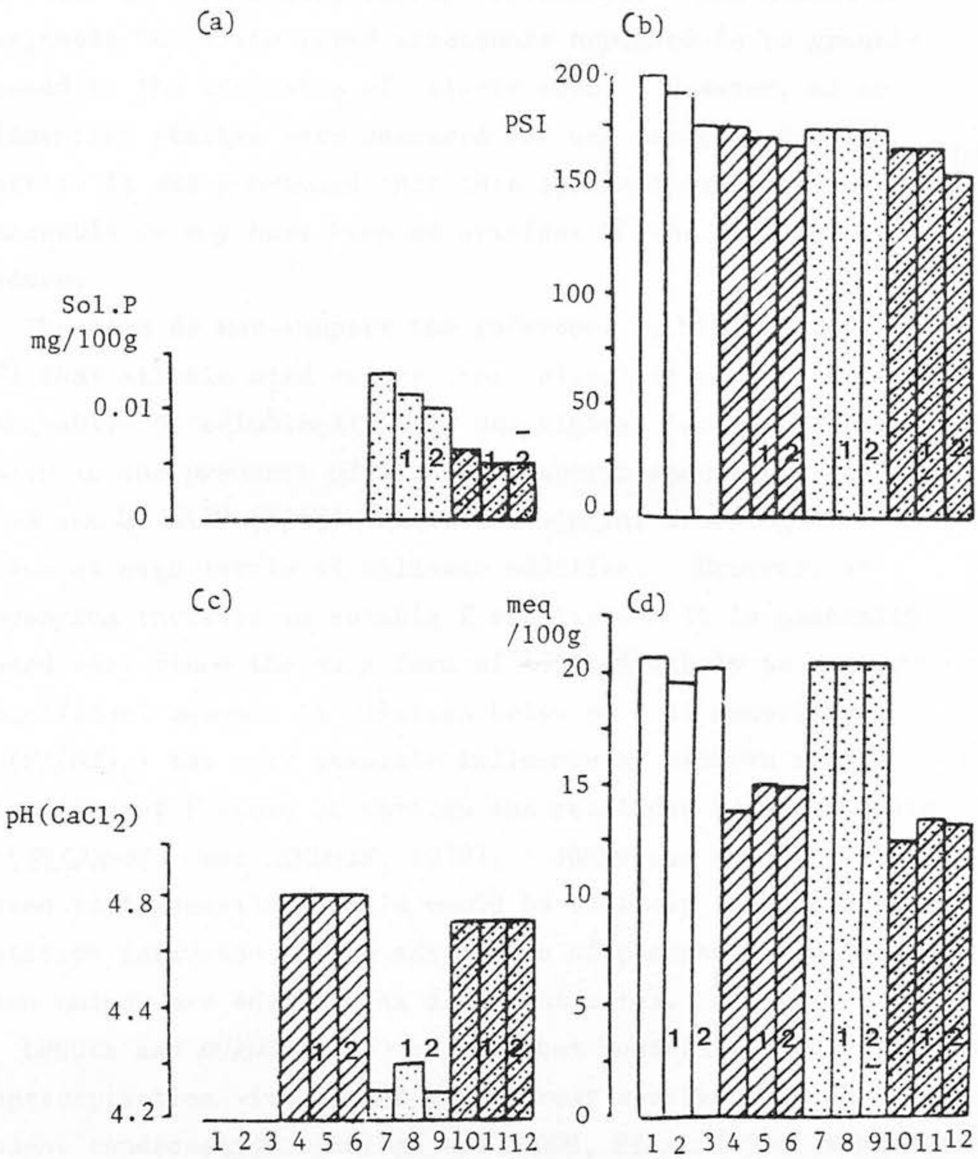
P was too low to measure in the absence of superphosphate but when this was added it was increased as observed in chapter 4 (section 4.3.4). However, when silicic acid and particularly silicic acid together with lime were also applied (treatments 8 to 12) the increases in soluble P were lower (Fig. 8.3a). The P sorption index was highest for the untreated soil (treatment 1) and was lowered slightly ($\sim$ 12%) where lime and superphosphate and silicic acid at the higher level were included (Fig. 8.3b). This effect was seen to be cumulative on treatment 12. The change in PSI due to superphosphate was much smaller than recorded for soil 11 in chapter 4 (section 4.3.3). The effect of silicic acid at the lower level of addition was negligible. Changes in PSI in the presence of silicic acid were not accompanied by corresponding increases in soluble P as observed by PEASLEE and FRINK (1969).

Silicic acid had little influence on pH or the levels of exchangeable- and soluble-Al which were only significantly ($P < 0.001$) changed by lime and also superphosphate (treatment 7). Although, when applied together (treatment 10), their effect was not cumulative (Fig. 8.4).

The level of exchangeable Ca was below detection limits in treatments 1 and 2 but a very small amount was recorded at the higher rate of silicic acid addition (treatment 3)(Fig. 8.4). Additions of lime and superphosphate both increased exchangeable Ca and their effects were additive as has been observed before (chapter 4, section 4.3.5). The addition of silicic acid in the presence of lime but not superphosphate, caused very large increases in exchangeable Ca with the increases at the higher rate of addition more than twice those at the lower rate of addition. Corresponding increases were not measured for soluble Ca although this was increased by lime and superphosphate treatments, and again their effects were additive.

Since silicic acid hardly influenced the concentrations of either soluble Al or soluble Ca it had little influence on the molar concentration ratio: lime and superphosphate on the other hand, significantly influenced M.C.R. (Fig. 8.4).

Fig 8.3 Changes in (a) Soluble P (b) PSI (c) pH and (d) Exchangeable Al in soil 11a treated with silicic acid lime and superphosphate.



8.4. DISCUSSION

8.4.1. EFFECT OF SILICIC ACID ON SOIL Al AND ASSOCIATED SOIL PROPERTIES

Silicic acid treatments resulted in only minor changes in the measured properties of soil 11a and neither exchangeable- nor soluble Al were significantly influenced. The amount of exchangeable Ca in the limed treatments appeared to be greatly increased by the inclusion of silicic acid. However, as no complimentary changes were measured for any associated soil properties it was concluded that this apparent increase in exchangeable Ca may have been an artefact of the leaching procedure.

The data do not support the inference by PEASLEE and FRINK (1967) that silicic acid reduces the solubility of either exchangeable- or soluble-Al. At the highest level of silicic acid addition in the presence of lime and superphosphate PSI was reduced and DE HAAN (1965) observed a similar lowering of P sorption at high levels of silicate addition. However, no accompanying increase in soluble P resulted. It is generally accepted that since the only form of silicon likely to occur in significant amounts in solution below pH 9 is monosilicic acid ($Si(OH)_4$) the only possible influence of silicon on the availability of P would be through the reactions of monosilicic acid (ELGAWHARY and LINDSAY, 1972). JONES and HANDRECK (1967) reported that monosilicic acid would be unlikely to have a large competitive influence on the adsorption of phosphate ions since the two anions are adsorbed at different sites.

LUCUIK and HUANG (1974) showed that monosilicic acid reacted by coprecipitation with Al and its hydroxy species in a pH dependent condensation reaction and CLOOS, ET AL. (1968) suggested that P sorption would be higher in the presence of these polynuclear hydroxy Al/Si complexes. The bulk of the reported evidence for the effects of silicic acid on P sorption together with the observations recorded here, therefore fails to explain or support the increases in phosphate potential recorded by FRINK and PEASLEE (1967).

Fig 8.4 Changes in (a) Soluble Al (b) Soluble Ca (c) Exchangeable Ca and (d) Molar Concentration Ratio in soil 11a treated with silicic acid, lime and superphosphate.

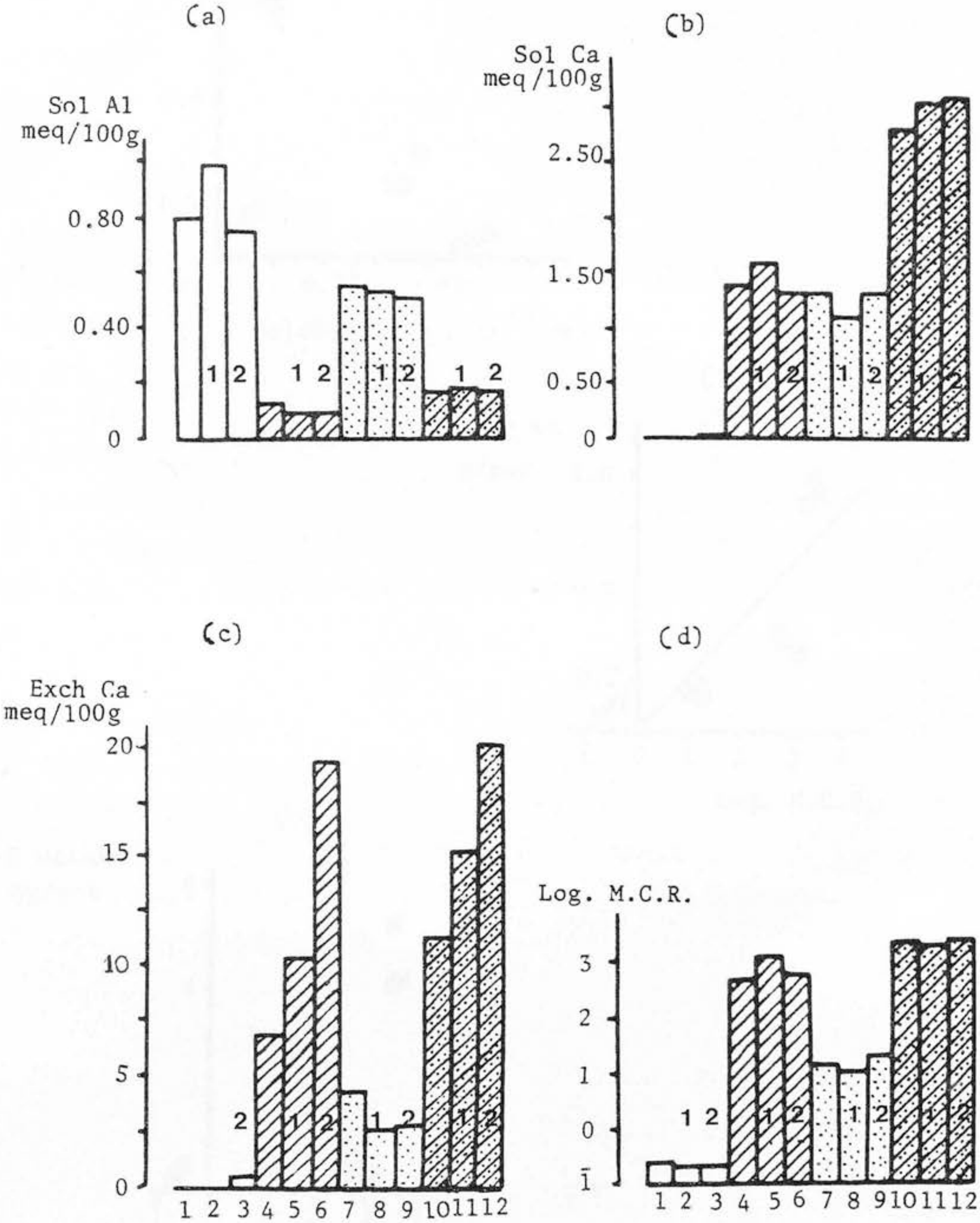
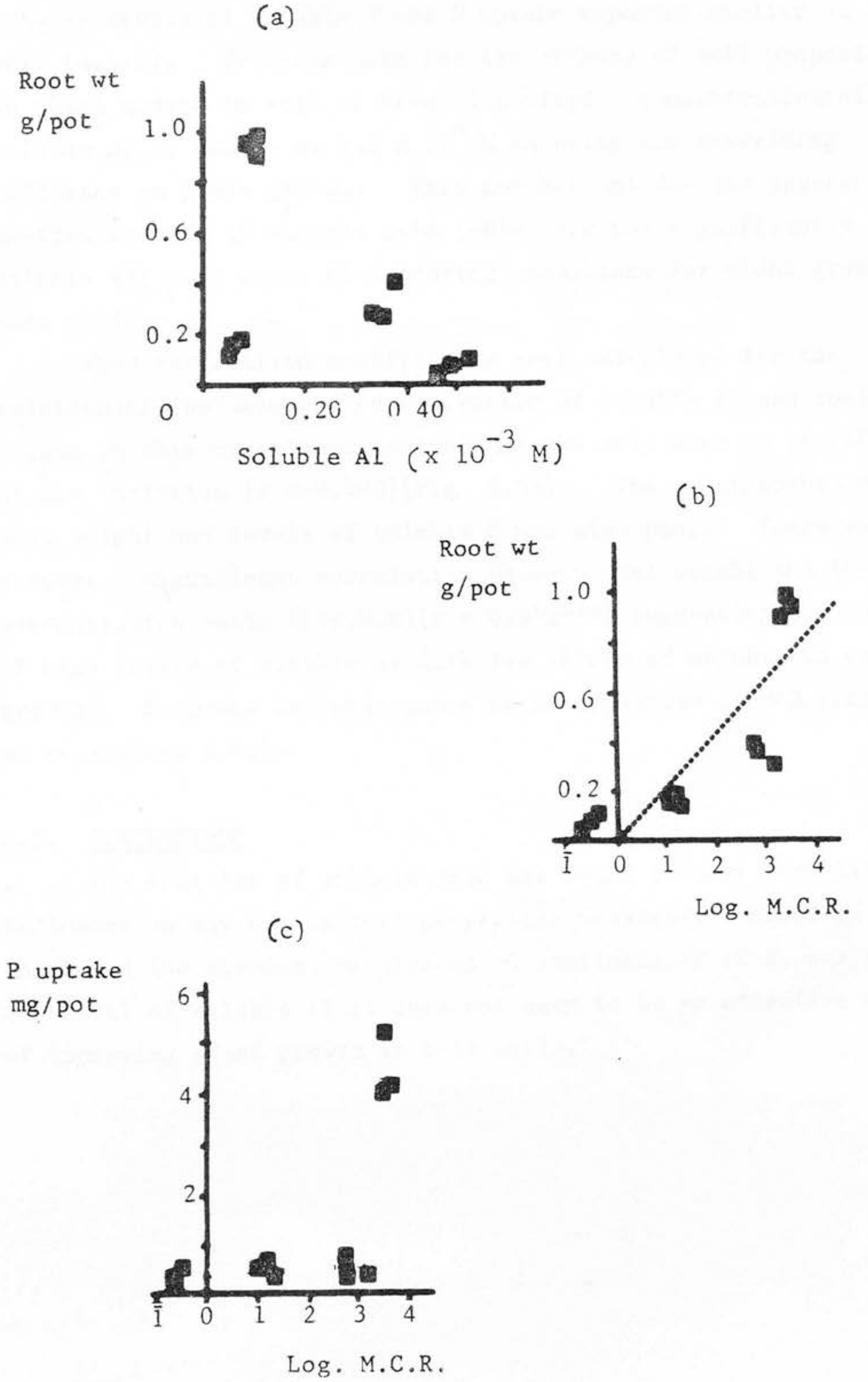


Fig 8.5 Relationships between (a) Root weight and soluble Al (b) Root weight and Molar Concentration Ratio (MCR) and (c) P uptake and MCR.



8.4.2. EFFECT OF SILICIC ACID ON THE GROWTH OF RYEGRASS

Any changes in soluble P due to silicic acid were not reflected by changes in P uptake which agreed with the lack of correlation between levels of soluble P and P uptake reported earlier on this soil (4.4.2). Previous data for the effects of soil properties on plant growth in soil 11 have identified concentrations of soluble Al in excess of 0.2×10^{-3}M as being the overriding influence on plant growth. This may account for the apparent ineffectiveness of silicic acid (which did not significantly reduce soluble Al) as a means of improving conditions for plant growth in this soil.

When correlation coefficients were calculated for the relationship between the concentration of soluble Al and root weight in this experiment, soluble Al was only seen to explain 20% of the variation ($r = -0.492$)(Fig. 8.5a). The relationship between root weight and levels of soluble P was also poor. There was however a significant correlation between root weight and the molar concentration ratio (Log.MCR)($r = 0.952^{***}$) suggesting a combined effect of high levels of soluble Al with low levels of soluble Ca on root growth. P uptake was also shown to be sensitive to MCR (Fig. 8.5c), as in section 4.4.6.

8.5. CONCLUSIONS

The addition of silicic acid was found to have very little influence on any of the soil properties measured. Since it neither increased the chemical or biological availability of P, nor reduced the level of soluble Al it does not seem to be an effective method of improving plant growth in hill soils.

CHAPTER 9

POT EXPERIMENT TO EXAMINE THE EFFECTS OF SUPERPHOSPHATE ON THE GROWTH OF RYEGRASS SEEDLINGS IN FOUR SOILS WITH DIFFERENT Al CONTENTS

9.1. INTRODUCTION AND OBJECTIVES

Observations from previous experiments have suggested that young roots are particularly susceptible to high concentrations of soluble Al and that inhibition of root growth at this stage could lead to early death of plants possibly due to indirect P deficiency. Here the aim was to use seedlings grown in conditions of adequate P and low Al to determine whether more mature plants were better able to withstand the adverse effects of Al. A further aim was to assess the effects of increasing levels of superphosphate addition on Al toxicity in ryegrass. The specific objectives of these experiments were as follows:-

1) Determine the effects of Al on the growth and uptake of P by established ryegrass seedlings.
2) Examine the effects of incremental additions of superphosphate on the levels of soil P, on the relationship between Al and P, and their consequences for plant growth.

9.2. EXPERIMENTAL

9.2.1. SOILS

The soils used in this experiment were located and sampled with help from the West of Scotland College soil advisors and staff of the Soil Survey of Scotland. It was the intention to select four soils which covered a wide and representative range in Al, and which differed only in their amounts of exchangeable- and soluble Al. Unfortunately, although 11 soils were sampled it was not possible to fully comply with these conditions and the 4 soils most closely meeting the specifications were chosen. Even these covered a narrower range in Al than was desirable, and one was high in organic matter.

All four soils were of the Darleith series (on basalt): soil 11a came from a second collection at Carron Forest; 12 was from Skye, while 13 and 14 were from the Carrick Hills. Soil

14 was sampled from an area limed 15 years earlier and adjacent to site 13. Site locations were given in Table 2.1 and Fig. 2.1.

Table 9.1. Selected properties of soils 11a, 12, 13 and 14

Soil	% C	CEC by Sum^{n}	Exch. Al	Exch. Ca	% Al Sat^{n}	* pH	Sol. Al	Extr. Al	Tot. P	PSI	Extr. P	Sol. P
		meq/100g					meq/100g		mg/100g		mg/100g	
11a	9.2	19.7	18.7	0.8	95	3.5	0.90	20.5	269	188	0.33	Tr.
12	2.1	22.1	14.3	5.8	65	4.0	0.19	22.9	562	211	0.31	Tr.
13	21.1	19.9	11.0	6.5	55	4.1	0.04	19.4	500	137	0.56	0.02
14	6.5	14.2	1.8	7.0	13	4.9	Tr	2.4	350	47	0.06	0.01

* $CaCl_2$

The carbon content of three of the soils was less than 10% but in soil 13, % C was more than 20%. CEC, by summation of the major cations, Al, Ca and Mg, was rather similar in 3 of the soils (around 21 meq/100 g) but was about 30% lower in soil 14 (Table 9.1). Percent Al saturation was highest in soil 11a and associated with the lowest pH (3.5). Soils 12 and 13 had similar but lower levels of Al saturation, (65 and 55% respectively) and higher pH values (4.0 and 4.1 respectively). Soil 14, with a past history of lime treatment, had both the lowest Al content and % Al saturation, associated with the highest soil pH. Soluble Al was very high in soil 11a(0.9 meq/100 g) compared with only 0.2 meq/100 g or less in the other soils. Extractable Al however was very high in three of the soils (11a, 12 and 13) and as a consequence of this their PSI values were also very high (> 130) while levels of soluble P were very low. Soil 14 contained very little extractable Al and had a low PSI, but the amounts of soluble and extractable P were as low in this soil as in the other 3 soils. From these data the differences between soils 13 and 14 do not appear to be confined solely to the effects of the lime applied 15 years previously. More information about the soils is provided in Table 9.1A.

9.2.2. POT EXPERIMENT

Six replicates of 6 superphosphate treatments equivalent to 0, 50, 100, 150, 200 and 300 kgP/ha ($P_0, P_1, P_2, P_3, P_4, P_6$) were prepared for each soil and left for one week to equilibrate (Table 9.2A). Ten day old ryegrass seedlings grown in sand plus nutrient solution (Table 9.2A) were washed free of sand and transplanted, 5 per pot, into 5 of the 6 replicates. The sixth replicate was used for soil analysis to assess the effects of applied treatments on:- extractable and soluble P, PSI, extractable-, exchangeable- and soluble-Al, pH, soluble-Ca and Mg: details of all analytical methods were given in chapter 2.

The pots containing the seedlings were transferred to the glasshouse and arranged in randomised blocks. In order to prevent wilting, the seedlings were kept at high humidity by erecting a polythene 'tent' around the pots for one week. Supplementary lighting was provided by 6 overhead lamps providing between 60 and 90 watts m^{-2}: the glasshouse temperature was maintained between 20 and $25^{\circ}C$.

Two harvests were taken, 40 and 80 days after transplanting leaving 1 cm of stubble which was included in the root weight and analysis. Herbage from each harvest was weighed and analysed for P while P and Al were measured in the roots after the 2nd harvest. On soil 11a there was insufficient root material for analysis and herbage analysis was limited to duplicates from the bulked replicates. Full details of the results are given in Tables 9.1A to 9.6A and the main features of these data are described and illustrated in the following sections.

9.3. RESULTS

Transplanted seedlings grew very badly in soil 11a and Al toxicity symptoms were observed at all levels of P addition. Seedlings growing on soils 12, 13 and 14 exhibited P deficiency symptoms in the absence of added P but showed no signs of adverse Al effects (Fig. 9.1).

9.3.1. ROOT AND HERBAGE DRY MATTER PRODUCTION

In contrast to the marked responses to superphosphate in

Fig. 9.1. Effect of different levels of superphosphate addition on seedling growth in soils 14 (Carrick + lime), 13 (Carrick - lime), 12 (Bay) and 11 (Darleith)

(photographed 28 days after planting out)

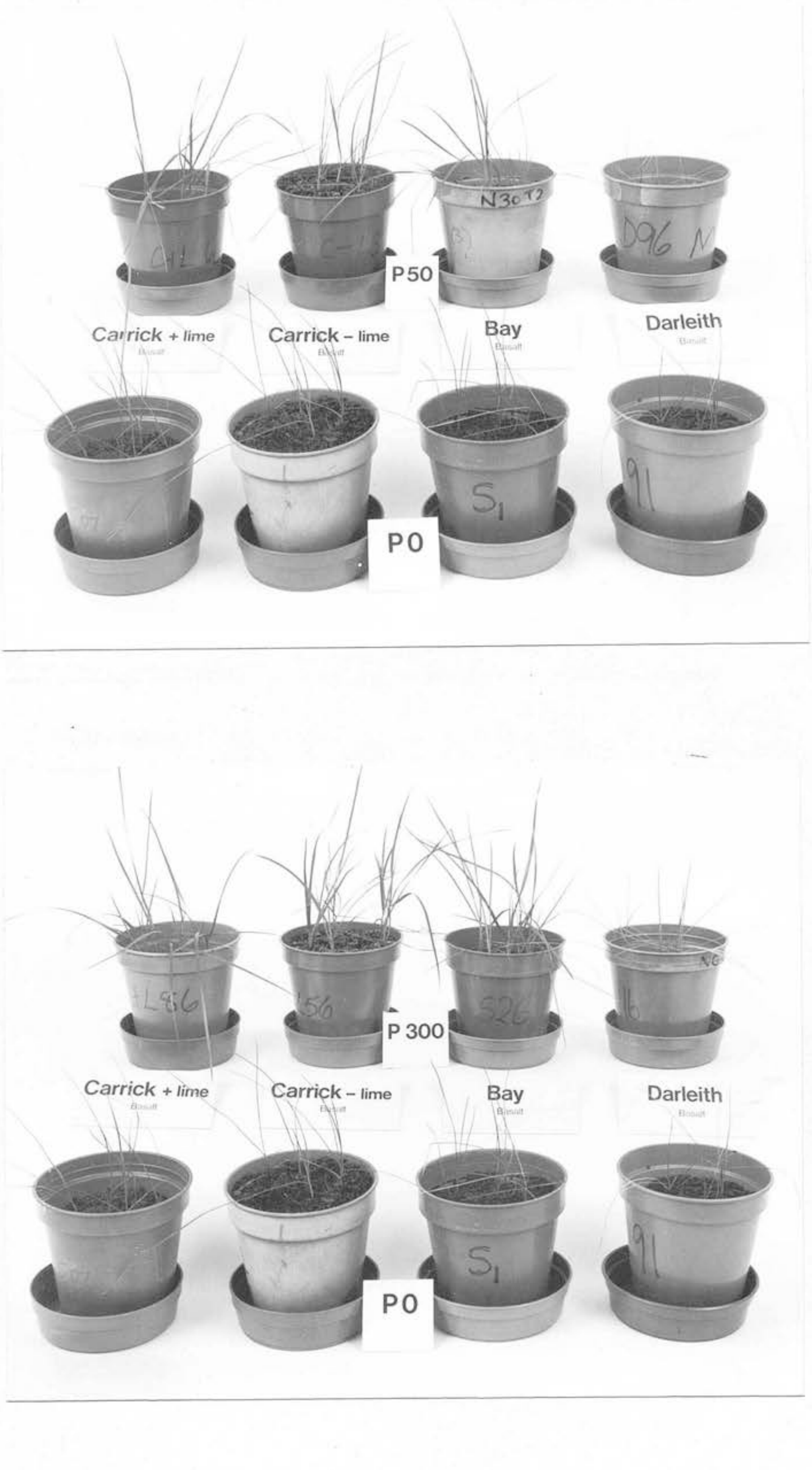
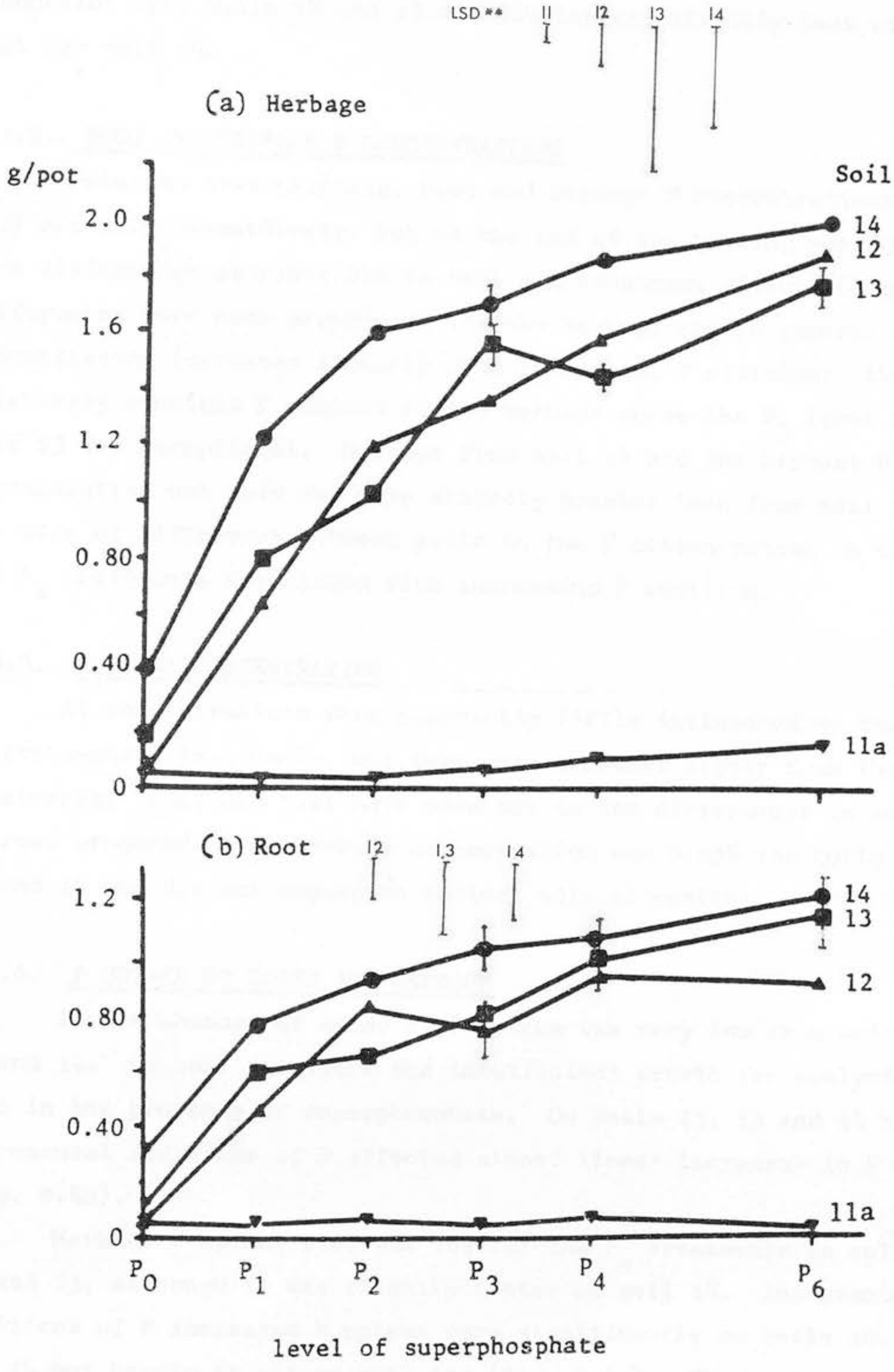


Fig. 9.2 Effect of increasing superphosphate addition on (a) Herbage and (b) Root DM from soils 11a, 12, 13 and 14.



SE < 0.05 not shown

soils 12, 13 and 14 (Fig. 9.2) there was only a very small response on soil 11a. Production of both root and herbage dry matter was highest on soil 14 throughout the range of P treatments, and the difference was especially marked in the absence of applied P. Herbage production from soils 12 and 13 was similar and slightly less than that for soil 14.

9.3.2. ROOT AND HERBAGE P CONCENTRATIONS

Prior to transplanting, root and herbage P concentrations were 0.27 and 1.0% respectively, but at the end of the growing period there were differences attributable to soil and treatment effects (Fig. 9.3). Differences were most pronounced for the herbage and in general the P concentration increased linearly with increasing P addition: the relatively constant P content of the herbage above the P_3 level in soil 13 was exceptional. Herbage from soil 14 had the highest P concentration but this was only slightly greater than from soil 12. The size of difference between soils in the P concentration in the P_o and P_1 treatments diminished with increasing P addition.

9.3.3. ROOT Al CONCENTRATION

Al concentrations were apparently little influenced by the superphosphate treatments, but they were somewhat higher from the P_o treatments: this may just have been due to the differences in amount of root produced. The average concentration was 0.45% for soils 12, 13 and 14 and did not appear to reflect soil Al content.

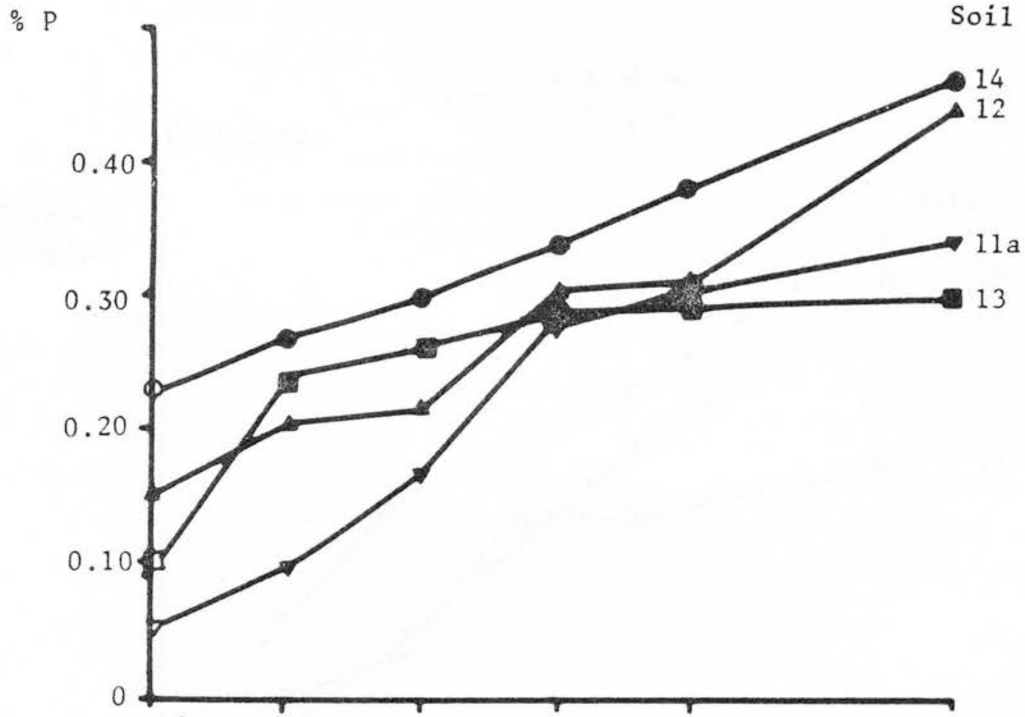
9.3.4. P UPTAKE BY ROOTS AND HERBAGE

In the absence of added P, P uptake was very low from soils 12, 13 and 14. On soil 11a there was insufficient growth for analysis, even in the presence of superphosphate. On soils 12, 13 and 14 however incremental additions of P affected almost linear increases in P uptake (Fig. 9.4b).

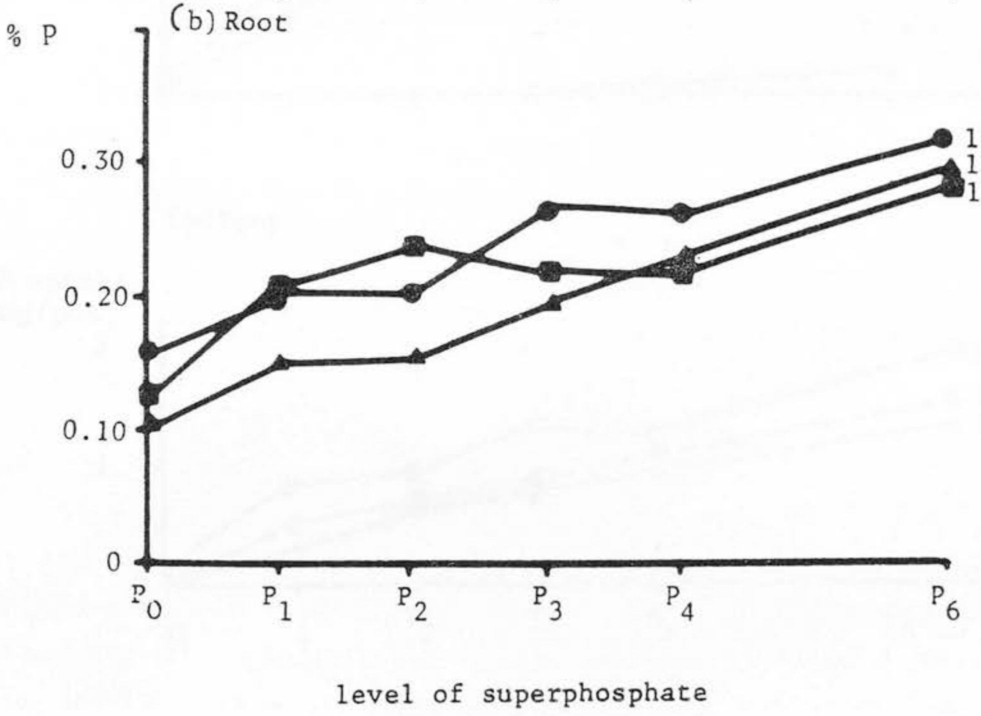
Herbage P uptake also was low for the P_o treatments on soils 11a, 12 and 13, although it was slightly better on soil 14. Incremental additions of P increased P uptake very significantly on soils 12, 13 and 14 but hardly at all on soil 11a (Fig. 9.4a). The pattern of increased uptake varied; on soil 12 the response was linear, but on soils 13 and 14 increases were greatest at the lower levels of P

Fig 9.3 Effect of increasing superphosphate addition on %P in (a) Herbage and (b) Roots from soils 11a, 12, 13 & 14.

(a) Herbage

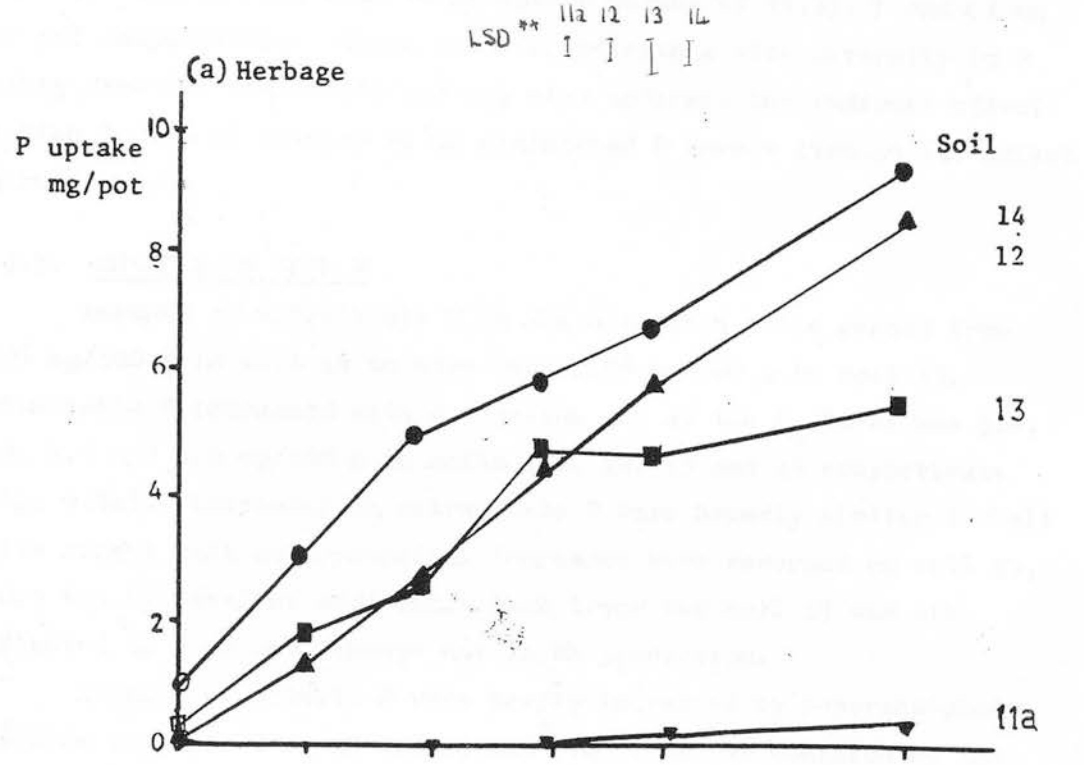


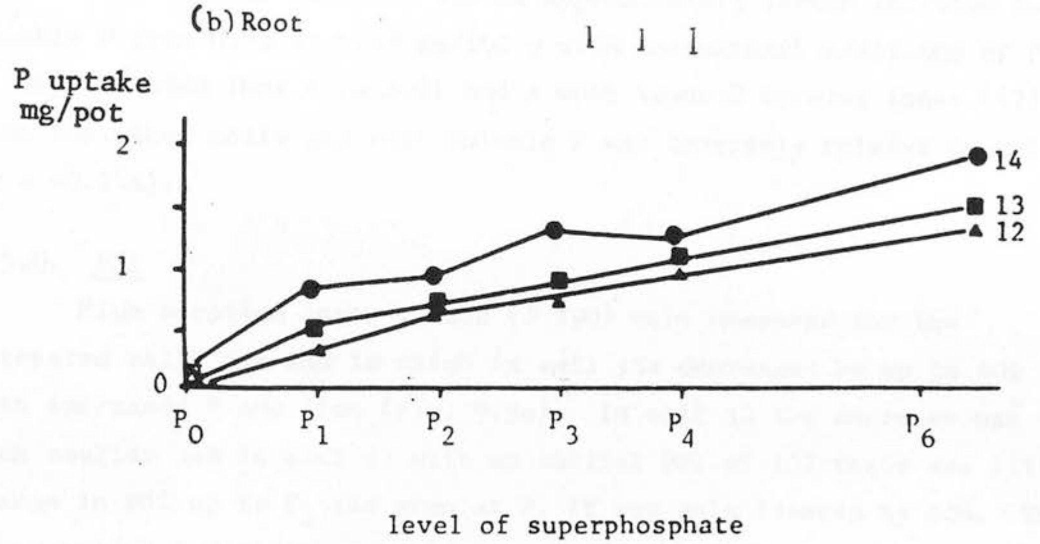
(b) Root



Footnote: Roots from Soil 11a not analysed.

Fig 9.4 Effect of increasing superphosphate addition on P uptake by (a) Herbage and (b) Roots from soils 11a, 12, 13 & 14.





Footnote: Roots from Soil 11a not analysed.

addition. Uncharacteristically, the response plateaued at P_3 for soil 13, with no further significant increase for the P_4 and P_6 addition.

Total P uptake (roots + herbage) was greatest at the highest level of P addition and at this level the soils were ranked in the order $14 > 12 > 13 \gg 11$, with total uptake values of 11, 10, 7 and < 1 mg per pot respectively. These results indicate a wide diversity in P supply from the four soils and may also indicate the indirect effect of high levels of soluble Al on diminished P uptake through its effect on root growth.

9.3.5. CHANGES IN SOIL P

Amounts of extractable P in the untreated soils ranged from 0.06 mg/100 g in soil 14 to more than 0.56 mg/100 g in soil 13. Extractable P increased with P addition and at the P_6 level was 5.4, 6.0, 3.3 and 6.2 mg/100 g in soils 11a, 12, 13 and 14 respectively (Fig. 9.5a). Increases in extractable P were broadly similar for all soils except that no substantial increases were recorded on soil 13, above the P_4 level of addition. This trend for soil 13 was also reflected in P uptake, though not in DM production.

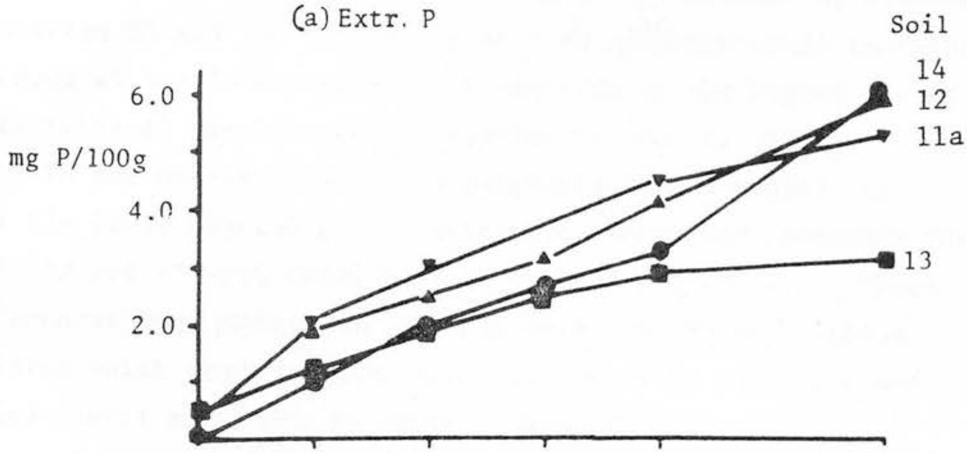
Amounts of soluble P were hardly increased by superphosphate addition in soils 11a, 12 and 13 and even with the addition of the equivalent of 300 kg P/ha remained below 0.10 mg/100 g (Fig. 9.5b). In contrast in soil 14 there was an approximately linear increase in soluble P from 0.01 to 0.49 mg/100 g with incremental additions of P. It may be noted that this soil had a much lower P sorbing index (47) than the other soils and that soluble P was inversely related to PSI ($r = -0.741$).

9.3.6. PSI

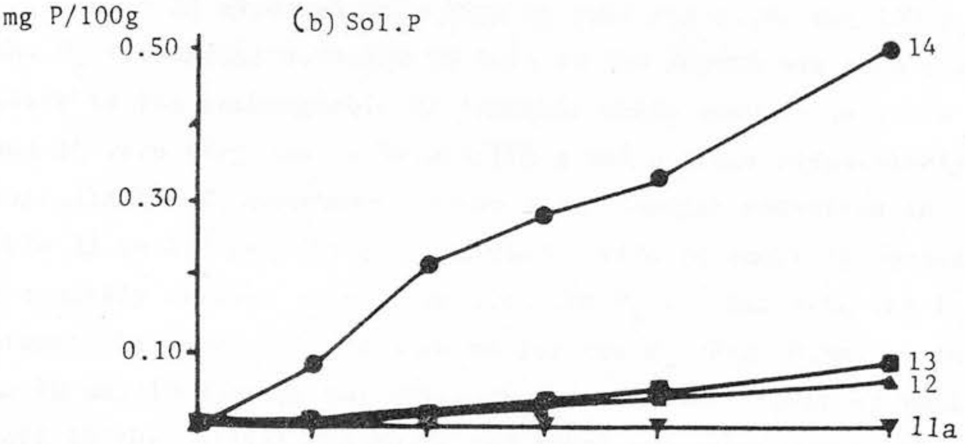
High sorption index values (> 190) were measured for the untreated soils 11a and 12 which in soil 11a decreased by up to 40% with increased P addition (Fig. 9.5c). In soil 12 the decrease was much smaller and in soil 13 with an initial PSI of 137 there was little change in PSI up to P_4 and even at P_4 it was only lowered by 10%. The low sorption index for soil 14 was reduced by 50% by P_1 addition but with higher increments of P there was no further reduction.

Fig 9.5 Changes in the amounts of (a) Extractable P (b) Soluble P and (c) PSI due to incremental additions of superphosphate in soils 11a, 12, 13 & 14.

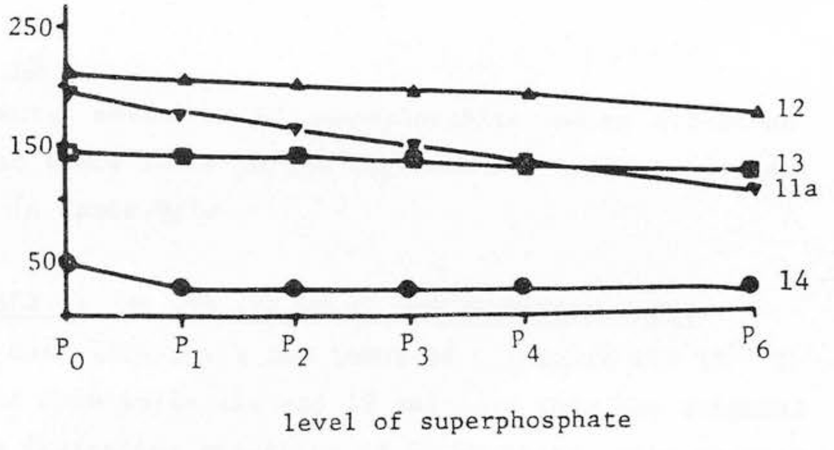
(a) Extr. P



(b) Sol.P



(c) PSI



9.3.7. CHANGES IN SOIL Al

Extractable Al was high in soils 11a, 12 and 13 (12 to 23 meq/100 g) but very low in soil 14 (2 meq/100 g)(Fig. 9.6a). However, despite this common high Al content soils 11a, 12 and 13 were influenced by superphosphate additions differently. In soils 11a, 13 and 14 extractable Al was progressively reduced by between 25 and 30% whereas in soil 12 although small increases occurred at the lower levels of P addition at the higher levels extractable Al was more nearly similar to that in the P_0.

In the untreated soils exchangeable Al was highest in soil 11a (18.7 meq/100 g), intermediate values were recorded for soils 12 and 13 with least in soil 14 (1.8 meq/100 g). These differences were maintained for all levels of superphosphate addition which produced only small increases in soils 11a and 12 and almost no change in soils 13 and 14.

Soluble Al also was very high in soil 11a (0.81 meq/100 g in the P_0 treatment) although in soil 12 the amount was much smaller relative to its exchangeable Al content, while amounts in soils 13 and 14 were very low (0.04 meq/100 g and a trace respectively). In soil 11a the P_1 treatment caused a substantial reduction in soluble Al to 0.5 meq/100 g but higher levels of addition caused progressively smaller reductions from the P_0 so that with the P_6 treatment the level was almost the same as for the P_0 (Fig. 9.6c). In soils 12 and 13 similar but diminished trends were observed while in soil 14 the initial, naturally low level was increased by the P_6 addition.

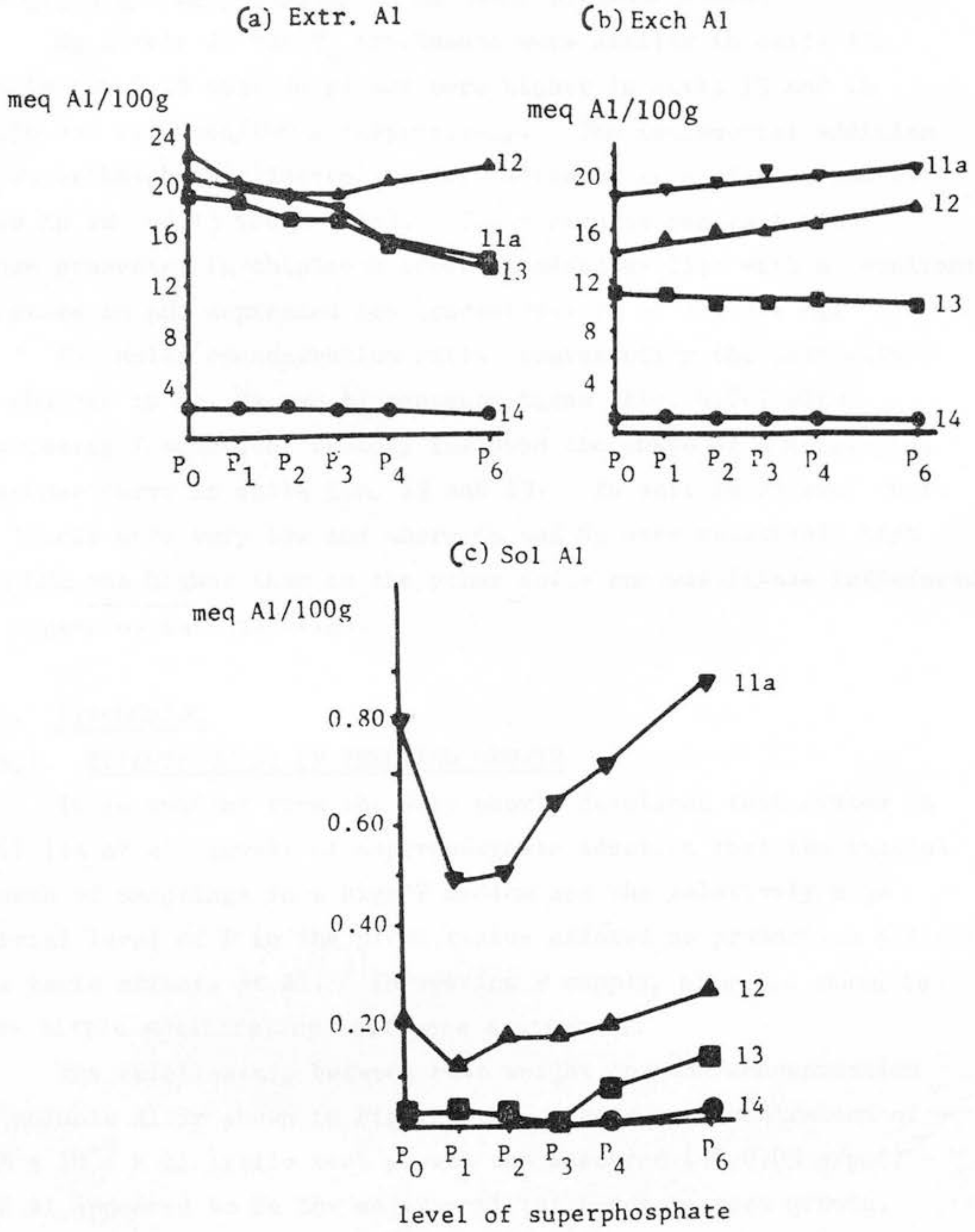
9.3.8. SOIL pH

Incremental additions of superphosphate had no effect on soil pH and in the 4 soils pH was consistently similar to the values given in Table 9.1.

9.3.9. SOLUBLE Ca, Mg AND THE MOLAR CONCENTRATION RATIO

In the untreated soils the level of Ca in the 10^{-3} M $CaCl_2$ extracts from soils 11a and 12 was less than the original concentration indicating retention of Ca by these soils whereas in soils 13 and 14 additional Ca was measured in the $CaCl_2$ extracts

Fig 9.6 Changes in the amounts of (a) Extractable Al (b) Exchangeable Al and (c) Soluble Al due to incremental additions of superphosphate to soils 11a, 12, 13 & 14.



(0.05 and 0.37 meq/100 g respectively). These differences reflect the range in % Ca saturation amongst the soils (3.8, 26, 33 and 49% for soils 11a to 14 respectively), which may also explain the individual patterns of increase in soluble Ca (Fig 9.7a), For soils 14, 12 and 13 especially the tendency was for Ca to be increased most by the highest levels of superphosphate. On soil 11a the increase in Ca was almost linear.

Mg levels in the P_o treatments were similar in soils 11a and 14 ($\sim$ 0.25 meq/100 g) but were higher in soils 13 and 12 (0.58 and 0.79 meq/100 g respectively. The incremental addition of superphosphate effected smaller increases in soils 11a and 14 than in 12 and 13 (Fig. 9.7b). These results contrast with those presented in chapter 6 where Ca added as lime with a resultant increase in pH, depressed the concentrations of soluble Mg.

The Molar concentration ratio, representing the nett effect of changes in Ca, Mg and Al concentrations (Fig. 9.7c) with increasing P addition, broadly followed the shape of a Mitserlich response curve in soils 11a, 12 and 13. In soil 14 however where Al levels were very low and where Ca and Mg were relatively high the MCR was higher than in the other soils and was little influenced by superphosphate addition.

9.4. DISCUSSION

9.4.1. EFFECTS OF Al ON SEEDLING GROWTH

It is evident from the very poorly developed root system in soil 11a at all levels of superphosphate addition that the initial growth of seedlings in a high P medium and the relatively high initial level of P in the plant tissue offered no protection against the toxic effects of Al. Increasing P supply, also was shown to have little ameliorating influence against Al.

The relationship between root weight and the concentration of soluble Al is shown in Figure 9.8a. Above a concentration of 0.3×10^{-3} M Al little root growth was measured ($<$ 0.05 g/pot) and Al appeared to be the major soil influence on root growth. In the range 0.1 to 0.2×10^{-3} M the adverse effects of Al were less pronounced and root weight was relatively high. It can be seen however that where the higher levels of P addition have

Fig 9.7 Changes in the amounts of (a) Soluble Ca (b) Soluble Mg and (c) Log. Molar Concentration Ratio due to incremental additions of superphosphate to soils 11a, 12, 13 & 14

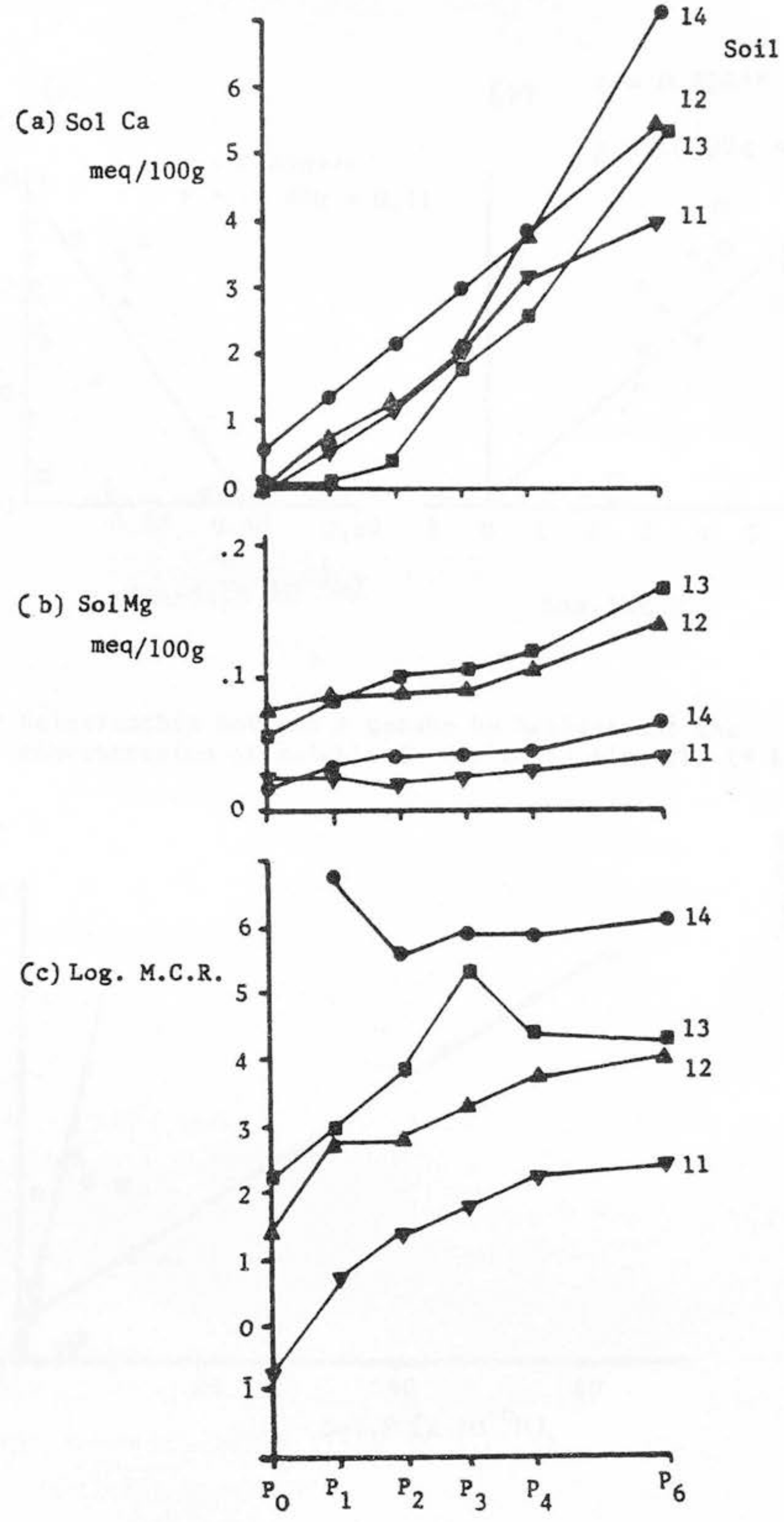


Fig 9.8 Relationship between Root weight and(a) the concentration of soluble Al and(b) Molar Concentration Ratio for soils 11a, 12, 13 & 14.

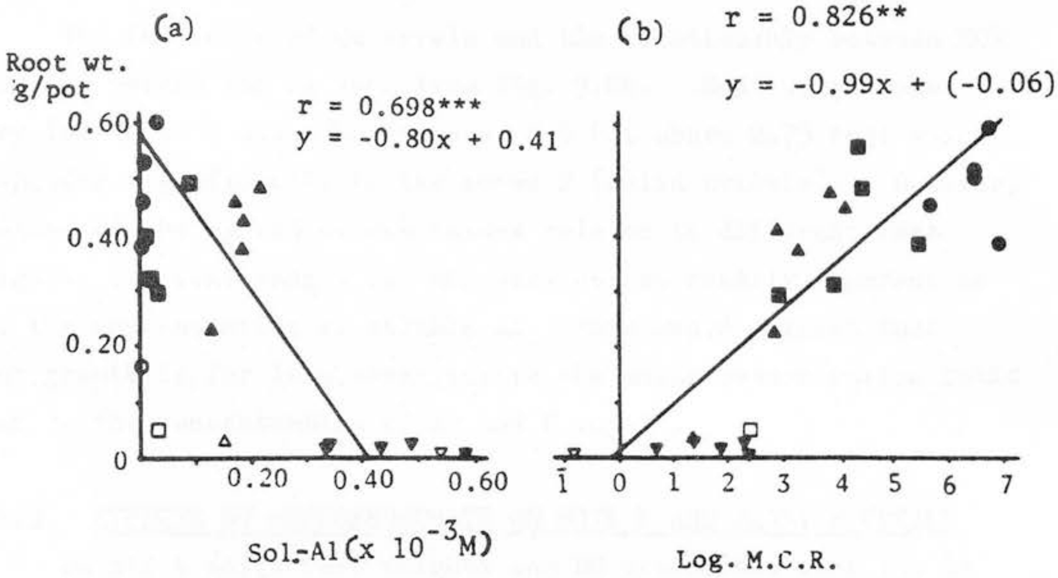
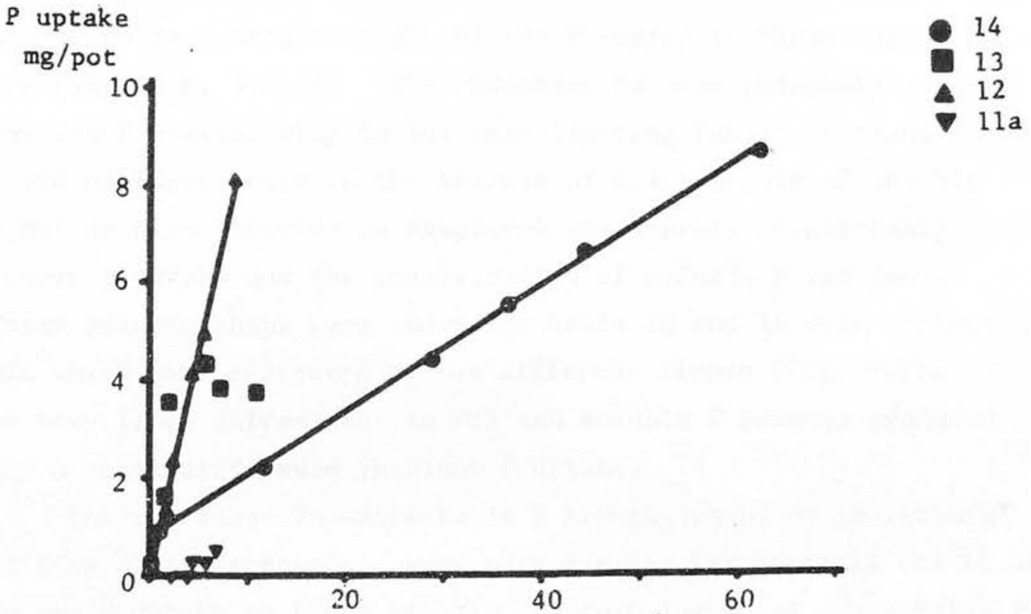


Fig 9.9 Relationship between P uptake by herbage and the concentration of soluble P for soils 11a, 12, 13 & 14



increased soluble and extractable P (Fig. 9.5) but also soluble Al (Fig. 9.6c) root growth in soil 12 (Fig. 9.2b) was increased less by increasing the supply of P. These observations provide further evidence of the restrictive influence of Al in the range 0.1 to 0.2×10^{-3}M.

The influence of Ca levels and the relationship between MCR and root weight can be seen from Fig. 9.8b. Root weight was very low below a log. MCR value of 2.5 but above 2.75 root weight responded significantly to the added P (solid symbols). However, because of the spread of MCR values related to different root weights, critical ranges for MCR were not so readily apparent as for the concentration of soluble Al. This would suggest that root growth is far less sensitive to the molar concentration ratio than to the concentration of Al and P supply.

9.4.2. EFFECTS OF SUPERPHOSPHATE ON SOIL P AND PLANT P UPTAKE

On all 4 soils root weights and DM production were low in the absence of added P (Fig. 9.2b) but in view of the lack of reliable symptoms of Al toxicity (brown, short, stubby roots) together with the low extractable P levels and presence of P deficiency symptoms on soils 12 to 14 the low root weights were thought to be a direct result of low P supply in these soils (see chapter 4, 4.4.2). The responses to superphosphate suggest that low P availability is the main limiting factor to plant growth on these soils in the absence of toxic levels of soluble Al, but as also observed in chapter 4 the overall relationship between P uptake and the concentration of soluble P was poor. Linear relationships were shown for soils 12 and 14 with contrasting PSIs, which were reflected by the different slopes (Fig. 9.9). The very large differences in PSI and soluble P however produced only a small difference in plant P uptake.

The increases in extractable P brought about by incremental addition of superphosphate were more similar for soils 12 and 14 as too was P uptake on these soils. In turn levels of extractable P from soil 13 showed a similar trend to P uptake. With the exception of soil 11a where Al was shown to be the overriding influence on plant growth extractable P was strongly correlated with P uptake ($r = 0.953^{**}$, $r = 0.968^{**}$, $r = 0.859^{*}$ for soils 12, 13 and 14 respectively).

The very small increases in soluble P in soils with such high P sorption properties, together with the increases in soluble Al, induced by the input of Ca ions from superphosphate, may help to explain why superphosphate did not ameliorate the adverse effects of Al on plant growth. The concentration of soluble P would need to be higher than that feasible when P fixation is so high to precipitate Al and render it harmless. CLARKSON (1965) also concluded the ameliorative effects of adding P on Al toxicity were limited to situations which favoured the precipitation of Al phosphate.

9.4.3. ANOMALOUS RESULT

The lack of increase in extractable P for the P_6 treatment on soil 13 was reflected in the results for P content of the herbage (Fig. 9.3a). One explanation for this might have been that an incorrect weight of superphosphate was added to this treatment however this seems unlikely as appropriate changes in soluble Ca, soluble P and extractable Al were obtained. A further possibility is that some other limiting factor was operating against P uptake but this fails to explain why the level of extractable P was also low. No satisfactory explanation has been found.

9.5. CONCLUSIONS

Ryegrass, planted as established 10 day old seedlings, was found to be just as susceptible to Al toxicity as germinating seedlings. In high P fixing soils the addition of superphosphate appears to offer little protection against the adverse effects of Al on root growth. Because of the Ca component of superphosphate its addition in larger amounts may increase the likelihood of Al toxicity in soils with high levels of exchangeable-Al. Concentrations of Al in excess of 0.3×10^{-3} M caused almost total inhibition of root growth while in the range 0.1 to 0.2×10^{-3} M the effects were apparent but less severe and because P supply was good the small reductions in root weight did not apparently influence P uptake.

P uptake was shown to be significantly correlated with extractable P although it did not reflect the variability in soil properties like soluble-P which was poorly related to P uptake. In the absence of excess Al and in the presence of added P yields on a high P fixing soil were almost as high as those on a low P fixing soil suggesting that sorption index 'per se' is not a limitation to growth. Because PSI was inversely related to soluble-P this further suggests that the intensity of P supply may not be critical. The absence of any clear relationship between P uptake and soluble P throughout this study (4.4.2, 6.5) also supports this view.

CHAPTER 10

EFFECTS OF SOLUBLE Al ON ROOT GROWTH

10.1. INTRODUCTION AND OBJECTIVES

From the experiments presented and discussed it appears that Al influences plant growth directly through its inhibitory effect on root development. The roots of ryegrass growing in soils 11 and 11a in the absence of lime exhibited symptoms characteristic of Al toxicity. The significant inverse correlation between soluble Al and root weight suggested that the concentration of Al soluble in 10^{-3} M $CaCl_2$ might provide a quantitative diagnostic assessment of the likelihood of Al toxicity. In the experiments described here several techniques were used in attempts to demonstrate, confirm and quantify the direct effects of Al on root growth using:- a) soil sandwich in root chamber; b) split root technique and c) seeds were grown in $CaCl_2$ soil extracts to determine the critical concentrations of Al. The specific objectives of these experiments were:-

1. Quantify the effects of Al on root elongation and development using a),
2. Distinguish between the direct adverse influence of Al on root growth and the secondary resultant effect of reduced P uptake as the prime causal influence on the growth of ryegrass using b),
3. Determine the effect of different concentrations of Al and Ca, and pH on radicle emergence and elongation using c),
4. Examine the effect of Al on mitosis in the root tip using c).

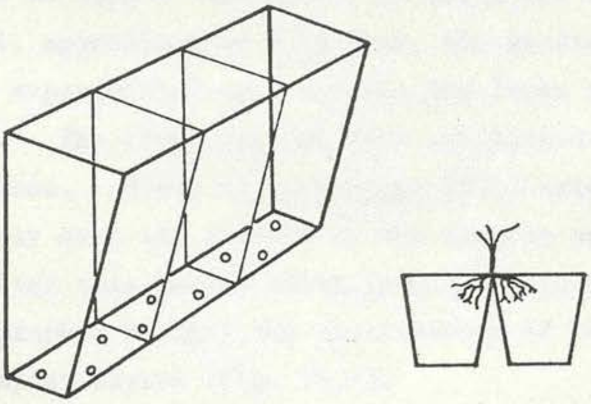
10.2. EXPERIMENTAL

10.2.1. SOILS

The soils used in techniques (a) and (c) were the same untreated soils used in chapter 9 (11a, 12, 13 and 14), technique (c) also included those from the P_6 treatment, while only soil 11a was used in technique (b).

Fig 10.1(a) Root observation chamber and pot arrangement for split root technique and(b) Root distribution in soil cores from root observation chamber.

(a)



(b)

Soil 14 13 12 11a

10.2.2. ROOT CHAMBER TECHNIQUE (a)

Four root chambers were made with clear perspex fronts (Fig. 10.1) to facilitate daily observations on root growth and morphology, and the measurement of root elongation. Glass fibre filter pads were soaked and placed in the bases of the chambers which were filled so as to form a "sandwich", of which the bottom layer was moist compost, approximately 8 cm deep, the middle layer (10 cm deep) was moist experimental soil and the top layer was the same as the bottom. The clear perspex face was masked with black,detachable,polythene. Seeds of L. perenne (S24) were sown along the edge and evenly over the surface of the compost and grown for a month. After this period cores from the soil sandwich were removed and photographed to show the distribution of roots within the soil and compost layers (Fig. 10.1).

10.2.3. SPLIT-ROOT TECHNIQUE (b)

Two square (10 cm) plastic pots each with one side ground to a knife edge at the top were glued together with a suitable adhesive. One pot was filled to the brim with a nutrient rich soil, with a very low level of soluble Al, and the other similarly filled with soil 11a(untreated). Five 16 day old seedlings with all five seminal roots developed were placed so that they had 3 roots in soil 11 and 2 roots in the nutrient rich soil (Fig. 10.1). The seedlings were supported abreast the 2 pots using foil until they became self-supporting.

10.2.4. RYEGRASS RADICLE GROWTH IN SOIL EXTRACT SOLUTIONS (c)

Soil from the P_o and P_6 treatments for soils 11a to 14 (chapter 9) was shaken with 10^{-3} M $CaCl_2$ at 1:5 and 1:10 soil: solution ratios for 1 hour, and then filtered in order to obtain solutions covering a range of Al concentrations. Seed testing paper was placed in 16 petri dishes and soaked with the soil extracts to keep the seedlings moist during the six day growing period. Samples of the extracts were analysed for pH, Al and Ca. 23 seeds were placed on a grid layout in petri dishes which were kept in an incubator at 23°C until the seeds had germinated whence they were returned to the laboratory. Following germination 6 daily measurements, to the nearest 1 mm, were taken for 20 main axial roots.

At the end of the six day period the root tips were removed and macerated as described in the Appendix (2.4A). However, even with the help of experienced staff at the Royal Botanic Gardens, Edinburgh, scoring of abundance of meristematic cells in each of the five stages of mitosis (CLARKSON, 1965) was confounded by the difficulties encountered with cell maceration. It was suggested that roots grown in soil might be macerated more successfully but unfortunately time did not permit a repeat of this experiment using modified techniques.

Ca and Al concentrations and pH were measured in the filtrates using the methods described in chapter 2.

10.3. RESULTS AND INTERPRETATION

10.3.1. ROOT CHAMBER OBSERVATIONS

The daily measurements were abandoned after 5 days when it became apparent that the roots were growing preferentially down the perspex face rather than within the soil. This method therefore proved unsatisfactory for the determination of the quantitative effects of soil Al on root elongation. However, sample cores taken at 40 days revealed many fewer roots in the experimental soil layer when it consisted of soil 11a than when the other soils were used. (Fig. 10.1b). This confirmed previous observations (chapters 4 to 9) that soil 11a was the least favourable for root growth.

10.3.2. SPLIT ROOT EXPERIMENT

14 days after transplanting the seedlings roots inserted into soil 11a had shrivelled but the transplanted seedlings were still growing as a result of better root growth in the adjoining nutrient rich, non-toxic soil. This phenomenon of the nutrient demands of the whole plant being satisfied by nutrient uptake from those roots growing in the better soil has been described as 'compensatory growth' (RUSSELL, 1978). When it occurs the roots growing in the poor soil become obsolete and sensece as observed here. Because of this phenomenon this method was unsuitable as a technique for

elucidating the effects of Al on plant growth.

Foliar sprays are an alternative method of overcoming nutrient stress (REED and TUKEY, 1978) although the aerial morphology of grasses does not provide a very suitable geometry or surface for efficient sorption. If time had permitted however this method would have been investigated as a means of counteracting the effects of Al on nutrient uptake.

10.3.3. CRITICAL CONCENTRATIONS OF SOLUBLE Al

More than 20 seeds germinated in all treatments confirming previous observations that Al and pH (over the range tested) had no effect on germination. Initially elongation of the main root was rapid (> 2 mm/day) in all 16 extracts and a single green leaf was seen on the second day which grew slowly in all extracts but without changing appearance. Roots, however, behave differently and by the 3rd day the root tips from seedlings in all extracts from soil 11a had begun to turn brown. A similar browning effect was also observed in the P_6 treatments (at both soil: solution ratios) from soil 12. By the 6th day no further elongation was measured for the roots growing in the solution from soil 11a; the thin brown roots had begun to curl and fewer laterals, which were themselves spindly, were noted compared with roots growing in extracts from the other soils.

Table 10.1. Effects of superphosphate treatment level, and soil: solution ratios on mean lengths of main root (mm ± SEM)

Treatment	P_o	P_6
1:5 ratio	22.2 ± 3.3	22.0 ± 3.9
1: 10 ratio	22.0 ± 3.9	23.4 ± 4.7

When the root lengths, based on 20 observations, were considered (Table 10.1), there were no significant differences due to either P treatment level (P_o - P_6) or soil:solution ratio (1:5, 1:10. However, when root growth and the maximum root lengths were compared for the individual treatments (Fig. 10.2) (Table 10.2) it can be seen that root growth in the extract from soil 11a was well below that from the other soils.

Fig 10.2 Root Elongation per day in 10^{-3} M $CaCl_2$ extracts from soils 11a, 12, 13 and 14 at two ratios of soil to solution (1:5 and 1:10) with and without added P (open and closed symbols).

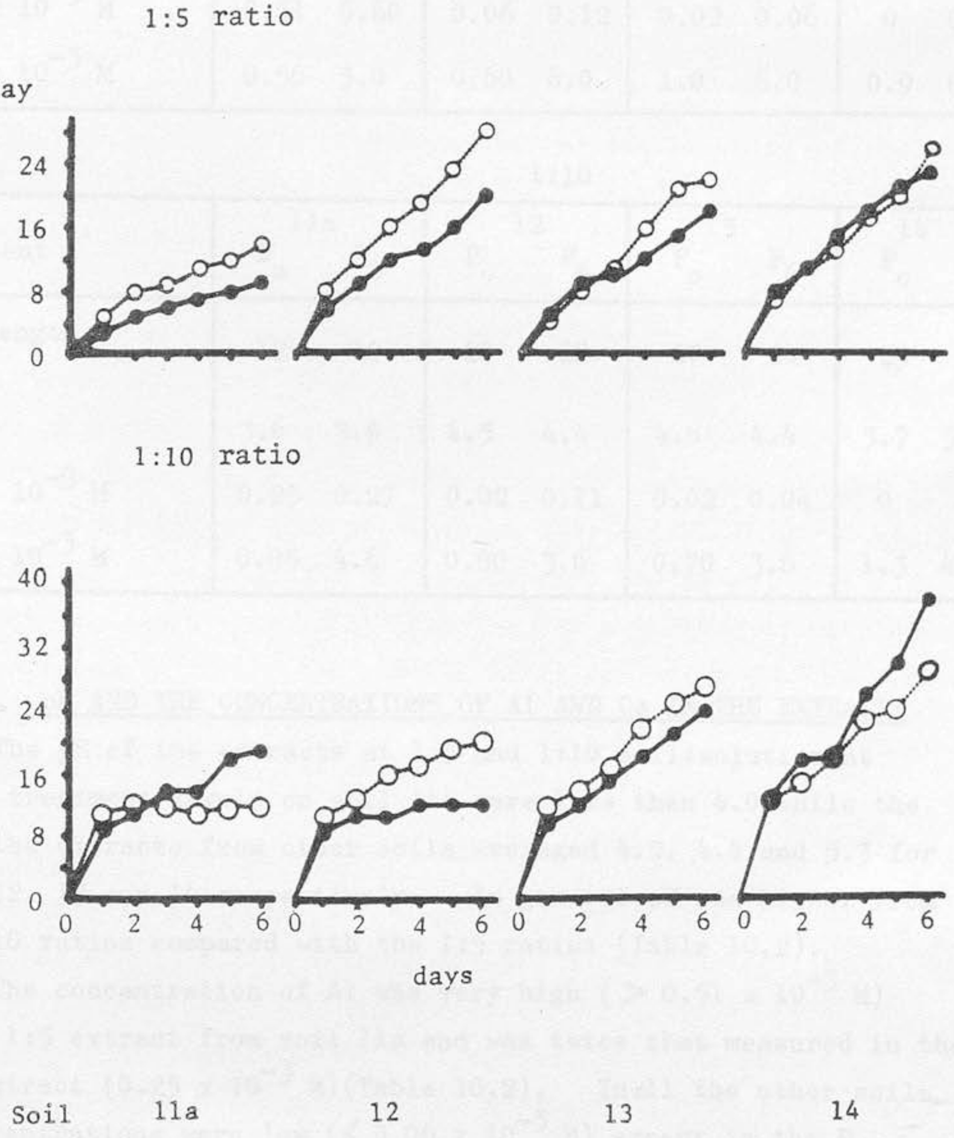


Table 10.2. Maximum root length, pH and the molar concentration of Al and Ca in the 1:5 and 1:10 $CaCl_2$ extracts

Ratio	1:5							
Soil	11a		12		13		14	
Treatment	P_o	P_6	P_o	P_6	P_o	P_6	P_o	P_6
root length mm	13	7	28	20	22	18	26	25
pH	3.4	3.6	3.9	4.0	4.4	4.4	4.9	4.7
$[Al] \times 10^{-3}$ M	0.51	0.60	0.06	0.12	0.02	0.06	0	0.01
$[Ca] \times 10^{-3}$ M	0.50	5.0	0.60	6.0	1.0	6.0	0.9	6.5
Ratio	1:10							
Soil	11a		12		13		14	
Treatment	P_o	P_6	P_o	P_6	P_o	P_6	P_o	P_6
root length mm	12	19	20	12	27	24	29	38
pH	3.6	3.9	4.5	4.4	4.6	4.4	5.7	5.9
$[Al] \times 10^{-3}$ M	0.25	0.27	0.02	0.11	0.02	0.04	0	0
$[Ca] \times 10^{-3}$ M	0.95	4.6	0.80	3.6	0.70	3.6	1.3	4.7

10.3.4. pH AND THE CONCENTRATIONS OF Al AND Ca IN THE EXTRACTS

The pH of the extracts at 1:5 and 1:10 soil:solution at both P treatment levels on soil 11a were less than 4.0 while the pH of the extracts from other soils averaged 4.2, 4.4 and 5.3 for soils 12, 13 and 14 respectively. In general pH was higher from the 1:10 ratios compared with the 1:5 ratios (Table 10.2).

The concentration of Al was very high ($> 0.51 \times 10^{-3}$ M) in the 1:5 extract from soil 11a and was twice that measured in the 1:10 extract (0.25×10^{-3} M)(Table 10.2). In all the other soils Al concentrations were low ($< 0.06 \times 10^{-3}$ M) except in the P_6 treatment from soil 12 where the concentration exceeded 0.1×10^{-3}M. In general Al concentrations were lower in the 1:10 than in the 1:5 extracts and from the P_o than the P_6 treatments coinciding with the higher pHs.

In the P_o extracts, with the exception of soil 14 (1:10) the concentration of Ca was equal to or less than that of the extracting solution indicating that Ca had been adsorbed by the soils in most cases (Table 10.2). At the high level of superphosphate addition (P_6) concentrations of Ca in the 1:5 extract were increased 10 fold over the P_o treatment in soils 11a and 12 and by 6 to 7 fold in soils 13 and 14. In the 1:10 extract increases were smaller, and more nearly similar in all four soils.

10.3.5. RELATIONSHIP BETWEEN ROOT ELONGATION, pH AND THE CONCENTRATIONS OF Ca and Al

The inhibition of root elongation and the browning of the root tips which are characteristic of Al toxicity were most clearly demonstrated in the extracts from soil 11a where they were also associated with low pH. Highly significant inverse relationships were demonstrated between maximum root length and both the concentration of Al and pH ($r = 0.782^{***}$ and 0.825^{***} respectively). Together pH and the concentration of Al explained 76% of the variation in root length while separately pH explained 68% and Al 61% respectively. The inclusion of the concentration of Ca into the regression analysis did not improve the amount of variation explained suggesting that the concentration of Ca did not significantly modify the effects of Al and pH on root elongation.

No results are available from the attempt to study the effect of Al on stages of mitosis.

10.4. DISCUSSION AND CONCLUSIONS

Neither technique a) nor b) proved successful for the examination of the direct effects of soil Al on root growth. Method c) for the identification of soils which may contain potentially toxic levels of Al to ryegrass (S24) was partly successful. When concentrations of Al exceeded 0.25×10^{-3} M the shrivelling of the roots confirmed suggestions from previous experiments that the inhibition of root growth by Al was the cause of the very limited growth and eventual death of ryegrass in that soil. The results also suggest that low pH may be more important than low Ca levels in accentuating the adverse effects of high concentrations of soluble Al.

Root appearance and reduced root length were demonstrated in soils and treatments with intermediate concentrations of Al, but in this case the effects were not as severe as when Al concentration exceeded 0.25×10^{-3} M. The concentration range of Al between 0.1 and 0.2×10^{-3} M was within that shown in chapter 4 to be associated with some reduction in growth. However results from the pot experiment reported in chapter 9 provided no evidence to suggest that DM production or P uptake were restricted in that range of soluble Al. A possible explanation for this discrepancy between the 2 sets of data may be that, where Al concentrations are only moderately toxic (0.1 to 0.2×10^{-3}M) the intensity of soluble Al in all parts of the soil system with which the root is in contact may not be as uniform as in the liquid phase in this experiment. Since toxic levels of Al were associated with the inclusion of superphosphate which contains Ca there is a greater chance of the Al concentrations not being uniform throughout the soil. It is also likely that where the level of P in the soil is higher due to fertiliser application a smaller root system can satisfy the plants nutrient uptake requirements.

It appears, therefore that the $CaCl_2$ bioassay technique described here might be useful for the identification of soils where Al toxicity may reduce the growth of ryegrass, although it may not be as useful for fertilised soils. Symptoms of Al toxicity which may be used to assess the concentration effects include reduced root elongation, browning and curling of the roots with poorly developed laterals.

CHAPTER 11

POT EXPERIMENT TO EXAMINE THE EFFECT OF DIFFERENT CONCENTRATIONS OF SOLUBLE Al IN VIRGIN SOILS ON THE GROWTH OF RYEGRASS IN THE PRESENCE AND ABSENCE OF LIME AND SUPERPHOSPHATE

11.1. INTRODUCTION AND OBJECTIVES

Virgin soils, characterised by concentrations of soluble Al between 0.05 and 0.20 x 10^{-3}M were collected for this experiment to study the effects of naturally occurring, intermediate levels of soluble Al on plant growth. Results from previous experiments, in which intermediate Al concentrations have resulted only from treatment effects, have suggested that under certain conditions concentractions of Al in the range 0.1 to 0.2 x 10^{-3}M may reduce the response of ryegrass to superphosphate. It was hoped to explore these conditions in this experiment in which the specific objectives were:-

1. Examine the effects of a 15 fold range in soluble Al on ryegrass growth and mineral composition.
2. Examine the effects of lime and superphosphate additions on pH, the concentration of soluble Al and P in these soils, and on the growth and composition of ryegrass.

11.2. EXPERIMENTAL

11.2.1. SOILS

The locations of soils 15 to 19 used here are indicated in Figure 2.1 and full analytical details in Table 11.1A. The main features are summarised here. Except for soil 16 with a carbon level of 18.5% the other four soils contained less than 8% carbon. Soil 16 was included to investigate the effect of organic matter in the reactions of soluble Al since it provided a direct comparison with soil 15 as both soils contained the same amounts of soluble-Al (0.22 meq/100g). The other three soils (17 to 19) had much lower levels of soluble Al ($<$ 0.1 meq/100 g: $<$ 0.08 x 10^{-3}M). pH was low in four of the soils (15 to 18: 4.1 in $CaCl_2$) but high in soil 19 (4.9). Al saturation was also high in these soils ($>$ 75%) but only 14% in soil 19 (Table 11.1). Levels of exchangeable Al however were not so similar for soils 15 to 18 with soil 18 containing the most (20 meq/100 g), soils 16 and 17 similar amounts (∼ 10 meq/100 g) and soil 15 intermediate between these. Soil 19 in contrast only contained 1.8 meq/100 g. There was an even wider range in exchangeable Ca from less than 0.3 meq/100 g in soils 17 to 10 meq/100 g in soil 19.

Table 11.1. Selected properties of Soils 15, 16, 17, 18 and 19.

Soil	% C	pH	Sol. Al	% Al sat^n	Exch. Al	Exch. Ca	Extr. Al	PSI	Extr. P	Sol.P
			meq/100g		—— meq/100 g		——		— mg/100 g —	
15	4.6	3.7	0.22	90	15.1	1.5	5.6	57	0.25	0.05
16	18.5	3.5	0.22	77	10.9	2.5	4.5	63	0.19	0.07
17	8.0	4.1	0.06	95	9.2	0.3	18.8	140	0.13	0.01
18	7.1	3.9	0.09	78	20.0	4.5	11.8	113	0.06	0.01
19	7.7	4.9	0.01	14	1.8	10.0	3.5	54	0.06	0.03

High values were recorded in both soils 17 and 18 for PSI and extractable Al (> 100 and > 10 meq/100 g respectively) while in soils 15, 16 and 19 PSI was around 60 and extractable Al around 4 meq/100 g (Table 11.1). Extractable P was low (< 0.25 mg/100 g) in all five soils and by comparison with data for other hill soils (chapters 4 to 9) would suggest a large expected response to superphosphate addition. Soluble P was very low especially in the soils (17 and 18) with the highest PSI values.

11.2.2. POT EXPERIMENT

Four replicates of each of the untreated soils, superphosphate (equivalent to 80 kgP/ha) and lime (equivalent to 1250 kg/ha) treatments were prepared using 10 cm pots as described in chapter 2. These amounts were equivalent to those used in chapter 4 (Table 4.2A) but in this case only a one week equilibration period was used. A separate replicate treatment for chemical analysis was not prepared but instead samples of soil for analysis were removed from the individual pots by taking 5 cores with a cork borer. Seeds of L. perenne (S24) were sown at the rate given in Table 4.2A; a single harvest was taken 28 days after germination.

pH was measured in the 10^{-3} M $CaCl_2$ solution used to extract soluble P and Al. P, Ca, Mg, K, Fe and Mn were measured in the herbage and P, Ca, Mg, K and Al determined in the roots. Statistical differences were tested using the Student's T test. Details of these methods were given in chapter 2.

11.3. RESULTS

Full details of analytical data are given in Tables 11.1A to 11.3A, and the main features are described in this section.

11.3.1. OBSERVATIONS ON PLANT GROWTH

Al toxicity symptoms were observed after 2 weeks but only in the untreated soil 15. Symptoms of P deficiency were just showing before harvest on the non P treatments on all five soils, and substantial responses were observed on all superphosphate treatments.

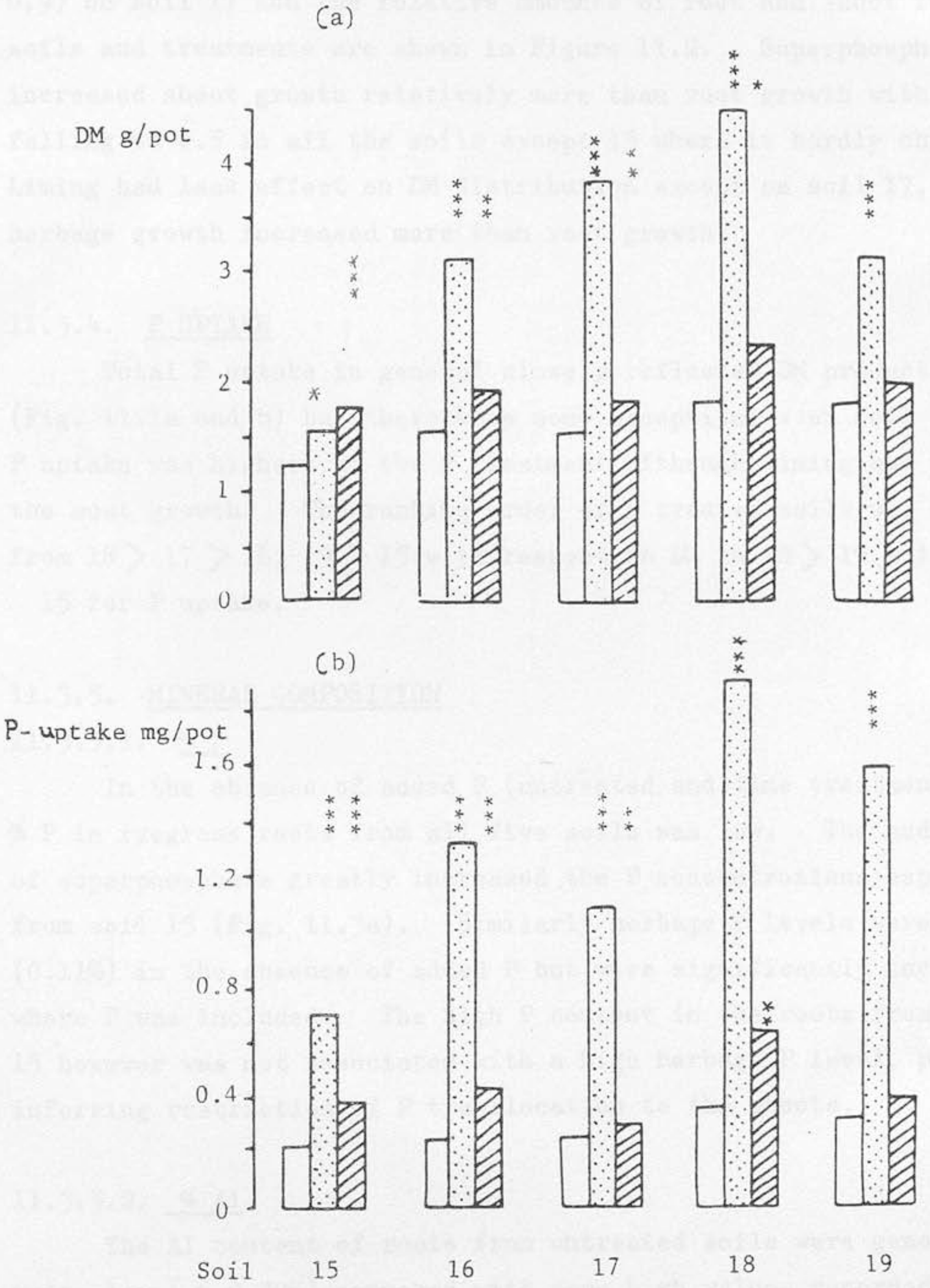
11.3.2. DRY MATTER PRODUCTION

Treatment effects were similarly shown by both roots and herbage production and their combined total DM production has been used for interpretation (Fig. 11.1a). On the untreated soils this was significantly ($P < 0.01$) lower from 15 than from 16 and 17 where amounts were not significantly different but were in turn significantly ($P \leq 0.01$) less than from soils 18 and 19.

Dry matter production was very significantly ($P < 0.01$) increased by the addition of superphosphate on soils 16 to 19. On soil 15 however, the increase was relatively small and barely significant ($P = 0.05$). Amounts of dry matter production on this treatment were not significantly different between soils 16, 17, 18 and 19 but the yield on soil 15 was significantly ($P < 0.05$) less than from these (Table 11.3A).

The addition of lime produced smaller but significant responoses in DM in soils 15 to 18 ($P < 0.001$, 0.01, 0.01 and 0.05 respectively). On soil 19 however where exchangeable Ca was very high there was no significant response to lime.

Fig 11.1 Effects of superphosphate and lime on(a) Total DM and(b) Total P uptake from soils 15, 16, 17, 18 & 19.



Footnote: Treatment symbols as for chapter 4.

* significantly different from control P< 0.05
** significantly different from control P< 0.01
*** significantly different from control P< 0.001

11.3.3. ROOT : SHOOT RATIOS (R/S)

There was quite a range in R/S values amongst the five untreated soils from 0.69 on soil 15, and 0.8 on soils 16, 18, 19, to 0.97 on soil 17 and the relative amounts of root and shoot for both soils and treatments are shown in Figure 11.2. Superphosphate increased shoot growth relatively more than root growth with R/S falling to 0.5 in all the soils except 15 where it hardly changed. Liming had less effect on DM distribution except on soil 17, where herbage growth increased more than root growth.

11.3.4. P UPTAKE

Total P uptake in general closely reflected DM production (Fig. 11.1a and b) but there were some exceptions : on soil 15 P uptake was highest on the P treatment although liming had produced the most growth. The ranking order of P treated soils was changed from 18 > 17 > 16, 19 > 15 with respect to DM to 18 > 19 > 16 > 17 > 15 for P uptake.

11.3.5. MINERAL COMPOSITION

11.3.5.1. % P

In the absence of added P (untreated and lime treatments) % P in ryegrass roots from all five soils was low. The addition of superphosphate greatly increased the P concentrations especially from soil 15 (Fig. 11.3a). Similarly herbage P levels were low (0.11%) in the absence of added P but were significantly increased where P was included. The high P content in the roots from soil 15 however was not associated with a high herbage P level, possibly inferring restriction of P translocation to the shoots.

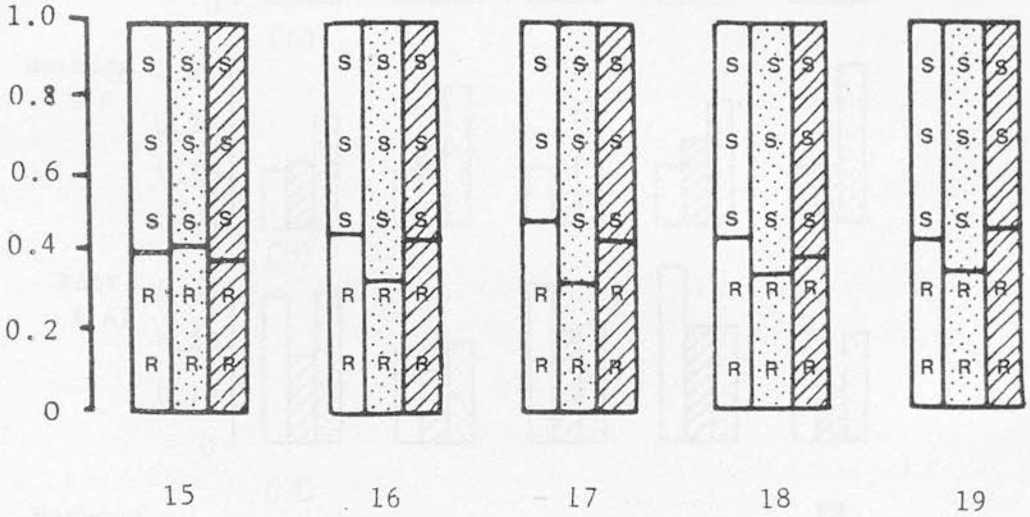
11.3.5.2. % Al

The Al content of roots from untreated soils were generally quite low (< 0.30%) compared with some high values recorded in chapter 4 (4.3.6). Root Al content was lowered by both liming and, to a lesser extent, by superphosphate treatments (Fig. 11.3c).

11.3.5.3. % Ca

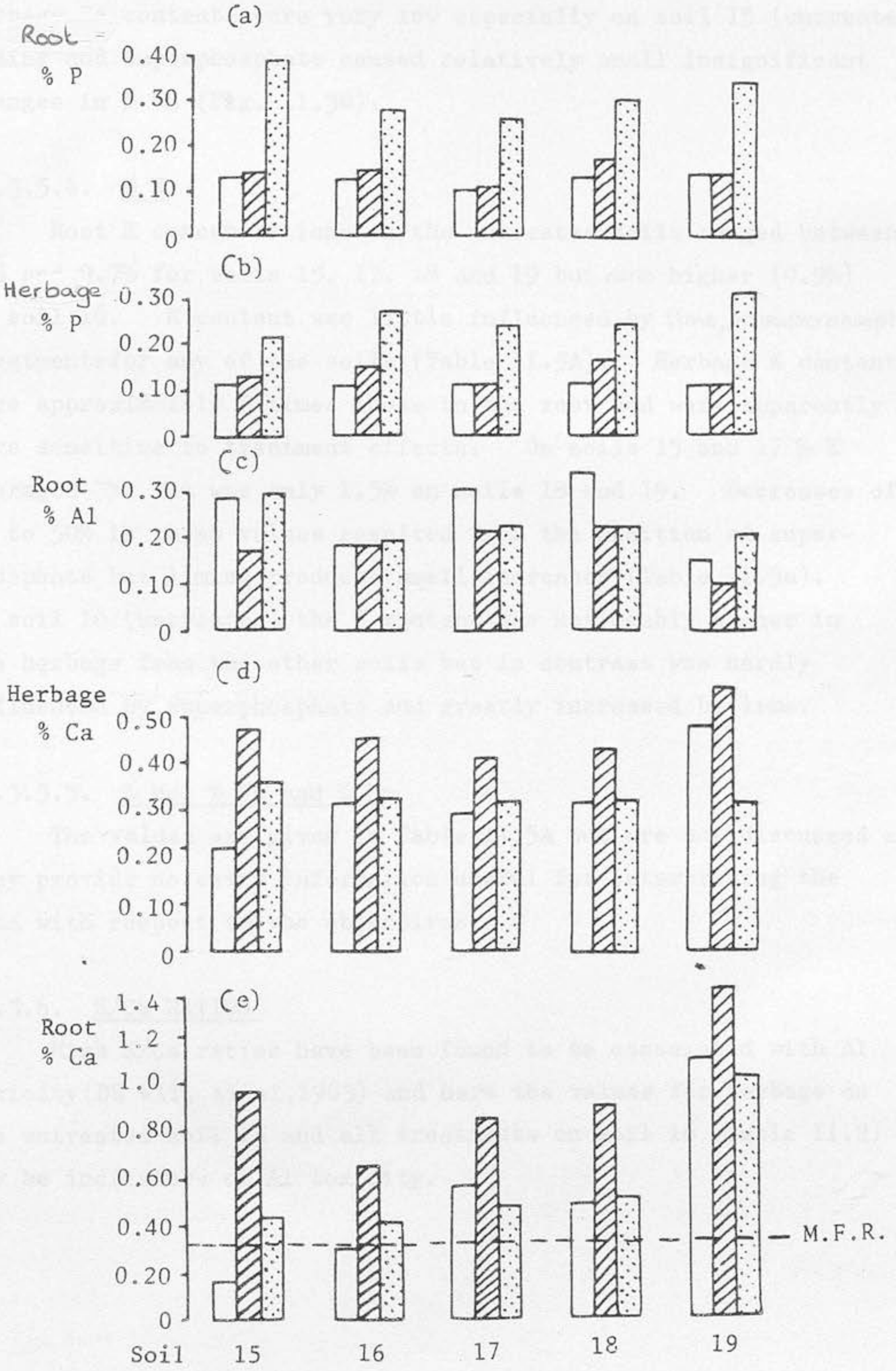
Root Ca concentrations were close to the minimum functional

Fig 11.2 Effect of superphosphate and lime on the proportion of shoot to root from soils 15, 16, 17, 18 & 19.



R = roots S = shoots

Fig 11.3 Changes in(a) % P Root (b) % P Herbage (c) % Al Roots (d) % Ca Herbage and(e) % Ca Roots in soils 15 to 19 treated with lime and superphosphate.



requirement (M.F.R) (0.3%) on soils 15 to 18 but were higher (0.48% on soil 19 (Fig. 11.3e). Liming increased Ca concentration to above 0.5% but superphosphate had little effect on % Ca. It did, however, increase DM production substantially. Similarly herbage Ca contents were very low especially on soil 15 (untreated). Liming and superphosphate caused relatively small insignificant changes in % Ca (Fig. 11.3d).

11.3.5.4. % K

Root K concentrations on the untreated soils ranged between 0.5 and 0.7% for soils 15, 17, 18 and 19 but were higher (0.9%) on soil 16. K content was little influenced by lime, or superphosphate treatments for any of the soils (Table 11.5A). Herbage K contents were approximately 5 times those in the root and were apparently more sensitive to treatment effects. On soils 15 and 17 % K averaged 3%, but was only 1.5% on soils 18 and 19. Decreases of up to 50% in these values resulted from the addition of superphosphate but liming produced small increases (Table 11.5a). On soil 16 (untreated) the K content was noticeably higher in the herbage from the other soils but in contrast was hardly influenced by superphosphate and greatly increased by lime.

11.3.5.5. % Mg, % Fe and % Mn

The values are given in Table 11.5A but are not discussed as they provide no extra information useful for interpreting the data with respect to the objectives.

11.3.6. K/Ca RATIOS

High K/Ca ratios have been found to be associated with Al toxicity (DE WIT, et al, 1963) and here the values for herbage on the untreated soil 15 and all treatments on soil 16 (Table 11.2) may be indicators of Al toxicity.

Table 11.2. K/Ca ratios in ryegrass roots and herbage from soils 15 to 19

Treatment Soil	Root			Herbage		
	Control	+Lime	+Superphosphate	Control	+Lime	+Super phosphate
15	3	1	2	30	3	5
16	2	2	2	16	8	11
17	2	1	1	6	3	3
18	2	1	1	6	3	3
19	1	1	1	2	1	1

11.3.7. pH OF THE $CaCl_2$ EXTRACTS

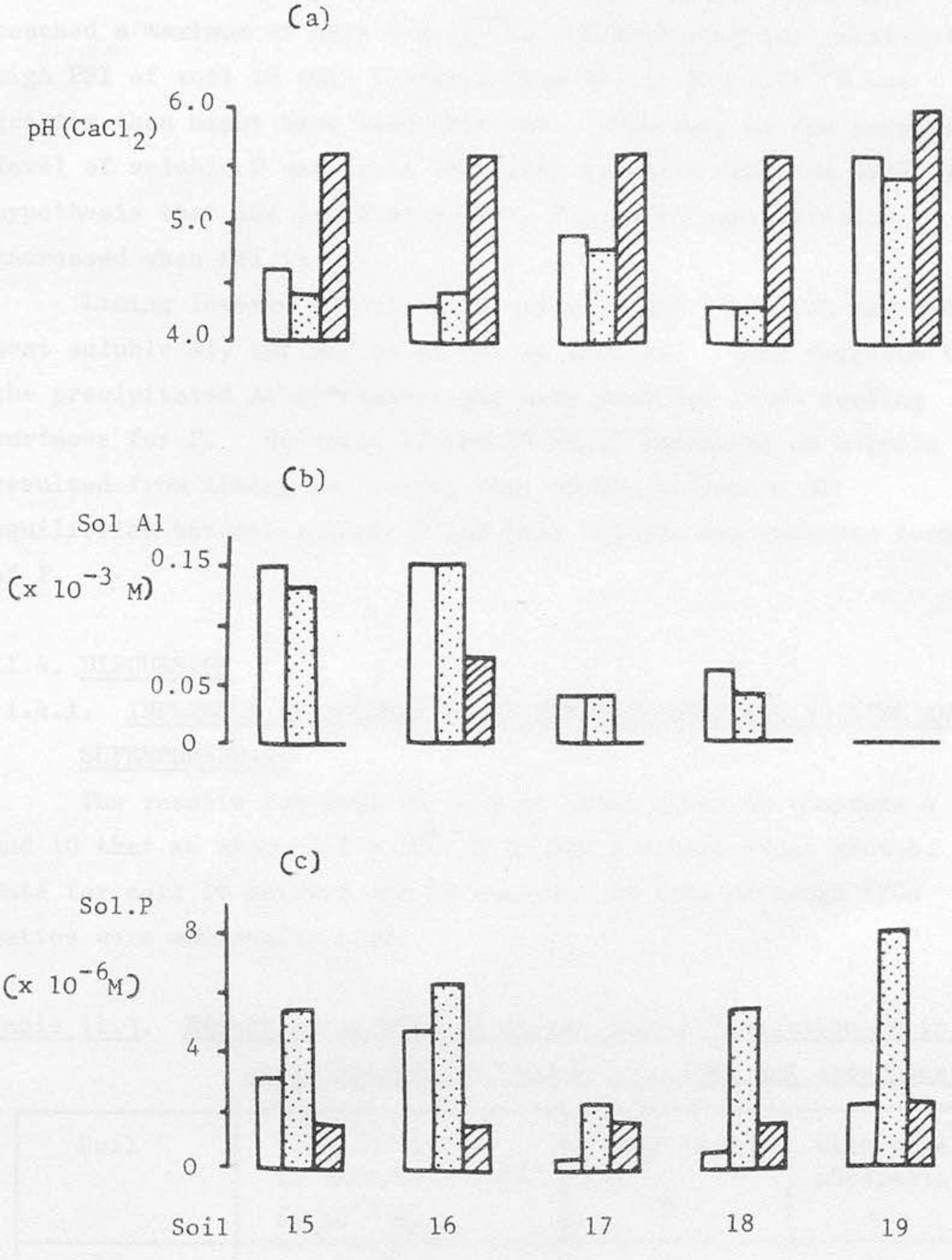
From the unlimed treatments for soils 15 to 18 the pH was below 5, however for soil 19 it was quite high (5.6)(Fig. 11.4). Only with the addition of lime were the pHs of soils 15 to 18 brought up to pH 5.6. The increases in pH due to lime were greatest in soils 16 and 18 which compared with soils 15 and 17 were lower in Al saturation (Table 11.1). The smallest change in pH due to lime was in soil 19 and it was observed in chapter 6 that when the pH of a soil was around 5.5 the increases for a given amount of lime were smaller than when the soil pH was in the range 4.5 to 5.5. Superphosphate had little affect on pH.

In general the pH of the 10^{-3} M $CaCl_2$ extracts was about 0.5 to 0.8 units higher than the soil pHs measured in 10^{-2} M $CaCl_2$ (Table 11.1).

11.3.8. SOLUBLE Al IN SOILS

The highest concentrations of Al were measured in the untreated soils, 15 and 16 (0.5×10^{-3}M) with much lower amounts in the other soils especially 19, which was too low to measure (Fig. 11.4). With superphosphate treatment on 2 soils (15, 18) Al was very slightly decreased, while there was no effect on soils 16 and 17. Liming reduced soluble Al to a neglible level in soils 15, 17 and 18, but had less effect on soil 16.

Fig 11.4 Effects of lime and superphosphate on(a) pH, (b) soluble Al and(c) soluble P in soils 15, 16, 17, 18 & 19.



11.3.9. SOLUBLE P IN SOILS

Soluble P was very low in the two untreated soils (17 and 18) with high PSI values and was highest at only 5 x 10^{-6} M in soil 16 (Fig. 11.4). Superphosphate increased soluble P in all the soils although by differing amounts. The amounts of increase were smaller and similar for soils 15, 16 and 17 but in soils 18 and 19 the level of soluble P was more than doubled although reached a maximum of only 8 x 10^{-6} M. Considering the relatively high PSI of soil 18 this increase from $\sim$1 to $>$ 5 x 10^{-6} M was greater than might have been expected. However, as the increased level of soluble P was still very low, it still conforms with the hypothesis that the level of soluble P is only substantially increased when PSI is low.

Liming lowered soluble P in soils 15 and 16, which had the most soluble Al, but had no effect on soil 19. This suggests that the precipitated Al hydroxides may have provided extra sorbing surfaces for P. On soils 17 and 18 small increases in soluble P resulted from liming indicating that pH may influence the equilibrium between soluble P and less soluble and adsorbed forms of P.

11.4. DISCUSSION

11.4.1. INFLUENCE OF SOLUBLE Al ON RYEGRASS RESPONSE TO LIME AND SUPERPHOSPHATE

The results for soil 15 support those given in chapters 4 and 10 that at above 0.1 x 10^{-3} M Al can restrict plant growth. Data for soil 16 however are in contrast to this although K/Ca ratios were abnormally high.

Table 11.3. Effect of soluble Al on dry matter production (% increase over control) in response to lime and superphosphate

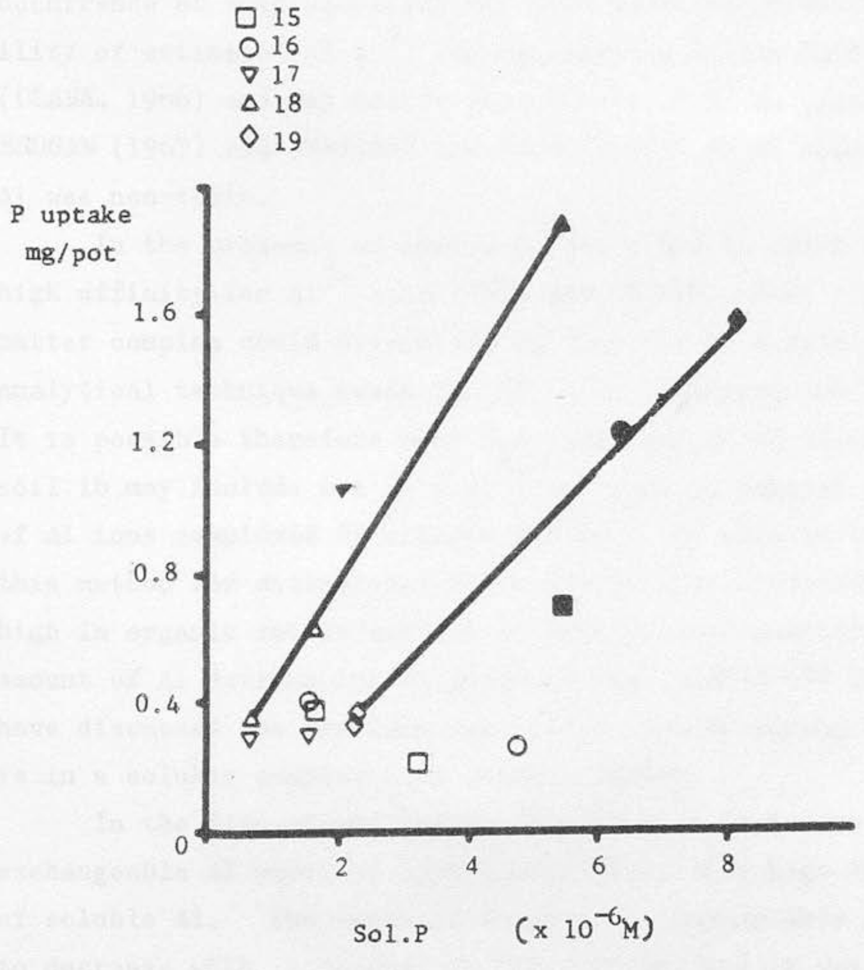
Soil	Concn. of Sol Al in untreated soil (x 10^{-3} M)	with lime %	with superphosphate %
15	0.15	+43	+27
16	0.15	+26	+105
17	0.04	+18	+147
18	0.06	+29	+147
19	0.01	+11	+75

The magnitude of treatment effects may be expressed as % response over the untreated soil, and when these values (Table 11.3) are compared the results for soil 15 stand out with the main response due to lime rather than superphosphate which was characteristic of the other soils. Soil 16, on the other hand, with the same soluble Al content as 15, has behaved in the same way as the other soils in which the levels of soluble Al are unlikely to be influencing growth. The significant responses to lime on soils 16 to 18 may be partly attributable to the input of calcium since in the untreated soils the plant material may have been deficient in Ca. However, as indicated from the increased levels of soluble P in soils 17 and 18 liming may have increased its availability slightly. Unfortunately, there was insufficient soil available for a lime + superphosphate treatment but it seems likely that the results from such a treatment would have facilitated the interpretation of these lime effects.

Where the level of soluble Al was below that shown to restrict growth, soil 16 excluded, the response to added P was substantial - as suggested from the low extractable P values. There was no overall linear relationship between P uptake and soluble P but as found in chapter 9 amongst individual soils P uptake did show linear increases for increases in soluble P (Fig. 11.5). As also observed in chapter 9 comparing soils 12 and 14 on Fig. 9.9. the slope was steepest for the soils (18 and 12) with the higher PSI values. This would suggest that although the P sorbing capacity of the soil may influence the level of soluble P resulting from the addition of P fertiliser the resultant effect on P availability and uptake by ryegrass is negligible.

The mechanism(s) by which Al reduces growth and the response to superphosphate are not obvious from the parameters measured here. Possible explanations will be presented in chapter 13 when all the results are available. However, it seems likely in view of the low Ca levels that these may have contributed to the adverse effects of Al.

Fig. 11.5 Relationship between P uptake and the concentration of soluble P from treatments with and without added P (closed and open symbols respectively) in soils 15 to 19.



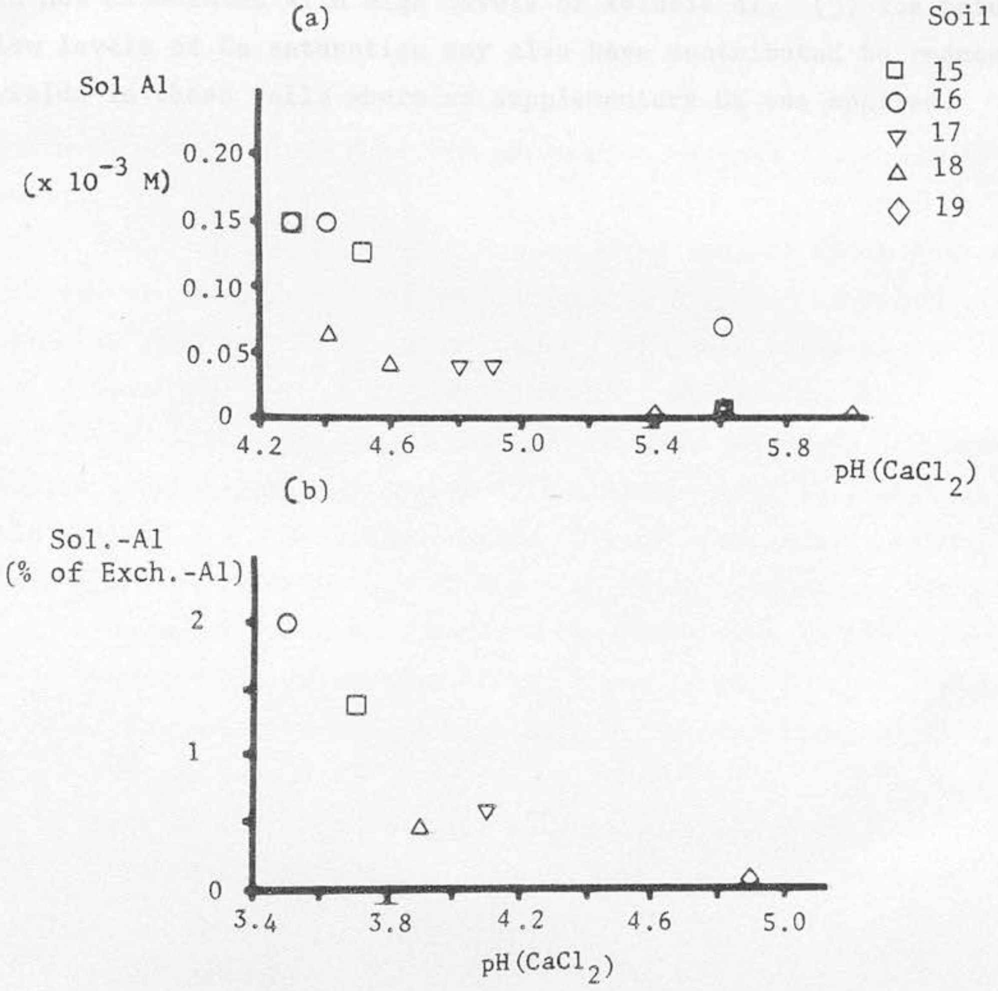
11.4.2. RELATIONSHIP BETWEEN THE LEVEL OF SOLUBLE Al AND OTHER SOIL PROPERTIES

The only difference between soils 15 and 16 in soil properties which might account for the lack of Al toxicity symptoms associated with the relatively high concentration of soluble Al measured in soil 16, was the high organic matter content of that soil (Table 11.1). SCHNITZER and SKINNER (1963) showed that organic matter can form water stable complexes in a 1:1 ratio with Al over the pH range 3 to 4.5. This range was extended to pH 5 by MARTIN and REEVE (1960) who found that complex formation was enhanced when Al occurred in polymeric forms of the hydrous oxide. The occurrence of such complexes has been shown to affect the reliability of estimates of Al^{3+} ion activity in dilute $CaCl_2$ extracts (CLARK, 1966) and may modify the effects of Al on plant growth. BROGAN (1967) and BARTLETT and RIEGO (1972) found that complexed Al was non-toxic.

In the presence of excess Alizarin Red S, which has a very high affinity for Al^{3+} ions (KING and PRUDEN, 1968) the Al/organic matter complex could dissociate so that the Al detected by the analytical technique could include both complexed and free Al ions. It is possible therefore that the measurements of soluble Al from soil 16 may include not only Al^{3+} but also an unknown proportion of Al ions complexed by organic matter. If this is the case this method for determining Al in dilute salt solutions from soils high in organic matter may not be suitable for quantifying the amount of Al detrimental to plant growth. KAURICHEV et al (1969) have discussed the problems associated with measuring Al when it is in a soluble complex with organic matter.

In the five virgin soils examined here high levels of exchangeable Al were not always associated with high concentrations of soluble Al. The ratio of soluble to exchangeable Al was found to decrease with increasing pH (Fig. 11.6a) and it was also observed that above pH 5 the concentration of soluble Al was low ($< 0.01 \times 10^{-3}$ M). Similar effects have been recorded for other soils (Chapters 4 and 6). It was also apparent from this set of data that there was no simple relationship between exchangeable- and extractable-Al (see also Section 3.3.2 and 9.3.7.) and it may be that the relationship established for soils 4, 9, 10 and 11 in chapter 4 was fortuitous.

Fig. 11.6 Relationships between pH and (a) concentration of Soluble Al, (b) Soluble Al as per cent of Exchangeable Al in soils 15 to 19.



11.5. CONCLUSIONS

These results provide further evidence that (1) when the concentration of soluble Al exceeds 0.1×10^{-3} M it is likely to interfere with plant growth reducing the response to added P. However, the seriousness of these effects may be mitigated by Al complex formation with organic matter when the carbon content of the soil is high. (2) When superphosphate is added to hill soils their sorbing ability, despite keeping the level of P in the soil solution low, has little influence on plant growth providing it is not associated with high levels of soluble Al. (3) The naturally low levels of Ca saturation may also have contributed to reduced yields in these soils where no supplementary Ca was applied.

CHAPTER 12

VIRGIN AND LIMED SOILS DERIVED FROM BASALT

12.1. INTRODUCTION AND OBJECTIVES

It has been noted in previous chapters that soils developed on basalt exhibit some outstanding properties : many of these differ from those of other Acid Brown soils both with respect to chemical characteristics, especially their high Al content, and to the effects of inherent properties and treatment induced changes on plant growth. In this chapter additional basaltic soils have been examined with a view to assessing the extent to which generalisations concerning the properties of such soils can be made.

Soils were sampled from forest sites with no known history of lime or fertiliser treatment (virgin soils) and adjacent sites known to have received lime at least five years previously. Limed soils were included so that the influence of lime on the effects of 'field' liming on pH and soil Al could be assessed. Floate (unpubl.) observed that the pH of Llansannan soil (re. soil 5) did not reflect a lime application 20 years previously although the amount of exchangeable Al was much lower than in the control.

The specific objectives of this survey were as follows:-

1. Compare the properties of limed and virgin soils and examine the relationship between base status and forms of Al in these soils.
2. Examine the relationships between soil Al, P sorption and the chemical availability of P in these two groups of soils.

12.2. EXPERIMENTAL

The surface organic layer was removed and bulk samples of soil were taken from between 0 and 15 cm depth. At each of 6 sites samples were obtained from 2 nearby locations. The soils have been classified within the Darleith series, apart from soil 24 from Canna, where soils have not been surveyed.

The soils were prepared for analysis as described in chapter 2; organic carbon, pH, exchangeable Al, Ca and Mg, extractable Al and P, soluble Al, P, Ca, Mg and PSI were measured as described in chapter 2. C.E.C. was calculated by summing the major exchangeable cations (Al, Ca and Mg).

The significance of the difference between the 2 group means (M_V and M_L) was calculated as follows:

$$LSD = T \text{ (for } 2n - 2 \text{ d f)} \times SED$$

where $SED = \sqrt{SEM_V^2 + SEM_L^2}$ and M_V = mean of Virgin soils

M_L = mean of Limed soils

12.3. RESULTS AND INTERPRETATION

12.3.1. COMPARISON OF SELECTED SOIL PROPERTIES AMONGST SOILS 20 TO 25

The values for selected properties indicated that soil 24 was very different from the other soils (Table 12.1). Base status and pH in this soil were high while all forms of Al and percent saturation by Al of the CEC were low. For these reasons, but particularly that of the low Al content compared with other basaltic (Darleith) soils analysed in other parts of this study (soils 7, 8, 11, 11a, 12 and 13) it was considered that this soil was atypical and may not be properly classified in the Darleith series. WHITTOW (1977) commented that the natural fertility of other soils on Canna was relatively high and indicated that they had been consistently modified by wind depositions of both shell sand and basic salts in sea-spray. WHITTOW also reported that the soils on the island of Canna were strongly weathered but less strongly leached than elsewhere, contributing to their high base saturation. Because of its atypical characteristics this soil (24) was excluded from further comparative studies to be discussed.

12.3.2. SOIL ACIDITY AND ASSOCIATED PROPERTIES

12.3.2.1. VIRGIN SOILS

Soils 20, 21, 22, 23 and 25 showed a considerable range in carbon content, from 8% in soil 21 to 29% in soil 22 (Table 12.1). Cation exchange capacity was high in all five soils (> 10 meq/100 g) and Al saturation was also high ranging from 65 to 90% (Table 12.2).

Table 12.1. Selected properties of 6 Acid Brown soils developed on basalt

Virgin Soils

Soil	% C	Tot.P	Extr.P	Sol.P	PSI	Extr. Al	Exch. Al	Sol.Al	Exch. Ca	Exch. Mg	Sol. Mg	pH $(CaCl_2)$
		mg/100 g				meq/100 g						
20 V	13.2	337	1.93	0.02	163	34.2	16.2	0.08	0.2	2.5	0.03	3.9
21 V	8.1	225	0.84	0.02	95	16.7	14.6	0.04	1.0	1.9	0.28	3.6
22 V	29.3	350	1.85	0.12	109	12.5	13.2	0.07	2.0	4.3	0.42	3.8
23 V	9.6	550	0.31	Tr	115	11.9	8.4	Tr	0.2	1.0	0.19	4.3
24 V	9.3	250	0.19	0.01	90	7.1	0.2	Tr	2.8	2.4	0.38	4.2
25 V	13.2	175	0.17	0.02	138	13.8	8.1	0.02	2.0	0.6	0.29	3.8
+Mean	14.7	327	1.02	0.04	124	17.8	12.1	0.04	1.1	2.1	0.24	3.9
S.E.M.	3.8	65	0.37	0.02	12	4.2	1.6	0.01	0.4	0.7	0.06	0.1

+ excluding soil 24

Limed soils

Soil	% C	Tot.P	Extr.P	Sol.P	PSI	Extr. Al	Exch. Al	Sol.Al	Exch. Ca	Exch. Mg	Sol. Mg	pH $(CaCl_2)$
		mg/100 g				meq/100 g						
20 L	5.4	550	0.34	Tr	108	18.3	8.4	Tr	4.3	2.6	0.31	4.1
21 L	6.6	187	0.14	Tr	107	26.0	11.6	0.02	2.0	0.6	0.24	4.0
22 L	5.3	363	0.62	Tr	147	32.8	6.4	0.02	3.0	0.2	0.15	4.4
23 L	9.1	200	0.13	Tr	118	9.0	7.6	Tr	2.3	1.1	0.09	4.3
24 L	9.2	387	0.19	0.14	66	1.9	0.2	Tr	13.5	5.8	0.42	5.1
25 L	4.5	675	0.34	0.03	71	9.3	4.4	Tr	6.5	1.1	0.25	4.4
+Mean	6.2	395	0.31	$<$0.11	110	19.1	7.7	$<$0.01	3.6	1.1	0.21	4.2
S.E.M.	0.8	96	0.09	-	12	4.4	1.2	-	0.8	0.4	0.04	0.1

+ excluding soil 24

Table 12.2 Difference between soil properties associated with acidity in virgin and limed soils (20, 21, 22, 23 and 25)

Property	Range		Mean			LSD		
	Virgin	Limed	Virgin	Limed	Difference	*	**	***
% Carbon	8-29	4.5-9	14.7	6.2	8.5NS	8.9	13.0	19.6
CEC meq/100g	10-20	10-16	15.2	12.4	2.8NS	4.1	5.9	8.9
Exch.Al meq/100g	8-16	0.2-11.6	12.1	7.7	4.4NS	4.6	6.7	10.1
Exch.Ca "	0.2-2.0	2-6	1.1	3.5	2.5*	2.1	3.0	4.5
% Al saturation	65-90	37-69	80	62	18**	11	17	25
pH	3.6-4.2	4.0-4.4	3.8	4.2	0.4*	0.3	0.5	0.7
Sol.Al meq/100g	Tr.-0.08	Tr.-0.02	0.04	<0.01	-		-	
Sol.Ca "	0-0.02	Tr.0.02	0	<0.01	-		-	

Al saturation was highest in soil 23 (88%) although with respect to the amount of exchangeable-Al soil 23 only had 8.4 meq/100 g compared to more than 13 meq/100 g in soils 20, 21 and 22. pH was low (< 4.0) except in soil 23 which had the least exchangeable Al. But this and the generally high levels of exchangeable-Al did not give rise to high levels of soluble-Al. Amounts of soluble-Al were very low (< 0.08 meq/100 g) in all five soils.

Base status was low and the soils had more than twice the amount of exchangeable-Mg than -Ca except in soil 25 (Table 12.1). Exchangeable-Ca did not exceed 2.0 meq/100 g and Ca saturation was less than 10%. The Ca deficit in these soils was further indicated by the adsorption of Ca from the 10^{-3} M$CaCl_2$ solution used to extract soluble cations.

12.3.2.2. LIMED SOILS

The range in carbon content amongst the limed groups of soils was more restricted than recorded for the virgin soils (4.5 to 9%, Table 12.2) with the mean contents of the 2 groups 6.2 and 14.7% almost significantly different at the 1% level. Both mean and maximum values for CEC were lower than in the virgin group although that of soil 25 was slightly higher than its virgin counterpart and the difference between the two groups was not significant (Table 12.2). In the limed soils 20, 22 and 25 exchangeable-Al was approximately 50% lower than in the virgin soils but in soils 21 and 23 the difference was slight. Overall, the difference between the means of the 2 groups was almost significant at the 5% level (Table 12.2) indicating the important long term effect of lime on exchangeable Al.

Levels of exchangeable Ca were very much higher in the limed soils 20 and 25 although the difference was less marked in soils 21, 22 and 23 and with the result that the difference between the means was just significant (Table 12.2). It may be noted that the large increases in exchangeable Ca in soils 20 and 25 were associated with large decreases in exchangeable Al.

As result of the effects of lime on CEC and levels of exchangeable Al and Ca, Al saturation (%) was significantly ($P < 0.01$) lower in the limed group of soils although the mean value was still just over 60% (Table 12.2). The highest level of soluble Al measured in the limed soils was 50% that of the virgin soils while levels of soluble Ca were about the same in the 2 groups (Table 12.2). It was also noted in chapter 4 that liming had no appreciable effect on soluble Ca levels in the more Ca deficient soils.

Soil pH was only slightly higher in the group of limed soils compared with their virgin counterparts (pH 3.8 and 4.2 ($CaCl_2$) respectively) and the difference was significant ($P < 0.05$). These results for the long term effects of lime on soil acidity fail to support the conclusions of FLOATE (unpubl.) that liming has a more permanent effect on exchangeable Al, whereas the influence on soil pH is not as prolonged.

12.3.3. RELATIONSHIP BETWEEN pH, BASE STATUS AND FORMS OF Al

For the group of virgin soils pH was not significantly correlated with any of the selected soil properties (see Table 12.3). In the limed soils pH was significantly ($P < 0.01$) and inversely correlated with exchangeable Al. There was also a significant inverse relationship between pH and the amount of Ca adsorbed from the 10^{-3} M $CaCl_2$ solution in the limed soils (Table 12.3).

Table 12.3 Correlation coefficients for the relationship between some selected soil properties and the level of soluble Al and pH

Property	% C	Extr. Al	pH	CEC	Exch. Al	% Al sat^n	Exch. Ca	Sol.Ca (amount adsorbed
Virgin								
pH	-0.156	-0.112	-	-0.627	-0.513	-0.306	0.524	-0.527
Soluble Al	0.593	0.651	-0.484	0.893*	0.864	0.054	0.076	0.931*
Limed								
pH	-0.173	-0.201	-	-0.811	-0.919*	-0.545	0.429	-0.897*
Soluble Al	-0.117	0.903*	-0.201	-0.277	0.458	0.655	-0.564	0.470

$P \leqslant 0.05$ $r > 0.878$*, $P \leqslant 0.01$, $r > 0.959$**, $P \leqslant 0.001$, $r > 0.991$***

The amount of soluble Al, shown elsewhere in this study to be critical for ryegrass growth, was significantly correlated ($r = 0.893$*) with CEC and also with Ca adsorbed from $CaCl_2$ ($r = 0.931$*) in the group of virgin soils. In the limed soils soluble Al was significantly correlated with extractable Al only. The amount of soluble Al was not correlated with pH, Al saturation or exchangeable Al in either groups of soils (Table 12.3).

12.3.4. SOIL PHOSPHORUS

12.3.4.1. VIRGIN SOILS

Total P was particularly high in soils 20, 22 and 23 and even in soils 21 and 25 it exceeded 175 mg/100 g (Table 12.1, 12.4). Extractable-P in contrast was very low ($<$0.4 mg/100 g) except in soils 20 and 22 where it was 1.93 and 1.85 mg/100 g respectively. Soluble P was very low in all the soils, with the highest level being measured in soil 22 (0.12 mg/100 g) and consistent with the high PSI values and levels of extractable Al. (Table 12.4).

Table 12.4. Difference between virgin and limed soils with respect to soil P (Soils 20, 21, 22, 23 and 25)

Property	Range		Mean		Difference	LSD		
	Virgin	Limed	Virgin	Limed		*	**	***
Total P mg/100 g	175-550	170-675	327	395	68 NS	267	389	584
Extractable P mg/100 g	0.17-1.93	0.13-0.62	1.02	0.31	0.71 NS	0.88	1.23	1.92
Soluble P mg/100 g	Tr.-0.12	Tr.-0.03	0.04	$<$0.01	$>$0.03	N.C.		
P.S.I.	95 -163	66-108	124	110	14 NS	39	57	85
Extractable Al meq/100 g	12-34	2-33	17.8	19.1	1.3 NS	14	20	30

N.C. not calculated

Table 12.5. Correlation coefficients for the relationships between both extractable-P and PSI and selected soil properties.

Property	% C	CEC	pH	Extr. Al	Exch. Al	Sol. Al	Tot. P	Extr. P	Sol. P
Virgin									
Extractable-P	0.596	0.911*	-0.264	0.588	0.835	0.957*	0.036	—	0.646
PSI	-0.092	-0.115	-0.418	0.749	0.118	0.332	-0.073	0.342	-0.239
Limed									
Extractable P	-0.658	-0.457	0.553	0.550	-0.531	0.302	0.314	—	0.092
PSI	0.289	-0.368	-0.056	0.695	0.244	0.563	0.729	0.428	-0.895

$P \leqslant 0.05$, $r > 0.878$*; $P \leqslant 0.01$, $r > 0.959$**; $P \leqslant 0.001$, $r > 0.991$***

12.3.4.2. LIMED SOILS

The range of total P was even greater for the group of limed soils and the means was not significantly different. The ranges in amounts of extractable- and soluble-P were smaller but because of the large variation between the soils in each group, the differences between the means for the 2 groups were not significant (Table 12.4). PSI was generally lower for this group of soils the means of 124 and 110 for the limed and virgin soils respectively were not significantly different There was no general trend in amount of extractable-Al: in soils 20, 23 and 25 levels were between 20 and 50% lower, while for soils 21 and 22 they were up to 60% higher (Table 12.1). The mean values for extractable-Al for the two groups were not significantly different (Table 12.4).

12.3.5. RELATIONSHIP BETWEEN 'P' AVAILABILITY AND SELECTED SOIL PROPERTIES

Amounts of soluble-P were too low in both groups to assess the influence of other soil properties on the amount extracted but in general, as found for other basalt soils examined, the trace amounts were associated with a PSI value greater than 100. Extractable-P was correlated with CEC and soluble-Al in the group of virgin soils ($r = 0.911^*$, $P < 0.05$; $r = 0.957^*$, $P < 0.05$ respectively) (Table 12.5). For the groups of limed soils extractable P was not correlated with any of the selected soil properties (Table 12.5).

PSI was not shown to be significantly correlated with % carbon, CEC, pH or any of the 3 forms of Al, although, as noted in chapter 4 the correlation coefficient was highest ($r = 0.749$) with extractable-Al. Considering the relatively high amounts of extractable-Al particularly in soil 20, PSI values were not as high as would have been predicted from a simple linear relationship between PSI and extractable-Al. PSI values of around 160 (similar to that of soil 20) were recorded for soil 11 and 11a in which less than 20 meq/100 g of extractable-Al were measured. PSI was not significantly correlated with total-, extractable- or soluble-P.

In the group of limed soils the correlation coefficients for the relationships between % C, CEC, pH and the 3 forms of Al were all non-significant and similar to those for the group of virgin soils (Table 12.5). In contrast to the results for the virgin soils in the limed soils total-P tended to be high when PSI was high. PSI was significantly and inversely correlated with soluble-P in the group of limed soils which is in agreement with results from other soils examined.

12.4. DISCUSSION AND CONCLUSIONS

As a result of the differential effects of lime on the selected soil properties inter-relationships between these amongst the virgin soils were not always duplicated in the limed group, and vice-versa. The tendency for the three forms of Al to be linearly correlated was smaller for the group of limed soils. This comparison between virgin and limed soils has shown that the reduction in all three forms of soil Al and Al saturation brought about by liming in short term pot experiments, chapters 4, 6 and 11 can be maintained for a considerable length of time . Similarly, the effects of lime on pH are long lasting.

In general, the % carbon and available P tended to be lower in limed soils, which may possibly be explained by the results from chapter 5 which showed that liming increased the utilisation of soil C and P by micro-organisms. PSI also tended to be lower amongst the limed soils. Plant growth experiments were not conducted on these soils, and no firm conclusion with regard to the effect of lime on P availability may be drawn from this data.

Despite the common parent material, basalt, there were wide ranges amongst the soils for most of the properties measured, with the exception of pH which was low in all five soils showing only a 0.4 unit spread. Despite the generally high levels of extractable-Al and high Al saturation, coupled with low pH, levels of soluble Al were low. Although ryegrass was not grown in the soils, on the basis of data already discussed for other basaltic soils it seems unlikely that root growth would be greatly influenced by Al. The generally low values for soluble-Al amongst these basaltic soils and also for soils 12, 13 and 15 to 19 suggest that very high soluble-Al contents are not common amongst basalt soils. It is possible though that agricultural practice and the high inputs of fertiliser without sufficient lime may increase the level of soluble-Al.

CHAPTER 13

DISCUSSION AND CONCLUSIONS

13.1. INTRODUCTION

The main objective of this study was to assess the relative importance of acidity, aluminium toxicity and deficiencies of phosphorus and calcium as factors limiting plant growth in Acid Brown hill soils. Other aspects of the work explored mechanisms by which these limiting processes might operate. A further objective was to examine soil and plant responses to the addition of calcium and phosphorus as means of overcoming, or at least reducing, these limitations to the production of high yielding, ryegrass dominated reseeded pastures.

Ryegrass was chosen as the test plant because of its importance in reseeded pastures and the conclusions will therefore be relevant to the requirements of this species in improved hill pastures. No work on clover was undertaken, despite its importance in such pastures, but attention will be drawn to conclusions which may be applicable to clover.

Discussion will focus on the points of interest in this study which contribute to the understanding of the following:-

1. Ranges in properties of Acid Brown hill soils related to acidity, Al, Ca and P status, and of their interrelationships (13.2).
2. Effects of Al and its interactions with Ca and P on plant growth (13.3).
3. Effects of Ca and P additions on soil properties and plant responses (13.4).

13.2 NATURAL VARIABILITY IN THOSE PROPERTIES OF ACID BROWN SOILS RELATED TO ACIDITY AND P SUPPLY

13.2.1. SOIL ACIDITY AND RELATED PROPERTIES

Of the soil properties examined here, those listed in Table 13.1. have been shown to have either direct or indirect effects on plant growth.

Table 13.1. Ranges in some important properties of the 25 hill soils examined

Property	Min.	Max.	Mean	±S.E.M.
pH ($CaCl_2$)	3.1	4.9	3.9	0.09
Exch. acidity meq/100 g	0.2	23.4	11.8	1.2
Exch. Al "	0.2	20.0	9.8	1.1
Al. sat^n %	4	97	71	5.2
+ Sol. A. meq/100 g	0	0.79	0.13	0.05
+ Sol. Ca p.p.m.	ND	15	-	-
Extr. Al meq/100 g	2.4	34.2	11.1	1.6
Extr. P mg/100 g	0	2.5	0.47	0.13
+ Sol. P "	0	0.12	0.03	0.007

+ Excluding soils 1, 2, 3, 5, 6, 7 and 8.

pH in the majority of soils was low ($<$ 4.0, $CaCl_2$) and reflected the high exchangeable acidity and exchangeable-Al contents of these soils. pH only explained 39% of the variation in exchangeable acidity but it can be seen from Figure 13.1 that generally exchangeable acidity was low when pH was above 5.3. The wide range in exchangeable acidity was consistent with similar variation in exchangeable-Al contents amongst the soils (Fig. 13.2). It seems likely that this variation is mainly attributable to the different Al contents of the parent materials.

Exchangeable-Al was inversely related to pH but there was no significant linear correlation ($r = -0.307$ N.S., Fig. 13.3). An almost linear decrease in exchangeable-Al with increasing pH was observed however, for individual soils where they had been limed or leached (6.3.1., 7.3.1./7.4.1.). This relationship demonstrated for individual soils was also observed by BACHE (1974), and he too found no overall significant correlation between pH and exchangeable-Al. FLOATE (1978) showed that the relationship between pH and exchangeable-Al was dependent upon both CEC and the extent of Al saturation.

pH was significantly correlated with Al saturation (%) ($r = -0.719$***) for this collection of Acid Brown hill soils although the inherent soil differences were still apparent from the spread

Fig 13.1 Relationship between exchangeable acidity and pH for 25 Acid Brown hill soils.

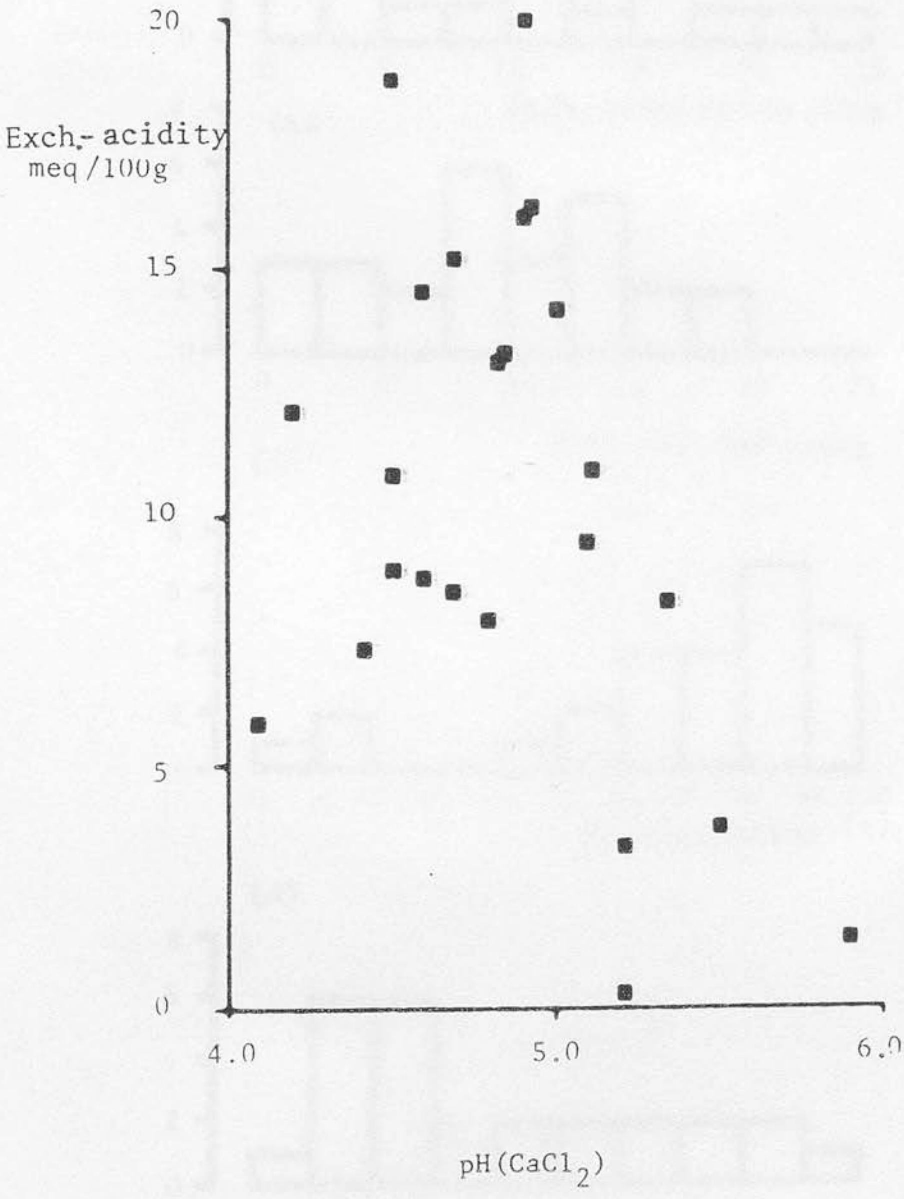
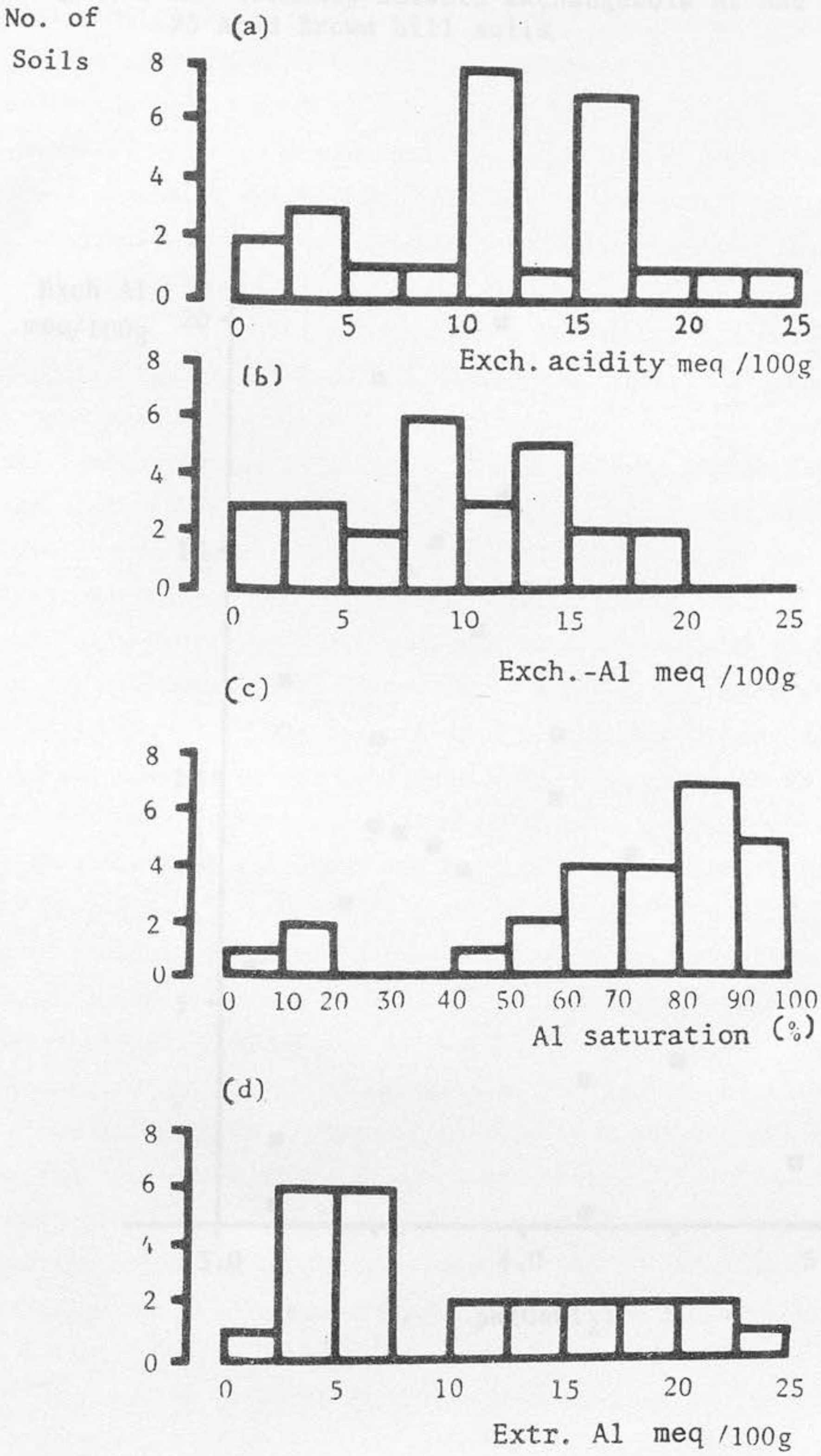


Fig 13.2 Distribution of soils with reference to ranges of (a) Exchangeable acidity (b) Exchangeable Al (c) Al saturation (%) and (d) Extractable Al.



of values for a particular pH (Fig. 13.4). Al saturation exceeded 70% in the majority of soils with only a few below 50% (Fig. 13.2). BLOSSER and JENNY (1971) reported highly significant correlations between soil pH and base saturation amongst groups of soils formed by similar environmental processes. BACHE (1974) showed pH to be dependent on the properties of Ca ions neutralising the negative charge but stressed the differences in the pattern of dependence between soils : which reflected the association between pH and the hydrolysis of Al and Ca-Al exchange equilibria. It may be concluded that reactions involving soil cations are dependent on their relative saturation of the CEC rather than their absolute amounts.

In addition to influencing plant growth through the generation of acidity, exchangeable-Al also acts as a 'reservoir' for soluble-Al. Although there was no significant correlation between amounts of soluble and exchangeable Al, (Fig. 13.5), soluble Al was low in most of the soils (< 0.1 meq/100 g) but those on basalt had above average amounts. The high content, (0.5 meq/100 g) in soil 11, was not, however, typical of the other basalt soils (Table 12.1). The amount of naturally occurring soluble-Al was negligible above pH 4.5 but as shown for exchangeable-Al there was no significant correlation with pH ($r = -0.468$ N.S.). The absence of a significant relationship between soluble-Al and pH was also recorded by MACLEOD and JACKSON (1967). The highest concentrations of soluble-Al were normally associated with high Al saturation but there was no significant correlation between these properties ($r = 0.435$ N.S.). WEBBER (1978, unpubl.) showed that the amount of soluble-Al was related to the proportion of exchange sites saturated with Al rather than to the amount of exchangeable-Al. EVANS and KAMPRATH (1970) suggested a critical level of between 60 and 70% for plant growth, but in many of these soils the concentrations of Al associated with such levels were well below that shown to influence ryegrass growth. The individuality of these hill soils and the complex nature of the reactions and properties which influence the concentration of soluble-Al is stressed by these observations and more work is required to understand them fully.

As might be expected from the inverse relationship between exchangeable-Al and base saturation almost all these soils were low in exchangeable- and especially soluble-Ca. In most of them there was a deficit between their soluble-Ca content and that of the 10^{-3}M $CaCl_2$ equilibrating solution (Table 13.1). BENIANS (pers. comm.) has also found very low soluble-Ca concentrations in soils derived from basalt. These inherently low Ca contents were shown to be a contributory factor to the poor growth of ryegrass in several of the soils examined (soil 4, section 4.4.4; soil 11, section 7.4.3.).

pH was not shown to exert the pronounced effect on reactions involving Al suggested by PIONKE and COREY (1967) (see 1.2.2.). The comment, 'that under natural conditions any relationship between pH and exchangeable-Al was merely an alternative manifestation of a common property' (REEVE and SUMNER, 1971), appears to be relevant for these Acid Brown hill soils.

In REEVE and SUMNER's alternative scheme describing factors influencing the distribution of Al account is taken of the effects of proportional saturation of the CEC and as such this scheme, given below, more appropriately describes the relationships between forms of Al in hill soils.

$$\begin{tikzcd}
\mathrm{FeAl}\,y(\mathrm{OH})^{x+}_{3y-x} \arrow[d, shift left] & \text{........ positively charged hydroxy polymers able to block CEC directly or neutralise it by double layer interaction.} \\
\text{Exch. } \mathrm{Al}^{3+} \arrow[u, shift left] \arrow[d, shift left] \arrow[r, phantom, "\rightleftharpoons"] & {[(\mathrm{CEC} - \mathrm{AEC}) - \text{Exch. bases}]} \\
\text{Al bound by organic matter} \arrow[u, shift left] &
\end{tikzcd}$$

(REEVE and SUMNER, 1971)

The influence of parent material on the amounts of the different forms of Al was most clearly seen for extractable-Al (Table 13.1, Fig. 13.2). Amounts were highest in soils derived from basalt ($>$10 and up to 34 meq/100 g). Because of the differential influences of other factors on the amounts of the 3 forms of Al there were no significant correlations between them and it was concluded that the significant correlations observed in Chapter 4 (section 4.3.1.) for soils 4, 9, 10 and 11 were fortuitous. Exctractable-Al was not significantly correlated with pH (r = 0.037 NS), although for soils 1 to 8 (3.3.2.) there was a tendency for extractable-Al to be higher in those soils with higher pH. The significance of extractable-Al for plant growth was attributed to its influence on P supply.

Fig 13.3 Relationship between exchangeable Al and pH for 25 Acid Brown hill soils.

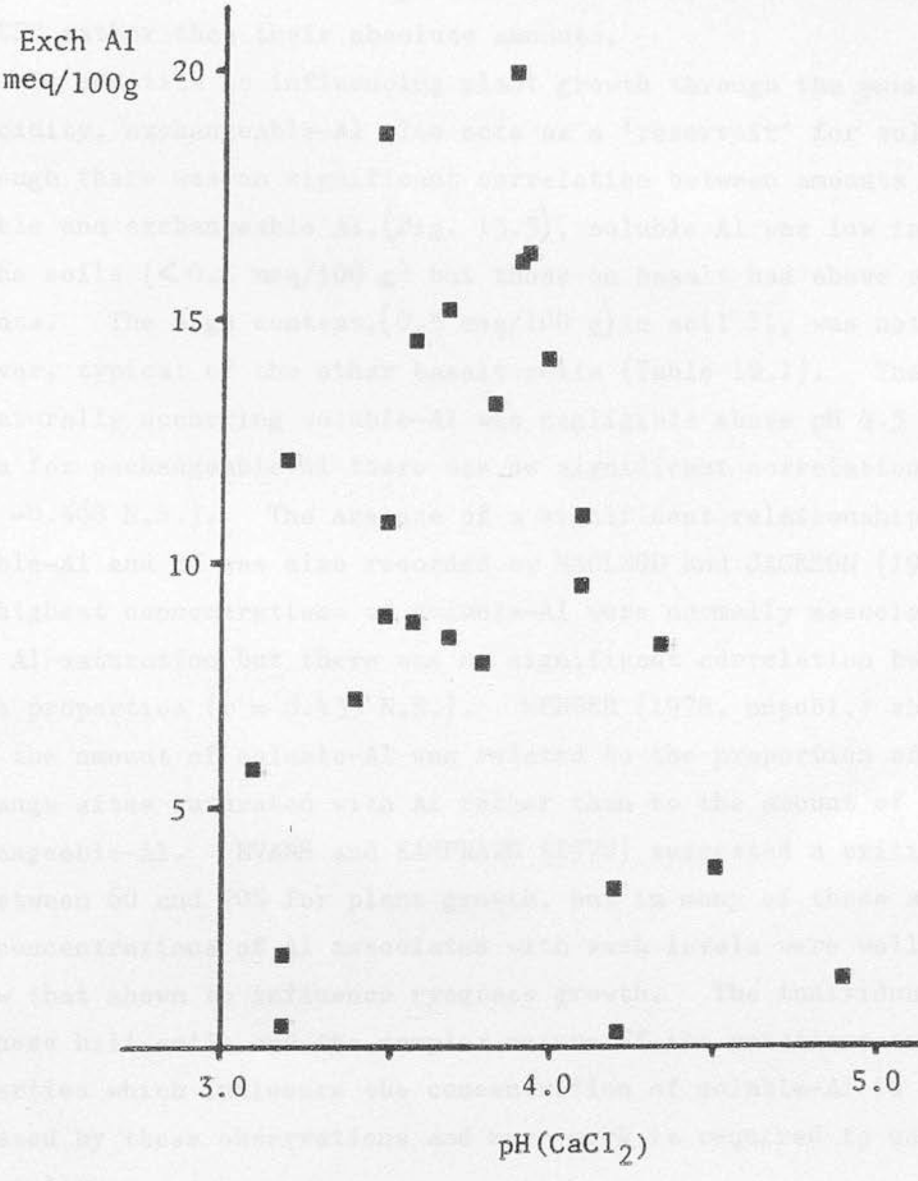


Fig 13.4 Relationship between Al saturation (%) and pH for 25 Acid Brown hill soils.

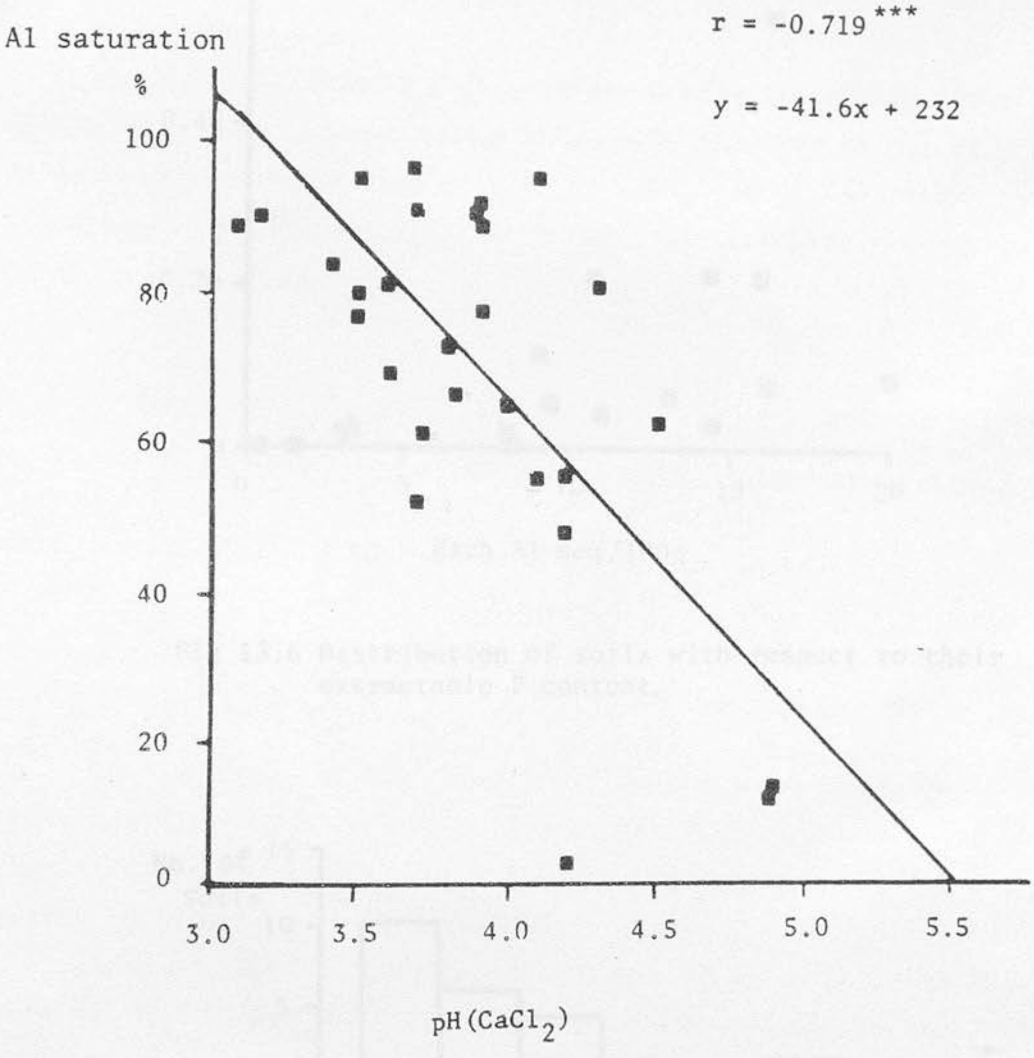


Fig 13.5 Relationship between soluble and exchangeable Al.

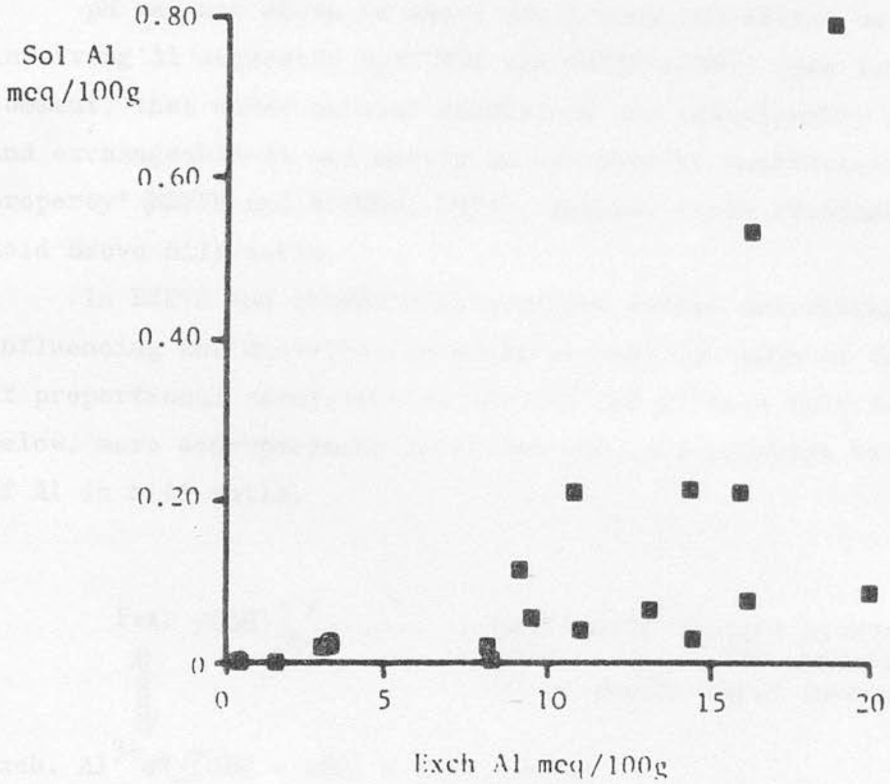
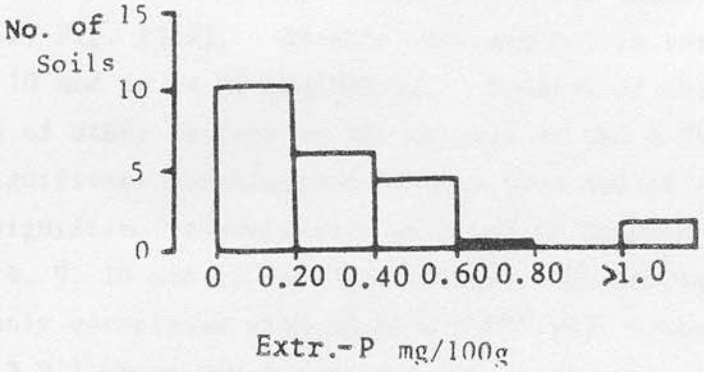


Fig 13.6 Distribution of soils with respect to their extractable P content.



13.2.2. EFFECTS OF Al ON P SUPPLY

Extractable-Al explained more than 80% of the variation in PSI for soils 1 to 8 (3.3.5), and the correlation coefficient for the relationship between it and PSI for the 25 soils was highly significant (r = 0.891***). Because of the high P fixation shown by the soils developed on basalt, a higher P concentration was used in the equilibrating solution so that actual values for PSI are not strictly comparable. However, some generalisations may be made; the P fixing characteristics of the soil appeared to exert a controlling influence on the concentration of soluble-P when the PSI exceeded 50 (section 4.4.1; 9.3.6). A significant inverse relationship between PSI and soluble-P has been consistently demonstrated throughout this study, and the latter was always very low when the PSI exceeded 50, and often below the detectable limit ($\sim 10^{-7}$M) when the PSI exceeded 100.

The active role of Al in P fixation is widely documented (WILLIAMS et. al, 1958, SAUNDERS, 1965; LOPEZ HERNANDEZ and BURNHAM, 1973, 1974a and b) although the relative contributions of the different forms of Al are less well established. LOPEZ HERNANDEZ and BURNHAM (1973) showed that extractable-Al was significantly correlated with PSI while exchangeable-Al was poorly correlated. SYERS et al. (1970) found the removal of exchangeable-Al had little effect on P adsorption contrasting the results from Chapter 7 (7.4.1.) and those of WILD (1953) which indicate that exchangeable-Al is involved in P fixation. PRAKASH and BHASKER (1974) showed that both forms were involved, as was indicated here (7.3.1/7.4.1.) where results inferred that a proportion of the so called extractable-Al included some exchangeable-Al. PRAKASH and BHASKER suggested that the first rapid stages of adsorption involved exchangeable-Al while the reaction with extractable-Al was slower and prolonged. It was demonstrated in Chapter 4 (4.4.1.) however, that in these Acid Brown soils extractable-Al was the more important form of Al with respect to P fixation. When extractable-Al was low (< 5 meq/100 g) PSI was also low (≤ 50) but in the majority of these soils these values were significantly exceeded and thus the soils could be described as strongly P-fixing.

The mechanisms involved in P fixation and the effects of other soil properties were not studied as such, although some relevant observations were made. The P adsorption isotherms (Fig. 3.2) illustrated the differences between soils with respect to the number and type of adsorption site available. Gypsum additions were shown to lower PSI (4.3.3.) although from the data available it is only possible to speculate about the mechanisms involved: 1) that sulphate competes with phosphate for adsorption sites or 2) that the exchange of Al for Ca lowers the soils' affinity for P. Evidence from the leaching experiment (7.4.2) supports both hypotheses although the absence of increases in soluble P (7.4.2., 4.3.4.) are less compatible with theory 1). It is likely that the displaced Al reacts with phosphate in solution precipitating as Al phosphate which is compatible with theory 2), however, no firm conclusions can be drawn from the limited data.

Extractable-P was found to be the best estimate of plant available P although it did not reflect the small changes in P availability to which plant roots were sensitive nor was it satisfactory when other soil factors had an overwhelming influence on plant and particularly root growth. Extractable-P was not correlated with any form of soil Al, acidity or PSI. In untreated soils it was low ($<$ 0.6 mg/100 g; Fig. 13.6.) falling into the lower end of the P availability index used by the East of Scotland College of Agriculture (E.S.C.A.) C71/28 (1971). The effect of these inherently low levels of available-P in hill soils will be discussed in the following section.

13.3. EFFECTS OF Al AND ITS INTERACTIONS WITH Ca AND P ON THE GROWTH OF RYEGRASS IN ACID BROWN HILL SOILS

This study highlighted 3 main causes for reduced yields of ryegrass attributable to Al:- interference with root growth, with Ca and also P uptake. Some possible mechanisms and the Al concentration ranges involved will now be discussed.

13.3.1. EFFECT OF Al ON GERMINATION AND ROOT DEVELOPMENT

Records of germination (4.3.7. and 10.3.3.) showed that within the concentration range covered by these soils (up to 0.8×10^{-3}M) Al had no affect on germination. MACRAE (1972, unpub.) and DESSUREAUX (1969) report similar findings and it is generally acknowledged (FOY et al. 1978) that the effects of Al follow radicle emergence.

It was shown that when the concentration of Al exceeded 0.3 x 10^{-3}M root growth in ryegrass (L. perenne S24) was almost totally inhibited (4.4.3; 8.4.2.; 9.3.1./9.4.1; 10.3.3.). As a result absorption of nutrients and water was severely restricted and the plants usually died. The time taken for this influence of Al to take effect was demonstrated in Chapter 10 (10.3.3.). COLLIER and GREENWOOD (1977) observed inhibitory effects of Al on the growth of lettuce seedlings within 10 days and commented that the time factor was inversely proportional to the concentration of Al. The relatively poorer growth in soil 11a compared with 11 supports this observation. MACLEOD and JACKSON (1965) showed that concentrations of Al in the soil solution above 0.5 ppm severely restricted legume establishment and found the seedlings to be particularly susceptible at 21 days. It was observed in Chapter 9 that the effect of Al on 10 day old seedlings of ryegrass was as pronounced as when the seeds were germinated directly in a high-Al soil (9.3.1.). The concentrations required to bring about these effects in ryegrass (between 3 and 5 p.p.m.) are much greater than for legumes.

Two distinct causes of inhibition of root development by Al have been recognised by the prevention of cell extension (AIMI and MURAKAMI, 1964) and the inhibition of DNA replication (CLARKSON, 1965, 1969 and HENNING, unpub. (1.7). Because the root cap protecting the meristematic cells is freely permeable to Al (RASMUSSEN, 1968) cell division is particularly susceptible to Al interference. It was not possible, however, to demonstrate these reported effects of Al on mitosis (10.2.4.).

Although there are many reports (FOY et al, 1978) of the adverse effects of Al on plant growth, together with inferences on its mode of action, the sequence of events is hard to establish. No direct evidence is available from this study but circumstantial evidence (i.e. the concomitant measurement of a number of soil and plant properties) allows some speculation as to the phytotoxic mechanism(s). Results obtained, together with evidence from the literature will next be considered in relation to i) uptake of Al into cells; ii) the interactions between Al and Ca and iii) the effects of Al on P uptake and translocation.

13.3.2. MOVEMENT OF Al INTO PLANT CELLS

For Al to interfere with mitosis and other intercellular processes it must be able to move across cell membranes. Results from the bioassay (10.3.4/10.4) suggested that pH influenced Al uptake. In the presence of a high H ion concentration membrane integrity is reduced because pore size tends to be larger with the substitution of H for Ca (MENGEL, 1962; HANDLEY et al, 1965, MARSCHNER et al, 1966; HIATT and LEGGET, 1974). This would expedite the movement of Al ions across the membrane, which is normally a very slow process. The rate of movement by diffusion (RANDALL, 1963 unpub.) would then only be influenced by the concentration gradient for Al.

In studies of plant growth in soil media it is hard to separate the effects of Al from those due to pH because of the inverse relationship between pH and the solubility of Al. In this study inhibition of root growth was most pronounced when soluble-Al exceeded 0.3 x 10^{-3}M and the pH ($CaCl_2$) was below 4.0 (3.5 to 3.8) (4.3.7; 8.3.1; 9.3.1.). pH 'per se' was not thought to be the cause of the poor growth since root growth was healthy under similar conditions when the concentration of soluble-Al was low (soil 10, 4.4.3, Fig. 4.12, Section 4.2). The evidence available, both from soil and plant studies, suggests that the effects of Al become more pronounced at low pH because of increased solubility and membrane permeability.

13.3.3. INFLUENCE OF Al ON Ca UPTAKE

In most of the soils examined concentrations of soluble-Ca were very low (Table 13.1) while those of soluble-Al and -Mg particularly in the basalts, (12.3.3.) were much higher. In several of the pot experiments (Fig. 4.7, sections 4.4.4/4.4.6; 7.4.3; 11.3.5 Fig. 11.3) Ca concentrations in the plant were only just equal to the minimum functional requirement. (LONERAGAN and SNOWBALL, 1962; 1.6.1.) Low herbage Ca concentrations were associated with high amounts of soluble-Al in soil 10 (4.4.4/4.4.6). It was also observed that although the addition of gypsum significantly increased soluble-Ca in this soil, amounts of soluble-Al also increased and Ca uptake was not improved. In contrast, on the lime treatment which hardly increased soluble-Ca but significantly decreased the amount of soluble-Al (Figs 4.4, 4.1, 4.7), Ca uptake was high.

It appears that interference by Al, together with the inherently low soil Ca contents, is responsible for Ca deficiency in ryegrass growing in these Acid Brown hill soils. FOY (1974) identified Al induced Ca deficiency as a means by which Al could reduce dry matter production. AWAD ET AL. (1976) concluded that the effects of Al were not distinguishable from those of Ca deficiency in a trial with Kikuyu grass. RANDALL (1963, unpub.) reported that ryegrass suffering from suspected Al toxicity had higher K/Ca ratios and were lower yielding. Similar symptoms, mineral imbalances and lower yields, were recorded for ryegrass growing on soil 15 (11.3.6/11.3.2). These adverse effects were observed when the Al concentration was between 0.1 and 0.3 x 10^{-3}M and were more noticeable on superphosphate treatments (soil 10, Fig. 4.9, treatment 7). This concentration range at pH 4 to 4.5 (in $CaCl_2$) was below that found to inhibit root growth, although sometimes, lower root weights were recorded.

An explanation for the interference with Ca uptake by Al was given by SHONE (1966) (see Section 1.6.1). Because of the uncertainty attached to the root Al contents in this study (4.3.6) it was not possible to show conclusively whether or not Ca concentrations were lower when those of Al were higher. However, the displacing effect of highly charged cations on Ca in the root was demonstrated with the lead acetate washing procedure described in 2.3.2: roots soaked in lead acetate had significantly less Ca than unsoaked roots (Table 2.1A).

Studies using solution culture (FOY et al, 1978) have shown that increasing the concentration of Ca with respect to Al can overcome Al induced Ca deficiency. It is much more difficult, however, when working with soil to manipulate Ca:Al ratios because of the high buffering capacity of the soil and the effect of pH on Al solubility. ADAMS and LUND (1966) and BACHE (pers. comm.) have, however, examined and are currently studying the relationship between cation activity ratios and plant growth. In Chapter 4, gypsum was included as a treatment in an attempt to vary Ca:Al ratios in the soils. In two of them (soils 10 and 11) which had high exchangeable-Al contents the amounts of Ca were increased with respect to Al, although soluble-Al also increased with the result that dry matter production and P uptake were low (Fig. 4.8). CLARKSON (pers. comm.) suggested that increase in the relative proportion of soluble-Ca would need to be very much greater than occurred here to overcome the Al effects. It was concluded from Chapter 4 that priority be given to lowering soluble-Al in preference to increasing soluble-Ca as both the most effective and the most appropriate method of overcoming Ca associated detrimental effects of Al in these Acid Brown hill soils.

It was not possible to calculate Activity Ratios for the treated soils and instead the Molar Concentration Ratio (MCR) based on the concentrations of Al, Ca and Mg (2.4.3.0) was used to assess the effect of changing the relative concentrations of Al to Ca plus Mg on ryegrass growth. Values of MCR plotted against P uptake (Fig. 4.14), however, gave no indication of a critical value for MCR nor was it apparent for these soils that the proportion of Ca:Al was influencing growth.

It was concluded for these hill soils in which the reservoir of exchangeable-Al tends to be high (13.2.1.), that the addition of Ca containing fertilisers may have a detrimental effect through the displacement of Al into solution. Results show that the only effective method for overcoming problems of reduced yields attributable to Al either directly or indirectly is adding lime to the soil which lowers the Al concentration and may also increase soluble-Ca slightly. It is recommended that because P fertilisers are usually Ca based they are added together with lime in these Acid Brown hill soils to prevent the adverse effects of Al reducing the response of ryegrass to added P.

13.3.4. INFLUENCE OF Al ON P UPTAKE AND TRANSLOCATION

Interactions between Al and P in the soil, and soil solution were discussed in the preceding section (13.2.2.). In this section the influence of Al on the 'biological' availability of P will be discussed. When the concentration of Al exceeded 0.3×10^{-3}M root growth by ryegrass was negligible, severely restricting the uptake of nutrients, especially P, which requires a dense root system (1.5.2.). At concentrations between 0.1 and 0.3×10^{-3}M, when root growth was not so severely inhibited, there were suggestions that Al was aggravating P deficiency in some soils.

It was not wholly clear from the results obtained whether or not the concentration of soluble-P 'per se' was influencing P uptake. P uptake from soils 12 and 14, when they had been treated with superphosphate was similar despite the wide variation in the concentrations of soluble-P in the two soils (Fig. 9.9). On soil 11, however, on the lime + P treatments where Al was not thought to be influencing the biological availability of P, the concentration of soluble-P rarely exceeded 0.005 mg/100 g and P uptake was well below that from the other soils (Fig. 4.10). This latter observation suggests that below a critical value the concentration of P in the soil solution does reduce P uptake and yield, however, this will be discussed again later (13.3.4). In the majority of these hill soils, however, the concentration of soluble-P 'per se' did not appear to be significantly influencing ryegrass yield. Because the concentration of soluble-P does not reflect the P supplying power of the soil (4.4.2) it gives little information for evaluating potential ryegrass growth in Acid Brown hill soils.

RORISON (1965) and CLARKSON (1967) showed that Al ions adsorbed in the root free space could precipitate P, confining it to the root, so that shoots become P deficient with the result that yields were lowered. For a few soils treated with superphosphate, with concentrations of Al between 0.1 and 0.3 x 10^{-3}M root P contents were below those of the corresponding herbage and there was a tendency for herbage yields to be low (soil 10, 4.3.7, Fig. 4.5; soil 15, 11.3.5.1., Fig. 11.1). Because the distribution of P within the root was not investigated it was not possible to be sure that Al/P precipitation was responsible for the higher root P contents. However, even if P precipitation were occurring the effects were not very pronounced and yields did not significantly suffer as a result.

WHITE (1977) found that Medicago sativa growing in solution, pH 5.0, absorbed between 16 and 36% of its P as polymeric aluminophosphates. It is just possible that above pH 4.5 when the concentration of Al is low the association of Al with P in such complexes might enhance P uptake from Acid Brown hill soils. RORISON (1965) showed that these Al/P complexes can move freely across the plasmalemma, and that once inside the cell they tend to move into the vacuole where organic acids become bound to Al in preference to P, which becomes free for use in metabolism and other cellular functions.

Such soluble Al/P complexes were not identified in this study, although their existance could account for the anomalous result reported in Chapter 4 (4.4.1.). More information concerning the formation of these complexes in hill soils is required in view of their possible significance for P uptake and the interpretation of Al shown to be associated with P inside the root cells.

Al concentration ranges quoted here with reference to toxicity and interference with Ca and P uptake apply only to ryegrass which is more tolerant of Al than clover (MUNNS, 1965). This study suggests that providing additional P is applied, the concentration of Al is below 0.1×10^{-3}M, and the native Ca content is not too low, ryegrass yields on Acid Brown hill soils should be high even when the pH is in the range 4 to 4.4 (in $CaCl_2$). N fixing clover, however, has a higher demand for Ca and requires a higher pH than ryegrass (5.5 to 6.0)(HFRO Jubilee Rep. 1979). Thus if, as common practise, clover is included in a reseed with ryegrass it seems unlikely that if the growing requirements of clover are satisfied the soil conditions will be limiting to ryegrass.

13.4. EFFECTS OF LIME AND SUPERPHOSPHATE ON RYEGRASS GROWTH IN ACID BROWN HILL SOILS

In this section only the most relevant changes in soil properties found to influence yield of ryegrass, namely acidity and P status influenced by lime and P treatments will be discussed. Additions of lime plus superphosphate or superphosphate alone were found to be the most effective methods of increasing herbage production from these soils. The role of nitrogen in hill soils has not been examined and N was included as a basal treatment in all the pot experiments to ensure its availability.

13.4.1. EFFECT OF LIME ON SOIL ACIDITY/Al AND BASE STATUS

The addition of lime lowered the amount of exchangeable-acidity and -Al in all the soils (4.3.1; 6.3.1; 12.3.2.2.) and increased pH which was associated with a significant reduction in soluble-Al (Fig. 4.1, Figs. 6.1/6.3, Fig. 11.4). These changes are typical of those brought about by lime (COLEMAN and THOMAS, 1967; MACLEOD and JACKSON, 1967; BEEK, 1969; McLEAN, 1971). The change in pH per unit of lime added appeared to be influenced by the exchangeable-Al content. Soils naturally high in exchangeable-Al gave the smallest increases in pH although the quantitative fall in exchangeable-Al was greatest in those soils (4.3.1/2), where the pH was above 4.4 ($CaCl_2$) or once it had reached this the influence of exchangeable-Al on pH was less obvious and the change in pH per unit of lime became more similar for soils with different, inherent, exchangeable-Al contents (Fig. 6.1).

The amount of lime needed to precipitate soluble-Al in these soils was less than that required to reduce the amount of exchangeable-Al to a negligible quantity, suggesting the solubility of Al was more pH sensitive than the exchange reactions. With the exception of soil 11/11a the application of the equivalent of 1250 kg/ha was sufficient to lower soluble Al in the soils used in the pot experiments to a concentration too low to measure (Fig. 4.1; Fig. 11.4).

The form of Al least affected by lime was extractable-Al. In all the soils the amount was lowered by lime, but the extent of the change varied between soils (Fig. 4.1, Fig. 6.2). Differences in carbon (organic matter)content may have contributed these differential effects of lime. PRATT and BLAIR (1961) showed that ammonium acetate extracted organically bound Al and it was seen here (Fig. 6.2) that the magnitude of change in extractable-Al with increasing lime addition was greatest in soil 11a which had twice the carbon content of soil 9.

Al/organic matter interactions were not examined in this study although there were suggestions that the organic matter content of the soil was modifying the effect of Al on plant growth (11.4.2). It was shown by DATTA and SRIVASTVA (1963) and SCHNITZER and SKINNER (1963) that Al/organic matter interactions influenced the availability of P. In Chapter 5 (5.4.1.) the addition of glucose was found to enhance fungal growth which immobilised a large proportion of the 'available P'. On soil 11, rich in Al with a high PSI, however, P uptake was significantly increased by the addition of glucose with P (treatment 6 Fig. 5.1.). Although the study of Al/organic matter interactions is fraught with problems (11.4.2.) those observations suggest that further investigations might be rewarding; The Macaulay Institute and the University of Newcastle on Tyne are currently pursuing the problems.

One of the objectives of this study was to attempt to identify the reasons for plant responses to lime as a basis for formulating a liming strategy for Acid Brown hill soils. Liming was found to overcome several causes of poor growth in these soils; it increased pH and lowered the amounts of all 3 forms of Al, slightly increased soluble-Ca and significantly increased Ca uptake. Of these changes, the fall in soluble-Al and the increased biological availability of Ca were most important for ryegrass growth (13.3.1; 13.3.3.). Responses to lime represented by increased yield from ryegrass, were limited to those soils in which the concentration of Al exceeded 0.1×10^{-3}M or concentrations of soluble-Ca were very low (e.g. soils 4, 10 and 11, 4.4.1; soils 15 and 16). The results from the pot experiments suggest that liming acid mineral hill soils to at least pH 4.4 (in $CaCl_2$) should overcome these adverse influences of Al.

DURING and BRIER (1973) and WEBBER ET AL. (1977) found the lime requirements (L.R.) to be significantly correlated with Al concentrations extracted in 8.5 and 10.0×10^{-3}M $CaCl_2$ respectively. DURING and BRIER also showed that orthodox determinations of pH and exchangeable-Al predicted the L.R. badly for clover, although WEBBER ET. AL., (1977) recorded good correlations between L.R. and pH (H_2O), exchangeable-Al and exchangeable-acidity. KAMPRATH (1970) discussed the use of exchangeable-Al as a criterion for liming naturally leached mineral soils such as these Acid Brown hill soils, and indicated that Al saturation would need to be reduced to below 30%.

It may be seen from Figures 6.1 and 6.3. that the amounts of lime required to lower exchangeable- and soluble-Al to suitably low levels for satisfactory ryegrass growth differ both because of their different amounts, and relationships with pH. The required pH levels appear to be 5.4 and 4.4 for exchangeable- and soluble-Al respectively. To raise the pH by this additional unit required a significant amount of lime, at some considerable cost. Results from the pot experiments do not justify this additional lime for ryegrass because it appears to be sensitive to amounts of soluble- rather than exchangeable-Al. Adding lime was also shown to be associated with some less desirable changes in nutrient availability. Mg, K and also Mn availability were found to decrease with increasing lime addition (Fig. 6.3; KAMPRATH and FOY, 1971). Excessive use of lime can therefore be counter-productive.

In the field experiment discussed in 6.4., however, it was reported that the pH needed to be around 5.5 (H_2O) to maintain ryegrass growing in the reseed. It appears that in the field environment factors other than soluble-Al but which may be associated with acidity and or Ca nutrition are influencing the growth of ryegrass. In the field many factors outwith the parameters which were examined in these pot experiments could have contributed to the higher pH requirement. Ryegrass evolved on these base rich soils and it is possible that under stresses imposed by climate and nutrient availability, it is less tolerant of Al, low pH, and low base status. It is also likely that the indigenous grasses and sedges, which are better adapted to strong acidity and low nutrient status, are better competitors for nutrients than ryegrass at low pH. These species also tend to reproduce vegetatively bipassing the vulnerable seedling establishment phase.

13.4.2. EFFECT OF LIME ON P AVAILABILITY

The addition of lime had little effect on PSI because it only slightly lowered the amount of extractable Al (13.4.1). The amount of soluble-P also was not found to be significantly changed by lime except where superphosphate had been added, then concentrations tended to be lower (Figs. 4.3; 8.3; 11.4.). The effects of lime on changes in PSI and the solubility of native P were examined in Chapter 6. Small changes in the concentration of soluble-P were just measurable with increases in pH although these were more obvious from changes in P uptake (Fig. 6.6). The poor detection of changes in P availability by chemical methods probably reflects the procedures involved. These impose a quite different set of equilibrium conditions compared to those imposed by the root which is constantly removing P through the growing period. It may be concluded that the influence of lime on P availability is closely connected with soil pH particularly with the effect of this on the affinity of Al for P. The results presented agree broadly with the view of AMARASIRI and OLSEN (1973) that liming lowers the solubility of labile and soluble-P to a minimum around pH 6.

Extractable-P, although showing a good overall correlation with P uptake, was even less sensitive than soluble-P to the relatively small changes in P availability, apparent from P uptake values, brought about by lime (e.g. Fig. 4.9.). However, this is understandable because the reagent is strongly buffered to pH 4.5. It is possible that these more strongly buffered reagents used to extract P lead HALSTEAD (1967) to make the comment that, 'regardless of the level of lime addition, or pH, in acid soils the greatest proportion of added P was always recovered from the Al fraction': implying that lime just caused the redistribution of P between the forms of Al rather than influencing the affinity of Al for P.

The main shortcoming of all the chemical methods used here, and elsewhere, to assess P availability is that they do not take into account the soil conditions influencing root growth which may aid or hinder P uptake. In soils such as 10, 11/11a and 15 where Al toxicity was shown to be influencing P uptake lime significantly enhanced P uptake (Fig. 4.9; 11.1). This effect was attributed to lime reducing the concentration of soluble-Al to below $0.1 \times 10^{-3}M$, the apparent critical concentration for ryegrass (13.3.4.). In this study it was not possible to distinguish between this effect and that of a change in the chemical availability of P (i.e. the conditions influencing P absorption and the equilibrium P concentration in solution).

In soils where Al toxicity was not a problem (e.g. soil 9) lime significantly reduced P uptake from added P (Fig. 4.9). This negative effect of lime in the presence of added P was recorded by WILD (1953) and RYAN (1971, unpub.) and was introduced in 1.8.2. LAWTON and DAVIES (1956) proposed that the decrease in the proportion of $H_2PO_4^-$ ions with increasing pH might contribute to this negative effect. Results from Chapter 5 (5.4.1.) suggested that the large increase in fungal growth brought about by lime could account for reductions in P availability in short term experiments.

It is concluded from this study and studies by THOMAS (1960) and RYAN and SMILLIE (1975) that the main benefits of liming these Acid Brown hill soils is the lowered amounts of soluble-Al and the generally improved rooting media which enables roots to explore more of the soils P reserves. This is likely to be even more important in the field situation where plants are grown continuously, as permanent pasture. In soils such as 11/11a liming is a prerequisite for growth and response to added P and in view of the experience with the field plot (6.4.) it is recommended that some lime be added with superphosphate to maximise the returns from adding P. The likely benefit from minimising competition from indigenous species may outweigh the small losses in P uptake on soils where Al is not a problem, but this needs to be assessed further. The results provided no conclusive evidence to suggest that liming Acid Brown hill soils influenced the soil properties controlling the concentration of P in the soil solution and the rate at which it is replenished.

13.4.3. EFFECTS OF SUPERPHOSPHATE ON SOIL ACIDITY AND Al

The addition of superphosphate did not produce any significant changes in soil acidity in the soils examined. As the level of addition was increased, however, increases in soluble-Al were recorded which were not apparently related to the inherent amount of exchangeable-Al, pH or even Al saturation (Fig. 9.6c, Table 9.1). Soluble-Al was also significantly increased where gypsum was included (Fig. 4.1.c) although in the case of gypsum the increases were most obvious in soils 10 and 11 where pH was low and exchangeable-Al was high. Increases in soluble-Al were most apparent at the higher applications of superphosphate ($>$100 kg/ha) (Fig. 9.6c) reflecting the increased displacing ability of Ca at higher concentrations. At the lower applications in these soils (e.g. 11a) with inherently high soluble-Al contents the concentrations of Al fell with the lower applications probably due to the formation of Al phosphate. PHILLIPS and WEBB (1971) showed that water soluble P fertilisers such as superphosphate, lowered the pH in the vicinity of their dissolution so that in acid soils most of the added P is precipitated as Al or Fe phosphates.

However, because of the tendency for concentrations of Al to increase as a result of the addition of superphosphate this method was found to be unsuitable for overcoming Al toxicity in hill soils. It seems likely that the increased use of superphosphate and other Ca based P fertilisers, as the availability of basic slag declines, will increase the incidence of Al toxicity in hill soils making it more imperative to add lime with the P as a preventative measure.

13.4.4. EFFECT OF SUPERPHOSPHATE ON THE AVAILABILITY OF P

The addition of superphosphate brought about large increases in extractable-P in all the soils but these were only associated with equally significant increases in P uptake when there were no adverse effects of Al. Without the addition of P to these soils growth was very restricted and P deficiency symptoms were observed in the early stages of plant growth (4.3.7; 9.3.1; 11.3.1). The low values of extractable-P in these soilscorresponded with low or very low P availability index ratings, (E.S.C.A. C71/28, 1971). Maximum responses to added P were recorded up to the addition of equivalent to 150 kgP/ha (Fig. 9.2). Above this level other nutrients and or environmental conditions appeared to be exerting a stronger influence on yield.

The P sorption index was lowered by the addition of superphosphate, but the proportional decrease varied between soils (4.3.3., Fig. 4.2; 9.3.6, Fig. 9.5). The content of extractable-Al did not account for these soil differences. Although PSI was inversely correlated with soluble-P decreases in PSI were not usually associated with increases in soluble-P indicating that factors other than just P adsorption were controlling the equilibrium P concentration. Where PSI was low, however ($<$50 as in soil 14) soluble-P was significantly increased by increasing the level of P addition and this was associated with a fall in PSI (9.4.2.). This suggests that in soils where there are fewer P adsorption sites, reflecting mainly lower extractable-Al contents, additions of P are more likely to be associated with a rise in soluble-P.

It was noted in Section 7.4.2., that Ca based P additions reduced PSI more than did a K salt of P. It was suggested in Section 4.4.1. that exchange by Ca for Al ions on exchange sites reduced the affinity of the surface for P, but K should also have this displacing effect (KCl was used to displace exchangeable-Al). Thus, although it was demonstrated here (7.4.1.) and by WILD (1953) that exchangeable-Al does 'fix' P this fails to explain why PSI was lowered by the Ca salt most. It seems likely that the sulphate in superphosphate competed with phosphate ions for adsorption sites and thus reduced the number of sites. This also explains why gypsum (4.3.3.) reduced PSI suggesting that sulphate can displace phosphate. However, because of the displacing effect of Ca on Al increasing the concentration of Al which then precipitated the P, there was no increase in soluble P.

The duration of contact between soil and fertiliser may have influenced the availability of P particularly in the high P fixing soils. In the experiment described in Chapter 4, the duration was 3 months compared to only 1 week in the experiment described in Chapter 9. P uptake from soil 12 with the highest PSI recorded for these soils was not significantly less than that from soil 14 (low PSI) (Fig. 9.9), whereas in soil 11 (which was limed also) P uptake was lower than from soils with lower PSIs (Fig. 4.10). JAMES et al. (1979) also reported reduced P availability from added P on high P fixing basalt soils. RYAN (1971, unpub.) showed that P availability from superphosphate was significantly reduced with time due to the change in solubility of the products of reaction between soil and fertiliser. The effect of duration of contact between soil and P fertiliser on the availability of added P for ryegrass has been examined for these soils at H.F.R.O. but the results are not yet available. The long term aspects of fertiliser P availability especially in limed soils requires further investigation so that P maintenance requirements can be drawn up. In this respect it would be worthwhile examining in more detail the reactions and soil properties which determine the availability of P with time. RYAN (1971, unpub. Ph.d) recommended that P fertiliser be applied simultaneously with the seed on high P fixing soils.

This study has identified the need for both lime and P applications to hill soils to improve ryegrass growth, confirming the introductory remarks that low P availability and Al were limiting production from these soils. Severe inhibition of root growth in ryegrass, however, does not appear to be very common and it seems that ryegrass does grow well above pH 4.4 (in $CaCl_2$) provided soluble-Al is low and there is adequate P and Ca, and competition from indigenous species is kept down.

13.5. CONCLUSIONS

In this ~~study~~ the effects of Al, low availability of P and Ca, and low pH on the growth of ryegrass in a controlled environment were investigated. Regular harvests were taken, N levels were optimum, weeds and environmental stresses were absent, there were no subsoil influences, lime and nutrients were evenly distributed and none of the experiments exceeded 6 months. The following is a summary of the main conclusions:

1. Wide ranges exist in many chemical properties for the ill-defined group of Acid Brown hill soils reflecting the diversity in parent materials.
2. Soils are characterised by their low pH (mean 3.9 in $CaCl_2$), large amounts of exchangeable acidity, exchangeable and extractable Al ($>$10 meq/100 g), high Al saturation ($>$70%), low levels of Ca, high PSI ($>$50) and very small amounts of extractable-P ($<$0.3 mg/100 g).
3. The low P supplying power of these soils is a major limitation to high productivity from reseeds.
4. The amount of extractable P (in NH_4OAc) was shown to be a satisfactory guide to the P requirement of these soils.
5. The form in which Al occurred in the soil was influenced by several factors including pH but the amount of each form was not simply or significantly related to pH. Soluble-Al was highest when Al saturation exceeded 80% and pH was low.
6. pH was influenced by the level of Al saturation and the amount of exchangeable-acidity, but was not significantly correlated with either.
7. Amounts of exchangeable- and soluble-Al were very low above pH 5.4 and 4.4 respectively.
8. Both the form and content of Al in the soil influenced the growth of ryegrass: extractable-Al through its affinity for P, being strongly correlated with PSI and inversely correlated with the concentration of soluble P; exchangeable-Al via its inverse relationship with pH and base saturation; and as soluble Al, which at certain concentrations was inhibitory to root growth, nutrient uptake and hence the establishment and growth of ryegrass
9. Ryegrass root growth and yields, in the presence of added P, were significantly and inversely correlated with soluble-Al (the concentration of Al in 10^{-3}M 1:5 soil to solution ratio); $[Al] > 0.3 \times 10^{-3}$M root growth was almost totally inhibited and ryegrass herbage production ceased.

$[\mathrm{Al}]$ range 0.1 to 0.3×10^{-3}M root growth and nutrient uptake (P and Ca) and translocation reduced and thus yields reduced.
$[\mathrm{Al}] < 0.1 \times 10^{-3}$ M no adverse effects of Al demonstrated.

10. The inhibitory effects of Al were enhanced with increased acidity and the concentration was strongly correlated with the extent of the inhibitory effect and the time taken for this to take affect.
11. Concentrations of Al up to 0.4×10^{-3}M were not found to influence germination.
12. Concentrations of Al above 0.3×10^{-3}M were not common in the soils examined and concentrations in the intermediate range were only measured in less than 20% of the soils. In the majority of these Acid Brown hill soils the amount of soluble-Al was below that shown to interfere with ryegrass growth.
13. Fertiliser treatments, in the absence of lime, are likely to increase the naturally occurring concentrations of soluble-Al in these soils, with deleterious effects.
14. Low P availability was a universal problem amongst these soils so that applications of P fertiliser proved to be essential to obtaining high or even moderately high yields. Responses to superphosphate in pot experiments were greatest up to the equivalent of 150 kg P/ha.
15. The effectiveness of P fertiliser was greatly enhanced by the simultaneous addition of Ca as most of these soils had only low levels, were deficient in Ca, or had its availbility reduced by the presence of Al.
16. Liming the soil was found to be a pre-requisite for ryegrass growth in soils where soluble-Al exceeded 0.3×10^{-3}M but was also shown to be worth while in all soils with low base status and high Al saturation (the majority of Acid Brown hill soils).
17. The addition of Ca as gypsum did not overcome the adverse effects of Al and neither did applications of silicic acid or large amounts of superphosphate.
18. In an optimum environment (pot experiments in the glasshouse with no competition from indigenous species) ryegrass was found to be tolerant of low pH (4.4 in $CaCl_2$), when Al

toxicity and Ca deficiency were not, themselves, a severe limitation, but in the field amidst competition a pH in excess of 5 was required to maintain vigorous ryegrass growth.

19. Liming was shown to reduce the chemical availability of added P in those soils as described in 18 (above) as it increased the affinity of Al for P, but the advantages associated with liming - improved rooting and competitive ability outweigh this relatively small reduction in yield found in only a small percentage of these soils.

13.6 FURTHER WORK

Several areas meriting further investigation have been highlighted in this stidy. Having demonstrated the need to add both lime and P to these Acid Brown hill soils means that the long term interactions between these amendments and the soil will need studying, in the field. Changes in acidity and the effects of P availability and composition of the sward need to be investigated. It would also be useful to see whether the tolerance range of ryegrass to levels of soluble-Al in pot experiments is duplicated in the field. Field observations suggest there are more factors than just soil chemical properties to be considered when assessing lime requirements and the need for other nutrient amendments in the field environment. The reasons why ryegrass performs less well in the field need to be established. It may prove helpful to examine the growth of indigenous hill species to see whether they are specially adapted or tolerant of particular sets of conditions.

It was shown that liming these soils improved conditions for micro-organisms and in view of the changes these bring about in P status through mineralisation and temporarily 'locking up' P it would be useful to monitor the long term changes in organic P and P availability. Interactions between Al and organic matter were found to have advantageous implications for plant growth and since these soils tend to have high contents of organic matter this subject would seem worthy of further work. The sets of conditions in the soil controlling the concentration of soluble-Al need to be better understood in view of the adverse effects of Al demonstrated. This study has shown how inadequate are some of the conventional methods for assessing P availability and indicated the need to examine the whole concept of P availability in hill soils to show how availability changes with time as P is being added and removed.

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APPENDIX

Table 2.1A. Effect of Lead Acetate Treatment on the mineral content of the Roots

Treatment	With Lead Acetate				Without Lead Acetate			
	% Si	% Al	% P	% Ca	% Si	% Al	% P	% Ca
Soil 10	1.40	.37	.11	.26	2.52	.51	.11	.44
Tr. 1	1.65	.51	.10	.26	1.35	.41	.11	.34
Soil 4	1.64	.88	.06	.27	1.58	.69	.06	.37
Tr. 1	1.56	.76	.06	.23	2.44	1.14	.07	.32
Soil 10	.48	.20	.13	.21	1.44	.53	.18	.23
Tr. 5	.65	.25	.16	.13	.76	.32	.18	.25
Soil 4	2.81	.41	.11	.21	4.04[c]	1.47[c]	.12	.32
Tr. 5	2.44	.78	.10	.16	1.39	.60	.12	.33
Soil 10	1.89	.47	.07	.32	1.50	.33	.08	.42
Tr. 2	.9	.25	.07	.28	.83	.21	.08	.46
Soil 4	3.05	1.02	.06	.41	1.55	.65	.06	.57
Tr. 2	1.34	.19	.06	.46	1.03	.16	.06	.63

c: suspect contamination.

Note: 2.2A. Preparation of discs for x-ray fluorescence

(C. C. Evans unpub.)

Samples of herbage were milled in an adapted Moulinex coffee grinder and oven dried overnight. 1.00 g of sample was added to 1.00 g dried cellulose powder (Whatman Standard grade). This was mixed and ground for 10 mins in a Glendevon M260 ball mill. The mixture was compressed into a self supported disc, in a hydraulic press. The sample was then inserted into a Philips PW 1540 1 kw X-ray Fluorescence Spectrometer, and the unknown peaks were compared with those of prepared standards, and the percent content of P, Al, Si, Ca, Mg and K were calculated.

Note: 2.3A. Calculations

(1) Nutrient concentrations measured in solutions by auto-analysis, atomic absorption: SOIL EXTRACTIONS.

$$\frac{\text{ppm nutrient x Mls extracting solution}}{1000} \times \frac{100}{\text{wt of soil}}$$

$$= \text{mg nutrient per 100 g soil.}$$

e.g. Morgan's extraction have 2.0 g air dry soil in 25 ml NH_4OAc.

Measure 0.11 ppm P. $\therefore$ amount of NH_4OAc extractable P =

$$\frac{.11 \times 25}{10\cancel{0}\cancel{0}} \times \frac{1\cancel{0}\cancel{0}}{2} = .11 \text{ ppm} \times 1.25 = 0.14 \text{ mgP}100\text{g}^{-1} \text{ soil}$$

(2) Meq. of a cation = $\frac{\text{mg x atomic wt. cation}}{\text{valency}}$

e.g. $Al^{3+} = \text{mg} \times \frac{27}{3} = \text{meq}$

PLANT ANALYSIS

Expressed as % or ppm = $\mu g\ g^{-1}$

100% = 1,000,000 ppm

1000 ppm = 0.1%, 1 ppm = 0.0001%

P uptake is calculated in mg.

= % P x 10 x dry weight (g)

e.g. if concentration of P in herbage = 1% in 2 g of dry matter

$\therefore$ 100% P of 1 g = 1000 mgP

$$1\% \text{ of } 2 \text{ g} = \frac{10\cancel{0}\cancel{0}}{1\cancel{0}\cancel{0}} \times 2$$

$$= 20 \text{ mg P}$$

Table 2.4A Method of Root Squashing

A single root tip was selected, cut from the root, and placed on a slide in a drop of proprione-carmine. The tip was then cut into the smallest lengths possible, macerated with a flat edged needle and a coverslip placed over them. Using the tip of the handle of a mounted needle the surface of the coverslip was tapped gently, holding the edge between the first and second fingers to prevent the coverslip from rolling the material. The slide was gently heated over a spirit lamp, to blood heat, to further break up the material. Then the slide was placed between folded filter paper and pressed firmly down on the surface of the coverslip with thumbs. To prevent rapid evaporation a drop of acetic-carmine was run round the edges of the coverslip.

The prepared slide was scanned using 4 x 10 magnification then the number of nuclei undergoing mitosis or in interphase were scored.

Stain recipes

Aceto-carmine	5 g Carmine 90 cc Acetic acid 100 cc Distilled H_2O

The ingredients were placed in a 500 cc round flask, attached to a Liebig condenser and slowly brought to the boil, allowed to cool, then filtered.

Propione-carmine 4 g of carmine were dissolved in 100 ml of 45% proprionic Acid.

Both stains can be stored for $\sim$ 3 months.

Table 2.5A Profile Description Soil 4.

Location: Lephinmore. 993 935 sheet 55 1st series 1:50,000

Classification: Stricken Association. Fungarth series. Brown earth.

Parent Material: Dalradian, Highland Schist. Metamorphic rock.

Slope : 30°

Altitude : 100 m N facing

Vegetation : Agrostis Fescue grassland

Drainage : Free

Horizon : Depth cm

A_1	0-19	Very dark greyish brown (10 YR 3/2) very fine sandy loam many small tabular stones, strongly developed crumb structure with many fine pores, intimately mixed organic matter, an abundance of fibrous roots, showing sharp boundary with
B	19-24	Brown (10 YR 5/6) sandy clay loam with very many small tabular stones - structure moderate, angular blocky, many fine pores and fissures, low in humus, fine fibrous roots abundant
B_x	44	Brown (10 YR 5/4) sandy loam small angular stones and large boulders, massive, structureless many pores, few fibrous roots.
C		Below water table.

Table 2.6A   Profile Description Soil 9

Location: Stanhope Glen 132288 Sheet 72 1st series 1:50,000

Classification: Ettrick Association - Linhope series, Brown Earth.

Parent material: Silurian, Tarannon & Llandovery, Sedimentary

Slope : 4°

Altitude : 200 m

Vegetation : Open Callunetum about 20 years old.

Drainage : Free

Horizon : Depth cm

L	0- 1	Fibrous organic matter, abundance of fine fibrous roots.
A	1- 9	Dark brown (10 YR 3/3) loam slightly stony, granular structure with mixed mineral and organic matter and an abundance of fine fibrous roots.
AB	9-20	Dark brown (10 YR 4/3) fine sandy loam with small stones, angular blocky structure, with intimately mixed organic matter and abundance of fine fibrous roots merging into
B_2	20-38	Brown (10 YR 5/4) loam with coarse sand, stony, angular block structure with roots.
B_3	38-55	Yellowish brown (10 YR 5/8) gritty loam with many distinct strong mottles (10 YR 5/8). Many large tabular stones weak structures of pores and fissures, veins of iron abundant, roots common, merging into
C	55-68	Strong brown (7.5 YR 5/6) gritty loam very stony with large tabular stones some stained yellowish brown (10 YR 5/8) weak structureless with pores, fissures and tubes of iron abundant, woody roots common.

Table 2.7A

Profile Description Soil 10

Location: Sourhope (Auchope Hill) 858215 sheet 74 1st series 1: 50,000

Classification: Sourhope Association - Sourhope Series - Brown podzolic

Parent material: Andesite Lava (Old Red Sandstone age), Igneous

Slope : 12^{o}

Altitude : 305 m

Vegetation : <u>Agrostis fescue</u> grassland dominated by <u>Juncus</u> and <u>Carex</u> species.

Drainage : Free

Horizon :	Depth cm	
L	0- 6	Structureless but differentiated into F & H layers fibrous, high organic matter abundance of living fleshy roots.
A	6-18	Black (5 YR 2/1) loamy sand with rounded stones structureless, crumbly, low organic matter, living fibrous roots, narrow boundary into
B	18-38	Yellowish brown (5 YR 5/6) loamy sand with many very large angular stones giving a weak crumbly structure, low in organic matter, roots common, thick and woody, merging into
C	38+	Yellowish brown (5 YR 5/6) sandy loam, extremely stony, brittle structure, brown fibrous roots common.

Table 2.8A <u>Profile Description Soil 11</u>

Location: Carron Forest, sheet 57, 1st series 1:50,000

Classification: Darleith Association - Darleith series, Brown Podzolic

Parent material: Basalt lavas of Carboniferous age, Extrusive Igneous.

Slope : 7°

Altitude : 250 m

Vegetation : Clear felled Spruce forest

Drainage : Free

Horizon :	Depth cm	
L	0-12	With differentiated F & H layers, high organic matter content of discrete humus.
A_1	12-22	Dark reddish brown (5 YR 3/2) loam, moderate subangular blocky structure, crumbly, pores and fissures rare, stony, high in organic matter with an abundance of fine roots, distinct change into
A_G	22-29	Dark brown (7 YR 4/2) silt loam, very stony, weak, subangular blocky, crumbly, few very fine pores, less organic matter, fewer thicker roots, merging into
B	29-57	Dark brown (7 YR 4/2) gritty loam, very stony moderate structure, weak subangular blocky and brittle very fine pores common, very few roots, sharp boundary with
C	57-80	Very dark greyish brown (10 YR 3/2), very gritty loam, extremely stony, mainly gravel structureless, very fragmented, strongly indurated, low in organic matter but evidence of humic acids, no roots.

Table 3.1A <u>Summary of P Sorption data for soils 1—8 (Fig. 3.1)</u>

Soil	Initial conc^{n} of P added ppm	Final conc^{n} P ppm/	(µM) (c)	P sorbed/ 100 g soil (x)	PSI $\frac{x}{\log c}$
1	40	14	452	52	27
	86	49	1582	74	
	126	87	2810	78	
2	40	5	161	70	29
	86	38	1227	96	
	126	77	2487	98	
3	40	14	452	52	31
	86	38	1227	96	
	126	73	2358	106	
4	40	6	194	72	27
	86	42	1357	88	
	126	80	2584	92	
5	40	5	161	70	35
	86	29	937	114	
	126	68	2196	116	
6	40	3	92	74	48
	86	17	549	138	
	126	49	1582	154	
7	40	1	32	78	92
	86	2	64	168	
	126	10	329	232	
8	40	0	0	80	105
	86	0.5	16	171	
	126	6	194	240	

Table 4.1A Chemical Properties of Soils 4, 9, 10 & 11.

	Soil 4	9**	10	11**
pH	4.2	4.2	3.5	3.9
% C	4.9	4.3	5.6	9.5
Bulk density g/cc	1.56	1.86	0.67	0.94
Total P mg/100 g	75.0	81.0	118	214
Organic P mg/100g	36.5	57.5	87.5	185
Arrion Exch. P	2.00	2.30	2.51	1.13
Extr. P	0.24	0.23	0.47	0.33
Truog P	4.24	0.57	1.62	1.96
PSI	44^{+}	27^{+}	46^{+}	168^{++}
Exch. Acid meq/100 g	3.3	3.5	9.3	16.4
Exch. Al "	3.3	3.1	9.1	16.3
Exch. Ca "	1.8	2.6	1.2	1.0
Exch. Mg "	0.8	0.8	1.1	1.0
Exch. Fe "	Tr	Tr	Tr	Tr
Tamms. Fe %	1.1	0.5	0.5	3.5
Extr. Al meq/100 g	4.9	3.6	5.3	20.2
Extr. Ma (pH) mg/100 g	0.25	0.78	1.10	0.26
Sol. P mg/100 g	0.03	0.06	0.05	Tr
" Al meq/100 g	0.02	0.02	0.11	0.54
" Ca meq/100 g	-(12)*	0.02	-(13)*	-(8)*
" Mg meq/100 g	0.32	0.32	0.34	0.24
" Mn g/g	6.10	2.90	0.90	4.50
Fe g/g	0.45	0.15	3.85	4.50

* Ca adsorbed from 10^{-3} M.$CaCl_2$ (amount adsorbed, ppm)

\+ Addition of ∿ 75 ppm P

++ " ∿ 150 ppm P

** Used in chapter 5.

Table 4.2A Diary and Experimental Details for Chapter 4

Duration: March to October 1977
Soils 4, 9, 10, 11 collected 24 March - 7 April 1977, sampled 0-5 cm below organic horizon.

Soil + treatment mixed and potted 15/16 April 1977

Pots 70 cm^2 at ridge, 500 ml vol. holding ~ 300 g AD. soil

Seeds sown 12/7/77

1st Harvest 9/8/77 temperature range 10 — 42^o

2nd Harvest 13/9/77 " " 14 — 32^o

3rd Final Harvest 11/10/77 " " 15 — 28^o

Test crop Lolium perenne S24 0.22 g seeds pot ≡ 280.2 kg/ha, P content 0.74 mg.

Treatments

Nutrient rate of application	Fertiliser	g/pot	Nutrient/ pot	Time of application
PO = 0 P1 = 80 kg/P	Superphosphate (≡916 kg/ha)	0 0.7228	71.3 mg/p 8.3 meqCa	At mixing stage (M.S.)
K = 100 kg/ha N = 36 kg/ha	KNO_3	0.2035	2 meq K 28.2 mg N	M.S.
Ca_0 = 0 Ca_1 = 20 meq/pot	Gypsum $CaSO_4,2H_2O$	1.7217	20 meq Ca	M.S.
Ca_0 = 0 Ca_1 = 1250 kg/ha*	Lime $CaCO_3$	1.00	20 meq Ca	M.S.
N = 30 kg/ha	NH_4NO_3	25 mls		Every 14 days

M.S. Mixing Stage

* Amount of Lime required to raise the pH of all the soils above 5.0 (H_2O) :-

Level, kg/ha	Lime Addition g.fresh weight per 10 g soil	pH to nearest 0.05 pH units			
		Soil 4	Soil 11	Soil 9	Soil 10
0	0	5.25	4.40	4.95	4.45
1250	0.025	5.70	5.30	5.55	5.05
2500	0.05	5.95	5.65	5.80	5.35
5000	0.10	6.15	5.80	6.15	5.65
10000	0.20	6.25	5.95	6.20	5.80

Table 4.3A pH (Fig. 4.2a) Amounts Exchangeable-, Extractable- and Soluble-Al (Fig. 4.1) of the 4 soils described in Chapter 4, arranged in limed and unlimed groups of treatments.

	L0				L1			
Treatment	G0P0	G1P0	G0P1	G1P1	G0P0	G1P0	G0P1	G1P1
Soil No.	1	3	5	7	2	4	6	8
			pH					
4	4.3	4.4	4.4	4.5	5.3	5.4	5.3	5.2
9	4.3	4.3	4.3	4.3	5.3	5.3	5.3	5.3
10	3.6	3.7	3.7	3.7	4.3	4.3	4.3	4.3
11	3.9	4.0	4.0	4.1	4.4	4.4	4.4	4.4
			Exch.-Al^{3+} meq/100 g					
4	1.84	1.23	1.04	1.23	0.41	0.20	0.20	0.20
9	2.10	2.20	2.00	1.80	0.20	0.25	0.30	0.30
10	8.64	7.91	8.02	8.32	2.50	2.66	2.66	2.70
11	15.64	14.84	14.84	13.89	6.82	8.21	9.22	7.62
			Extr. Al^{3+} meq/100 g					
4	4.86	4.97	4.28	4.31	3.43	3.13	2.99	3.13
9	3.82	3.68	3.13	3.16	2.53	2.45	2.13	2.09
10	5.42	5.35	4.29	4.76	4.45	4.81	4.03	4.06
11	20.80	20.80	20.80	20.00	18.80	18.80	18.80	17.40
			Sol.-Al meq/100 g					
4	0.02	0.08	0.04	0.12	$<$0.01	0.01	0.01	0.01
9	0.02	0.07	0.02	0.14	$<$0.01	$<$0.01	$<$0.01	$<$0.01
10	0.11	0.59	0.22	0.60	0.03	0.07	0.07	0.14
11	0.54	0.33	0.31	0.41	0.08	0.13	0.04	0.17
			Sol.-Al x 10^{-3} M					
4	0.013	0.053	0.027	0.080	trace	0.007	0.007	0.007
9	0.013	0.047	0.013	0.090	trace	trace	trace	trace
10	0.067	0.390	0.150	0.400	0.020	0.047	0.047	0.090
11	0.360	0.220	0.210	0.270	0.053	0.087	0.027	0.110

Table 4.4A PSI (Fig. 4.2b) and Amounts of Soluble and Extractable-P (Fig. 4.3) in the 4 soils described in Chapter 4, arranged in P-treated and non-treated groups of treatments.

Treatment	P_0				P_1			
Soil No.	L_0G_0 1	L_1G_0 2	L_0G_1 3	L_1G_1 4	L_0G_0 5	L_1G_0 6	L_0G_1 7	L_1G_1 8
	PSI							
4+	36	38	16	15	12	11	11	11
9+	22	21	6	6	1	1	3	3
10+	41	42	21	18	14	11	15	12
11++	158	144	126	107	107	102	121	119
	Sol.-P mg/100 g							
4	0.03	0.04	0.03	0.03	0.06	0.07	0.06	0.07
9	0.06	0.07	0.04	0.03	0.10	0.07	0.07	0.09
10	0.05	0.06	0.02	0.03	0.14	0.12	0.11	0.10
11	Tr.	Tr.	Tr.	Tr.	0.005	$<$0.005	$<$0.005	$<$0.005
	Sol.-P x 10^{-6} M							
4	1.9	2.6	1.9	1.6	3.5	4.5	3.9	4.5
9	3.9	4.5	2.6	1.9	6.5	4.5	4.5	5.5
10	3.2	4.2	1.3	1.9	9.0	7.7	7.1	6.5
11	Tr.	Tr.	Tr.	Tr.	0.2	$<$0.1	$<$0.1	$<$0.1
	Extr.-P mg/100 g (pre growth)							
4	0.19	0.21	0.21	0.19	1.02	1.02	1.09	0.91
9	0.22	0.20	0.20	0.22	2.07	2.03	2.07	1.86
10	0.50	0.47	0.40	0.49	1.62	1.63	1.66	1.63
11	0.33	0.33	0.33	0.25	1.49	1.44	1.41	1.31
	Extr.-P mg/100 g (post growth)							
9	0.21	0.19	0.20	0.22	1.02	1.08	1.08	1.04
11	0.33	0.33	0.33	0.25	1.41	0.93	1.31	0.94

\+ 75 ppm P added

++ 150 ppm P added

Table 4.5A Amounts of Exchangeable- and Soluble-Ca (Fig. 4.4) Soluble-Mg and Log MCR (Fig. 4.14) in the 4 soils described in Chapter 4.

Soil No.	Treatment No. 1	3	5	7	2	4	6	8
	Exch.-Ca meq/100 g							
4	3.0	9.1	5.0	12.0	8.2	18.7	11.6	21.8
9	5.4	10.1	8.0	13.7	8.0	15.7	11.3	17.5
10	3.0	12.3	5.6	12.8	9.7	20.2	14.2	23.2
11	0.4	7.2	3.6	9.2	6.3	13.6	9.5	14.5
	Sol.-Ca meq/100 g							
4	-	1.36	0.26	2.10	0.09	2.40	0.65	2.77
9	-	2.02	0.41	2.35	0.28	2.20	0.76	2.62
10	-	1.73	0.23	0.79	-	2.33	0.62	2.91
11	-	0.85	0.24	1.63	0.33	1.58	0.73	1.51
	Sol. Mg meq/100 g							
4	0.32	0.57	0.40	0.54	0.22	0.32	0.47	0.51
9	0.32	0.57	0.40	0.61	0.25	0.34	0.47	0.47
10	0.34	0.78	0.44	0.54	0.18	0.71	0.34	0.61
11	0.24	0.79	0.21	0.23	0.13	0.16	0.18	0.23
	Log. MCR							
4	2.740	4.005	4.347	5.133	4.340	6.396	5.681	7.564
9	3.013	5.602	5.502	5.366	5.836	7.377	6.766	7.730
10	2.590	3.043	2.166	3.663	2.196	5.687	4.120	5.506
11	0.439	3.175	2.659	3.357	4.931	4.631	5.441	4.325

Table 4.6A Mean % P Content of Herbage (H) and Roots (R) (Fig. 4.5)
(where Herbage = $H_1 + H_2 + H_3/3$)

	Treatment No.									
	1	2	3	4	5	6	7	8	SED	CV%
		P_0				P_1				
Soil 4										
H.	0.08	0.09	0.08	0.08	0.22	0.25	0.22	0.29	0.01	9
R.	0.07	0.06	0.07	0.06	0.12	0.11	0.12	0.11	0.01	12
Soil 9										
H.	0.09	0.06	0.06	0.09	0.31	0.29	0.29	0.38	0.01	7
R.	0.11	0.12	0.13	0.12	0.19	0.15	0.12	0.18	0.01	8
Soil 10										
H.	0.09	0.10	0.10	0.09	0.21	0.32	0.21	0.30	0.02	11
R.	0.11	0.08	0.10	0.08	0.16	0.15	0.22	0.16	0.01	13
Soil 11										
H.	0.06	0.10	0.06	0.09	0.16	0.13	0.13	0.13	0.01	10
R.	0.10	0.11	0.10	0.11	0.16	0.15	0.19	0.12	0.01	11

Table 4.7A Mean % Ca Content of Herbage (H) and Roots (R) (Fig. 4.7)

	Treatment No.									
	1	2	3	4	5	6	7	8	SED	CV%
		P_0				P_1				
Soil 4										
H.	0.66	1.44	0.85	2.18	0.60	0.78	0.78	0.87	0.09	12
R.	0.33	0.53	0.52	0.87	0.32	0.62	0.42	0.58	0.07	19
Soil 9										
H.	0.78	1.94	1.18	2.56	0.64	0.81	0.77	0.91	0.06	8
R.	1.24	2.00	2.00	2.81	1.04	1.14	1.12	1.34	0.10	9
Soil 10										
H.	0.32	0.60	1.00	0.79	0.35	0.63	0.50	0.62	0.12	27
R.	0.32	0.30	0.51	0.53	0.24	0.43	0.34	0.43	0.02	8
Soil 11										
H.	0.74	1.10	1.98	0.90	0.74	0.80	0.76	0.73	0.06	9
R.	0.43	1.37	0.36	1.78	1.38	0.99	1.59	1.08	0.15	19

Table 4.8A Mean % Al Content of Herbage (H) and Roots (R) (Fig. 4.6)

	Treatment No.								SED	CV%
	1	3	5	7	2	4	6	8		
	L_0				L_1					
	Soil 4									
H.	0.03	0.07	0.01	0.12	0.01	0.01	0.01	0.01	0.01	21
R.	0.73	0.70	0.48	0.39	0.55	0.56	0.35	0.37	0.07	20
	Soil 9									
H.	0.04	0.01	0.01	0.01	0.02	0.02	0.12	0.12	0.01	36
R.	0.16	0.32	0.14	0.16	0.08	0.16	0.08	0.17	0.17	26
	Soil 10									
H.	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	12
R.	0.11	0.66	0.16	0.42	0.08	0.06	0.28	0.42	0.12	26
	Soil 11									
H.	0.08	0.06	0.08	0.11	0.03	0.02	0.02	0.01	0.01	10
R.	1.14	0.96	0.46	0.54	0.12	0.12	0.35	0.09	0.02	27

Table 4.9A <u>Dry Weight and P uptake from Soil 4</u>

Mean Dry Weight g/pot

Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.31	0.16	0.18	0.14	0.49	1.15
2	0.31	0.16	0.22	0.13	0.54	1.18
3	0.33	0.24	0.35	0.19	0.44	1.55
4	0.36	0.18	0.25	0.13	0.39	1.21
5	1.66	2.60	1.54	0.78	3.54	9.63
6	1.85	2.40	1.60	0.61	2.98	9.44
7	2.09	2.59	1.60	0.82	2.83	9.90
8	1.84	2.42	1.70	0.70	2.88	9.55
SE	0.11	0.09	0.05	0.03	0.15	0.29
SED	0.16	0.12	0.06	0.05	0.21	0.41
LSD*	0.34	0.26	0.14	0.10	0.44	0.86
**	0.46	0.35	0.18	0.13	0.59	1.17
***	0.62	0.47	0.25	0.18	0.80	1.59
CV%	21.1%	13.0%	9.9%	15.0%	18.1%	10.8%

Mean P Uptake mg/pot (Fig. 4.9)

Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.18	0.12	0.19	0.10	0.37	0.96
2	0.24	0.10	0.23	0.12	0.37	1.20
3	0.24	0.16	0.32	0.17	0.32	1.23
4	0.23	0.13	0.33	0.16	0.26	1.12
5	4.93	3.73	3.42	1.19	2.97	16.24
6	7.24	3.85	3.78	1.20	3.27	19.26
7	5.80	4.09	3.71	1.44	3.52	18.56
8	8.38	4.32	4.17	1.36	3.27	20.61
SE	0.24	0.14	0.13	0.05	0.09	0.55
SED	0.34	0.20	0.18	0.07	0.11	0.78
LSD*	0.95	0.49	0.38	0.14	0.20	1.61
**	0.95	0.57	0.52	0.20	0.41	2.20
***	1.29	0.77	0.70	0.26	0.67	2.96
CV%	14.0%	13.0%	12.9%	13.6%	12.9%	11.0%

Table 4.10A Dry weight and P Uptake from Soil 9

	Mean dry weight, g/pot					
Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.32	0.28	0.36	0.22	0.52	1.70
2	0.33	0.21	0.26	0.17	0.48	1.46
3	0.34	0.35	0.44	0.21	0.53	1.87
4	0.34	0.21	0.30	0.14	0.45	1.44
5	1.84	2.74	1.54	0.86	3.97	9.95
6	1.47	2.66	1.70	0.80	3.22	9.84
7	1.69	2.72	1.74	0.82	2.75	9.79
8	1.42	2.71	1.76	0.81	3.46	10.17
SE	0.06	0.05	0.03	0.03	0.11	0.16
SED	0.08	0.07	0.04	0.04	0.15	0.23
LSD*	0.17	0.14	0.08	0.08	0.32	0.48
**	0.24	0.19	0.10	0.11	0.44	0.66
***	0.32	0.26	0.14	0.15	0.59	0.88
CV%	12.0%	6.4%	5.1%	10.8%	12.1%	5.4%

	Mean P Uptake, mg/pot (Fig. 4.9)					
Tr.	H1	H2	Hs	Stubble(S)	Root(R)	Total
1	0.19	0.24	0.44	0.18	0.56	1.60
2	0.20	0.15	0.32	0.12	0.54	1.34
3	0.21	0.24	0.58	0.18	0.70	1.94
4	0.20	0.17	0.46	0.16	0.55	1.49
5	8.11	5.67	4.40	1.17	5.64	25.18
6	4.21	5.00	4.89	0.95	5.54	20.85
7	5.00	6.00	5.07	1.15	4.96	22.12
8	5.24	5.67	5.24	1.04	5.98	23.27
SE	0.32	0.07	0.05	0.04	0.23	0.34
SED	0.45	0.10	0.08	0.06	0.33	0.48
LSD*	0.95	0.21	0.16	0.12	0.68	1.01
**	1.29	0.29	0.21	0.16	0.93	1.37
***	1.74	0.39	0.29	0.21	1.25	1.85
CV%	22.0%	5.0%	4.0%	13.1%	15.2%	5.6%

Table 4.11A Dry Weight and P Uptake from Soil 10

Mean Dry Weight, g/pot

Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.29	0.27	0.34	0.15	0.45	1.51
2	0.39	0.34	0.39	0.19	0.68	1.99
3	0.21	0.14	0.16	0.12	0.10	0.74
4	0.42	0.39	0.45	0.18	0.52	1.96
5	1.77	2.78	1.44	0.88	1.69	8.56
6	1.64	2.51	1.59	0.77	2.47	8.99
7	0.83	2.14	1.60	0.72	0.81	6.10
8	1.50	2.87	1.63	0.68	2.52	8.96
SE	0.08	0.10	0.04	0.03	0.07	0.22
SED	0.12	0.15	0.06	0.04	0.10	0.30
LSD*	0.25	0.30	0.13	0.08	0.21	0.63
**	0.34	0.41	0.17	0.11	0.29	0.86
***	0.46	0.56	0.23	0.15	0.39	1.16
CV%	19.1%	14.5%	9.0%	12.4%	12.5%	8.9%

Mean P Uptake, mg/pot (Fig. 4.9)

Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.17	0.18	0.44	0.16	0.48	1.43
2	0.26	0.28	0.53	0.22	0.41	1.67
3	0.15	0.08	0.14	0.14	0.11	0.61
4	0.47	0.37	0.59	0.20	0.40	2.11
5	3.53	4.45	3.38	1.34	3.64	16.34
6	6.00	5.55	5.23	1.39	3.74	21.89
7	1.48	4.01	3.45	1.54	1.67	12.14
8	5.98	6.05	4.77	1.30	4.09	22.18
SE	0.25	0.22	0.14	0.10	0.14	0.46
SED	0.35	0.31	0.20	0.14	0.21	0.64
LSD*	0.73	0.65	0.42	0.29	0.43	1.34
**	1.00	0.88	0.58	0.39	0.58	1.82
***	1.34	1.19	0.78	0.53	0.78	2.46
CV%	22.0%	16.9%	12.4%	24.8%	16.0%	9.3%

Table 4.12A Dry Weight and P Uptake from Soil 11

Mean Dry Weight, g/pot

Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.17	0.07	0.05	0.08	0.08	0.45
2	0.34	0.30	0.40	0.17	0.51	1.74
3	0.16	0.07	0.06	0.10	0.10	0.50
4	0.32	0.28	0.33	0.20	0.52	1.75
5	0.22	0.41	0.43	0.20	0.41	1.71
6	1.07	2.34	1.21	0.63	2.38	7.87
7	0.22	0.41	0.50	0.20	0.38	1.75
8	1.07	2.36	1.21	0.69	2.28	7.62
SE	0.04	0.05	0.05	0.02	0.05	0.16
SED	0.06	0.07	0.07	0.03	0.07	0.23
LSD*	0.12	0.14	0.14	0.07	0.15	0.48
**	0.17	0.19	0.19	0.10	0.20	0.65
***	0.23	0.25	0.25	0.13	0.27	0.88
CV%	18.8%	11.9%	17.8%	17.3%	12.1%	11.2%

Mean P Uptake, mg/pot (Fig. 4.9)

Tr.	H1	H2	H3	Stubble(S)	Root(R)	Total
1	0.14	0.06	0.01	0.06	0.07	0.34
2	0.30	0.33	0.64	0.22	0.58	2.06
3	0.12	0.05	0.02	0.14	0.10	0.44
4	0.25	0.23	0.40	0.24	0.54	1.68
5	0.23	0.54	0.69	0.40	0.68	2.54
6	1.58	2.53	2.43	0.72	3.50	10.75
7	0.24	0.56	0.70	0.34	0.73	2.65
8	1.61	2.07	2.16	0.81	2.53	9.18
SE	0.08	0.07	0.07	0.03	0.07	0.18
SED	0.11	0.10	0.10	0.04	1.10	0.25
LSD*	0.23	0.20	0.21	0.09	0.21	0.53
**	0.31	0.27	0.29	0.13	0.28	0.72
***	0.42	0.37	0.39	0.17	0.38	0.97
CV.	20.7%	17.1%	16.5%	17.6%	11.7%	9.48%

Table 4.13A. Analysis of Variance - Two way interaction tables for % Ca for Soils 4 and 9

Soil 4

Treatment	DF	Herbage Mean Square	Variance Ratio	Roots Mean Square	Variance Ratio
P	1	2.216	150.338 ***	0.051	5.409 *
G	1	0.708	40.046 ***	0.174	18.389 **
L	1	2.880	195.428 ***	0.500	52.827 ***
P x G	1	0.221	15.004 **	0.113	11.919 **
P x L	1	1.684	114.245 ***	0.005	0.477 NS
G x L	1	0.101	6.871 *	0.0	0.012 NS
PGL	1	0.208	14.115 **	0.045	4.754 NS
rep	3	0.050	3.423	0.006	0.642
error	21	0.015		0.009	
CV%		11.9		18.6	

Two Way Interaction Table

	Lo	L1	Go	G1	Mean
Po	0.75	1.81	1.05	1.51	1.28
Pi	0.68	0.83	0.69	0.82	0.75
Go	0.63	1.11			
Gi	0.81	1.52			
	0.72	1.31	0.87	1.16	

Lo	Li	Go	G1	Mean
.43	.70	0.43	.70	0.56
.37	.60	0.47	.50	0.49
.33	.57			0.45
.47	.72			0.59
.40	.65			

Soil 9

P	1	5.569	663.065 ***	5.823	267.989 ***
G	1	0.772	91.898 ***	1.707	78.549
L	1	4.04	480.966 ***	1.800	82.858
P x G	1	0.322	38.336 ***	0.803	36.972
P x L	1	2.492	296.686 ***	0.778	35.814
G x L	1	0.018	2.093 NS	0.013	0.608 NS
PGL	1	0.018	3.358 NS	0.002	0.076 NS
rep	3	0.013	1.509 NS	0.005	0.211 NS
error	21	0.008		0.022	
CV%		7.7		9.3	

Two Way Interaction Table

	Lo	L1	Go	G1	Mean
Po	0.98	2.25	1.36	1.87	1.62
P1	0.71	0.86	0.73	0.84	0.76
Go	0.71	1.38			1.04
G1	0.98	1.73			1.35
Mean	0.84	1.55			

Lo	Li	Go	G1	Mean
1.62	2.41	1.62	2.40	2.01
1.08	1.24	1.09	1.23	1.16
1.14	1.57			1.36
1.56	2.08			1.82
1.35	1.82			

Table 4.14A. Analysis of Variance - Two way interaction tables for % Ca for Soils 10 and 11

Soil 10

Treatment	DF	Tops Mean Square	Variance Ratio	Root Mean Square	Variance Ratio
P	1	0.188	7.113 *	.048	44.972 ***
G	1	0.513	19.438 **	.092	86.527 ***
L	1	0.109	4.144 NS	.074	69.364 ***
P x G	1	0.272	10.313 *	.025	23.691 ***
P x L	1	0.057	2.160 NS	.016	15.162 **
L x G	1	0.216	8.197 *	.013	11.98 **
PGL	1	0.052	1.972 NS	.001	0.573 NS
rep	3	0.016	0.604	0.00	0.378 NS
error	21	0.026		.001	
CV%	27			8.2	

Two Way Interaction Table

	Lo	L1	Go	Gi	Mean
Po	0.66	0.69	0.46	0.90	0.68
Pi	0.42	0.62	0.49	0.56	0.52
Go	0.33	0.61			
Gi	0.75	0.70			
	0.54	0.65	0.48	0.73	

	Lo	L1	Go	G1	Mean
Po	0.41	.46	0.36	0.52	0.43
Pi	.29	.43	0.34	0.39	0.36
Go	0.28	0.41			0.35
Gi	0.42	0.48			0.45
	0.35	0.44			

Soil 11

P	1	1.441	172.407 ***	0.619	13.078
G	1	0.488	58.346	0.200	4.227 NS
L	1	0.233	27.87	1.055	22.293 **
P x G	1	0.613	73.388	0.001	0.015 NS
P x L	1	0.291	34.787	5.371	113.507 ***
L x G	1	1.174	140.519	0.066	1.389 NS
PGL	1	0.915	109.449	0.179	3.772 NS
rep	3	0.008	0.969 NS	0.003	0.054 NS
error	21	0.008		0.047	0.047
CV%		9.4		19.4	

Two Way Interaction Table

	Lo	L1	Go	G1	Mean
Po	1.36	1.00	0.92	1.44	1.18
P1	0.75	0.77	0.77	0.74	0.76
Go	0.74	0.95			0.84
G1	1.37	0.82			1.09
	1.055	0.88			

	Lo	L1	Go	G1	Mean
	0.39	1.57	0.90	1.07	.98
	1.49	1.03	1.19	1.33	1.26
	0.91	1.18			1.04
	0.97	1.43			1.20
	0.94	1.30			

Table 5.1A.

Mean Dry Weights g/pot

Treatment		Soil 9 H_1	H_2	H_3	St	R	Soil 11 H_1	H_2	H_3	St	R
GloPoLo	1	0.32	0.28	0.36	0.22	0.52	0.16	0.07	0.05	0.15	0.08
GlıPoLo	2	0.19	0.13	0.24	0.12	0.34	0.12	0.09	0.11	0.10	0.11
GloPoLı	3	0.38	0.17	0.29	0.11	0.41	0.32	0.27	0.42	0.17	0.55
GlıPoLı	4	0.21	0.16	0.27	0.12	0.36	0.11	0.19	0.31	0.14	0.05
GloPıLo	5	0.97	1.79	1.22	0.56	1.93	0.14	0.07	0.08	0.08	0.11
GlıPiLo	6	0.19	1.07	0.77	0.35	1.16	0.12	0.12	0.19	0.13	0.15
GloPiLı	7	0.88	1.68	1.07	0.59	2.26	0.45	1.20	0.92	0.41	1.28
GlıPiLı	8	0.21	1.43	0.84	0.41	1.41	0.16	0.71	0.73	0.25	0.84
SE		0.031	0.04	0.03	0.03	0.06	0.01	0.04	0.03	0.01	0.04
SED		0.04	0.05	0.05	0.04	0.08	0.02	0.05	0.04	0.01	0.06
CV%		12.8	7.9	9.6	17.3	9.3	10.5	18.6	15.3	11.2	14.5

Mean P Uptake mg P/pot

Treatment		Soil 9 H_1	H_2	H_3	St	R	Soil 11 H_1	H_2	H_3	St	R
GloPoLo	1	0.24	0.22	0.38	0.18	0.56	0.16	0.07	0.01	0.09	0.07
GlıPoLo	2	0.14	0.08	0.19	0.09	0.26	0.10	0.05	0.08	0.07	0.16
GloPoLı	3	0.23	0.20	0.34	0.11	0.32	0.23	0.25	0.58	0.22	0.53
GlıPoLi	4	0.18	0.11	0.30	0.10	0.27	0.13	0.16	0.42	0.19	0.36
GloPiLo	5	1.31	1.21	1.54	0.48	1.55	0.11	0.03	0.09	0.10	0.15
GliPıLo	6	0.41	1.03	1.23	0.44	0.80	0.21	0.15	0.15	0.22	0.19
GloPıLı	7	1.40	1.17	1.49	0.50	1.43	0.53	0.93	1.54	0.59	1.21
GliPiLı	8	0.67	0.97	1.10	0.42	1.04	0.31	0.56	1.39	0.37	0.85
SE		0.05	0.07	0.06	0.03	0.05	0.02	0.02	0.03	0.02	0.06
SED		0.07	0.10	0.09	0.04	0.07	0.04	0.03	0.04	0.04	0.08
CV%		15.5	18.7	12.9	18.3	11.4	19.8	13.5	9.1	18.6	16.8

Table 5.2A. Analysis of Variance - Two way interaction tables for P uptake on Soils 9 and 11

Effect	DF	Soil 9		Soil 11	
		Mean Square	Variance Ratio	Mean Square	Variance Ratio
P	1	92.591	1849 ***	8.461	2568 ***
L	1	0.00	0.00 NS	24.584	7461 ***
Gl	1	9.475	189 ***	2.118	642 ***
P.L	1	0.049	0.97 NS	5.033	1527 ***
P.Gl	1	3.168	63 ***	0.732	222 ***
L.Gl	1	0.331	6.62 NS	4.225	1282 ***
P.L.Gl	1	0.016	0.3 NS	1.712	519 ***
residual	14	0.05		0.003	
replicates	2	0.031	0.61 NS		1.97 NS

Total P Uptake (mg P/pot)

Soil / Tr.	1	2	3	4	5	6	7	8	Mean
9	1.58	0.76	1.20	0.96	6.09	3.93	6.00	4.20	3.09
11	0.40	0.46	1.81	1.26	0.49	0.92	4.80	2.80	1.62

Two Way interaction table

Soil 9						Soil 11					
	Lo	Li	Glo	Gli	Mean		Lo	Li	Glo	Gli	Mean
Po	1.17	1.08	1.39	0.86	1.12	Po	0.43	1.54	1.11	0.86	0.98
Pi	5.01	5.10	6.05	4.06	5.05	Pi	0.70	3.64	2.64	1.70	2.17
Glo	3.84	2.34				Glo	0.44	3.31			
Gli	3.60	2.58				Gli	0.69	1.87			
	3.09	3.09	3.72	2.46			0.56	2.59			1.58

Table 5.3A pH, Carbon Content (Fig. 5.3a and b) and Truog P, pre- and post-growth (Fig. 5.2a and b)

Soil 9

Treatment	pH (pre-growth)	Organic Carbon mg/100 g	Truog P mg/100 g (pre-growth)	Truog P mg P/100 g (post-growth)
GL_0 P_0 L_0(1)	4.3	4.22	0.85	0.45
GL_0 P_1 L_0(5)	4.3	4.32	2.56	1.31
GL_0 P_0 L_1(3)	5.3	4.37	0.81	0.42
GL_0 P_1 L_1(7)	5.3	4.01	2.40	1.74
GL_1 P_0 L_0(2)	4.4	4.57	0.62	0.60
GL_1 P_1 L_0(6)	4.4	4.54	2.00	1.90
GL_1 P_0 L_o(4)	5.5	4.24	0.77	0.64
GL_1 P_1 L_1(8)	5.4	4.32	1.81	1.53

Soil 11

Treatment	pH (pre-growth)	Organic Carbon g/100 g	Truog P mg/100 g (pre-growth)	Truog P mg/100 g (post-growth)
GL_0 P_0 L_0(1)	3.9	9.51	1.90	1.88
GL_0 P_1 L_0(5)	4.0	9.57	4.40	4.12
GL_0 P_0 L_1(3)	4.4	9.60	1.86	1.74
GL_0 P_1 L_1(7)	4.4	9.63	4.29	3.14
GL_1 P_0 L_0(2)	4.0	9.86	1.60	1.65
GL_1 P_1 L_0(6)	4.0	9.90	2.73	2.73
GL_1 P_0 L_1(4)	4.5	9.63	1.74	1.74
GL_1 P_1 L_1(8)	4.0	9.28	3.16	2.56

Table 6.1A.1 Soil Analyses after 1 month's equilibration
(Figs. 6.1a, 6.2a, 6.3a)

Treatment level	Exch.Acidity meq/100g	Exch.Al meq/100g	pH	Extr.Al meq/100g	PSI	Extr.P mg/100g
SOIL 9						
0	5.5	3.3	4.2	3.7	33	0.22
1	3.5	1.9	4.7	2.9	31	0.20
2	1.5	0.6	5.2	2.1	31	0.19
3	0.9	Tr.	5.6	2.1	33	0.23
5	0.8	"	6.1	2.2	34	0.20
8	0.4	"	6.5	1.7	34	0.21
10	0.4	"	6.7	1.8	35	0.21
15	<0.1	"	6.8	1.7	36	0.22
SOIL 11						
0	20.1	13.3	3.8	16.1	176	0.32
1	17.2	11.4	4.1	15.7	173	0.33
2	15.4	10.0	4.2	15.1	171	0.33
3	12.8	8.7	4.4	14.1	171	0.32
5	5.2	4.0	4.9	13.0	169	0.31
8	1.0	Tr.	5.4	11.8	169	0.30
10	0.6	"	5.7	11.3	166	0.32
15	0.5	"	6.5	9.8	165	0.33

Table 6.1A.6 Soil Analyses after 6 month's equilibration (prior to seeding)

Treatment level	Exch.Acidity meq/100g	Exch.Al meq/100g	pH	Extr.Al meq/100g	PSI	Extr.P mg/100g
SOIL 9						
0	3.8	3.3	4.2	4.0	34	0.20
1	3.6	2.1	4.8	3.8	33	0.19
2	2.0	1.0	5.3	3.3	31	0.18
3	1.8	0.2	5.6	2.5	32	0.18
5	0.8	Tr.	0.2	2.1	32	0.20
8	Tr.	"	6.7	1.9	29	0.21
10	"	"	6.8	1.6	29	0.18
15	"	"	6.9	1.4	29	0.16
SOIL 11a						
0	14.4	13.0	3.9	16.8	168	0.34
1	16.0	11.5	4.2	16.0	168	0.32
2	13.0	10.9	4.3	15.7	168	0.32
3	12.1	7.9	4.5	15.4	164	0.31
5	8.8	5.9	5.0	14.4	164	0.30
8	2.0	2.1	5.4	13.4	164	0.32
10	0.8	Tr.	5.7	12.8	160	0.31
15	Tr.	Tr.	6.6	10.2	160	0.30

Table 6.2A <u>Effects of Liming on the Amounts of Soluble-P, Al, Ca, Mg, K, Fe, Mn, pH and MCR (Fig. 6.3 and 6.4)</u>

SOIL 9

Treatment	(a) P	(b) Al	(c) Ca	(d) Mg	(e) K	(f) Fe	(g) Mn
	mg/100 g	meq/100 g				mg/100 g	
0	0.02	0.09	0	0.03	0.02	0.06	0.40
1	"	0.06	0.7	0.02	0.01	0.09	0.20
2	"	0	1.2	0.01	0.01	0.07	0.08
3	"	"	1.6	0.005	0.01	0.09	0.06
5	"	"	2.3	"	Trace	0.09	Trace
8	"	"	3.3	Trace	"	0.09	"
10	"	"	3.5	"	"	0.07	"
15	"	"	3.8	"	"	0.08	"

	(h) pH	(i) $Al \times 10^{-3}M$	(j) $Ca \times 10^{-3}M$	(k) $Mg \times 10^{-3}M$	(l) MCR
0	3.9	0.06	0	0.03	0.0075
1	4.3	0.04	0.7	0.02	233
2	4.6	Trace	1.2	0.007	ND
3	4.7	"	1.6	0.006	"
5	4.9	0	2.3	0.005	"
8	5.8	0	3.3	Trace	"
10	6.2	0	3.5	"	"
15	6.4	0	3.8	"	"

SOIL 11a

	(a)	(b)	(c)	(d)	(e)	(f)	(g)
0	Trace	0.69	0	0.22	0.02	0.16	0.56
1	"	0.24	0.03	0.16	0.02	0.09	0.28
2	"	0.16	0.06	0.12	0.01	0.06	0.16
3	"	0.06	0.09	0.11	"	0.13	0.10
5	"	0.01	0.13	0.09	"	0.12	0.08
8	0.01	Trace	0.34	0.07	"	0.12	Trace
10	0.01	"	0.44	0.05	Trace	0.10	"
15	0.01	"	0.58	0.05	Trace	0.16	"

	(h)	(i)	(j)	(k)	(l)
0	3.6	0.46	0	0.21	0.044
1	3.8	0.16	0.03	0.16	0.228
2	4.0	0.11	0.06	0.12	0.661
3	4.1	0.04	0.09	0.11	6.60
5	4.3	0.01	0.13	0.09	689
8	5.1	Trace	0.34	0.07	ND
10	5.8	"	0.44	0.05	"
15	6.3	"	0.58	0.05	"

Table 6.3A Dry Matter Production, P Uptake and Mineral Composition of Roots and Herbage in Soils 9 and 11a (Figs.6.7, 6.8 and 6.9)

Treatment level	DM g/pot	Root DM g/pot	Total DMg/pot	P up.Herbage mg/pot	P up.Root mg/pot	Total P up. mg/pot
SOIL 9						
0	0.11	0.06	0.17	0.24	0.10	0.34
1	0.10	0.06	0.16	0.22	0.10	0.32
2	0.10	0.06	0.15	0.19	0.09	0.28
3	0.09	0.05	0.14	0.18	0.09	0.27
5	0.08	0.07	0.15	0.18	0.10	0.28
8	0.10	0.06	0.16	0.21	0.12	0.33
10	0.11	0.07	0.18	0.25	0.13	0.38
15	0.13	0.08	0.21	0.26	0.15	0.41
SOIL 11a						
0	0.04	0.02	0.06	0.05	0.01	0.06
1	0.05	0.04	0.09	0.09	0.07	0.16
2	0.07	0.06	0.13	0.10	0.07	0.17
3	0.07	0.06	0.13	0.11	0.08	0.19
5	0.07	0.05	0.12	0.12	0.08	0.20
8	0.06	0.04	0.10	0.09	0.05	0.14
10	0.06	0.05	0.11	0.07	0.06	0.13
15	0.07	0.05	0.12	0.12	0.08	0.20

MINERAL COMPOSITION

Treatment level	Herbage			Root		
	% P	% Fe	% Mn	% P	% Al	% Ca
SOIL 9						
0	0.22	0.01	0.02	0.16	0.81	0.80
1	0.22	0.01	0.01	0.16	0.52	1.21
2	0.19	0.01	0.01	0.15	0.49	1.20
3	0.20	0.01	0.01	0.16	0.47	1.33
5	0.22	0.01	0.01	0.15	0.43	1.55
8	0.21	0.01	0.01	0.20	0.38	2.11
10	0.20	0.01	0.01	0.18	0.46	2.36
15	0.23	0.01	0.01	0.19	0.44	2.43
SOIL 11a						
0	0.13	0.04	0.02	0.10	1.0	0.61
1	0.17	0.04	0.02	0.16	0.75	0.75
2	0.14	0.02	0.01	0.12	0.50	0.80
3	0.15	0.01	0.01	0.14	0.44	1.00
5	0.17	0.01	0.01	0.14	0.37	1.20
8	0.16	0.01	0.01	0.15	0.23	1.40
10	0.12	0.01	0.01	0.13	0.44	1.52
15	0.18	0.01	0.01	0.15	0.40	1.68

Table 8.1A Dry Matter Production and P Uptake by Herbage and Roots, and TI (Fig. 8.1)

Mean Dry Matter, g/pot

Treatment	DM H	DM R	Total DM
L_0 P_0 Si_0(1)	0.20	0.10	0.30
L_0 P_0 Si_1(2)	0.22	0.04	0.26
L_0 P_0 Si_2(3)	0.18	0.06	0.25
L_1 P_0 Si_0(4)	0.28	0.18	0.45
L_1 P_0 Si_1(5)	0.24	0.16	0.40
L_1 P_0 Si_2(6)	0.23	0.13	0.36
L_0 P_1 Si_0(7)	0.35	0.40	0.75
L_0 P_1 Si_1(8)	0.34	0.27	0.61
L_0 P_1 Si_2(9)	0.30	0.27	0.57
L_1 P_1 Si_0(10)	1.91	0.90	2.81
L_1 P_1 Si_1(11)	1.90	1.00	2.89
L_1 P_1 Si_2(12)	1.45	0.95	2.34
SED	0.03	0.02	0.05
LSD*	0.07	0.04	0.10
**	0.09	0.06	0.16
***	0.12	0.08	0.18
CV%	7.2%	8.2%	7.2%

Mean P Uptake, mg/pot

Treatment	P Up.H.	P Up.R.	Total P Up.	TI
L_0 P_0 Si_0(1)	0.16	0.14	0.30	51
L_0 P_0 Si_1(2)	0.18	0.07	0.25	72
L_0 P_0 Si_2(3)	0.28	0.11	0.39	71
L_1 P_0 Si_0(4)	0.30	0.26	0.56	54
L_1 P_0 Si_1(5)	0.29	0.26	0.56	52
L_1 P_0 Si_2(6)	0.26	0.19	0.46	58
L_0 P_1 Si_0(7)	0.33	0.39	0.72	46
L_0 P_1 Si_1(8)	0.25	0.25	0.50	49
L_0 P_1 Si_2(9)	0.22	0.23	0.45	48
L_1 P_1 Si_0(10)	2.59	1.58	4.18	62
L_1 P_1 Si_1(11)	3.46	2.00	5.46	68
L_1 P_1 Si_2(12)	0.49	1.74	4.23	59
SED	0.06	0.10	0.19	3
LSD*	0.12	0.21	0.38	5
**	0.17	0.28	0.52	7
***	0.22	0.37	0.68	9
CV%	9.4%	22.5%	18.3%	5.9%

Table 8.2A Mineral Composition of Herbage and Roots (Fig. 8.2)

	HERBAGE					
Treatment	% P	% Fe	% Ca	% Mg	% K	% Mn
1	0.12	0.009	0.09	0.09	2.32	0.011
2	0.15	0.015	0.19	0.10	2.37	0.012
3	0.15	0.013	0.19	0.14	2.31	0.010
4	0.09	0.013	1.03	0.07	3.16	0.009
5	0.08	0.014	1.04	0.05	3.20	0.007
6	0.07	0.017	1.33	0.07	3.32	0.007
7	0.11	0.018	0.90	0.10	3.07	0.012
8	0.12	0.014	0.94	0.10	3.05	0.007
9	0.12	0.012	0.75	0.07	2.54	0.007
10	0.13	0.012	0.81	0.08	3.06	0.009
11	0.18	0.014	0.85	0.09	2.94	0.009
12	0.18	0.014	0.82	0.10	3.42	0.010
LSD*	0.01	0.006	0.17	0.02	0.46	0.002
**	0.02	0.009	0.23	0.03	0.62	0.003
***	0.03	0.011	0.30	0.04	0.83	0.004
CV%	7%	14%	12%	15%	11%	14%
	ROOTS					
1^+	0.14	0.54	0.15	0.03	0.89	0.89
2^+	0.17	0.60	0.18	0.05	0.97	0.94
3^+	0.17	0.75	0.22	0.02	0.87	1.15
4	0.10	0.28	0.50	0.03	1.02	0.91
5	0.10	0.30	0.55	0.03	0.96	1.00
6	0.09	0.24	0.53	0.03	0.90	0.98
7	0.14	0.43	0.48	0.05	0.87	0.96
8^+	0.17	0.44	0.46	0.05	1.04	0.87
9	0.15	0.46	0.54	0.05	0.82	1.07
10	0.17	0.27	0.42	0.08	0.79	0.85
11	0.20	0.25	0.47	0.07	0.79	0.81
12	0.18	0.30	0.46	0.08	0.84	1.14

\+ single determination.

Table 8.3A Chemical Properties of Soil 11 treated with silicic acid, Lime and Superphosphate

Treatment	PSI	Sol.P mg/100g	10^{-3}M $CaCl_2$ pH	Exch.Al meq/100g	Sol.Al meq/100g	Exch.Ca meq/100g
L_0 P_0 Si_0	197	Tr.	4.0	20.7	0.78	0.3
L_0 P_0 Si_1	190	Tr.	4.0	19.2	0.97	0.3
L_0 P_0 Si_2	176	Tr.	4.0	20.2	0.74	0.5
L_1 P_0 Si_0	169	Tr.	4.8	13.6	0.11	7.0
L_1 P_0 Si_1	176	Tr.	4.8	14.8	0.08	10.4
L_1 P_0 Si_2	163	Tr.	4.8	14.6	0.09	19.0
L_0 P_1 Si_0	176	0.01	4.1	20.9	0.55	3.8
L_0 P_1 Si_1	176	0.01	4.2	20.9	0.52	2.7
L_0 P_1 Si_2	176	0.01	4.1	20.7	0.51	3.1
L_1 P_1 Si_0	163	$<$ 0.01	4.7	12.2	0.16	11.5
L_1 P_1 Si_1	163	$<$ 0.01	4.7	13.8	0.17	15.5
L_1 P_1 Si_2	155	$<$ 0.01	4.7	13.2	0.16	20.5
SED				0.4	0.07	0.7
LSD*				0.7	0.14	1.7
**				1.0	0.18	2.0
***				1.3	0.25	2.7

Treatment	Sol. Ca meq/100g	Sol. K meq/100g	Sol. Mg meq/100g	Sol. Mn mg/100g	Sol. Fe µg/g	log.MCR
L_0 P_0 Si_0	0	0.400	0.224	3.53	3.78	$\bar{1}.395$
L_0 P_0 Si_1	0	0.425	0.267	4.00	3.93	$\bar{1}.333$
L_0 P_0 Si_2	0.02	0.385	0.220	3.90	2.50	$\bar{1}.348$
L_1 P_0 Si_0	1.40	0.285	0.165	1.77	0.73	1.153
L_1 P_0 Si_1	1.62	0.321	0.187	1.52	1.13	1.063
L_1 P_0 Si_2	1.33	0.292	0.146	1.32	1.15	1.283
L_0 P_1 Si_0	1.30	0.359	0.287	3.85	2.05	2.686
L_0 P_1 Si_1	1.13	0.317	0.225	3.20	1.70	3.108
L_0 P_1 Si_2	1.30	0.404	0.264	3.17	1.90	2.813
L_1 P_1 Si_0	2.82	0.317	0.211	1.72	0.98	3.309
L_1 P_1 Si_1	3.09	0.353	0.191	1.60	0.95	3.358
L_1 P_1 Si_2	3.18	0.365	0.202	1.72	1.38	3.465
SED	0.06	0.014	0.016	0.24	0.19	
LSD*	0.12	0.029	0.032	0.48	0.38	
**	0.16	0.039	0.044	0.64	0.51	
***	0.22	0.052	0.058	0.85	0.68	

Table 9.1A <u>Chemical Properties of Soils 11 to 14</u>

	Soil 11a	12	13	14
pH ($CaCl_2$)	3.5	4.0	4.1	4.9
% C	9.2	2.1	21.1	6.5
Bulk density, g/cc	0.95	–	0.73	1.65
Total P mg/100 g	269	562	500	350
Organic P, mg/100 g	230	230	180	110
Extr. P. "	0.58	0.31	0.56	0.06
PSI ++	188	211	137	47
Exch. Acid, meq/100 g	21.6	15.8	12.4	2.40
Exch. Al "	18.7	14.3	11.0	1.80
Exch. Ca "	0.75	5.75	6.50	7.00
Exch. Mg "	0.25	2.04	2.40	5.40
Exch. Fe "	Tr.	Tr.	Tr.	Tr.
Extr. Al "	10.5	22.9	19.4	2.43
Extr. Mn (pH 7) mg/100 g	0.26	0.57	1.07	1.27
Sol. P mg/100 g	Tr.	Tr.	0.02	0.01
Sol. Al meq/100 g	0.79	0.22	0.04	Tr.
Sol. Ca "	– (16)*	–(3)*	0.05	0.37
Sol. Mg "	0.25	0.79	0.58	0.24
Sol. Mn μg/g	3.06	4.02	3.12	4.09
Sol. Fe "	2.21	0.26	0.73	1.26

++ addition of ~ 150 ppm P

* – Ca adsorbed from 10^{-3}M $CaCl_2$ (amount adsorbed ppm)

Table 9.2A Experimental Details

(October 78 - January 79)

Date started	27.10.78		
Date Transplanted	9.11.78		
1st Harvest	19.12.78	Temperature	20 — 25° C
2nd Harvest (finish)	29. 1.79	"	"

Test Crop - 5 ten day old seedlings of <u>L. perenne</u> S24 per pot
Soils Four (11a, 12, 13, 14)
Replicates 5 Total 150 pots in 5 blocks of 30 in
P levels 6 random arrangement

= P_0, P_1, P_2, P_3 P_4, P_6 increments $\equiv$ 50 kgP/ha.

Pots : 10 cm containing equivalent 300 g AD Soil

Nutrient	Rate of Application = Fertiliser kg/ha			G/pot	Nutrient/pot	
					P.mg	Ca. meq
P	0 kg P/ha		Superphosphate			
	50	" 575	"	0.4518	44.6	5
	100	1150	"	0.9036	89.2	10
	150	1725	"	1.3554	133.8	15
	200	2300	"	1.8072	178.4	20
	300	3450	"	2.7108	267.6	30
K N	Basal KNO_3			0.2035	78.6 mg K 28.2 mg N	
N	+ 3 applications of NH_4NO_3 = = 30 kg/ha = 90 kg N/ha					

* Theoretical solubility of P in superphosphate is 22.6% using formula $0.4\ (H_3PO_4) + 1.0\ [Ca(H_2PO_4)_2\ H_2O] + 3.4\ (CaSO_4)$.
Measured solubility = 20%

<u>Composition of nutrient solution</u>:- (HEWITT 1952.)

2.0 g/L $Mg(NO_3)_2$
3.2 g/L NH_4NO_3
0.9 g/L KH_2PO_4
0.5 g/L $MgSO_4$
0.5 g/L $CaSO_4 \cdot 2H_2O$
0.12 g/L feric citrate

Table 9.3A Dry Matter and P Uptake from Soils 11 to 14

Dry Matter g/pot (Fig. 9.2)

	Soil 11a				Soil 12			
	H_1	H_2	R	ΣH_1H_2	H_1	H_2	R	ΣH_1H_2
P_0	0.03	0.03	0.01	0.06	0.03	0.02	0.03	0.05
P_1	0.03	0.02	0.02	0.05	0.22	0.43	0.23	0.65
P_2	0.03	0.02	0.03	0.05	0.38	0.85	0.42	1.23
P_3	0.04	0.04	0.02	0.08	0.38	0.98	0.37	1.36
P_4	0.07	0.05	0.03	0.12	0.45	1.14	0.48	1.59
P_6	0.09	0.08	0.01	0.17	0.46	1.47	0.46	1.93
SED	0.01	0.01	0.01	0.02	0.04	0.08	0.05	0.09
LSD*	0.01	0.02	0.10	0.03	0.08	0.15	0.10	0.18
**	0.02	0.03	0.14	0.04	0.11	0.21	0.13	0.25
***	0.03	0.04	0.19	0.06	0.15	0.29	0.18	0.34
CV%	21.72	39.75	38.10	27.60	18.89	14.36	22.26	12.36
	Soil 13				Soil 14			
	H_1	H_2	R	ΣH_1H_2	H_1	H_2	R	ΣH_1H_2
P_0	0.04	0.12	0.05	0.16	0.12	0.31	0.16	0.43
P_1	0.20	0.61	0.29	0.81	0.32	0.92	0.38	1.24
P_2	0.26	0.77	0.32	1.03	0.42	1.19	0.46	1.61
P_3	0.26	1.32	0.39	1.58	0.41	1.29	0.51	1.70
P_4	0.30	1.15	0.49	1.45	0.46	1.41	0.53	1.87
P_6	0.38	1.42	0.57	1.80	0.46	1.62	0.60	2.08
SED	0.04	0.16	0.08	0.19	0.04	0.12	0.07	0.14
LSD*	0.09	0.41	0.14	0.41	0.08	0.26	0.14	0.29
**	0.12	0.55	0.19	0.55	0.11	0.35	0.19	0.40
***	0.17	0.75	0.26	0.75	0.16	0.47	0.26	0.53
CV%	29.08	28.23	37.20	27.22	17.65	17.33	24.53	14.93

Mean P Uptake mg/pot (Fig. 9.4)

	* Soil 11a	Soil 12		Soil 13		Soil 14	
	ΣH_1H_2	ΣH_1H_2	R	ΣH_1H_2	R	ΣH_1H_2	R
P_0	0.07	0.09	0.03	0.13	0.06	0.97	0.24
P_1	0.05	1.42	0.35	1.89	0.61	3.35	0.82
P_2	0.05	2.71	0.67	2.61	0.77	4.83	0.94
P_3	0.22	4.28	0.74	4.41	0.84	5.66	1.38
P_4	0.37	5.67	1.10	4.15	1.08	6.56	1.25
P_6	0.60	8.63	1.38	5.40	1.62	9.05	1.92

* No roots analysed from Soil 11a

Table 9.4A Mineral Composition of Herbage and Roots from Soils 11 to 14 (mean of 2 harvest cuts)

	Soil 11a			Soil 12		
	%P	%Fe	%Mn	%P	%Fe	%Mn
P 0	.06	.014	.022	.16	.021	.022
P 50	.10	.014	.015	.21	.019	.013
P 100	.17	.014	.020	.22	.016	.011
P 150	.28	.015	.017	.31	.016	.012
P 200	.31	.016	.015	.31	.015	.010
P 300	.35	.017	.015	.45	.014	.013
	Soil 13			Soil 14		
	%P	%Fe	%Mn	%P	%Fe	%Mn
P 0	.10	.021	.025	.23	.024	.020
P 50	.24	.013	.019	.27	.018	.014
P 100	.26	.016	.020	.30	.014	.011
P 150	.28	.016	.016	.34	.015	.013
P 200	.29	.015	.019	.35	.012	.011
P 300	.30	.015	.018	.47	.012	.013
	% P concentration in Roots (Fig. 9.3b)					
Soil *	P_0	P_1	P_2	P_3	P_4	P_6
12	0.10	0.15	0.16	0.20	0.23	0.30
13	0.11	0.21	0.24	0.22	0.22	0.29
14	0.15	0.21	0.21	0.27	0.26	0.32
	% Al concentration in Roots					
12	0.71	0.38	0.40	0.40	0.34	0.37
13	0.39	0.40	0.38	0.43	0.31	0.49
14	0.50	0.52	0.53	0.63	0.58	0.65
	Composition of 10 day old Transplants					
	% P	% K	% Ca	% Mg	% Al	
Tops	1.01	6.54	1.12	0.36	0.07	
Roots	0.28	0.99	0.74	0.10	0.47	

* No roots analysed from soil 11a

Table 9.5A Amounts of Extractable P, Soluble P and PSI (Fig. 9.5) and Extractable, Exchangeable and Soluble Al (Fig. 9.6) from Soils 11a to 14

	Extr. P mg/100g	Sol. P mg/100g	PSI	Extr.Al meq/100g	Exch.Al meq/100g	Sol.Al meq/100g
Soil 11a						
P_0	0.33	Tr.	198	20.8	18.7	0.81
P_1	2.00	0.02	175	20.0	19.5	0.49
P_2	3.19	0.02	165	19.4	20.0	0.51
P_3	3.88	0.03	158	18.0	21.0	0.64
P_4	4.41	0.05	140	15.7	20.6	0.72
P_6	5.44	0.06	120	14.0	21.0	0.87
Soil 12						
P_0	0.31	Tr.	211	22.9	14.3	0.22
P_1	2.19	0.01	211	20.1	15.6	0.13
P_2	2.50	0.02	188	19.3	16.0	0.18
P_3	3.19	0.03	188	19.3	16.0	0.18
P_4	4.22	0.04	188	20.4	16.8	0.21
P_6	6.03	0.07	174	21.5	18.0	0.27
Soil 13						
P_0	0.56	0.02	137	19.8	11.0	0.04
P_1	1.22	0.02	140	18.8	11.1	0.04
P_2	1.75	0.03	142	17.1	10.3	0.03
P_3	2.47	0.04	144	17.1	10.4	0.01
P_4	2.88	0.05	135	15.3	10.9	0.08
P_6	3.34	0.09	123	13.2	10.4	0.13
Soil 14						
P_0	0.06	0.01	47	2.43	1.8	Tr.
P_1	1.00	0.09	22	2.36	1.6	Tr.
P_2	1.94	0.23	22	2.31	1.3	<0.01
P_3	2.69	0.28	23	2.22	1.2	<0.01
P_4	3.25	0.30	23	2.20	1.4	0.01
P_6	6.19	0.49	23	1.80	1.2	0.03

Table 9.6A Concentrations of Soluble Al, Ca, P, Mg and LogMCR in Soils 11 to 14, Superphosphate levels 0-6 (Figs. 9.5, 9.6)

	pH	Sol.-Al x10^{-3}M	Sol.-Ca x10^{-3}M	Sol.-P x10^{-3}M	Sol. Mg x10^{-3}M	MCR log
Soil 11a						
P_0	3.4	0.54	Tr.	Tr.	0.25	$\bar{1}.22$
P_1	3.9	0.33	0.56	1.3	0.26	0.70
P_2	3.7	0.34	1.21	1.6	0.21	1.39
P_3	3.7	0.43	2.05	2.3	0.26	1.82
P_4	3.7	0.48	3.27	3.2	0.31	2.30
P_6	3.7	0.58	4.04	3.9	0.44	2.42
Soil 12						
P_0	4.0	0.15	Tr.	Tr.	0.79	1.34
P_1	4.1	0.09	0.89	1.0	0.87	2.83
P_2	4.2	0.12	1.20	1.6	0.89	2.80
P_3	4.1	0.12	2.08	1.9	0.88	3.26
P_4	4.2	0.14	3.97	2.9	1.11	3.82
P_6	4.1	0.18	5.60	4.5	1.48	4.04
Soil 13						
P_0	4.5	0.03	0.04	1.3	0.58	2.42
P_1	4.5	0.03	0.10	1.6	0.83	2.95
P_2	4.3	0.02	0.40	1.9	1.06	3.89
P_3	4.3	0.01	1.85	2.6	1.16	3.44
P_4	4.3	0.06	2.62	3.6	1.23	4.47
P_6	4.3	0.09	5.40	5.8	1.69	4.36
Soil 14						
P_0	5.2	Tr.	0.47	0.7	0.24	–
P_1	4.7	Tr.	1.47	6.1	0.38	6.82
P_2	4.6	$<$0.01	2.25	14.8	0.44	5.61
P_3	4.6	$<$0.01	3.60	18.4	0.47	5.93
P_4	4.9	0.01	3.85	22.3	0.47	5.91
P_6	4.6	0.02	7.25	31.6	0.65	6.11

Table 11.1A Chemical Properties of Soils 15 to 19

	Soil 15	16	17	18	19
pH ($CaCl_2$)	3.7	3.5	4.1	3.9	4.9
% C	4.6	18.5	8.0	7.1	7.7
Total P mg/100 g	95	175	138	175	113
Extr. P "	0.25	0.19	0.12	0.06	0.06
PSI ++	57	63	140	113	54
Exch.Acid.meq/100 g	16.7	16.4	12.0	23.4	2.60
Exch.Al "	15.1	10.9	9.44	20.0	1.78
Exch.Ca "	1.52	2.54	0.2	4.54	10.0
Exch.Mg "	0.25	0.79	0.17	1.25	1.25
Exch.Fe "	0	0	0	0	0
Extr.Al "	5.55	4.50	18.8	11.8	3.47
Extr.Mn (pH7) mg/100 g	1.70	1.64	0.94	1.98	0.33
Sol. P mg/100 g	0.05	0.07	0.01	0.01	0.03
Sol.Al meq/100 g	0.22	0.22	0.06	0.09	Tr.
Sol.Ca "	-*(11)	-*(14)	-*(12)	-*(7)	-*(2)
Sol.Mg "	0.13	0.27	0.33	0.24	0.33
Sol. K "	0.05	0.31	0.07	0.05	0.09
Sol.Mn µg/g	0.90	2.60	3.13	4.30	0.51
Sol.Fe "	0.60	11.2	1.15	2.05	4.30

* - ppm Ca adsorbed from 10^{-3}M $CaCl_2$ solution.

++ calculated from addition of 130 ppmP

Table 11.2A Concentration of Soluble P, Al and pH in soils 15 to 19 treated with lime and superphosphate. (Fig. 11.4)

	15			16			17			18			19		
	L_0P_0	L_0P_1	L_1P_0	L_0P_0	L_0P_1	L_1P_0	L_0P_0	L_0P_1	L_1P_0	L_0P_0	L_0P_1	L_1P_0	L_0P_0	L_0P_1	L_1P_0
pH (10^{-3}M $CaCl_2$)	4.3	4.5	5.6	4.3	4.4	5.6	4.9	4.8	5.6	4.4	4.6	5.6	5.6	5.4	6.0
Al x 10^{-3}M	0.15	0.13	Tr.	0.15	0.15	0.07	0.04	0.04	Tr.	0.06	0.04	Tr.	<0.01	0.02	0
P x 10^{-6}M	3.2	5.5	1.6	4.8	6.4	1.6	0.6	2.2	1.6	0.6	5.5	1.6	2.2	8.1	2.2

Table 11.3A Dry Weights and P Uptake from Soils 15 to 19 (Fig. 11.1)

H.	Dry Matter g/pot ± SD < 0.01			P Uptake, mg/pot ± SD < 0.02		
Soil	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
15	0.29	0.43**	0.35	0.30	0.57*	0.71**
16	0.33	0.41	0.82**	0.37	0.63**	2.25**
17	0.30	0.40**	1.01***	0.33	0.42**	2.39***
18	0.40	0.57	1.15**	0.45	0.91***	2.73***
19	0.39	0.43	0.84**	0.41	0.49	2.55***
R.	Dry Matter g/pot ±SD < 0.003			P Uptake mg/pot ± SD < 0.02		
Soil	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
15	0.20	0.27*	0.26	0.26	0.38*	1.02**
16	0.28	0.32	0.44**	0.30	0.48*	1.11***
17	0.31	0.31	0.51**	0.31	0.34	1.31***
18	0.33	0.37	0.62**	0.44	0.61	2.04***
19	0.31	0.36	0.43**	0.40	0.45	1.47***
Total	Dry Matter g/pot ± SD < 0.01			P Uptake mg/pot ± SD < 0.04		
Soil	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
15	0.49	0.70**	0.62	0.56	0.95**	1.75***
16	0.61	0.77*	1.25**	0.67	1.10**	3.33***
17	0.62	0.73*	1.53***	0.65	0.77*	2.70***
18	0.73	0.94	1.80***	0.89	1.56***	4.77***
19	0.72	0.80	1.27**	0.81	0.97	3.98***

* Significantly different from L_0P_0 by T Test

* T > 3.18 ** T > 5.84 *** T > 12.92

	R/S Ratios		
15	0.69	0.63	0.74
16	0.85	0.78	0.54
17	0.97	0.70	0.50
18	0.82	0.65	0.54
19	0.79	0.84	0.51

Table 11.4A Matrix of T Statistic for Difference Between Means on Soils 15, 16, 17, 18 and 19 Treated with Lime and Superphosphate

Soils	16	17	18	19
DM L_0P_0				
15	6.2**	6.8***	17.2***	9.4***
16		0.2	4.9**	3.5*
17			4.9**	3.4*
18				0.3
L_1P_0				
15	2.2	2.0	3.6**	2.5*
16		0.9	2.1	0.2
17			2.8*	1.2
18				2.0
L_0P_1				
15	8.2***	19.3***	19.3***	9.0***
16		3.8**	6.9***	0.2
17			0.9	1.0
18				4.5**
D of F = 2(n-1)	L.S.D.	$>2.5^{*}$	$>3.7^{**}$	$>6.6^{***}$
P Uptake L_0P_0				
15	3.3*	2.9*	9.1***	7.8***
16		0.8	5.7**	4.1**
17			7.1***	5.5**
18				2.0
L_1P_0				
15	2.7*	4.5**	17.5***	0.2
16		6.6***	7.6***	1.9
17			17.5***	3.2*
18				8.7***
L_0P_1				
15	10.6***	7.7***	21.2***	12.8***
16		5.2**	3.8**	10.5***
17			18.9***	8.5***
18				4.8**

Table 11.5A <u>Mineral Composition of L. perenne</u> (Fig. 11.3)

	<u>SOIL 15</u> Herbage			Root		
	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
% P	0.106	0.133	0.210	0.13	0.14	0.38
% Al	ND	ND	ND	0.28	0.17	0.39
% Ca	0.131	0.974	0.427	0.22	0.47	0.36
% Mg	0.093	0.133	0.084	0.04	0.07	0.06
% K	3.880	3.170	2.300	0.68	0.59	0.59
% Fe	0.044	0.016	0.023	ND	ND	ND
% Mn	0.048	0.026	0.031	ND	ND	ND
	<u>SOIL 16</u>					
	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
% P	0.109	0.150	0.266	0.12	0.14	0.27
% Al	ND	ND	ND	0.18	0.18	0.19
% Ca	0.299	0.650	0.410	0.31	0.45	0.32
% Mg	0.130	0.161	0.137	0.06	0.08	0.07
% K	4.667	5.060	4.420	0.95	0.90	0.79
% Fe	0.021	0.016	0.020	ND	ND	ND
% Mn	0.014	0.012	0.016	ND	ND	ND
	<u>SOIL 17</u>					
	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
% P	0.109	0.106	0.236	0.10	0.11	0.26
% Al	ND	ND	ND	0.30	0.21	0.22
% Ca	0.549	0.847	0.480	0.29	0.41	0.32
% Mg	0.212	0.233	0.238	0.06	0.09	0.11
% K	3.190	2.810	1.330	0.57	0.58	0.44
% Fe	0.027	0.020	0.018	ND	ND	ND
% Mn	0.019	0.015	0.020	ND	ND	ND
	<u>SOIL 18</u>					
	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
% P	0.110	0.158	0.236	0.13	0.17	0.30
% Al	ND	ND	ND	0.32	0.24	0.22
% Ca	0.490	0.900	0.513	0.32	0.43	0.32
% Mg	0.244	0.309	0.250	0.10	0.14	0.10
% K	3.050	2.820	1.950	0.63	0.57	0.44
% Fe	0.026	0.010	0.021	ND	ND	ND
% Mn	0.020	0.014	0.020	ND	ND	ND
	<u>SOIL 19</u>					
	L_0P_0	L_1P_0	L_0P_1	L_0P_0	L_1P_0	L_0P_1
% P	0.106	0.113	0.310	0.13	0.13	0.34
% Al	ND	ND	ND	0.15	0.10	0.21
% Ca	1.120	1.400	1.020	0.48	0.56	0.32
% Mg	0.391	0.506	0.404	0.13	0.31	0.10
% K	2.110	1.470	1.040	0.52	0.51	0.52
% Fe	0.023	0.017	0.016	ND	ND	ND
% Mn	0.014	0.013	0.014	ND	ND	ND