

**AN EVALUATION OF THE USE OF ORGANIC AMENDMENTS
TO AMELIORATE ALUMINIUM TOXICITY AND PHOSPHORUS
DEFICIENCY IN AN ACID SOIL**

by

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ABSTRACT

The effects of the additions of some commonly-available organic residues to an acid, P-deficient soil (typical of those used by small-scale farmers in KwaZulu-Natal) on soil pH, exchangeable and soil solution Al, P availability and maize yield response was investigated in a number of laboratory and glasshouse experiments. The organic amendments used were ground-up grassveld residues, household compost, filter cake (a waste product from a sugar mill) and layer poultry manure. The soil used was a Hutton form (Farmingham series) (Rhodic Ferrasol, FAO).

In an initial laboratory study, addition of all of the organic residues, at rates equivalent to 10 and 20 Mg ha⁻¹, raised soil pH significantly and as a result there was a marked reduction in exchangeable Al concentrations. The increase in pH and decrease in exchangeable Al was more pronounced at the higher rate of addition and followed the order: poultry manure > filter cake > household compost > grass residues. The major mechanism responsible for the increase in pH was thought to differ depending upon the type of organic residue being considered. Whilst the relatively high content of CaCO₃ was probably the main mechanism in the case of poultry manure and filter cake, the proton consuming ability of humic material probably predominated for household compost and decarboxylation of organic acids during decomposition was probably the main mechanism in the case of grass residues.

Additions of organic amendments also decreased concentrations of total Al (Al_T) in soil solution but the concentration of monomeric Al (Al_{Mono}), as estimated by pyrocatechol violet 60 sec. method, was unchanged or even increased. This latter effect was attributed to the high cation

content of residues (particularly that of poultry manure) which increased soil salinity and exchangeable Al^{3+} was consequently displaced into soil solution.

Additions of amendments also increased the Olsen-extractable P levels in the order: poultry manure > filter cake > household compost > grass residues and their addition also decreased the P adsorption capacity of soils. Concentrations of exchangeable Ca, Mg and K, and Na in the case of poultry manure, were increased by additions of organic amendments.

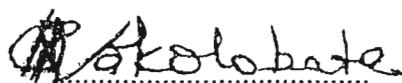
In a glasshouse experiment, the four organic residues were applied to soils at a rate equivalent to 20 Mg ha^{-1} with or without the addition of either lime (equivalent to 0, 5 or 10 Mg ha^{-1}) or P (equivalent to 0, 10 or 50 kg ha^{-1}). Lime applications to the control (unamended) treatment resulted in a marked reduction in exchangeable Al, Al_T , Al_{Mono} and in the proportion of Al_T present as Al_{Mono} in soil solution. The addition of organic amendments increased soil pH and reduced Al_T and Al_{Mono} to low concentrations regardless of whether lime was applied or not. There was no yield response in maize to applied lime in any of the amended treatments. There was a yield increase in response to applied P in the control, household compost and grass residue treatments but none for the filter cake and poultry manure treatments. In agreement with this, Olsen-extractable P values in soils followed the order: poultry manure > filter cake > household compost > grass residues > control.

It was concluded that the addition of organic amendments to acid soils is a practicable way of liming them and reducing the potential for Al toxicity and that it can also reduce fertilizer P requirements. This research now needs to be extended into the field situation.

DECLARATION

I hereby certify that the research reported in this thesis is my own work, except where otherwise indicated in the text, and that the work has not been submitted for a higher degree in any other university.

Signed:

A handwritten signature in black ink, appearing to read 'M.S. Mokolobate', written over a dotted line.

M..S. MOKOLOBATE

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CHAPTER 1

GENERAL INTRODUCTION AND STUDY OBJECTIVES

Acid soil infertility is a major limitation to crop production on highly weathered and leached soils in both tropical and temperate regions of the world (Rowell, 1988). In addition, soil acidification induced by the activities of mankind has become of increasing concern in recent years. Common anthropogenic causes of acidification include leaching with acid rainfall (the result of industrial pollution) and nitrification following applications of nitrogenous fertilizers (Wild, 1988). Two fundamental factors limit the fertility of acid soils, nutrient deficiencies (e.g. P, Ca and Mg) and the presence of phytotoxic substances (e.g. soluble Al and Mn).

In South Africa soil acidity is a serious problem that limits crop production in both large and small-scale agriculture. Acid soils predominate in the Western and Eastern Cape coastal belts, KwaZulu -Natal, Eastern Mpumalanga and Northern Province (Beukes, 1997). In these regions about 5 million ha of topsoils are seriously acidified having a $\text{pH}_{(\text{KCl})} < 4.5$. High potential (red and yellow apedal) soils make up 49% of this area. A further 11 million ha of soils have $\text{pH}_{(\text{KCl})}$ between 4.5 and 5.5 and are regarded as moderately acidic. In summary, Beukes (1997) concluded that in summer rainfall cropping areas west of the Drakensberg ranges, a minimum of 2.7 million ha of topsoils are acidic which represents about 37% of the cropped area. In addition, he estimated that some 2 million ha of land in summer rainfall areas of the country are also affected by subsoil acidity. Beukes (1997) further concluded that in order to ameliorate soil acidity in the summer rainfall areas of South Africa it would require an annual application of about 4.5 million tonnes of agricultural lime; present estimates of annual lime sales are about 1

million tonnes. Thus, a back-log in liming has developed and soil acidity is likely to become an increasing problem.

In most situations, poor crop growth in acid soils can be correlated directly with Al saturation (the percentage of the effective CEC occupied by exchangeable Al) (Sartain and Kamprath, 1977); Abruna-Rodriguez *et al.*, 1982). The practice of liming acid soils (i.e., applying CaCO_3) in order to raise soil pH and precipitate exchangeable Al as insoluble hydroxy-Al has long been recognized as necessary for optimum crop production (Haynes, 1984). However, in many undeveloped acid soils large quantities of lime (e.g., 5 - 20 tonne ha^{-1}) are commonly required to achieve adequate growth of many crops.

The low P status of highly-weathered acid soils is a particular problem because large amounts of P typically need to be applied in order to raise concentrations of available soil P to an adequate level (Sanchez and Uehara, 1980). This is because such soils contain large quantities of Al and Fe hydrous oxides which have the ability to absorb P to their surfaces. Thus, much of the added P is “fixed” and is not readily available for crop use.

In intensive agricultural systems, repeated applications of water-soluble P fertilizers (e.g., superphosphate) and lime are common practice, and indeed necessary, when farming is carried out on highly-weathered acid soils. However, acidic soils are common in many parts of Southeast Asia, South America and Africa, where much of the agriculture that is practiced is semi-subsistence farming. For both economic and logistic reasons, it is often not practicable for the resource-poor farmers who are involved in such agriculture to apply high rates of lime and P fertilizer to their soils. There is, therefore, a need to develop practicable alternatives.

Recent research has shown that the addition of green manures and animal wastes to acid soils can reduce Al toxicity and increase crop yields (Hue, 1992; Berek *et al.*, 1995). Additions of organic residues have also been shown to increase P uptake and crop growth in P-deficient soils (Hue, 1990; Hue *et al.*, 1994). The application of organic residues to soils in order to minimize the need for lime and fertilizer P would be of considerable benefit to small scale farmers. For this reason, the present study was initiated.

The specific objectives of the study were to:

- (i) Determine if organic waste materials that would be potentially available to small scale farmers could be used to ameliorate soil acidity and P deficiency in an acid soil typical of that used by resource-poor farmers in KwaZulu-Natal.
- (ii) Determine what effects the addition of such waste materials to soils have on nutrient availability.
- (iii) Determine what effects their application have on concentrations of exchangeable and soil solution Al and evaluate the mechanisms involved in any observed changes.
- (iv) Determine the overall effect of the additions of these organic wastes to soil on crop response in a glasshouse experiment.

This thesis is divided into five main sections. Following this introduction, the literature pertaining to the effects of organic waste additions on Al toxicity and P deficiency in acid soils is reviewed

in detail in chapter 2. In chapter 3, the results of a preliminary experiment to determine the effects of the additions of four organic waste materials are outlined and discussed. In chapter 4, the interaction of organic waste additions with modest applications of either lime or P is investigated in a glasshouse experiment. Conclusions and suggestions for further research are outlined in Chapter 5.

CHAPTER 2

REVIEW OF LITERATURE

In this chapter, the reactions and role of Al in soil acidity (section 2.1) and the processes of P fixation by soils (section 2.2) are reviewed and discussed. Particular attention is paid to the role that additions of organic residues to soils could have in affecting the solubility and phytotoxicity of Al and the availability of P in acid soils.

2.1 SOIL ACIDITY AND SOIL Al

2.1.1 Introduction

Soil pH is a universally employed diagnostic measurement in studies of soil acidity. There is, however, no standard critical pH below which a crop will be adversely-affected. The critical pH varies from soil-to-soil and with crop species. Because Al is the predominant phytotoxic substance present in acid soils, an index of its concentration is often used as both a measure of potential phytotoxicity and as a basis for making lime recommendations.

The important aspects of soil Al relevant to soil fertility are considered in this section. More detailed reviews of various aspects of the chemistry of soil Al are available elsewhere (Huang, 1988; Lindsay and Walthall, 1989; Ritchie, 1989, 1994; Stevenson and Vance, 1989; Zelazny and Jardine, 1989).

2.1.2 Exchangeable and Reactive Al

In acid soils, an appreciable portion of the cation exchange capacity is satisfied by Al ions.

Exchangeable Al is normally determined by extracting with an unbuffered salt, e.g. 1M KCl (Little, 1964). At $\text{pH}_{(\text{water})}$ values of 5.5 to 6.0, exchangeable Al precipitates as insoluble hydroxy-Al compounds. Thus, very little exchangeable Al is found in soils with a pH greater than 6.0 (see Section 2.1.3). Concentrations of exchangeable Al have been found to be closely related to plant response in acid soils and exchangeable Al levels have been used successfully to calculate lime requirements of soils (Hargrove and Thomas, 1981; McLean, 1976; Farina *et al.*, 1980; Sanchez, 1976).

Exchangeable Al does not always relate well to plant response because of differences between soils in mineralogy, surface charge, organic matter, and other factors. A closer relationship with plant growth is often found with percentage Al saturation. Aluminium saturation is calculated by dividing the exchangeable Al by the sum of the exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ , Na^+) plus exchangeable Al. Since Al is precipitated at a pH of about 5.5 to 6.0, soils are essentially base saturated above such pH values. Farina *et al.* (1980) found that there is a strong correlation between yield and Al saturation whereas there was only a weak correlation between the yield and pH. Growth limiting Al saturation levels have been found to vary from approximately 20 - 70% depending on soil and crop type (Kamprath, 1970; McCray and Sumner, 1990).

In addition to exchangeable Al there is a buffering reserve of reactive Al present in acid soils. Levels of exchangeable Al are partially controlled by this buffering reserve.

As noted by Wild (1988) reactive Al includes:

1. Positively charged hydroxy-Al polymers (see Section 2.1.3) of various sizes and degrees of hydration that may be coating soil colloids or be present on exchange sites;

2. Hydroxy-Al present in the interlayers of 2:1 clay mineral such as vermiculite and montmorillonite;
3. Al^{3+} and hydroxy-Al in forms complexed with organic matter (see Section 2.1.5);
4. Amorphous aluminosilicates (allophane and allophane-like constituents) in volcanic soils.

It is important to note that exchangeable Al is a poorly defined property of soils. The average charge per Al in 1M KCl extracts is between 2 and 3, decreasing as pH rises (Wild, 1988). This is presumably the result of a mixture of monomeric species of Al^{3+} , AlOH^{2+} and $\text{Al}(\text{OH})_2^+$ with polymeric forms also being present. Indeed, although exchangeable Al is often simplistically considered as Al^{3+} that is bound electrostatically to permanently charged sites on soil colloids (i.e. by cation exchange), the 1M KCl-extractable Al fraction consists of exchangeable Al *per se*. plus a variable amount of hydroxy-Al (Amedee and Peech, 1976). Exchangeable Al is, therefore, a mixture of unbuffered, salt-extractable forms of Al.

Factors such as concentration and pH of the extracting solution, valence of the extracting cation, and nature of the balancing anion can greatly influence the amount of Al extracted with an unbuffered salt. Skeen and Sumner (1967a), for example, extracted Al with 0.2N NH_4Cl solutions adjusted to different pH values from grey-brown ferralitic soils of KwaZulu-Natal. They showed that there was an increase in the total amount of Al extracted with a decrease in pH of the extracting solutions. This increase was ascribed to dissolution of non-exchangeable Al. In the same study, Skeen and Sumner (1967a) found that with an increase in the concentration of the extracting solution (e.g. NH_4Cl) there was an increase in the quantity of Al that was extracted. In a related study, Skeen and Sumner (1967b) investigated the effect of balancing anions in the extracting solution. They found that Cl^- and NO_3^- were the most effective anions

since they effectively minimized the processes of deolation (i.e. the release of non-exchangeable Al, e.g. from the interlayers of 2:1 clay minerals). In their study to demonstrate the effect of the valence of the extracting cation on extractable Al, Bache and Sharp (1976) showed that Al concentrations were greater in CaCl_2 than KCl solutions because divalent ions are more effective than monovalent ions in desorbing Al.

Sometimes extracts are used to deliberately measure exchangeable Al plus a proportion of the reactive buffering reserve of Al (Haynes, 1984). Copper chloride solution has a strong complexing ability (e.g. can extract Al bound to organic matter and some that is in the clay interlayers) (Hargrove and Thomas, 1981). Lanthanum chloride also removes organically-bound Al plus exchangeable Al (Oates and Kamprath, 1983). Such extractants can be used to calculate the lime requirement in soils where there is a large buffering reserve of reactive Al (Ritchie, 1989).

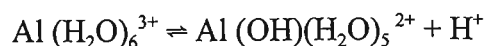
2.1.3 Aluminium Solubility in Soils

As noted by Wild (1988), Al concentrations in soil solution can be considered to depend primarily upon:

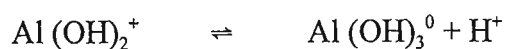
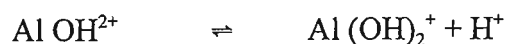
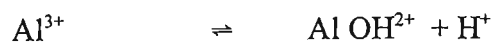
1. The solubility of gibbsite (i.e. crystalline $\text{Al}(\text{OH})_3$);
2. The hydrolysis products (ion species) of Al in solution, both monomeric and polymeric;
3. The interaction of Al with soluble inorganic and organic ligands.

Aluminium concentrations in soil solution can most simply be explained in relation to the solubility of gibbsite [i.e., crystalline $\text{Al}(\text{OH})_3$] and the hydrolysis products of Al in soil solution

(McLean, 1976). In aqueous solution, Al^{3+} is hydrated as $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Protons can be dissociated from the water molecules:



The sequence of H^+ dissociations is usually illustrated as follows:



The solubility of these monomeric Al species in equilibrium with gibbsite is shown in Figure 2.1.

It is evident that below pH 4 the dominant species is Al^{3+} . Aluminium solubility decreases with increasing pH until at about pH 6 where insoluble $\text{Al}(\text{OH})_3$ (gibbsite) is the predominant form.

At higher pH values increasingly soluble, negatively charged aluminate ions form.

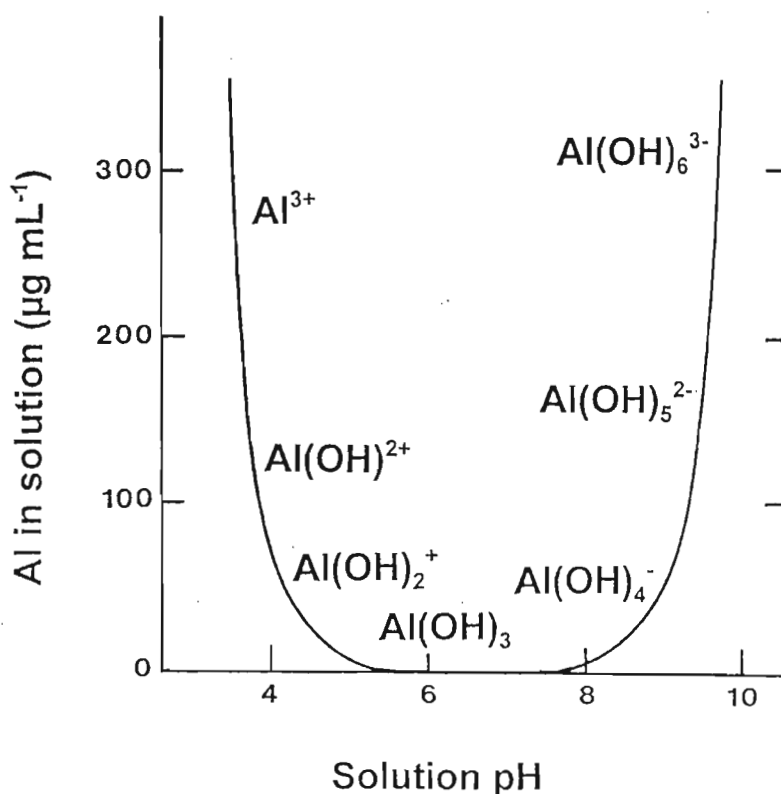


Figure 2.1 Effect of pH on the solubility of aluminium in solution (after McLean, 1976).

In soil solution, the extent of Al hydrolysis may be reduced by the presence of other anions such as NO_3^- , Cl^- , SO_4^{2-} and F^- and organic acids (Ritchie, 1989). As discussed below (Section 2.1.4.2) Al may form ion pairs with SO_4^{2-} (i.e. AlSO_4^+) and fluoride thus reducing the activity of Al^{3+} in solution. Aluminium may also form soluble monomeric complexes with organic acids and humic material (Section 2.1.5).

As noted above, Al is present in solution predominantly in octahedral coordination with OH^- or water. That is, Al^{3+} is present as $\text{Al}^{3+} \cdot 6\text{H}_2\text{O}$ and Al(OH)^{2+} as $\text{Al(OH)}^{2+} \cdot 5\text{H}_2\text{O}$. Polymerization of these octahedra characteristically occurs. Polymer formation is greatly influenced by pH of the solution. Hsu (1966), for example, found that hydrolysis of Al in distilled water yielded only monomeric species whereas when OH^- ions were added to Al solution, polymers were produced. The type of the polymer formed (chain-like or cyclic) depends on the OH^- :Al ratio (see Figure 2.2). Coalescence of rings ultimately results in the formation of planar sheets in which Al shares three pairs of hydroxide ions with three Al ions. This is the crystalline structure of gibbsite.

In soils, Al hydroxides are seldom, if ever, present in pure form. As the soil pH increases, Fe also precipitates as hydroxy-Fe species and Mn precipitates as Mn oxides. Fey and Le Roux (1977) found that both amorphous oxides of Al and Fe are present in some Oxisol clays, and Schwertmann *et al.* (1977) found that Al may substitute Fe in the hematite structure and lead to crystalline phases.









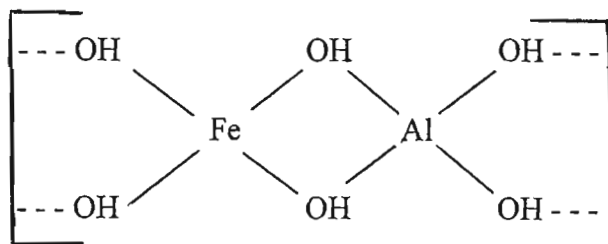
								
	Al^{3+}	$Al_2(OH)_2^{4+}$	$Al_3(OH)_4^{5+}$	$Al_6(OH)_{12}^{6+}$	$Al_9(OH)_{18}^{9+}$	$Al_{10}(OH)_{22}^{10+}$	$Al_{16}(OH)_{38}^{16+}$	$Al_{24}(OH)_{60}^{12+}$
Average charge/Al	3.0	2.0	1.67	1.0	1.0	0.80	0.63	0.50
OH/Al ratio	0	1.0	1.33	2.0	2.0	2.20	2.36	2.50

Figure 2.2 Summary of Al species present in solution which can be deduced from the solid state structures. The OH/Al ratio refer to the molar ratio in the complexes and not the OH/Al ratio of the system (after Stol *et al.*, 1976).

Rengasamy and Oades (1979) showed that positively charged Al- and Fe- hydroxy copolymers can form by bridging of Al(III) and Fe(III) through hydroxyl groups as follows:



Thus any condition that leads to a higher concentration of OH^- in the soil solution; is likely to result in the precipitation of mixtures of Al and Fe hydroxides and Mn oxides.

As well as forming polymers with hydroxyl ions alone, Al can form polymers in conjunction with other ligands such as phosphate and silicate (Ritchie, 1989). Evidence for the presence of soluble hydroxy-Al phosphate polymers in the pH range 4.1 - 4.8 at Al and phosphate concentrations of less than $100 \mu\text{M}$ and $25 \mu\text{M}$ respectively and at ionic strengths less than $910 \mu\text{M}$ has been presented by White *et al.* (1976) and Blamey *et al.* (1983). Higher concentrations and pH values resulted in precipitation of these polymers. The formation of hydroxy-Al silicate polymers at pH values less than 5.5 has been demonstrated by Luciuk and Huang (1974) and Farmer *et al.* (1988).

Two approaches have been made to experimentally distinguish the various forms of Al that are present in soil solution. The first involves the use of various complexing agents used for colorimetric analysis of Al. Three commonly used methods for spectroscopic determination of phytotoxic Al use 8-hydroxyquinoline (James *et al.*, 1983), pyrocatechol violet (Kerven *et al.*, 1989) and chrome-azurol-S (Close and Powell, 1989). In these methods it is assumed that Al species that react rapidly (e.g. < 2 min.) with a coloured complex are predominantly monomeric and species that react more slowly are complexed or polymeric in nature.

In a second approach, the proportion of soluble Al in each category is estimated theoretically using thermodynamic principles. The concentrations of the various cations and anions, as well as Al, are measured and a speciation programme (e.g. GEOCHEM; Sposito and Mattigod, 1980) is used to calculate the proportion of the various Al species present. This approach can be somewhat limited by the lack of reliable thermodynamic constants for some Al-ligand reactions and assumptions inherent in their formulation (Ritchie, 1989).

2.1.4 Soil Solution Al

The concentration of Al in soil solution is a more direct measurement of conditions to which the plant responds than either exchangeable Al or Al saturation. Indeed, Al concentrations in soil solution have been observed to be closely related to inhibition of plant growth in acid soils (Evans and Kamprath, 1970; Adams and Moore, 1983). However, inhibition of plant growth is not only related to the quantity of Al in soil solution but also the species of soluble Al present.

2.1.4.1 Quantities in Solution

Concentrations of Al in soil solution are highly pH-dependent (see Section 2.2) and are negligible above pH 5.5. Even at lower pH values exchangeable Al is very tightly held on exchange sites. As a result, the concentration of Al in soil solution is characteristically low (Sanchez, 1976). Data of Kamprath (1978), Curtin and Smillie (1983) and Adams and Moore (1983) indicate that total soluble Al (Al_T) is usually between 10 - 250 μM (i.e. 0.27 - 9.4 ppm) in acid soils.

Two important factors influencing concentrations of Al in soil solution are the salt content of the solution and the degree to which exchange sites are saturated with Al^{3+} . Brenes and Pearson (1973), for example, showed that a small addition of KCl to their soil samples increased the concentration and activity of Al in soil solution (Table 2.1). The reason for this is that added cations displace the exchangeable Al from the adsorption sites on the layer silicates and/or layer silicate oxide-coated systems. It is also clear from Table 2.1 that as pH was increased by additions of $Ca(OH)_2$, soil solution Al declined markedly.

Table 2.1 Soil pH, conductivity and aluminium content of solutions displaced from Humatas and Coto clays treated with varying amounts of $\text{Ca}(\text{OH})_2$ and KCl (after Brenes and Pearson, 1973).

	Treatment		Soil pH	Conductivity of soil solution	Soil solution Al	
	$\text{Ca}(\text{OH})_2$	KCl			Concentration	Chemical activity
	(<i>me/100 g</i>)	(<i>me/100 g</i>)		(<i>mmhos/cm at 25°C</i>)	(<i>mM</i>)	(<i>mM</i>)
Humatas	None	None	4.18	0.63	0.141	0.047
	0.50	None	4.20	0.70	0.185	0.061
	1.00	None	4.28	0.79	0.118	0.036
	1.25	None	4.30	0.80	0.070	0.021
	0.50	0.50	4.01	1.55	0.626	0.188
	1.00	0.50	4.07	1.69	0.474	0.135
	1.25	0.50	4.11	1.70	0.555	0.154
	1.75	1.00	4.08	2.90	0.804	0.199
Coto	None	None	4.45	1.55	0.111	0.029
	None	0.25	4.50	2.55	0.207	0.049
	None	0.50	4.24	3.55	0.485	0.112
	None	1.00	4.30	5.80	0.785	0.152

Because Al is held very tightly to exchange sites on soil colloids, concentrations of Al in soil solution are only high when the Al saturation is also high. An example of the relationship between the two parameters for Ultisols from North Carolina is shown in Figure 2.3. It is evident that concentrations of Al in soil solution rose sharply beyond 60% Al saturation.

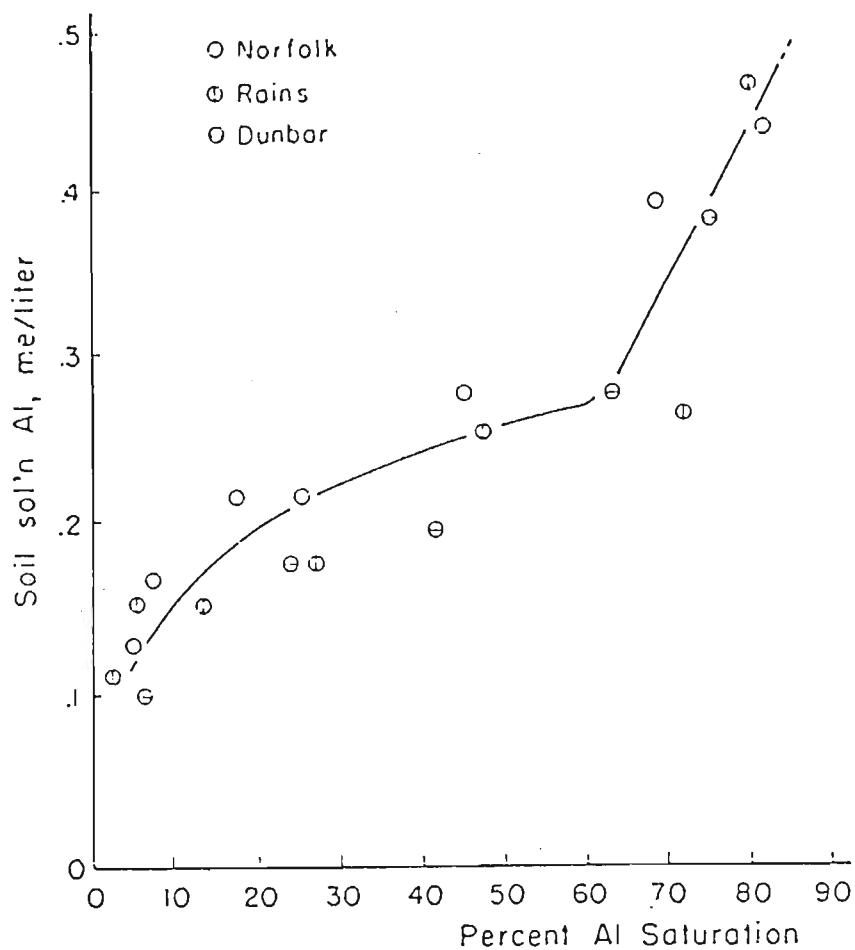


Figure 2.3 Relationship between percent Al saturation and soil solution Al for some Ultisols from North Carolina (after Evans and Kamprath, 1970).

Another important factor influencing Al concentrations in soil solution is soil organic matter content. Aluminium in soil solution often decreases as soil organic matter content increases since organic matter forms strong complexes with Al (see Section 2.1.5). This was demonstrated by Evans and Kamprath (1970) who used mineral and organic soils (with a range of organic matter contents) and found that as the organic matter increased, there was a decrease in soil solution Al.

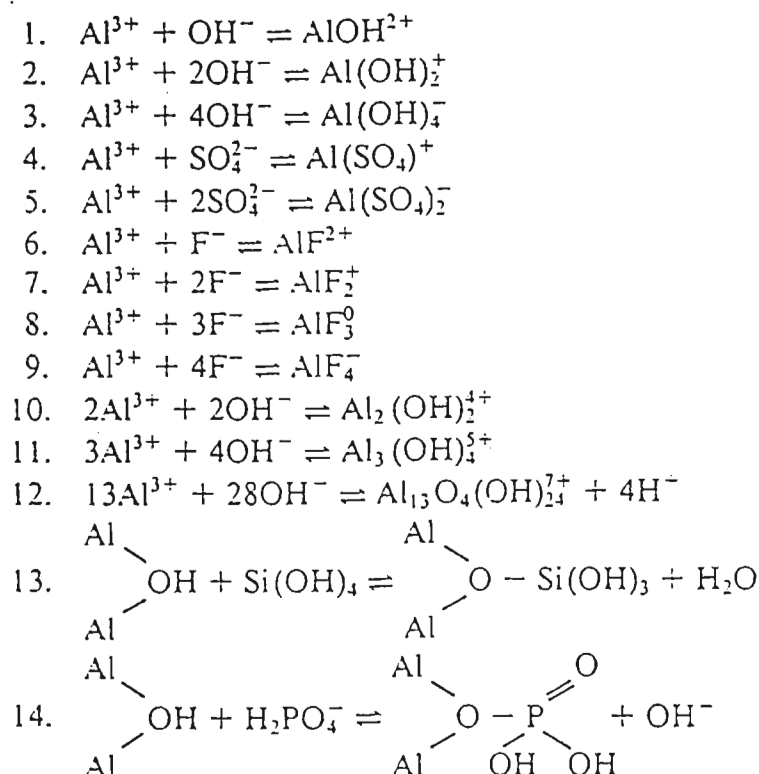
2.1.4.2 Speciation of Al in Soil Solution

There is increasing evidence that toxicity of Al is reduced in the presence of inorganic and organic complexing ions in soil solution (Hue *et al.*, 1986). It seems that it is the activity of Al^{3+} and/or monomeric hydroxy-Al species (e.g. AlOH^{2+} , $\text{Al}(\text{OH})_2^+$) that are the forms of solution Al most negatively correlated with depressed yields due to Al toxicity (Wright, 1989). Some research has certainly suggested that monomers of Al species other than Al^{3+} may be toxic to root growth. Blamey *et al.* (1983), for instance, found that near maximum Al toxicity to soybean root growth occurred with an Al monomer activity of $20 \mu\text{M}$. They were, however, unable to identify a specific Al monomer as being responsible for the toxicity.

In most soil solutions a significant proportion of the Al is likely to be present as hydroxy-Al monomers. As discussed in Section 2.1.3, monomeric hydrolysis of Al (reactions 1-3; Table 2.2) usually becomes significant at pH values greater than pH 4.0 and by 4.9 more than 80% of Al_T is hydrolyzed (Ritchie, 1989).

In soil solution, the extent of Al hydrolysis may be reduced by the presence of ligands (anions) such as NO_3^- , Cl^- , SO_4^{2-} and F^- (Singh, 1982). The extent of complexation will depend on ionic strength and pH of the solution and the relative concentrations and complexing ability of the inorganic ligands (Ritchie, 1989). In particular F^- , and to a lesser extent SO_4^{2-} , can complex strongly with Al (Table 2.2). Ion pair formation between Al and SO_4^{2-} or F^- may occur in soil solution where the concentration of these anions is high (Ritchie, 1989). Indications are that Al complexed with F^- and SO_4^{2-} is not toxic to root growth (Cameron *et al.*, 1986; Kinraide and Parker, 1987; Tanaka *et al.*, 1987).

Table 2.2 Possible inorganic reactions of aluminium in the soil solution (after Ritchie, 1989).



Aluminium also forms stable complexes in soil solution with simple aliphatic organic acids and soluble soil humic material. The nature of these complexes is discussed in detail in Section 2.1.5.2. It is, however, important to note here that complexation of Al by soluble organic matter is a very important mechanism in detoxification of soil solution Al (Hue *et al.*, 1986).

As noted previously, positively charged hydroxy-Al monomers characteristically polymerize and can form soluble hydroxy-Al polymers alone, or in association with phosphate and silicate ions (see Table 2.2). Whilst polynuclear hydroxy-Al ions have been found to exist in dilute acid solutions and in dilute salt extracts taken from acid soils (Bache and Sharp, 1976; White *et al.*,

1976), they have not been demonstrated to be present in significant quantities in soil solution (Wild, 1988; McCray and Sumner, 1990). It is possible that preferential adsorption of polynuclear Al by clay minerals and organic matter may prevent substantial concentrations from remaining in solution (Zelazny and Jardine, 1989). As demonstrated by Parker *et al.* (1988) polynuclear hydroxy-Al is toxic to plants when grown in nutrient solutions.

2.1.5 Aluminium-Organic Matter Complexes

During decomposition of plant and animal debris a whole range of substances are released and/or synthesized by the decomposer microorganisms. These include carbohydrates, lignin, nucleic acids, pigments, hormones, organic acids and humic substances. Aluminium can bind strongly to many of these compounds. Soil organic matter complexes with Al can be grouped into two main categories (Stevenson and Vance, 1989). These are (i) well-defined biochemical compounds such as simple aliphatic organic acids, phenols, sugar acids etc. and (ii) complex humic molecules. Of the well-defined biochemical compounds, simple organic acids are usually present in highest concentrations and as a result, their reactions with Al have received most attention.

The relative importance of specific biochemical compounds versus humic substances in binding Al in soil solution is unknown and will vary with soil and environmental conditions. It is, however, generally considered that humic substances may be of greater importance in reducing phytotoxicity of Al in acid soils (Stevenson and Vance, 1989; Harper *et al.*, 1995).

2.1.5.1 Organic Acids

Tan (1986) compiled a list of some organic acids that are commonly present in soils (Table 2.3). Concentrations of organic acids in soils are generally low but can vary greatly depending upon soil type, soil management practice and type of organic amendments added (Iyamuremye and Dick, 1996). Hue *et al.* (1986) compared subsoils of cultivated and non-cultivated soils and found that oxalic acid concentrations ranged from 4 - 22 μM in forested soil and from < 1.0 - 3.4 μM in cultivated soil. Similar trends were observed among other organic acids measured. Stevenson and Ardakini (1972) reported values as high as 3.7 - 5.0 and 1.0 - 4.0 μM for acetic and malic acid respectively. Takijima (1960) observed that the concentration of organic acids in soils decreased with increasing structural complexity as follows:

acetic > butyric > fumaric, propionic, valeric, succinic and lactic acids.

Table 2.3 Partial list of non-humified organic acids present in soils (after Tan, 1986).

Organic acid	Formula
Acetic acid	CH_3COOH
Amino acids	
Ascorbic acid	$\text{C}_6\text{H}_8\text{O}_6$
Aspartic acid	$\text{HOOCCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Benzoic acid	$(\text{C}_6\text{H}_5)\text{COOH}$
Butyric acid	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
Cinnamic acid	$\text{C}_9\text{H}_8\text{O}_2$
Citric acid	$\text{HO}(\text{CH}_2\text{COOH})_2\text{COOH}$
Coumaric acid	$\text{C}_9\text{H}_8\text{O}_2$
Ferulic acid	$\text{C}_{10}\text{H}_{10}\text{O}_4$
Formic acid	HCOOH
Fumaric acid	$\text{HOOCCH}=\text{CHCOOH}$
Gallic acid	$\text{C}_7\text{H}_6\text{O}_5$
Glutamic acid	$\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Hydroxybenzoic acid	$\text{C}_7\text{H}_6\text{O}_4$
Lactic acid	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$
Nucleic acids	
Oxalic acid	HOOCCOOH
Propionic acid	$\text{CH}_3\text{CH}_2\text{COOH}$
Pyruvic acid	CH_3COCOOH
Salicylic acid	$(\text{C}_6\text{H}_4) \begin{cases} \text{OH (1)} \\ \text{COOH (2)} \end{cases}$
Succinic acid	$\text{HOOCCH}_2\text{CH}_2\text{COOH}$
Syringic acid	$\text{C}_9\text{H}_{10}\text{O}_5$
Tannic acid	$\text{C}_{14}\text{H}_{12}\text{O}_{14}$
Tartaric acid	$\text{HOOCCH}(\text{OH})\text{CH}(\text{OH})\text{COOH}$
Vanillic acid	$\text{C}_8\text{H}_8\text{O}_4$

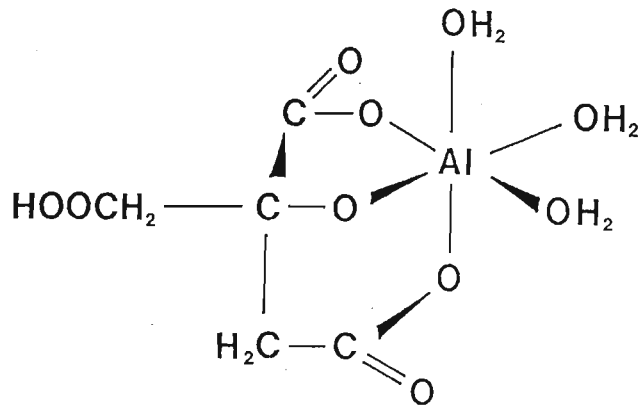
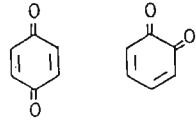
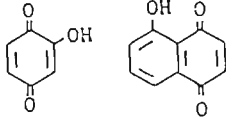
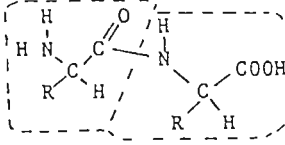


Fig. 2.4 The chelate structure of an Al-citrate complex (after Stevenson and Vance, 1989).

The role of these organic acids in detoxifying Al under field conditions is still somewhat speculative. Hue *et al.* (1986) demonstrated in pure solution cultures that soluble organic acids were effective at detoxifying Al and improving plant growth. The organic acids most effective were citric, oxalic and tartaric acids in that decreasing order, while malic, malonic and salicylic acids were less effective in that decreasing order. Hue *et al.* (1986) observed that the detoxifying capacity of these organic acids was positively correlated with the relative position of OH/COOH groups on their main C chain; positions that favoured formation of 5- or 6- bond ring structures with Al were most effective. Bartlett and Riego (1972) also showed that in solution culture citric acid could react rapidly with soluble monomeric hydroxy-Al and thus markedly increase root growth. The chelate structure of an Al-citrate complex is shown in Figure 2.4.

Table 2.4 Some important structural groups of humic molecules (after Stevenson, 1994).

Amino	$-\text{NH}_2$	Anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R}' \end{array}$
Amine	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{NH}_2 \\ \\ \text{H} \end{array}$	Imine	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}=\text{NH} \end{array}, \text{R}-\text{CHNH}$
Amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \\ \\ \text{H} \end{array}$	Imino	$=\text{NH}$
Alcohol	$\text{R}-\text{CH}_2\text{OH}$	Ether	$\text{R}-\text{CH}_2-\text{O}-\text{CH}_2-\text{R}'$
Aldehyde	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}=\text{O} \end{array}, \text{R}-\text{CHO}$	Ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}, \text{R}-\text{COOR}'$
Carboxyl	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}, \text{R}-\text{COOH}$	Quinone	
Carboxylate ion	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \ominus, \text{R}-\text{COO}^-$	Hydroxyquinone	
Enol	$\text{R}-\text{CH}=\text{CH}-\text{OH}$	Peptide	
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}, \text{R}-\text{CO}-\text{R}'$		
Keto acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{COOH} \end{array}$		
Unsaturated carbonyl	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ -\text{C}=\text{C}-\text{C}=\text{O} \end{array}$		

It is important to recognize that many of the organic acids capable of complexing Al may be present in soil solution for relatively short periods of time since they are susceptible to microbial degradation (Ritchie, 1989). In this regard it is interesting to note that an easily decomposable soluble component of lucerne meal was found by Hoyt and Turner (1975) to complex Al more strongly than organic substances that remained after 4 weeks incubation of the plant material with a soil.

2.1.5.2 Humic Substances

Humic substances make up 70-80% of the soil organic matter content of most mineral soils. Humic substances are complex systems of high molecular weight organic molecules made up of a core of phenolic polymers produced from the product of biological degradation of plant and

animal residues and the synthetic activity of microorganisms (Stevenson, 1994). They exist as heterogeneous, complex, three dimensional amorphous structures. Humic substances are classically fractionated into humic acid (HA) and fulvic acid (FA). Humic acid is the material extracted from soil with an alkaline solution and precipitated upon acidification whilst FA is the fraction that remains in solution. Fulvic acids are lower in relative molecular weight than humic acids and for this reason they are the major form of humic material present in soil solution.

Humic substances are able to form complexes with polyvalent metal ions, such as Al, due to their unusually high number of O - containing functional groups which include COOH, phenolic, enolic, alcoholic OH and C=O. The large range of functional groups present on humic substances is shown in Table 2.4. Due to the heterogeneous nature of humic substances, complexation may be regarded as occurring at a large number of reaction sites with binding affinity that ranges from weak forces of attraction (i.e., ionic) to formation of stable coordinate linkages (Stevenson and Vance, 1989). As a result, the mechanisms involved in the reactions of Al with organic matter are complex and probably involve simultaneous chelation, complex formation, adsorption and coprecipitation. (Haynes, 1984). The coordination of Al to part of a humic molecule through a single linkage or through a chelate complex is shown in Figure 2.5.

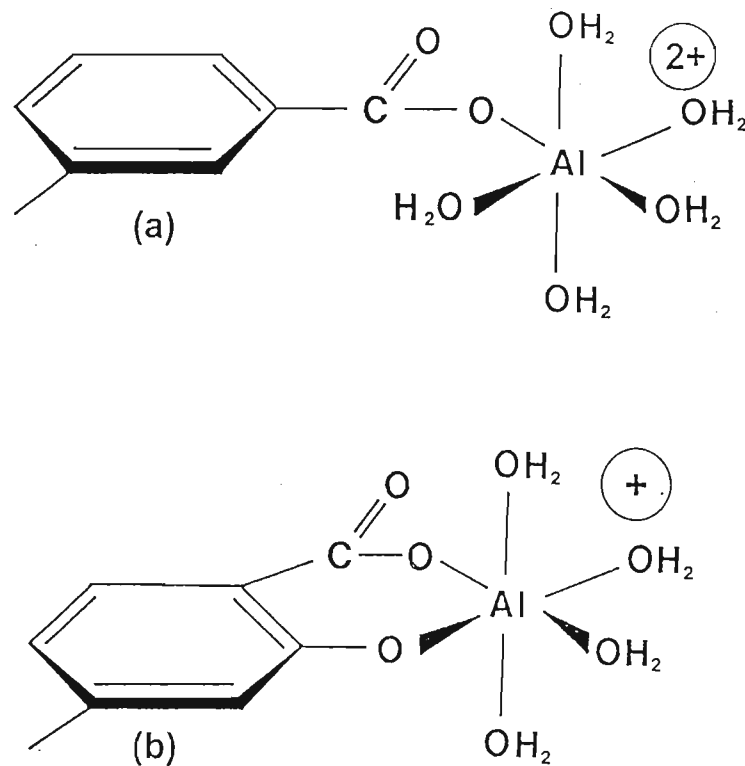


Figure 2.5 Binding of Al to humic substances by coordinate linkage with (a) single donor group and (b) the formation of a chelate complex (after Stevenson and Vance, 1989).

Aluminium complexed by organic matter is not readily exchangeable and is non-phytotoxic. Suthipradit *et al.* (1990) studied the effects of FA on tap-root elongation of soybean, cowpea and green gram in the presence of Al. In the absence of FA, from 85 to 96% of the total Al in solution was present as monomeric species. At 25 and 50 μM Al concentrations, only 10 to 12% of the added Al remained uncomplexed when FA was added and consequently root growth was greatly stimulated. Similarly, in greenhouse experiments in sand culture, Tan and Binger (1986) investigated the effects of HA on the growth of maize with increasing additions of Al. They found

that in the absence of HA, dry weight of maize leaves decreased linearly with increasing Al additions whilst Al concentrations in the leaves increased linearly from 57 to 83 $\mu\text{g g}^{-1}$. However, addition of 100 to 350 mg kg^{-1} HA to the pots decreased the Al concentrations in maize leaves and increased yields.

Fulvic acid and HA do not necessarily complex soil solution Al equally effectively. Harper *et al.* (1995), for example, found that in a comparison of FA and HA at 40 mg C L^{-1} in the presence of Al, HA complexed Al more strongly than FA.

Fulvic acid forms soluble complexes with Al, and this characteristic can be used to ameliorate subsoil acidity (Smith *et al.*, 1995). Smith *et al.* (1995) examined the chemical reactions and movement through a soil column of calcium fulvate in order to determine the factors that affect amelioration of subsoil acidity. They found that calcium fulvate was effective in decreasing the concentration of toxic Al present in the soil solution and on the exchange sites. The leachate from the soil column showed an increase in complexed Al. Aluminium complexed to the fulvate appeared not to be attracted to the exchange sites so that it was highly mobile. The exchange sites were then occupied by other cations (e.g. Ca^{2+}).

2.1.6 Influence of Additions of Organic Residues on Soil Al

A number of workers have shown that addition of green manures and animal wastes to acid soils can reduce the concentration of total Al (Al_T) and/or Al^{3+} activity in soil solution and thus reduce Al phytotoxicity and increase crop growth (Asghar and Kanehiro, 1980; Hue and Amien, 1989; Hue, 1992; Wong *et al.*, 1995). Controversy surrounds the mechanisms by which such Al

detoxification occurs (Hue and Amien, 1989). Proposed mechanisms include an increase in soil pH (Noble *et al.*, 1996), a reduction in exchangeable Al due to complexation of Al by solid phase organic material (Hoyt and Turner, 1975) and complexation of Al in soil solution by soluble organic matter thus reducing solution Al^{3+} activity (Hue *et al.*, 1986).

2.1.6.1 Effect on Soil pH

Additions of organic residues to soils can result in an increase in soil pH (Hoyt and Turner, 1975; Hue, 1992; Noble *et al.*, 1996). Hoyt and Turner (1975), for example, recorded an increase in soil pH of about 0.5 of a pH unit when lucerne meal was added to an acid soil (Figure 2.6). Although pH declined again after about 20 days incubation, it still remained above the initial soil pH value. Several other workers have also observed an initial rise in soil pH due to additions of organic residues which is then followed by a decline in pH (Hue, 1992; Wong *et al.*, 1998a).

Mechanisms suggested to be involved in the increase in pH include oxidation of organic acid anions present in decomposing organic residues, mineralization of organic residue N, specific adsorption of organic molecules produced during the decomposition process and reduction reactions induced by anaerobiosis. Plant material generally contains an excess of cations over inorganic anions with the balance being maintained by synthesis of organic acid anions (Noble *et al.*, 1996). Oxidation of these organic acid anions with the release of OH^- during decomposition of leaf material is likely to make a major contribution to the increase in pH (Helyar and Porter, 1989; Ulrich, 1991; Yan *et al.*, 1996). Ashing plant material and measuring the alkalinity of the ash provides an estimate of the organic anion content (Pierre and Banwart, 1973). Noble *et al.* (1996) compared the effect of leaf litter from 16 tree species on soil pH in an 8-week incubation

study. They found that leaf litter raised soil pH and that the increase was proportional to the ash alkalinity of the litter added.

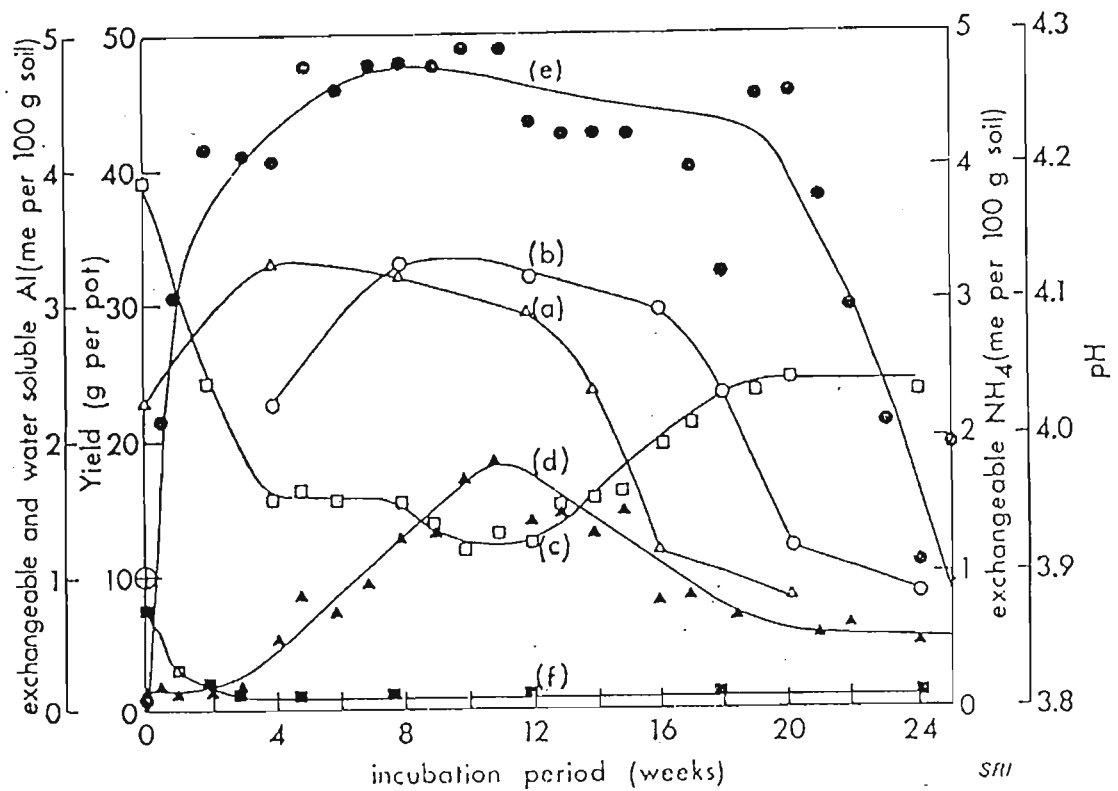
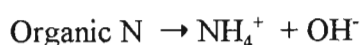


Figure 2.6 Effect of incubation on soil pH, exchangeable Al and NH_4 , water-soluble Al, and yield of barley after adding lucerne meal at 3 % of soil weight: \ominus barley yield with no alfalfa meal, barley yield (a) before and (b) after adjusting for incubation period; (c) exchangeable Al; (d) exchangeable NH_4 ; (e) pH; (f) water-soluble Al (after Hoyt and Turner, 1975).

The ash alkalinity of plant tissue will be greatly affected by the magnitude of cation accumulation by the plant. Noble *et al.* (1996), for example, found that ash alkalinity of plant litter was closely

correlated with tissue Ca content. Thus, it is not surprising that several workers have observed that the increase in soil pH during decomposition of leaf and shoot material is closely related to the total base content (e.g. Ca + Mg + K + Na) of the material (Bessho and Bell, 1992; Wong *et al.*, 1998 a, b).

During decomposition of organic residues, organic N in the residues will be mineralized. This will influence pH through the process of ammonification and nitrification (Pocknee and Sumner, 1997; Yan *et al.*, 1996). During ammonification there will be a rise in pH.



However, when NH_4^+ is nitrified to NO_3^- there is a release of two protons.



Thus, if soil conditions are not conducive for nitrification mineralization will induce a rise in pH. If, however, nitrification proceeds rapidly, and NH_4^+ does not accumulate in the soil, then there will be a net release of H^+ ions and the soil pH will decline. These effects will be additional to those related to the organic acid anion content. That is, ash alkalinity measures the excess of base-over-acid forming elements (excluding N which is volatilized during ignition). Nitrification is, in fact, thought to be the main reason why a rise in pH following residue addition is often followed by a decline (see Figure 2.6; Hoyt and Turner, 1975).

Another possible mechanism for the organic residue - induced increase in soil pH is specific adsorption of humic material and/or organic acids (the products of the decomposition of organic

residues) onto Al and Fe hydrous oxides with the consequent release of OH^- ions (Hue *et al.*, 1986; Iyamuremye and Dick, 1996). Such ligand exchange reactions are discussed in more detail in Section 3.1. An example of adsorption of oxalate onto a hydrous oxide surface with the release of OH^- ions is shown in Figure 2.7.

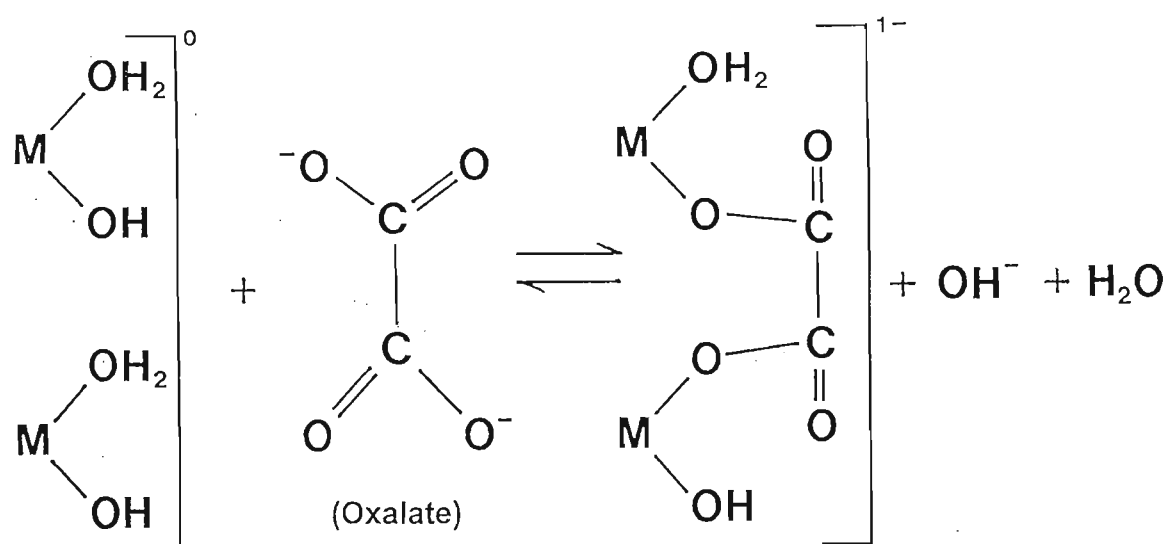
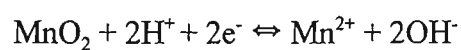


Figure 2.7 Specific adsorption of oxalate to an Al or Fe (M) hydrous oxide surface (after Hue, 1992).

It has also been suggested that the rise in pH could be attributable to reduction of higher valence Mn oxides and/or Fe oxides and hydrous oxides in soils (Hoyt and Turner, 1975; Hue, 1992). Such reactions characteristically occur under anaerobic conditions and lead to a rise in soil pH:



Hue and Amien (1989) suggested that localized anaerobic conditions could develop around rapidly decomposing pieces of organic residues in soils (due to intense microbial activity) thus promoting the above reduction reactions.

Wong *et al.* (1998b) suggested that in short term (14 day) incubations, the major mechanisms of acid amelioration by composts, manures and peat is proton exchange between the soil and organic matter buffer systems. They measured the proton consumption capacity of various organic amendments by titrating the organic matter from their natural pH values down to pH 4.0. It was shown by Wong *et al.* (1998b) that the increased soil pH was directly proportional to the proton consumption capacity of the organic materials.

2.1.6.2 Effect on Exchangeable Al

Since addition of organic residues to soils often results in an increase in soil pH, a decrease in the concentration of exchangeable Al would also be expected to occur. Indeed, several workers have measured an increase in soil pH with a concomitant decrease in exchangeable Al and Al saturation during the decomposition of organic residues in soils (Figure 2.7; Hoyt and Turner, 1975; Noble *et al.*, 1996; Wong *et al.*, 1998a, b).

The reduction in exchangeable Al is not necessarily only a function of the increase in pH. Complexation of Al by the solid phase of the decomposing organic residues would also tend to reduce exchangeable Al levels (Hoyt and Turner, 1975). There is little direct evidence for this mechanism since the partitioning of Al between exchangeable and organic forms (i.e. using 1*N*

KCl and 1N CuCl₂) does not appear to have been attempted on soils amended and unamended with organic materials.

However, in unamended soils, Thomas (1975) found that there was a strong negative correlation between organic matter content and exchangeable Al. He found that the effect of organic matter was greater at lower pH values; at pH 3.5 an increase in organic matter content from 1 to 2% lowered exchangeable Al from 6.0 to 4.2 meq 100 g⁻¹. Similarly, Evans and Kamprath (1970) observed less exchangeable Al in organic than mineral soils even when the pH of the organic soils was lower. Such findings suggest that increases in soil organic matter content caused by additions of organic residues will decrease exchangeable Al through Al complexation by the newly formed organic matter.

2.1.6.3 Effect on Soluble Al

Several workers have shown that additions of decomposing organic residues to soils can reduce both Al_T and monomeric Al in soil solution (Kretzschmar *et al.*, 1991; Bessho and Bell, 1992; Wong *et al.*, 1995; Noble *et al.*, 1996). The decrease in exchangeable Al and Al saturation caused by increased pH and/or complexation of Al by solid-phase organic matter (see above) will result in the reduction in Al concentrations in soil solution. In addition, soluble organic molecules (organic acids and phenolic humic-type substances) produced during decomposition of the organic residues will complex with monomeric Al in soil solution thus greatly reducing the proportion of Al_T present in phytotoxic monomeric forms.

In some cases, Al_T in soil solution is unaffected or is even increased during organic residue decomposition (Berek *et al.*, 1995; Slattery and Morrison, 1995). In such cases it is thought that the large amounts of soluble organic matter present, originating from the decomposition of residues, complex with Al and maintain it in the solution phase. Nevertheless, the formation of these soluble Al-organic matter complexes greatly reduces the amount of monomeric Al present in solution (Berek *et al.*, 1995).

Under field conditions, applications of organic residues can have significant effects on Al speciation in soil solution. Slattery and Morrison (1995) compared stubble retention with stubble burning on an acid soil. They found that soil pH was not significantly altered, whilst exchangeable Al and Al_T in soil solution tended to be higher under stubble retention. Nevertheless, in the stubble retention plots, there was a higher concentration of soluble low molecular weight organic acids and as a result monomeric Al as a proportion of Al_T in soil solution was decreased markedly.

In a field experiment on a tropical Oxisol in Burundi, Wong *et al.* (1995) showed that additions of the prunings of various trees and farmyard manure all greatly decreased the concentration of monomeric Al in soil solution. Grain yields of maize and beans on these soils were correspondingly increased due to alleviation of Al toxicity.

2.2 PHOSPHORUS AVAILABILITY IN SOILS

2.2.1 Introduction

Phosphate sorption (the loss of orthophosphate from soil solution to solid phases) occurs by both specific adsorption and precipitation reactions (Sanchez and Uehara, 1980). Specific adsorption (or ligand exchange) occurs when phosphate anions replace the hydroxyl groups on the surface of Al and Fe oxides and hydrous oxides (Parfitt, 1980). Precipitation reactions occur when insoluble phosphate compounds form with cations such as Al, Fe and Ca. At low pH (i.e. < 4.5 - 5.0), additions of phosphate to soil can result in precipitation of Al and Fe phosphates whilst at high pH (> 6.0 - 6.5) insoluble calcium phosphates form (Haynes, 1984). In many situations, however, specific adsorption reactions are the main regulators of soil solution phosphate concentrations (Parfitt, 1980).

2.2.2 Adsorption of P by Soils

Aluminium and Fe oxides and hydrous oxides can occur as discrete compounds in soils or as coatings on other soil particles. They can also occur as amorphous Al hydroxy compounds between the layers of expandable Al silicates. Highly weathered acid soils contain large quantities of these compounds and therefore have the ability to adsorb large amounts of added phosphate. The surface charge on amphoteric metal (M) hydrous oxides arises as a result of deprotonation and protonation of the potential-determining $\text{MOH}_2^{0,5+}$ and $\text{MOH}^{0,5-}$ groups. The surface charge is highly pH-dependant. As the activity of OH^- ions increases, relative to the H^+ ions, the pH rises and the surface becomes increasingly negatively charged; when the pH decreases the reverse is true. The point of zero charge (PZC) (i.e. the pH at which there are equal numbers of positive

and negative charges on the surface) of soils is usually in the pH range of 3 to 6 (Parfitt, 1980) so that most soils carry a net negative charge.

Phosphate ions (H_2PO_4^- and HPO_4^{2-}) can be specifically adsorbed by metal hydroxides by affecting a ligand exchange, displacing $\text{OH}_2^{0,5+}$ or $\text{OH}^{0,5-}$ groups at the surface. Examples of probable ligand exchange reactions are shown in Figure 2.8.

The adsorption process can be visualized in three planes (Bowden *et al.*, 1980): (1) the charged adsorbent plane, (2) the specific adsorbing plane, and (3) the outside plane of balancing indifferent counterions. Potential determining ions plus ligand exchanged (specifically adsorbed) ions, confer a charge at the surface. Electroneutrality at the charged adsorbing surface is maintained by counterions with a charge equal in magnitude and opposite in sign to the surface charge.

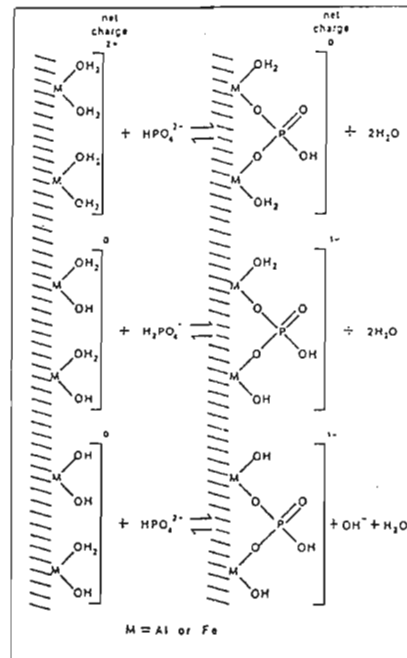


Figure 2.8 Examples of phosphate adsorption mechanisms (after McLaren and Cameron, 1990).

2.2.3 Factors Affecting P Adsorption

Specific adsorption of P is affected by many factors including pH, ionic strength of the background electrolyte and anion competition (Bowden *et al.*, 1980).

Generally, phosphate adsorption by soil and soil components is a maximum in the pH range 2 - 4 (Parfitt, 1978) and it decreases with increasing pH. The effect of increasing pH on adsorption of P by goethite is shown in Figure 3.2. Adsorption decreased from pH 2 to 12 but the decrease is

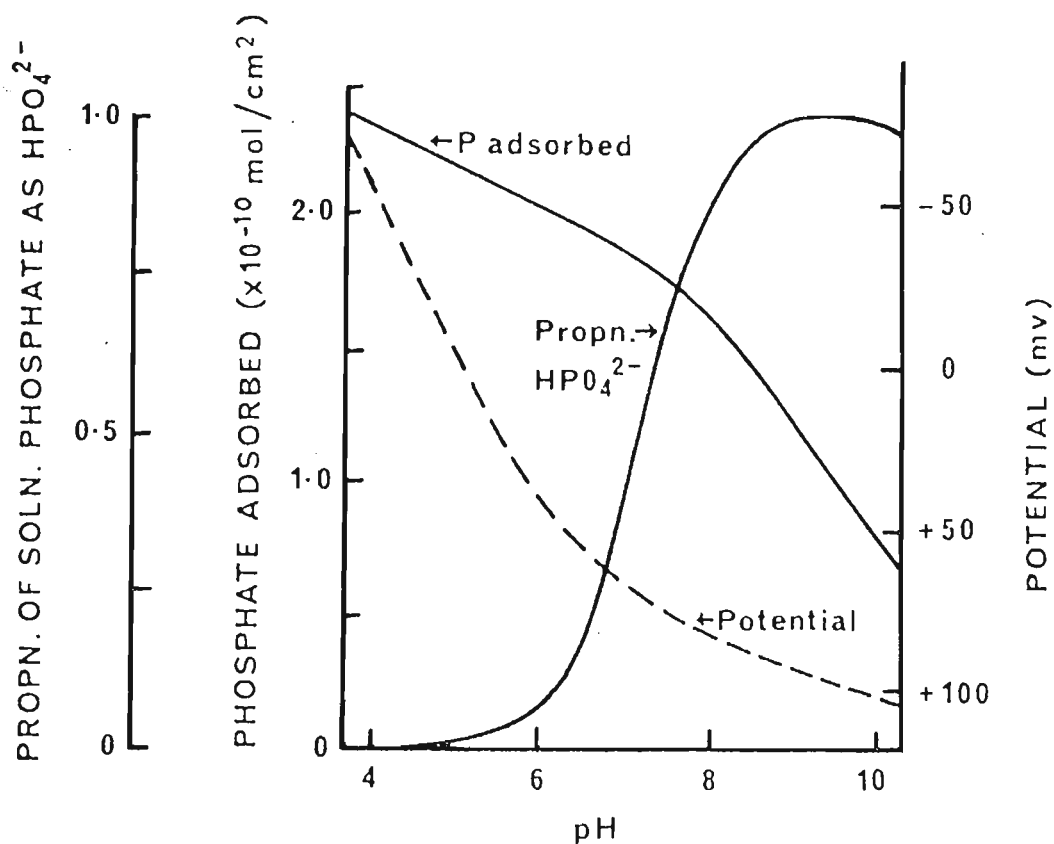


Figure 2.9 Effect of pH on the adsorption of P by goethite at a solution concentration of $200 \mu\text{M}$ together with the electrostatic potential in the plane of adsorption and the proportion of the solution P present as divalent anion (after Bowden *et al.*, 1980).

more rapid above pH 7. As pH is increased, the surface becomes increasingly negatively charged, thereby causing increased electrostatic repulsion and hence a decrease in P adsorption. The concentration of HPO_4^{2-} increases 10-fold over that of H_2PO_4^- when pH is increased from 2 to 7 (Bowden *et al.*, 1980). At approximately pH 7, both ions are present in nearly equal proportions (Figure 2.9). Phosphate is thought to be preferentially adsorbed as HPO_4^{2-} rather than H_2PO_4^- . As a result, P adsorption decreases relatively slowly until about pH 7 is reached. Above pH 7, the increase in concentration of HPO_4^{2-} is progressively slower whereas the decrease in surface potential continues; hence adsorption decreases more sharply.

Both the concentration and cation species of the background electrolyte affect P adsorption through their effect on electrostatic potential in the plane of adsorption (Bowden *et al.*, 1980; Barrow, 1984). Increasing the concentration of electrolyte cations near a negatively charged adsorption surface makes the potential in the plane of adsorption less negative and so phosphate adsorption is increased (Barrow, 1984).

Since divalent cations have greater positive charge than monovalent ones, their presence in the background electrolyte induces a greater effect on P adsorption (Barrow and Shaw, 1980). The relative effect of common cations in increasing P adsorption by soils and soil colloids has been reported (Haynes, 1984) to increase in the order:



If electrolyte cations have a specific affinity for the adsorbing surface then this may induce a further effect on P adsorption. For example, a specific effect of Ca in promoting P adsorption has been reported (Barrow, 1984; Bolan *et al.*, 1988).

Several studies have shown that inorganic anions can compete for P adsorption sites and thus decrease its adsorption. There are two main mechanisms by which anions compete for P adsorption sites. Firstly, the presence of other adsorbed anions physically blocks phosphate from being adsorbed. Secondly, electrostatic competition occurs when an anion is adsorbed onto a surface and makes the surface charge more negative (Bowden *et al.*, 1980). Conditions are therefore less favourable for adsorption of another anion. Ryden *et al.* (1987) showed that, at equivalent concentrations, inorganic anions are adsorbed onto hydrous Fe oxide in the order:

phosphate > arsenate = selenite > silicate > molybdate > sulphate > selenate > chloride = nitrate.

When P was added together with the other anions, sulphate, selenate, chloride and nitrate did not affect P adsorption, whereas the other anions reduced P adsorption in the order: arsenate > selenite > silicate > molybdate. The competitive effects of organic anions of P adsorption are discussed below.

2.2.4 Influence of Organic Matter on P Adsorption

The adsorption of organic compounds such as humic material and organic acids onto soil minerals such as Al and Fe hydrous oxides or other clay minerals occurs and this may decrease subsequent P adsorption (Iyamuremye and Dick, 1996).

2.2.4.1 Humic Material

Adsorption of humic material onto the surfaces of Al and Fe hydrous oxides and soils is well documented (Moshi *et al.*, 1974; Perrott, 1978; Sibanda and Young, 1986). Evans and Russell (1959), for example, showed that FA extracted from a podzol was adsorbed onto the surface of lepidocrite and goethite. Moshi *et al.* (1974) reported that adsorption of organic matter by soils increased the negative charge on surfaces and electrostatic competition resulting in a decrease in adsorption of P. Similarly, Perrott (1978) found that treatment of aluminosilicates with humified clover extracts caused the surface charge to become more negative and P adsorption was consequently decreased. Hajra and Debnath (1985) showed that application of HA to soils decreased Fe-bound P and Al-bound P suggesting the release (desorption) of P adsorbed to Fe and Al oxides. The competitive effect of organic matter on P adsorption is thought to be primarily due to the chelating ability of hydroxyl and carboxyl ligands found on humic material (Reddy *et al.*, 1980; Parfitt, 1980).

Sibanda and Young (1986) studied competition between HA, FA and P on synthetic goethite, gibbsite and two tropical soils. Their results showed that HA and FA competed strongly with P for adsorption sites on both soils (Figure 2.10) and synthetic oxides. It was shown that although the presence of HA and FA on oxide surfaces was able to restrict the adsorption of P, when P adsorption was increased, there was virtually no release of either HA or FA into solution. Sibanda and Young (1986) suggested that the reason for this lies in the nature of the adsorption mechanisms of both P and humus. That is, the competitive ability of HA for P does not lie exclusively in the occupation of adsorption sites by humic carboxyl groups. It may be that the unfavourable electrostatic field generated around the adsorbed humic molecule is more important

in preventing P adsorption. In addition, part of the adsorption mechanism for HA will be physical in nature (e.g. Van der Waals forces) and this will not be involved in competition with P.

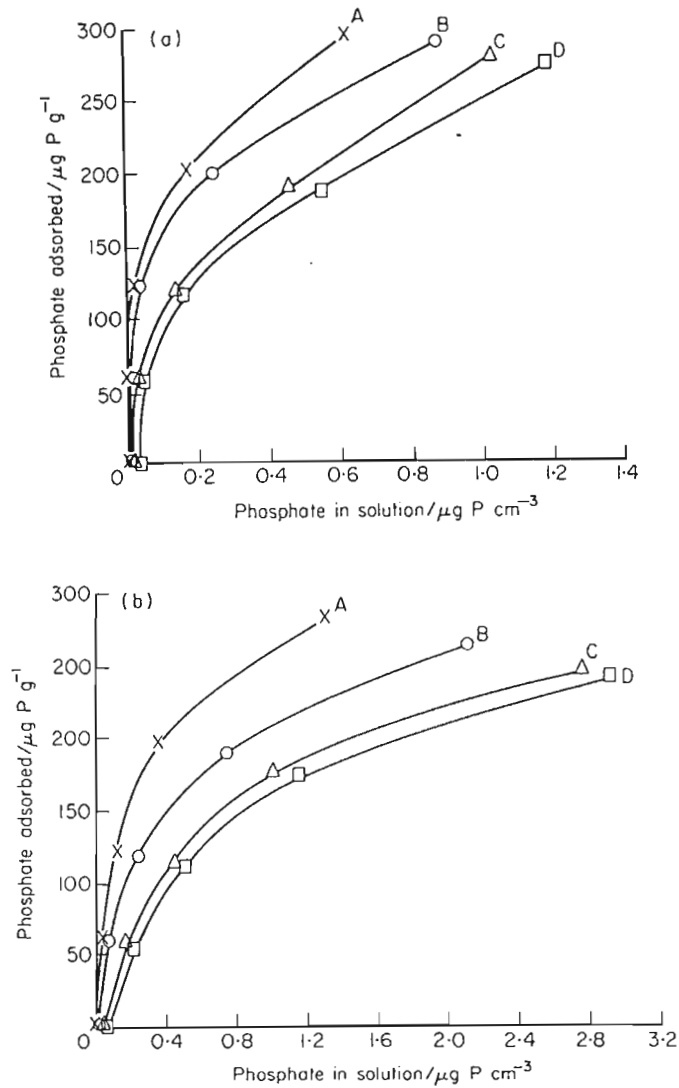


Figure 2.10 Phosphate adsorption isotherms for two soils as affected by addition of four levels of humic acid. Soils are (a) Salisbury (Harare) 5G2 series and (b) Marandellas (Marondera) 752. Four levels of humic acid are compared: A, 0; B, 0.4 %; C, 1.6 %; D, 3.0 % (after Sibanda and Young, 1986).

The effect of organic matter on P adsorption is not, however, clear cut. Yuan (1980), for example found that organic matter pretreatment had no effect on P adsorption in one soil, a slight effect in another and a large effect in a third soil they studied. Borggaard *et al.* (1990) found that removal of organic matter did not alter P adsorption by soils and concluded that organic matter did not compete with P for adsorption sites in the soils they studied. Appelt *et al.* (1975) reported that HA and FA did not decrease P sorption on a volcanic soils. They concluded that new organic matter-hydroxy-Al complexes were formed and these constituted new P adsorption sites.

2.2.4.2 Organic Acids

Organic acids such as citrate, malate and oxalate can compete with P for adsorption sites (Struthers and Sieling, 1950; Hue, 1992; Violante and Gianfreda, 1993). Nagarajah *et al.* (1970), for example, in a study of the effect of a wide range of organic anions on P adsorption by kaolinite and metal surfaces, found that organic anions reduced P adsorption in the order: citrate = oxalate > malonate = tartrate > acetate = succinate. Polygalacturonate was also observed to markedly reduce P adsorption. Similarly, Earl *et al.* (1979) found that in both soils and synthetic Al and Fe oxides, citrate caused a larger reduction in P adsorption than did tartrate, whereas acetate had little or no effect. Evans (1985) showed that addition of phytic acid to soil strongly reduced P sorption whereas cinnamic and benzoic acid had no effect on P adsorption. The competitive effect of organic acids on P adsorption is generally believed to occur because organic acids are adsorbed to Al and Fe oxides by ligand exchange (see Figure 2.7).

Violante and Gianfreda (1993) have studied the competition between orthophosphate ions and oxalate and showed that on a hydroxy-Al/montmorillonite (chlorite-like) complex, more

orthophosphate than oxalate was sorbed in a system containing a constant amount of orthophosphate even when the initial concentration of oxalate was higher than that of orthophosphate. Of the sites on the clay mineral that were available for adsorption by both anions, 51 to 79 % of the sites were occupied by orthophosphates. Many sites were highly specific for orthophosphate, whereas others were common to both oxalate and orthophosphate; these sites still had greater affinity for orthophosphate than oxalate. Yet other sites were specific for oxalate. Maximum reduction of adsorption of orthophosphate occurred when oxalate was added before orthophosphate addition and conversely, the minimum occurred when orthophosphate was added first.

2.2.5 Effect of Additions of Organic Residues on Soil P Availability

A number of studies have demonstrated that addition of organic amendments to soils can significantly increase the availability of P to plants and decrease the P adsorption capacity of soils (Hue *et al.*, 1994; Hue, 1990). The reduced P adsorption and increased P availability following applications of organic amendments to soils are thought to be the cumulative result of several mechanisms (Hue, 1990; Iyamuremye and Dick, 1996).

Firstly, organic materials generally contain significant quantities of P. Some of this P is mineralized during decomposition of the material and orthophosphate is released into soil solution. The released phosphate will then be rapidly adsorbed to soil surfaces thus increasing the proportion of adsorption sites occupied by phosphate. As a result the phosphate adsorption capacity of the soil is decreased in relation to subsequently added P. Several workers have suggested that this is the main mechanism by which addition of organic residues decrease the P

adsorption capacity of soils (Singh and Jones, 1976; Reddy *et al.*, 1980; Iyamuremye and Dick, 1996). For example, Singh and Jones (1976) observed that all organic residues they used (lucerne, barley, beans, corn, poultry manure, sawdust and wheat) returned P to the soil through mineralization and organic materials that contained more than 0.31% P decreased the amount of P sorbed by the soil and increased the level of P in solution. Similarly, Iyamuremye *et al.* (1996) showed that P-rich organic amendments (animal manure and lucerne residues) decreased subsequent P adsorption by soils. By contrast, wheat straw, which had a very low P content, had a much lesser effect on subsequent P adsorption.

As discussed above (Section 2.2.4) organic acids and humic substances produced during decomposition of the organic materials will also be adsorbed onto soil surfaces. This will block potential phosphate adsorption sites and tend to increase the availability of P originating from the organic materials and P subsequently added as in organic fertilizers. Indeed, several workers have suggested that the release of soluble humic material and/or organic acids from decomposing organic residues and manures contributes greatly to the decrease in P adsorption capacity and increased P availability that occurs in soils following their application (Easterwood and Sartain, 1990; Hue, 1991, 1992; Iyamuremye and Dick, 1996).

The increased pH that often accompanies application of organic residues to soils will also influence P adsorption. An increase in pH will confer a greater negative charge on adsorption surfaces and thus tend to reduce P adsorption. Thus, a decrease in P adsorption may be partially attributable to the increased soil pH (Mnkeni and MacKenzie, 1985; Iyamuremye *et al.*, 1996).

Other mechanisms may also be operative. For example, in acid soils, high levels of soluble Al (and Fe) can play a significant role in controlling phosphate concentrations in soil solution. Soluble P may precipitate as insoluble Al and Fe phosphates. Complexation of Al^{3+} (and Fe^{3+}) in soil solution by various organic anions lowers the activities of these free cations in soil solution. This in turn would tend to increase P availability (Iyamuremye and Dick, 1996). Thus far, there is little evidence that this mechanism has a significant effect on P solubility in residue-amended soils. Iyamuremye *et al.* (1996) considered it of minor importance even in soils of pH less than 5.

2.3 CONCLUSIONS

An understanding of the chemistry of Al is central to the understanding of the fertility of acid soils. Since phytotoxic concentrations of soluble and exchangeable Al often limit crop production in such soils, lime requirements are often based on estimates of exchangeable Al. The most phytotoxic forms of Al in soil solution are the monomeric species [Al^{3+} , AlOH^{2+} and $\text{Al}(\text{OH})_2^+$] with Al^{3+} thought to be the most toxic.

Both soluble humic substances and organic acids such as citrate (produced during decomposition of organic residues) can strongly complex with monomeric Al in soil solution. The toxicity of solution Al is greatly reduced when it is complexed with such organic compounds. Applications of large amounts of solid organic wastes to acid soils can also reduce exchangeable Al levels. Aluminium becomes strongly complexed to the solid-phase organic material. In addition, when organic residues decompose in the soil, the soil pH often rises and this results in the decline in exchangeable Al as hydroxy-Al species precipitates out. As a consequence of the above effects, a number of workers have observed that additions of organic residues to soils can result in a reduction in Al toxicity and greatly increased crop growth in acid soils.

Highly weathered acid soils have a mineralogy dominated by oxides and hydrous oxides of Al and Fe. Phosphate is strongly adsorbed (by ligand exchange) to the surfaces of these oxides and when it is added to such soils it is rapidly adsorbed and thus not readily available to plants. Management of P fertility is therefore a critical issue and P deficiencies in crops are common.

Both soluble humic material and organic acids can be adsorbed to the surfaces of Al and Fe oxides principally by ligand exchange. The adsorption of such compounds blocks potential P adsorption sites and thus increases the availability of subsequently added fertilizer P. In addition, organic residues often contain significant amounts of P which are released as orthophosphate during residue decomposition. This residue-derived P becomes adsorbed so that proportionately less of subsequently added fertilizer P is adsorbed and it is therefore more plant available. As a result, a number of workers have observed that additions of organic residues to P deficient soils has increased the availability of subsequently added fertilizer P and improved crop yields.

Applications of organic residues to soil in order to minimize the need for lime and fertilizer P would be of considerable benefit to small scale farmers. Indeed, the recycling of crop residues, composted wastes and animal manures should be a central component of soil fertility management for such farmers. Organic residues are readily available to resource-poor farmers whilst lime and fertilizer are expensive commodities.

CHAPTER 3

EFFECTS OF ADDITIONS OF ORGANIC WASTE MATERIALS TO AN ACID SOIL ON SOIL SOLUTION AND EXCHANGEABLE Al, P AVAILABILITY AND PLANT RESPONSE.

3.1 Introduction

Aluminium phytotoxicity together with deficiencies of nutrients such as Ca, Mg, K and P are major causes of acid-induced soil infertility. Conventionally, soil acidity is corrected by large applications of calcitic or dolomitic lime. However, in many developing countries, where resource-poor farmers carry out semi-subsistence agriculture, the unavailability and/or high cost of lime effectively prevents its use. Under such conditions, alternative means of managing soil acidity need to be developed.

Several experiments have shown that additions of suitable organic materials to soils can be effective substitutes for liming (Noble *et al.*, 1996; Yan *et al.*, 1996; Pocknee and Sumner, 1997; Tang *et al.*, 1999) and the use of such materials is likely to be a cost-effective alternative for small-scale farmers. The increase in pH can be highly significant. Kretzshmar *et al.* (1991) for example, showed that incubation of pearl millet straw with soil for 14 days increased soil pH from 4.54 to 6.15 whilst in a longer-term field experiment a less pronounced but significant increase in soil pH was recorded. An increase in soil pH is only one way in which additions of organic residues to acid soils are thought to reduce the phytotoxicity of Al.

Another important factor is believed to be the formation of organic-Al complexes in soil

solution since this lowers the concentration of phytotoxic Al^{3+} in solution (Kretzchmar *et al.*, 1991; Bessho and Bell, 1992).

Additions of organic residues will result in the addition of nutrients to the soil which are not present in significant quantities in lime (e.g. K, P and micronutrients). Thus, nutrient availability will be increased. In particular, enhanced P availability following the addition of organic residues to soils has been noted and attributed to a number of factors (Iyamuremye and Dick, 1996). These include a decreased P adsorption capacity of the soil due to an increased pH or blockage of adsorption sites on soil colloids by organic molecules and/or inorganic P released during residue decomposition (Singh and Jones, 1976; Easterwood and Sartain, 1990; Iyamuremye *et al.*, 1996).

The purpose of this study was to investigate the effects of additions of some commonly-available organic residues to an acid, P-deficient soil (typical of those used by small-scale farmers in the KwaZulu-Natal midlands) on soil pH, exchangeable and soil solution Al, P availability and plant response.

3.2 Materials and Methods

Soil (0 - 15cm) was collected from a site in the Bergville district of KwaZulu-Natal close to the main entrance to the Royal Natal National Park which is being used by the KwaZulu-Natal Department of Agriculture for small-scale farming trials. The soil was a dystrophic Hutton form (Rhodic Ferralsol, FAO). The soil had a $pH_{(water)}$ of 4.2, organic C content of $22g\ kg^{-1}$ and exchangeable Al was $13\ mmol_c\ kg^{-1}$. The soil has a clay content of about 42% and its

mineralogy is dominated by kaolinite plus halloysite and there are also appreciable amounts of crystalline sesquioxides, gibbsite and interlayered chlorite.

The organic amendments used were ground (<0.5 mm) veld grass (mainly *Digitaria sanguinalis* L. and *Tristachya leucothrix* L.), sieved (<2 mm) compost made from household and garden wastes, sieved (<2 mm) filter cake obtained from a commercial sugar-mill and sieved (<2 mm) layer poultry manure obtained from a commercial egg producer. The total N content of the amendments was measured by kjeldahl digestion with colorimetric determination of liberated ammonium (Foster, 1995) and organic C content was measured by the Walkley and Black dichromate wet oxidation procedure (Blakemore *et al.*, 1972). Samples were digested in nitric and perchloric acids and the P content was measured by the molybdenum blue method (John, 1970). The K, Ca, Mg, Na, Fe, Mn, Zn, Cu and Al contents of the digests were measured by atomic absorption spectrophotometry. The pH of organic amendments was measured in suspensions of 1.5 g sample in 30 ml of 2 mM CaCl₂ (Wong *et al.*, 1998a). Their proton consumption capacity was measured by slowly titrating them from their natural pH values down to pH 4.0 with 0.05 M H₂SO₄ (Wong *et al.*, 1998b). The CaCO₃ content of amendments was measured by the titrimetric method of Bundy and Bremner (1972). Ash alkalinity of amendments was measured as described by Slattery *et al.* (1991).

Soil was air-dried and sieved (<2 mm). The incubation experiment had five sources of organic amendment [control; grass residue, (G. residue); household compost, (H. compost); filter cake, (F. cake); and poultry manure, (P. manure)] and these were added to the soil at two rates [10 (R₁) and 20 (R₂) mg g⁻¹] which are equivalent to about 10 and 20 Mg ha⁻¹ respectively. Amendments were thoroughly mixed with the soil samples (1 kg) and placed in 2 litre plastic

containers (fitted with lids), rewetted to 70% of water holding capacity and incubated at 25°C in a controlled temperature room. Six samples of each treatment were made and three replications were removed after four weeks incubation and the remainder after 8 weeks. Samples were arranged in a randomized block design and containers were opened each week to allow for aeration and water was added where necessary to maintain the soil at the predetermined soil water content.

Forty eight hours prior to sampling for chemical analysis, soils were wetted to 100% water holding capacity. Soil solution was extracted by centrifugation (Elkhatib *et al.*, 1987). Monomeric Al (Al_{Mono}) in soil solution was measured in the filtrate (0.05 μm millipore filter extract) by the pyrocatechol violet (PCV) method of Kerven *et al.* (1989) and total soluble Al (Al_{T}) was measured by a modified PCV method using a LaCl_3 -Fe reagent after passing the solution through a 0.22 μm filter (Menziez *et al.*, 1992).

A subsample of soil was air-dried and sieved (<2 mm) and used for other chemical analyses. Soil pH was measured in a 1:2.5 soil : solution ratio (in both water and 1M KCl) using a glass electrode. Soluble salts were measured with a conductivity meter using a 1:5 soil : water ratio (Blakemore *et al.*, 1972). Exchangeable cations were extracted with 1M ammonium acetate (1:50 soil : extractant ratio for two hours) and the filtered extract was analysed for K, Ca, Mg and Na by atomic absorption spectrophotometry. Exchangeable Al was extracted with 1M KCl (1:2.5 soil:extractant ratio for 1h) and Al was measured by atomic absorption spectrophotometry. Soil Al was also fractionated sequentially with (a) 1M KCl, (b) 0.01M CuCl_2 , and (c) 1M ammonium acetate (Soon, 1993) after eight weeks incubation. These extracts were designated as exchangeable, organically-bound and sorbed Al respectively.

Available P was extracted from soils using 0.5 M NaHCO₃ (Olsen *et al.*, 1954) and P in the extract was analysed using the molybdenum blue method (John, 1970). Adsorption of P by soils treated with the high rate (R₂) of amendments after eight weeks incubation was determined by weighing duplicate samples of soil (1g) into centrifuge tubes together with 15 ml of 0.02 M CaCl₂ solution containing a few drops of toluene to limit microbial growth. After the addition of an appropriate quantity of P (as KH₂PO₄ solution) the solutions were made up to 30 ml with distilled water to give a final CaCl₂ concentration of 0.01 M. The tubes were shaken for 72 h at 20°C and were then centrifuged. The P concentration in the filtered supernatant solution was analysed by the molybdenum blue method. The amount of P adsorbed was calculated as the difference between P added and that remaining in the supernatant solution.

A subsidiary experiment was set up to determine the effect of additions of the organic amendments to the acid soil on plant growth. The four sources of organic amendments were added to 1 kg samples of air-dried soil (six replicates of each treatment) at a rate of 20 mg g⁻¹ (equivalent to 20 Mg ha⁻¹) and samples were placed in plastic pots. Basal dressings of N, K, Mg, Mn, Mo, Zn, Cu and B at rates equivalent to 200, 200, 100, 25, 0.28, 15, 15 and 10 kg ha⁻¹ respectively were applied to pots (no lime or P was added) and soils were wetted to 70% of water holding capacity. Pots (three replicates of each treatment) were planted with six maize seeds (*Zea mays* L. cv. Silver King) and later thinned to three per pot. Pots were arranged in a randomized complete block design and were maintained in a glasshouse with an air temperature held between 20 and 25°C. Plants were grown for 6 weeks. Herbage was harvested, dried at 70°C, weighed and ground.

Immediately after harvest of the planted replicates, soil solution was extracted from the three unplanted replicates and Al_T and Al_{Mono} were analysed as previously described. The pH and electrical conductivity of soil solutions was also measured. A subsample of soil was air-dried, sieved (<2 mm) and analysed for Olsen-extractable P, exchangeable Ca, Mg, K, Na, Al, $pH_{(water)}$ and $pH_{(KCl)}$ as outlined above. Ground plant samples were analysed for N, P, K, Ca, Mg, Na, Cu, Zn, Fe, Mn and Al as described previously for the organic amendments.

Both soil and plant data were analysed by analysis of variance using the Genstat V package.

3.3 Results

The elemental content of the organic amendments is shown in Table 3.1 and 3.2. Poultry manure was notably high in N, P, K, Ca and Na while filter cake had a relatively high Ca, Fe and Al content. The P content of poultry manure was approximately double that of filter cake and household compost which were in turn nearly double that of grass residue. In comparison with the other amendments, filter cake had a relatively low N content. For properties related to the effects of the organic amendments on pH following their addition to soils (i.e. proton consumption capacity, CaCO₃ content and ash alkalinity) a clear trend was evident and followed the order: poultry manure > filter cake > household compost > grass residues.

Table 3.1 Nutrient content of organic amendments used in the study.

Organic Material	P	K	Ca	Mg	Na	Fe	Mn	Zn	Cu	Al
	(g kg ⁻¹)					(mg kg ⁻¹)				
Household compost	11	14	32	3.9	1.0	0.8	341	24	38	131
Grass residues	5.8	14	7.1	2.1	1.3	0.4	99	24	8.1	27
Filter cake	11	8.5	60	5.5	0.6	2.5	335	25	28	274
Poultry manure	21	20	77	5.7	2.6	0.3	108	26	47	121

Soil pH_(water) generally followed the order: filter cake > poultry manure > household compost > grass residues > control (Figure 3.1). Changes in pH_(KCl) induced by organic amendments (Figure 3.1) were less marked than those measured in water and generally followed the order: poultry manure > filter cake > household compost > grass residues > control. After both four and eight weeks incubation, soil pH was increased by applications of organic amendments and the higher rate of addition generally caused a greater increase. Whilst soil pH_(water) was lower for poultry manure than filter cake, the reverse was generally the case for pH (KCl).

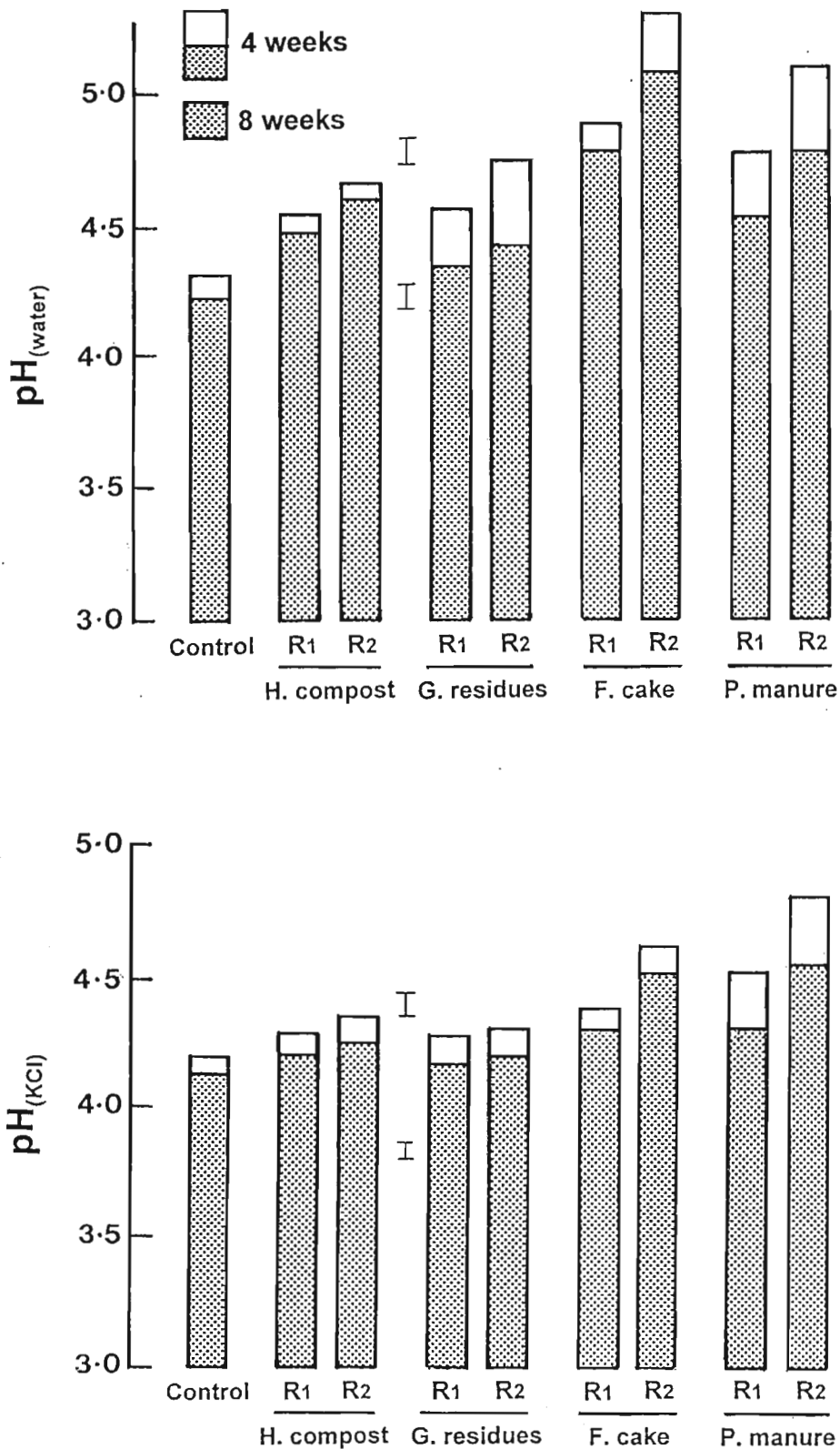


Figure 3.1 Effect of incubation of organic residues at two rates with an acid soil for 4 and 8 weeks on soil pH measured in water and 1M KCl. Rates of residue addition were R₁ = 10 mg g⁻¹ R₂ = 20 mg g⁻¹. Organic residues used were household compost (H. compost), grass residues (G. residues), filter cake (F. cake) and poultry manure (P. manure). LSD (P ≤ 0.05) shown at the two sampling times.

Extractable soluble salts, as measured by the electrical conductivity in 1:5 soil : water extracts, were increased by additions of all the amendments (Figure 3.2) and were notably high for the poultry manure treatments. Electrical conductivity was higher after eight than four weeks incubation.

Exchangeable Al was generally decreased by additions of amendments and this decrease was greater at the higher rate of addition (Figure 3.2). Exchangeable Al followed the order : poultry manure < filter cake < household compost < grass residues < control and was greater after eight than four weeks incubation.

Table 3.2 Some selected chemical properties of organic amendments used in the study.

Organic Material	Organic C ----- (g kg ⁻¹)-----	Total N	pH (CaCl ₂)	Proton Consumption capacity (cmol _c kg ⁻¹)	CaCO ₃ Content (%)	Ash Alkalinity (cmol _c kg ⁻¹)
Household compost	231	37.3	6.7	57	1.5	137
Grass residues	669	40.3	5.8	23	-	58
Filter cake	103	12.1	8.2	195	11.9	235
Poultry manure	239	62.6	7.8	280	25.0	375

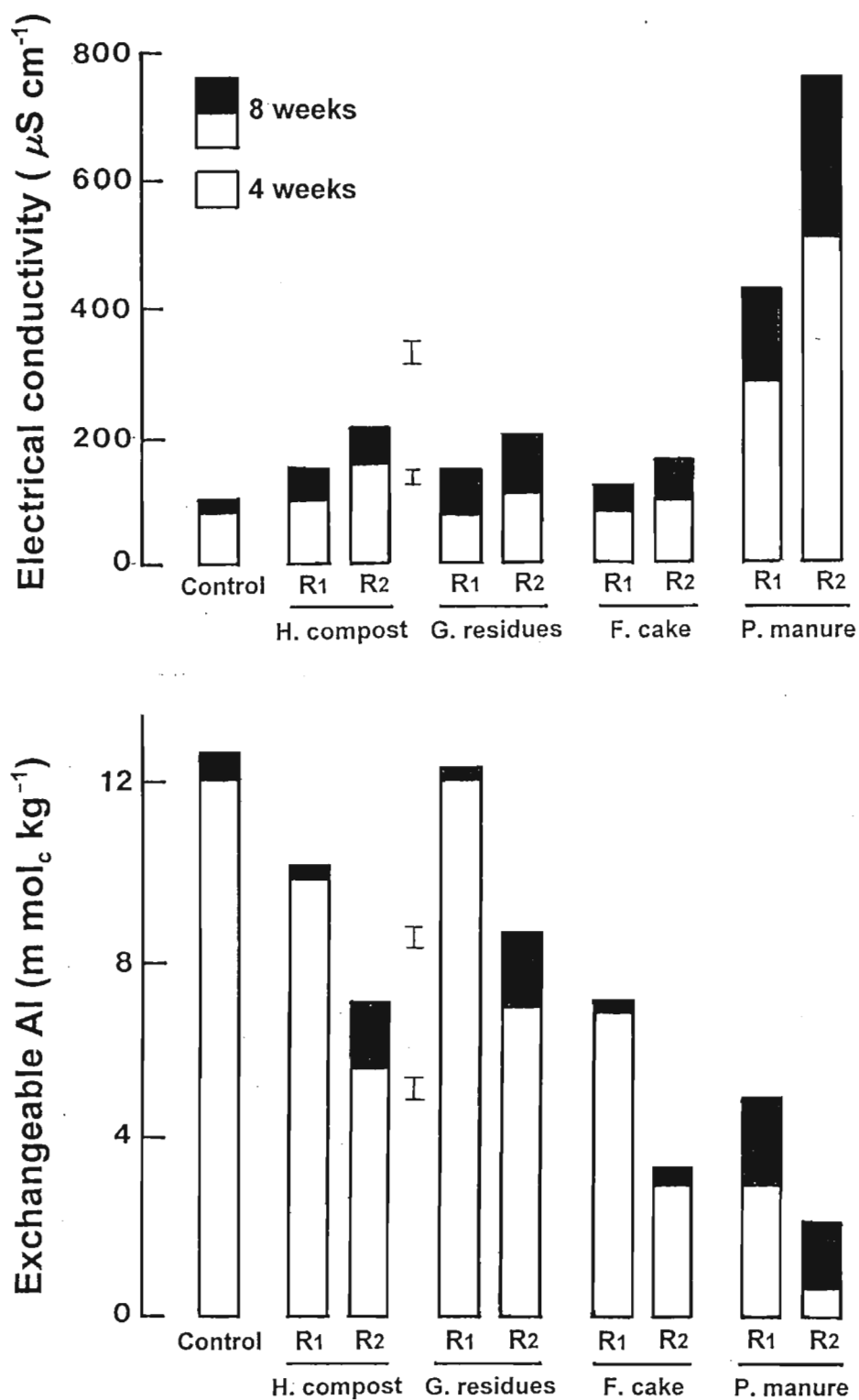


Figure 3.2 Effect of incubation of organic residues at two rates with an acid soil for 4 and 8 weeks on electrical conductivity in a 1:5 soil : water extract and exchangeable Al. For explanation of terms, see Figure 3.1.

The Al fractionation procedure showed that after eight weeks incubation, additions of household compost, filter cake and poultry manure tended to increase concentrations of organically bound (CuCl_2 extractable) Al but had no effect on quantities of sorbed amorphous (ammonium acetate-extractable) Al (Table 3.3).

Table 3.3 Sequential fractionation of soil Al from an acid soil as affected by incubation with organic residues for 8 weeks.

Treatment	Al fraction ($\text{mmol}_c \text{ kg}^{-1}$)		
	Potassium chloride	Copper chloride	Ammonium acetate
Control	13	27	2.5
Household compost	7.0	33	2.6
Grass residues	7.4	27	2.6
Filter cake	6.6	30	2.5
Poultry manure	3.1	33	2.6
LSD ($P \leq 0.05$)	1.3	2.8	0.31

After four weeks incubation, Al_T was decreased by additions of all amendments and the higher rate of addition had a greater effect (Figure 3.3). At both sampling times, filter cake had a very marked effect on decreasing Al_T , and to a lesser extent Al_{Mono} compared with the control. For the other amendments, Al_{Mono} either remained unaffected or was, in fact, increased compared with the control. After eight weeks Al_T was reasonably similar to control for the household compost and poultry manure amendments at the low rate and for grass residues at both rates of addition. The above trends are reflected in the proportion

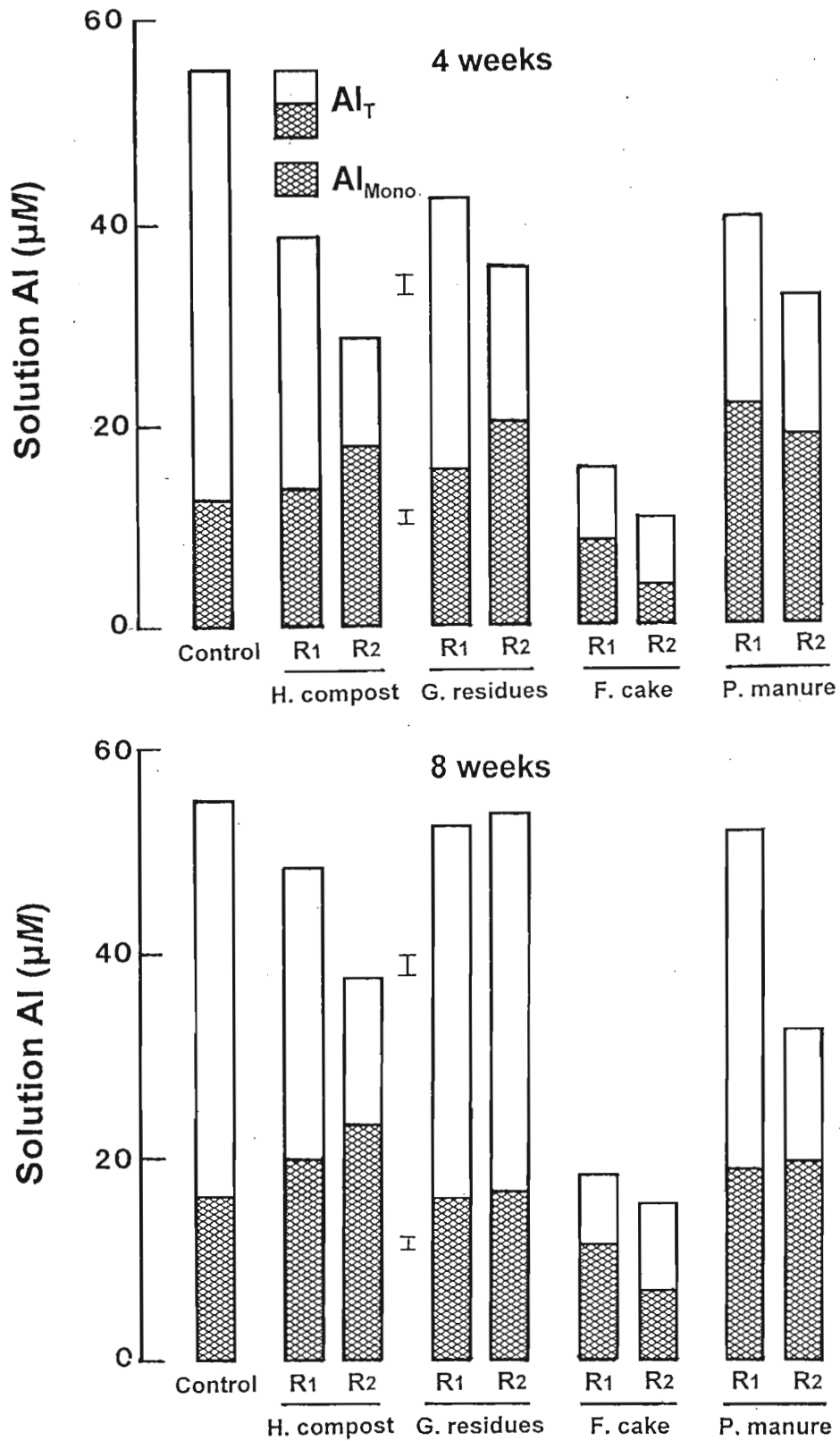


Figure 3.3 Effect of incubation of organic residues at two rates with an acid soil for 4 and 8 weeks on concentrations of total soluble (Al_T) and monomeric (Al_{Mono}) Al in soil solution. For explanation of terms, see Figure 3.1.

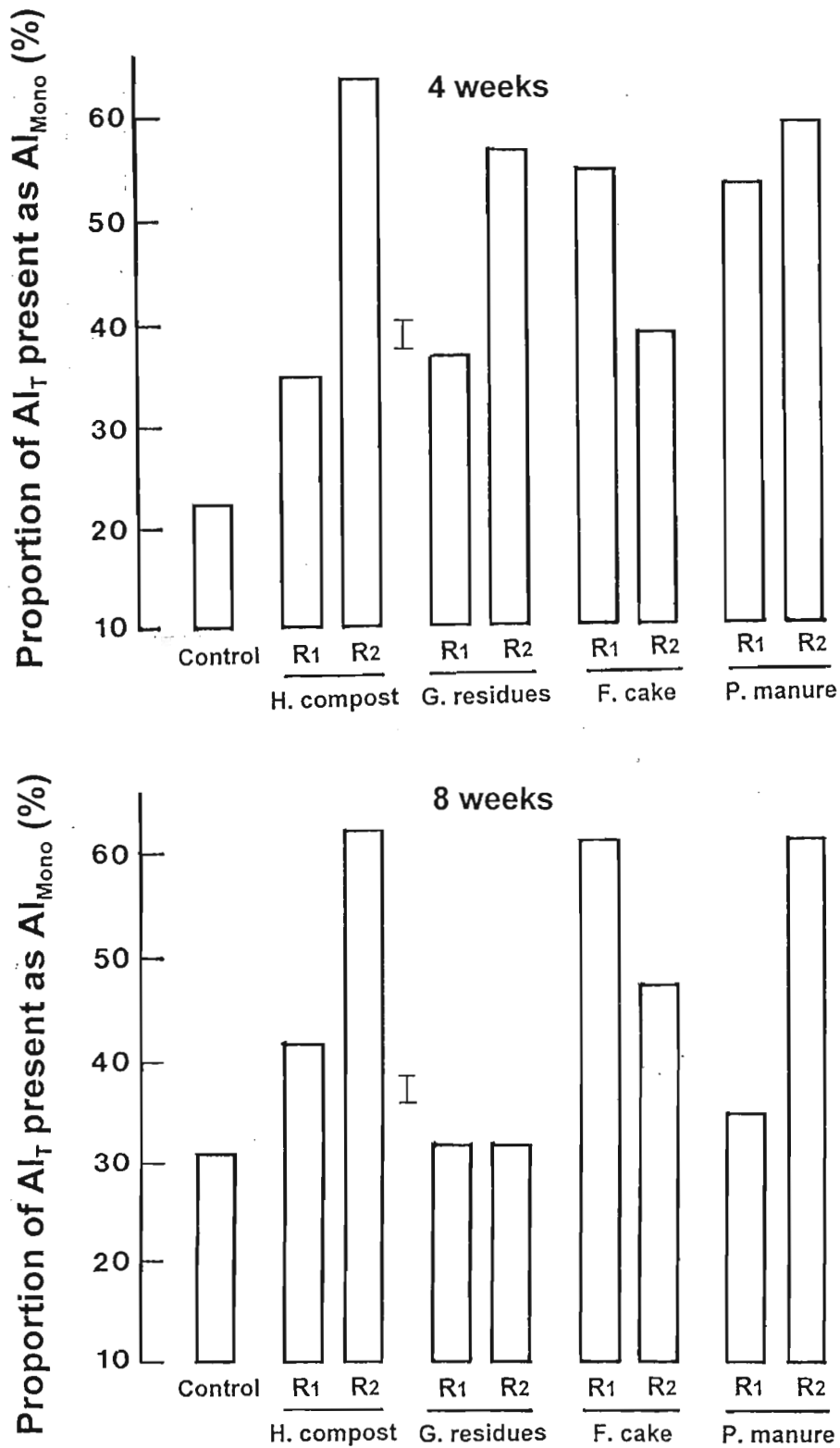


Figure 3.4 Effect of incubation of organic residues at two rates with an acid soil for 4 and 8 weeks on the proportion of total soluble Al (Al_T) in soil solution present in monomeric (Al_{Mono}) form. For explanation of terms, see Figure 3.1.

of A_T present as Al_{Mono} (Figure 3.4) which showed that after four weeks incubation all the amended treatments had higher values than the control and even after eight weeks none had values less than the control.

Additions of amendments increased concentrations of exchangeable Ca and Mg with the effect being most pronounced for poultry manure at the higher rate (Figure 3.5). For exchangeable Ca the order was: poultry manure > filter cake > household compost > grass residues > control. For exchangeable Mg the order was: poultry manure > filter cake = household compost > grass residues > control. Concentrations of exchangeable Ca and Mg were generally higher at eight than four weeks incubation for amended treatments, except for grass residues (Figure 3.5).

Concentrations of exchangeable K and Na were similar after four and eight weeks incubation and only data for eight weeks incubation is shown in Figure 3.6. Concentrations of exchangeable K were also increased by additions of amendments and followed the order: poultry manure > grass residues \geq household compost > filter cake > control (Figure 3.6). Additions of poultry manure increased exchangeable Na concentrations markedly (Figure 3.6).

Additions of amendments increased concentrations of extractable P in the order: poultry manure > filter cake = household compost > grass residues > control (Figure 3.7). For the control and grass residues treatments at the lower rate, concentrations of extractable P were lower after eight than four weeks incubation. By contrast, for the other treatments, concentrations of extractable P increased between four and eight weeks incubation.

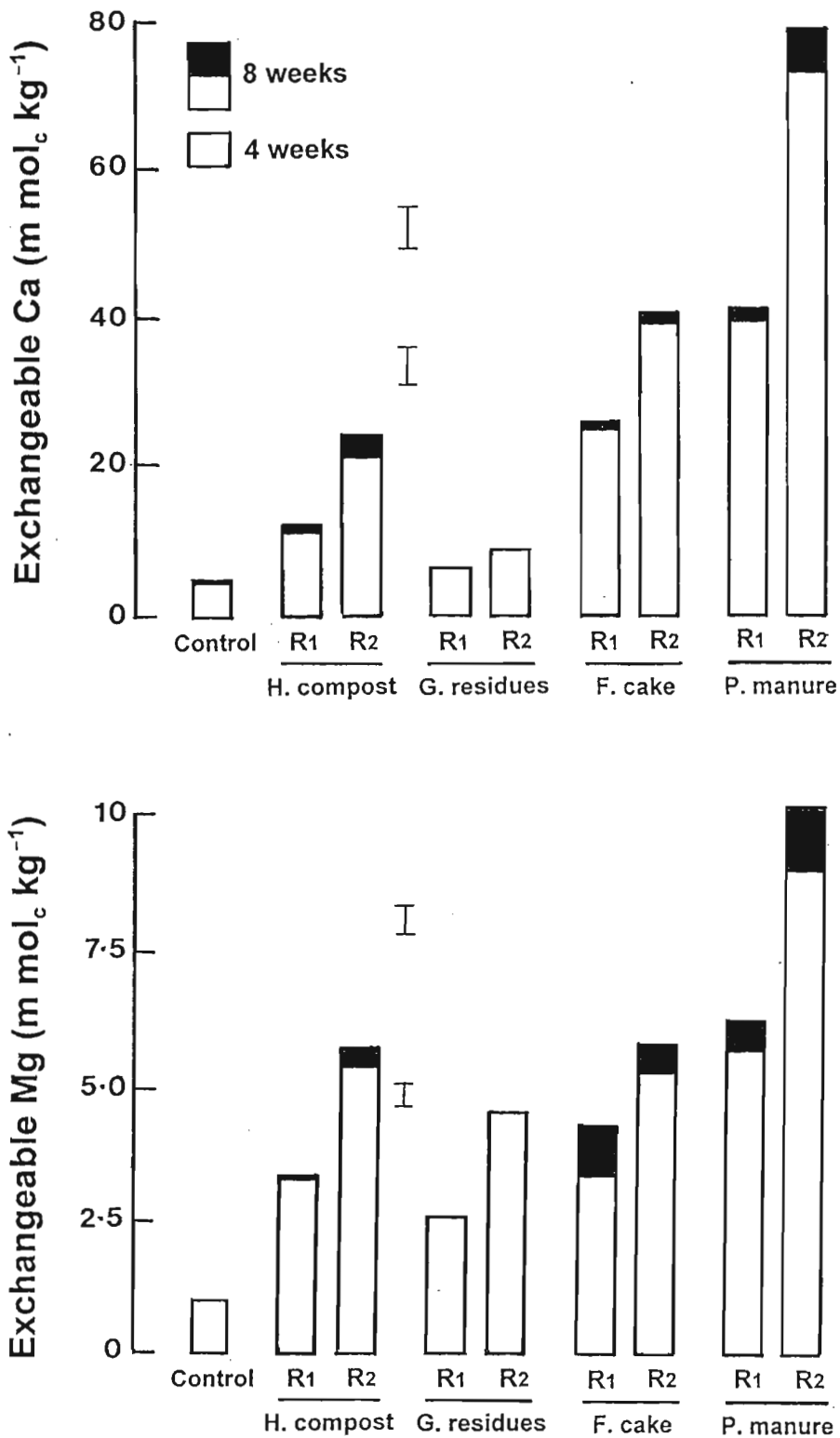


Figure 3.5 Effect of incubation of organic residues at two rates with an acid soil for 4 and 8 weeks on concentrations of exchangeable Ca and Mg. For explanation of terms, see Figure 3.1.

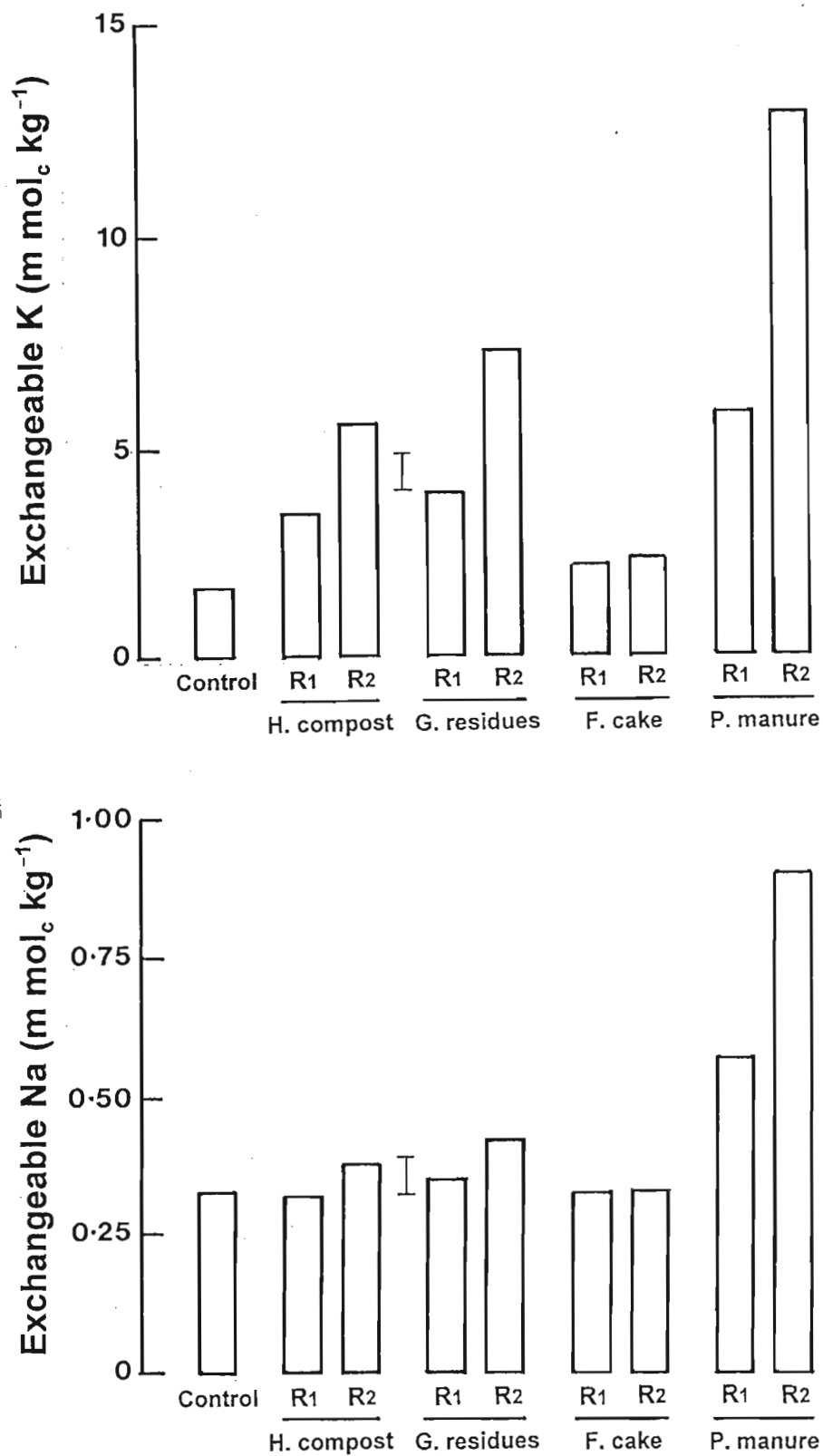


Figure 3.6 Effect of incubation of organic residues at two rates with an acid soil for eight weeks on concentrations of exchangeable K and Na. For explanation of terms, see Figure 3.1.

Construction of P adsorption isotherms after eight weeks incubation showed that additions of all amendments at the high rate (R_2) reduced the P-adsorption capacity of the soil in the order: poultry manure > household compost > filter cake \geq grass residues > control (Figure 3.8).

Results of analysis of soil solutions from the subsidiary experiment after 6 weeks incubation are shown in Figure 3.9. Solution pH was significantly increased by additions of all amendments and the greatest pH increases were recorded for filter cake additions (although pH values were not significantly different from other amended treatments). Electrical conductivity was also increased; particularly so by poultry manure. Additions of household compost and filter cake also tended to increase the electrical conductivity of solutions. The concentration of both Al_T and Al_{Mono} in soil solution were greatly decreased by additions of amendments and the proportion of Al_T present as Al_{Mono} was also decreased (Figure 3.9). As occurred in the main experiment, concentrations of Al_T tended to be reduced more by additions of filter cake than poultry manure even though solution pH tended to be higher with filter cake.

Exchangeable Al decreased with additions of amendments in the order: poultry manure < filter cake < household compost < grass residues < control. Changes in Olsen-extractable P, exchangeable Ca (Figure 3.10) and exchangeable Mg, K and Na (data not shown) showed similar trends to those recorded in the main experiment. The $pH_{(water)}$ was 4.3, 4.5, 4.4, 4.8 and 4.7 respectively for the control, household compost, grass residues, filter cake and poultry manure treatments and $pH_{(KCl)}$ was 4.1, 4.2, 4.1, 4.3 and 4.4 respectively. Maize yields followed the order: poultry manure > filter cake = household compost > grass residues > control (Figure 3.10).

Nutrient concentrations in tops of the maize plants are shown in Table 3.4. It is notable that plants grown in poultry manure treatment had higher concentrations of N, P, K and Ca as well

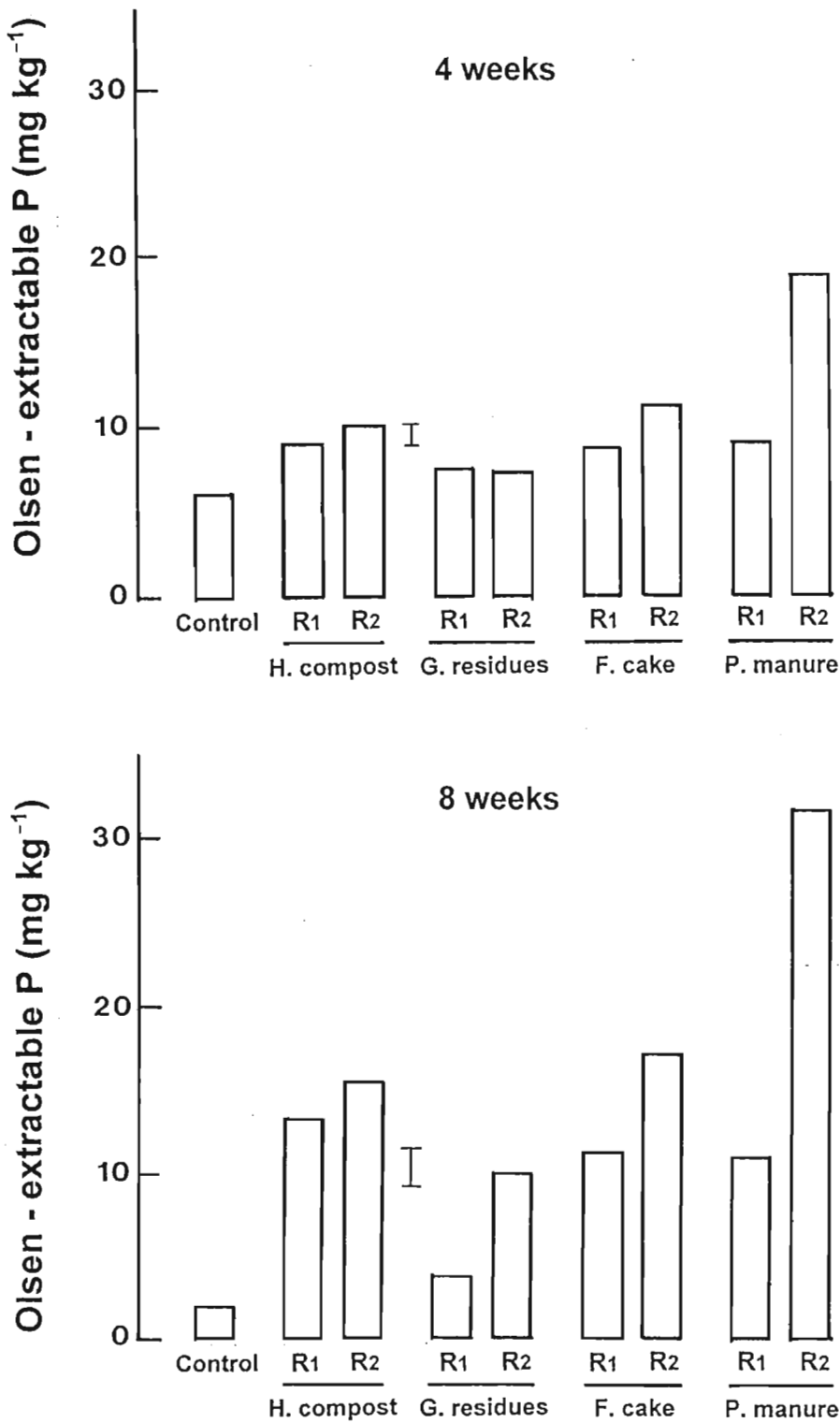


Figure 3.7 Effect of incubation of organic residues at two rates with an acid soil for 4 and 8 weeks on concentrations of Olsen-extractable P. For explanation of terms, see Figure 3.1.

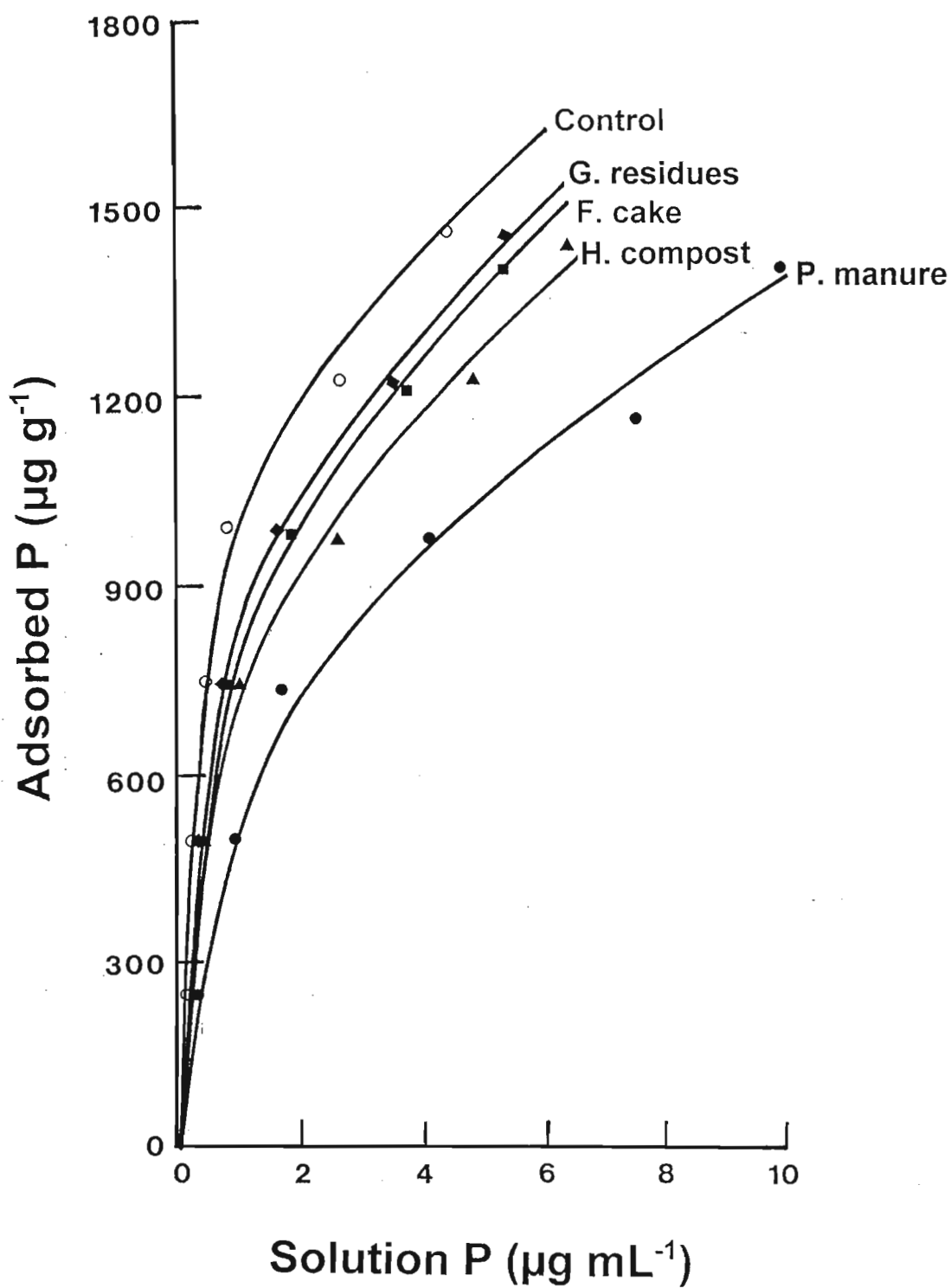


Figure 3.8 Phosphate adsorption isotherms for soils incubated with organic residues at the high rate (R_2) for eight weeks.

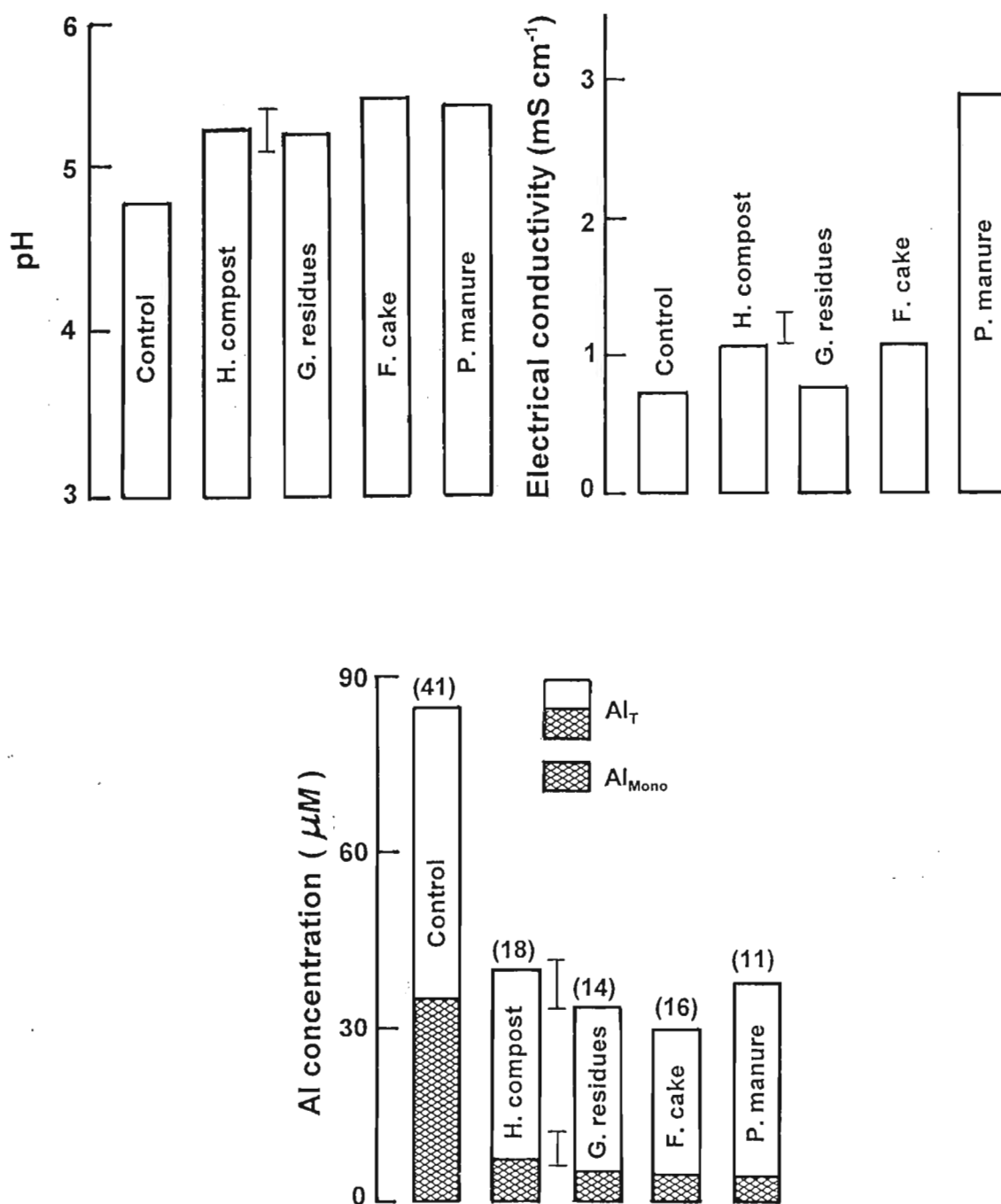


Figure 3.9 Effect of incubation of organic amendments with an acid soil for 6 weeks on the pH, electrical conductivity and concentrations of total soluble (Al_T) and monomeric (Al_{Mono}) Al in soil solution. The proportion of Al_T present as Al_{Mono} is shown in brackets. Organic amendments used were household compost (H. compost), grass residues (G. residues), filter cake (F. cake) and poultry manure (P. manure). LSD ($P < 0.05$) shown.

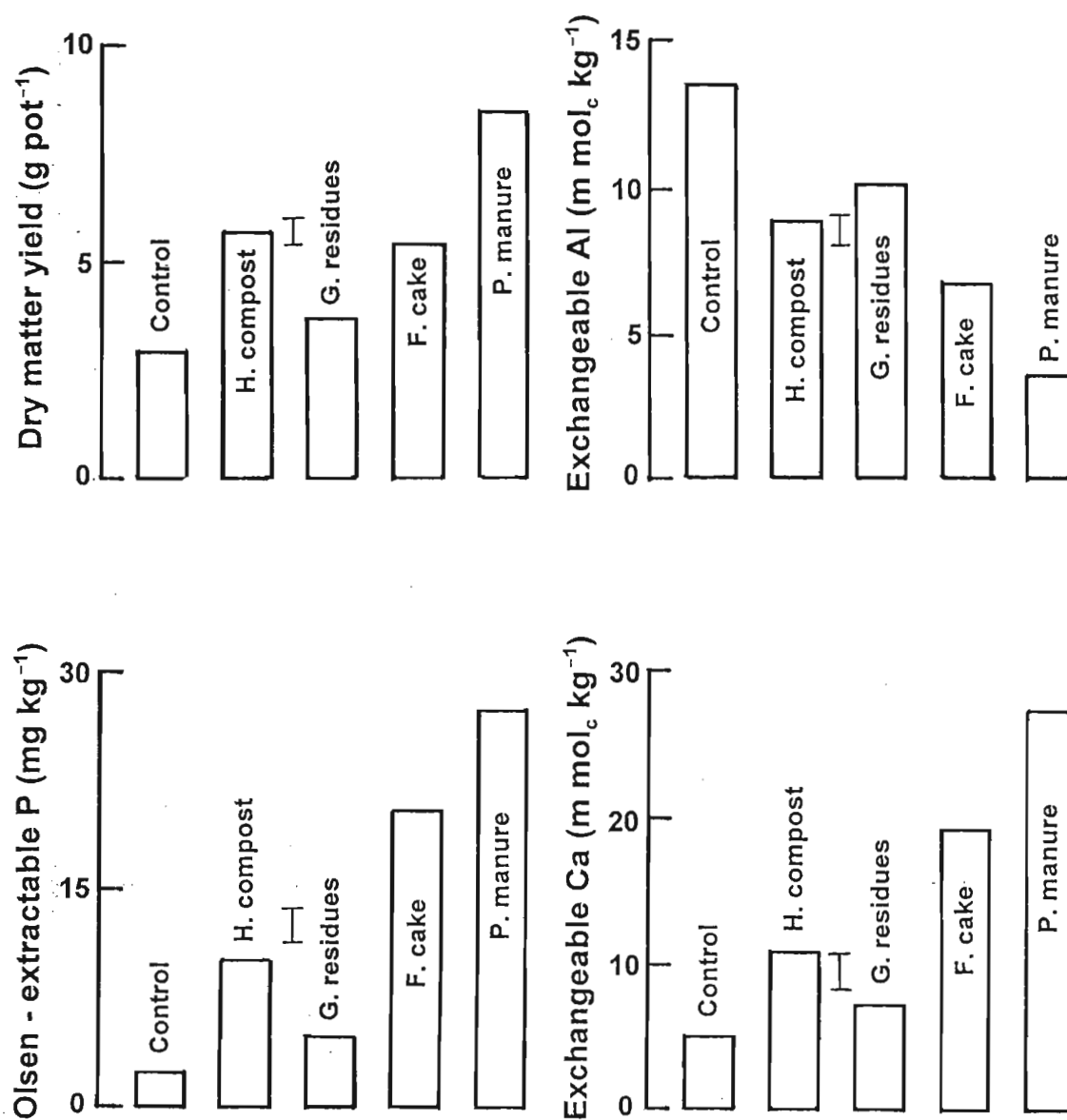


Figure 3.10 Effect of incubation of organic residues with an acid soil for six weeks on dry matter yields of maize and on concentrations of exchangeable Al and Ca and Olsen-extractable P present in the soil. For explanation of the terms, see Figure 3.9.

as higher yields (Figure 3.10). Plants grown in the grass residue treatment had higher P and K contents than the control. Tissue Mn concentrations were decreased by poultry manure, filter cake and household compost additions in agreement with their effect in markedly increasing soil pH (Figure 3.9). Tissue Al concentrations did not, however, show a similar trend.

Table 3.4 Nutrient concentrations in tops of maize plants grown in soils amended with organic residues.

Treatment		N	P	K	Ca	Mg	Mn	Al
		-----(g kg^{-1})-----					----(mg kg^{-1})----	
Control	18	7.6	24	3.6	1.3	40	62	
Household compost		12	7.8	29	3.3	1.1	26	53
Grass residues		9.5	9.0	36	2.5	1.0	44	66
Filter cake		10	8.6	22	4.9	1.1	23	61
Poultry manure		25	11.8	40	7.8	1.5	21	71
LSD ($P \geq 0.05$)		1.5	1.7	6.0	1.8	0.17	5.2	18

3.4 DISCUSSION

3.4.1 Nature of Organic Amendments

Grassy veld material is present throughout South Africa. Its use as an organic amendment in small-scale arable agriculture will only be sustainable, in the long-term, if the area from which grassy residues is removed is much greater than the arable area. That is, there will be a transfer of nutrients from the grassy area to the arable one via the grass residues. Indeed, although relatively low in P, the residues contained substantial quantities of N, K as well as other nutrients (Table 3.1). Thus, in the long-term soil fertility below the grassveld will decline. Nevertheless, grass residues represent a readily-available organic residue and if their application could decrease the need for heavy lime and P applications it would be warranted, particularly in the short-term.

The composting of organic wastes and their return to soils is an excellent way of recycling nutrients and organic matter. Household compost, as used in this study, is derived from home (e.g., vegetable peelings, unwanted leaves, fruit skins, egg shells, tea leaves, etc.) and garden waste (remains of vegetable crops, stalks and thin prunings). The controlled biological decomposition of this material results in the formation of humified material which is termed compost. The nutrient content of this material varies greatly depending upon that of the various constituents but is generally greater than that of municipal compost (Dalzell, 1987). Composting of household wastes in village-based communities is being actively

promoted by both national and international agencies and compost is therefore, a potential source of organic matter for small-scale farming.

The poultry industry is large in South Africa and as a result, large amounts of manure are produced. There are two types of confinement housing for poultry: the deep litter system and the caged pit system. Manure from the former system (used for broiler poultry) contains significant amounts of absorbent material such as sawdust; the type of manure from this system is usually referred to as poultry litter. By contrast, in the caged pit system, which is used mainly for layer-poultry, cages are suspended above a pit and manure falls into a pit and is removed periodically. The layer manure used in this study was of the latter type. Poultry manure is a material that is likely to be available to small-scale farmers since many villages now have simple cage pit systems for layer poultry whilst free range poultry are common.

Commercial layer poultry are commonly fed dietary supplements such as limestone (CaCO_3) grit, common salt (NaCl) and trace elements such as Cu (Robinson, 1961; Sims and Wolf, 1994) and this is reflected in the relatively high (CaCO_3), Ca, Na and Cu content of the poultry manure (Tables 3.1 and 3.2). The high N and P content of the poultry manure is a characteristic of this type of manure (Sims and Wolf, 1994).

Filter cake (also known as filter press mud) is a waste product of sugar mills. In order to

clarify (purify) the juice produced following its extraction by milling, lime is added to the heated juice and the suspended soluble organic material are then filtered in filter presses and collected as a solid cake. The filter cake contains large amounts of calcium carbonate (Table 3.2) and with the filtered impurities it constitutes a valuable fertilizer/lime material. Phosphorus and N are the nutrients of particular importance in filter cake (Table 3.1 and 3.2; Moberly and Meyer, 1978; Ng Kee Kwong and Deville, 1988). Approximately 800,000 Mg of the product are produced in South African mills (Moberly and Meyer, 1978) and the bulk of this is left, unused, in dumps close to the mills. The material represents a valuable resource to both large and small-scale farmers who are situated close to the mills.

A rapid release of Na and K but a slower release of Ca and Mg from poultry manure, filter cake and household compost is demonstrated by the increase in exchangeable Ca and Mg (Figure 3.5) between four and eight weeks incubation but no increase in exchangeable Na and K. This relatively slow release of Ca and Mg is typical of animal excreta and is thought to be principally because much of the Ca and Mg is present in sparingly soluble carbonate form (Barrow, 1984; Haynes and Williams, 1993). This is presumably also the case for the filter cake (due to its high lime content) and to a lesser extent household compost.

The increase in Olsen-extractable P for poultry manure, filter cake and household compost between four and eight weeks incubation (Figure 3.7) also demonstrates that not all the P in these materials is released immediately. For animal manures, this is believed to be due to the presence of sparingly-soluble dicalcium phosphates and organic forms of P that require

mineralization before orthophosphate is released (Barrow, 1975). This is also likely to be the case for filter cake and for household compost where much of the P is probably in organic form.

The decreased P adsorption capacity of the soil after incubation with the various residues is not surprising since each contained significant quantities of P (Table 3.1). This P was released during residue decomposition and consequently Olsen-extractable soil P was increased. Not surprisingly, the increase in available P followed the same order as P content of the residues, i.e., poultry manure > filter cake = household compost > grass residues > control. This released inorganic P is rapidly adsorbed onto soil colloid surfaces thus increasing the proportion of adsorption sites occupied by P. As a result, the P adsorption capacity of the soil is decreased with respect to subsequently applied P. Nonetheless, even though the extractable P content of the household compost and filter cake treatments was similar (Figure 3.7), the P adsorption capacity of household compost-treated soil was less than that of filter cake-treated soil (Figure 3.8). The reason for this is presumably that humic substances from the household compost became adsorbed to soil colloid surfaces. Humic molecules can be specifically adsorbed onto metal oxide surfaces and are known to have a competitive effect on P adsorption (Moshi *et al.*, 1974; Sibanda and Young, 1986).

3.4.2 Soil pH

Many of the beneficial effects of the application of crop residues, organic manures and compost to acid soils can be attributed to their effect on increasing soil pH and decreasing

phytotoxic Al in soluble and/or exchangeable form (Hoyt and Turner, 1975; Bessho and Bell, 1992; Noble *et al.*, 1996). However, the reasons for the elevation in pH are unclear and a number of different mechanisms have been forwarded. These include: (a) the immediate proton-consuming ability of organic materials (Wong *et al.*, 1998b), (b) decarboxylation of organic acid anions during decomposition of organic materials (Yan *et al.*, 1996), (c) ammonification of organic N held in residues (Hoyt and Turner, 1975), (d) specific adsorption of organic compounds released during decomposition (Hue and Amien, 1989) and (e) localized reduction reactions in the soil in the vicinity of decomposing residues (Hue, 1992).

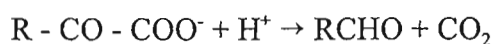
Composts and manures contain humic type substances with functional groups such as carboxyl and phenolic groups that are able to consume protons at their natural pH values (Tan *et al.*, 1971; Senesi and Brunetti, 1996). These materials are formed during the decomposition process and are relatively stable against further decomposition. Their capacity to consume protons should, therefore, control the buffer characteristics of these materials and their ability to neutralize soil acidity. For this reason, Wong *et al.* (1998a) proposed the measurement of the proton consumption capacity of such materials by titration with 0.05 M H₂SO₄. They showed that the increase in pH when composts, manure and peat were added to a spodosol, was directly proportional to the proton consumption capacity of the materials. In agreement with such findings it was found that both the increase in soil pH_(KCl) and the proton consumption capacity of materials followed the order: poultry manure > filter cake > household compost > grass residues.

However, the H⁺ consumption capacity (measured by titration with acid) of materials used is not only attributable to the presence of humic substances since some of them contained substantial amounts of CaCO₃ (Table 3.2).

For example, as already noted, CaCO₃ is an important component of filter cake since it is used to flocculate impurities out of juice produced by rolling harvested canes. Layer poultry birds have a significant intake of limestone dust and therefore fresh droppings characteristically contain considerable quantities of CaCO₃ (Robinson, 1961). The household compost also contained some CaCO₃.

The organic acid anion content of organic materials is another important factor involved in the rise in soil pH. Plant material generally contains an excess of cations over anions and the balance is maintained by the synthesis of organic acid anions (e.g., oxalate, citrate, malate) (De Wit *et al.*, 1963). Ashing the plant material and measuring the alkalinity of the ash provides an estimate of the organic anion content (Slattery *et al.*, 1991).

During microbial decomposition of the plant material, organic acid anions are decarboxylated and this results in both consumption of protons and release of CO₂:



In agreement with this, it has been shown that increases in soil pH following the addition of malate and citrate are highly correlated with CO₂ evolution during the decomposition of these two anions (Yan *et al.*, 1996). Thus, decomposition of plant residues has a liming effect.

Indeed, Pocknee and Sumner (1997) showed that the addition of calcium oxalate and calcium gluconate to soils had identical effects on soil pH to addition of CaCO_3 when added in equimolar rates. However, they found that the biological decomposition of the organic materials (and thus the concomitant rise in pH) was markedly slower than the chemical dissolution of CaCO_3 .

The ash alkalinity of the grass residues ($58 \text{ cmol}_c \text{ kg}^{-1}$) will have been the major factor leading to a rise in pH during the decomposition of the residues. The ash alkalinity of the other materials will, however, not only reflect organic acid anion content but also the CaCO_3 content of the ashed materials. Indeed, for poultry manure and filter cake the organic acid anion content seems unlikely to have been the major contributor leading to a rise in pH following their application to the soil.

The N content of organic residues is another factor that can contribute to a change in soil pH during their decomposition (Hoyt and Turner, 1975; Pocknee and Sumner, 1997). During residue decomposition, organic N is first ammonified to form NH_4^+ and then nitrified to form NO_3^- . During ammonification of one unit of organic N there is a release of one OH^- ion whilst during nitrification two H^+ ions are produced. Several workers have suggested that the main reason that, following additions of organic residues to soils, a decline in pH often follows, is that nitrification precedes (Hoyt and Turner, 1975). Indeed, Yan *et al.*, (1996) showed that while the addition of malate to soil caused an immediate increase in pH, addition of malate plus NH_4^+ resulted in an immediate increase in soil pH followed by a decrease which was associated with nitrification. The decrease in pH between four and eight weeks incubation observed in

this study was suspected to have been caused by nitrification. Recent analysis of the soils from after eight weeks incubation showed the presence of low concentrations of 2 M KCl - extractable NH_4^+ but high concentrations of NO_3^- - N.

There are several other factors which may have contributed to the residue-induced increase in soil pH. Ligand exchange between hydroxyl groups on Al and Fe hydrous oxides and low molecular weight organic acids and/or humic substances (produced during residue decomposition) could tend to raise pH (Hue and Amien, 1989). An increase in pH due to the reduction of Mn and Fe as suggested by Hue and Amien (1989) or caused by denitrification (Glinski *et al.*, 1992) could also occur. The extent and importance of these mechanisms in this particular study are unknown but are suspected to be minor.

3.4.3 Exchangeable and Soil Solution Al

As expected, the decrease in pH that occurred between four and eight weeks incubation caused an increase in exchangeable Al concentrations (Figure 3.2). While exchangeable Al concentrations followed the order: poultry manure < filter cake < household compost < grass residues, the soil $\text{pH}_{(\text{KCl})}$ was, in fact higher for the household compost than grass residue treatment (Figure 3.1). The lower than expected exchangeable Al concentrations in the household compost treatment may well be attributable to complexing of Al by the added composted material. Mature compost is essentially humified organic matter (Senesi and Brunetti 1996) and the unusually high number of functional groups (e.g., COOH, OH etc.) present on humic substances means they are able to complex strongly with polyvalent metal

ions such as Al (Stevenson and Vance, 1989). The lower Al_T in soil solution for the household compost than grass residue treatment may also reflect complexation of Al in solid phase caused by household compost additions.

Inorganic monomeric Al in soil solution was analysed in this study using pyrocatechol violet 60 sec. (PCV) method (Kerven *et al.*, 1989). This is designated as Al_{Mono} but it is accepted that PCV will also react with some Al in Al-organic matter complexes (Close and Powell, 1989; Kerven *et al.*, 1989; Parfitt *et al.*, 1995). Surprisingly, the pattern of Al_T and Al_{Mono} in soil solution with treatment did not follow that of exchangeable Al. In particular, both Al_T and Al_{Mono} were unexpectedly high for the poultry manure treatment. This is likely to be due to the very high basic cation content of the poultry manure. When these cations are released from the decomposing manure the cation content and ionic strength in soil solution will be greatly increased as are exchangeable cation concentrations. The poultry manure treatment had considerably higher concentrations of exchangeable Ca, Mg, K and Na than the others. Electrical conductivity in a 1:5 soil : water extract was also much greater and in the subsidiary experiment, the electrical conductivity in soil solution from the poultry manure treatment was more than double than that in the other treatments.

Other workers have observed similar phenomena. Brenes and Pearson (1973), for example, showed that a small addition of KCl to soil samples increased the concentration and activity of Al in soil solution. Mason and Fey (1989) demonstrated that additions of Na, K Ca and Mg at increasing ionic strengths resulted in a lower pH and higher Al concentrations and activities in soil solution. These effects occur because the added cations displace exchangeable Al^{3+} and

H^+ from exchange sites on soil colloids thus increasing their concentrations in soil solution.

This “salt-effect” with poultry manure was also evident by comparing the pH measured in water and KCl (Figure 3.1). That is, $pH_{(water)}$ is lower for the poultry manure than filter cake treatment at both sampling times. By contrast $pH_{(KCl)}$ (where the salt -effect is eliminated by measuring pH in 1 M KCl) is higher for the poultry manure than filter cake treatment after four weeks and similar after eight weeks incubation. Soil salinity induced by heavy applications of poultry manure has been reported previously (Sims and Wolf, 1994) and it has also been reported to reduce crop yields (Liebhardt and Shortall, 1974; Moberly and Stevenson, 1971). The salinity has been attributed primarily to high concentrations of K^+ in soil solution although Na^+ and NH_4^+ can also contribute to the problem (Liebhardt and Shortall, 1974; Liebhardt, 1976).

No doubt, much of the Al_T in soil solution that was not measured as Al_{Mono} was present in forms complexed with soluble organic matter. Surprisingly, this proportion was, in fact, generally reduced by additions of organic amendments. In the main experiment, filter cake reduced Al_T much more than the other amendments and was, in fact, the only treatment to reduce Al_{Mono} values below those of the control. Even then, the proportion of Al_T present as Al_{Mono} was not reduced. It is interesting to note that the filter cake treatments also had the lowest electrical conductivity values (Figure 3.2). This, again, suggests that the additions of cations in the organic materials, and the consequent increase in electrolyte concentration in soil solution, is a major factor that influences concentrations of Al_T and Al_{Mono} in soil solution when organic amendments are applied to soils. To some extent, this is, however, an artifact

of the closed laboratory incubation systems used in this experiment. For example, under field conditions, these accumulated salts can be leached out of the surface soil by rainfall or irrigation.

3.4.4 Subsidiary Experiment

In the subsidiary experiment additions of amendments had similar effects on electrical conductivity, exchangeable bases and Al and Olsen- extractable P to the main experiment. Nevertheless, the $\text{pH}_{(\text{water})}$ was higher particularly in the amended soils where it reached above 5. The mean $\text{pH}_{(\text{water})}$ for amended soils was 5.0 in the subsidiary experiment compared with 4.6 in the main experiment. The reason for this is unknown but may be due to ammonification without nitrification which would raise soil pH (Haynes and Swift, 1989).

Surprisingly, Al_T and Al_{Mono} were considerably lower in the subsidiary experiment than in the main one, yet exchangeable Al concentrations were in a similar range in both experiments. Indeed, additions of all amendments decreased both Al_T and Al_{Mono} and the proportion of Al_T present as Al_{Mono} (Figure 3.9). The reason for this difference is unclear but could well be related to the higher pH values measured in the subsidiary experiment. As the soil pH rises, the Al on the exchange sites will become increasingly hydrolyzed and polymerized and will therefore participate much less effectively in exchange reactions with cations in soil solution than will Al^{3+} . Despite this, poultry manure tended to have a higher Al_T concentration than filter cake even though $\text{pH}_{(\text{water})}$ and pH in soil solution tended to be lower for filter cake

treatment. The higher $\text{pH}_{(\text{KCl})}$ for poultry manure than filter cake treatment suggest that there was still a salt-effect operative.

Limiting factors to crop growth in this soil are likely to be principally P deficiency and Al toxicity. The critical Olsen-extractable P level is likely to be about 10 to 15 mg kg^{-1} (Kamprath and Watson, 1980) so that additions of poultry manure, filter cake, and possibly household compost, would have overcome this yield-limiting factor. Exchangeable Al was reduced to some extent by all amendments and the Al_T and Al_{Mono} concentrations in soil solution were also low for all the amended treatments. However, maize yields in poultry manure-amended soil were greater than those with either filter cake or household compost amendments. Tissue N, P, K and Ca concentrations were also higher in the poultry manure treatment reflecting the higher inputs of these nutrients in that treatment. The higher overall fertility in the poultry manure-amended soil apparently resulted in a greater yield potential than, for example, the filter cake treatment even though a basal application of nutrients was applied to all treatments. The accumulation of soluble salts in the poultry manure-amended soil did not apparently have a negative effect on the growth of maize. Even so, nutrient uptake (particularly of K) by the rapidly growing maize plants would have rapidly decreased salt concentrations in soil solution.

3.5 CONCLUSIONS

It is evident that additions of all four of the organic residues used in this study caused an increase in soil pH and a decrease in exchangeable and soluble Al. The major mechanisms responsible for this increase probably differed depending upon the type of residue being

considered. Whilst the relatively high content of CaCO_3 was presumably the main mechanism in the case of poultry manure and filter cake, the proton consuming ability of humic material probably predominated for household compost and decarboxylation of organic acids during decomposition was probably the main mechanism in the case of grass residues.

In relation to Al concentrations in soil solution, the high cation content of residues (particularly that of poultry manure) appeared to interact with their effect on pH. That is, the high concentration of cations in soil solution resulting from residue addition tends to displace exchangeable Al^{3+} into soil solution.

Additions of all the organic residues to an acid, P-deficient soil (where a basal fertilizer addition devoid of lime and P was applied) increased maize yields in a glasshouse experiment. Poultry manure and filter cake acted as substantial sources of both lime and P and household compost also increased pH and P fertility. Even additions of grass residues increased P availability and decreased exchangeable and soluble Al concentrations. It is concluded that the additions of organic residues to acid soils seems to be a practicable way of reducing lime and fertilizer P requirements. The relative effects of these residues versus moderate rates of lime and P that small-scale farmers might be able to afford is, as yet, unknown and is the subject of chapter 4.

CHAPTER 4

ALUMINIUM TOXICITY, PHOSPHORUS AVAILABILITY AND GROWTH OF MAIZE IN AN ACID SOIL AS AFFECTED BY THE ADDITIONS OF LIME, PHOSPHORUS AND ORGANIC WASTE MATERIALS

4.1 INTRODUCTION

Soil acidity and P deficiency are often the major limiting factors for small-scale farmers in KwaZulu-Natal. In large-scale commercial farming, these problems are conventionally corrected by heavy applications of lime and soluble P fertilizer (e.g., Superphosphate or ammonium phosphates). Due to economic and logistic constraints, fertilizer P, and more particularly lime, are not commonly applied in small-scale farming. This severely limits crop yields. While applications of low rates of lime and P may be possible for small-scale farmers, such rates are unlikely to generate high crop yields even when practices such as banding are used. Practical alternatives using inputs readily available to small-scale farmers must therefore be sought.

Recent research has shown that additions of green manures, animal wastes and composts to acid soils can reduce Al toxicity and increase crop yields (Hoyt and Turner, 1975; Ahmad and Tan, 1986; Hue and Amien, 1989; Berek *et al.*, 1995; Wong *et al.*, 1995). An increase in soil pH and/or complexation of soil solution Al by decomposition products of organic residues (e.g., organic acid anions and soluble humic material) have been implicated as the main factors in such Al detoxification (Haynes and Mokolobate, 2000).

Additions of organic residues have also been shown to increase P uptake and dry matter yields of crops in P-deficient soils (Hundal *et al.*, 1987; Hue, 1990, 1992; Hue *et al.*, 1994). Part of this effect is undoubtedly due to the release of P along with other nutrients from the manure (Iyamuremye and Dick, 1996). However, it is thought that manure-derived organic anions may become adsorbed onto surfaces of Fe and Al oxides and thus reduce the adsorption of added P (Easterwood *et al.*, 1990; Hue, 1992). Thus the plant availability of added fertilizer P to the plant is greatly increased.

The purpose of this chapter was to compare applications of lime or P, at rates practicable for use by small-scale farmers, with additions of readily available organic materials, on the availability of P and other nutrients, solubility of soil Al, plant growth and nutrient uptake in a glasshouse experiment. A P-deficient soil typical of those found in the midlands of KwaZulu-Natal was used. The organic waste materials used were household compost, grassveld residues, poultry manure and filter cake; the rates of P addition were equivalent to 10 and 50 kg P ha⁻¹ and lime rates were 5 and 10 Mg ha⁻¹.

4.2 MATERIALS AND METHODS

The soil used was a Hutton form (Farmingham series) [Rhodic Ferralsol (FAO)] and the sample was taken from the same site as the soil used in Chapter 3. That site is a small-scale farming demonstration trial administered by the KwaZulu-Natal Department of Agriculture which is situated in the KwaZulu-Natal midlands, close to the Royal Natal National Park. The soil had an organic C content of 27.5g kg⁻¹, total N content of 2.41g kg⁻¹, exchangeable Al, Ca, Mg, K and Na content of 11.38, 2.17, 0.45, 1.66 and 0.57 mmol kg⁻¹ respectively and an Olsen-extractable

P content of 6 mg P kg^{-1} . A bulk soil sample was dug from the 0 - 20 cm layer of soil, air-dried and sieved ($<2 \text{ mm}$). It had a clay content of 42% and a $\text{pH}_{(\text{water})}$ of 4.1.

The research consisted of two main experiments. In the first experiment, there were five main treatments (i) control, (ii) household compost, (iii) grassveld residues, (iv) poultry manure and (v) filter cake which were applied at a rate of 20 mg g^{-1} (equivalent to 20 Mg ha^{-1}). A description of organic amendments and their properties is provided in chapter 3. To these treatments, three rates of lime 0, 5 and 10 mg g^{-1} (equivalent to 0, 5 and 10 Mg ha^{-1}) were applied to give a total of 15 treatments.

For the second experiment, the same five organic amendment treatments were applied. To these treatments, three rates of P [as $\text{Ca}(\text{H}_2\text{PO}_4)_2$] 0, 10, $50 \mu\text{g P g}^{-1}$ (equivalent to 0, 10 and 50 kg P ha^{-1}) were applied to give 15 treatments.

For both experiments there were six replications of each treatment. The organic amendments were mixed with bulk samples of the soil. Subsamples (1kg) of these treatments were then taken and appropriate amounts of lime (Ca_2CO_3) or $\text{Ca}(\text{H}_2\text{PO}_4)_2$ were mixed with the soil and the samples were then placed in plastic pots. A basal fertilizer application was applied to all treatments of N, K, Mg, Mn, Mo, Zn, Cu and B at rates equivalent to 200, 200, 100, 25, 0.28, 15, 15 and 10 kg ha^{-1} respectively. The pots of four replicates were sown with seven maize seeds (*Zea mays* L. cv Silver King) and later thinned to four per pot. The other two replicates remained unplanted. Pots were arranged in a randomized complete block design and maintained at 70% of water holding capacity in a glasshouse with an air temperature held between 20 and 25°C . Plants were grown for 6 weeks. Above-ground herbage was harvested, oven-dried, weighed and ground.

Forty eight hours prior to harvest, the unplanted pots were wetted to 100% water holding capacity. After that period, solution was extracted by centrifugation and monomeric (Al_{Mono}) and total (Al_T) Al were measured as described in section 3.2. The pH and electrical conductivity of soil solutions was also measured. A subsample of soil was air-dried, sieved, and analysed for Olsen-extractable P and exchangeable cations by methods described in section 3.2. Ground plant samples were analysed for N, P, K, Ca, Mg, Cu, Zn, Al, Fe and Mn content by methods described previously (section 3.2).

Both soil and plant data were analysed by analysis of variance using the Genstat V package.

4.3 RESULTS

As expected, lime applications increased soil solution pH, $pH_{(water)}$ and $pH_{(KCl)}$ as well as the electrical conductivity of soil solution (Figures 4.1 and 4.2). Applications of P, however, had no measurable effect on either pH or electrical conductivity. In unlimed soils (i.e., the P experiment), values for pH measured in soil solutions, or in a water slurry, generally followed the order: poultry manure > filter cake > grass residues = household compost > control (Figures 4.1 and 4.2). Soil solution pH was generally 0.2 to 0.6 of a pH unit greater than that measured in a water slurry. Values for $pH_{(KCl)}$ were lower than those for water (Figure 4.2) and pH changes caused by additions of organic amendments were less marked when measured in KCl rather than water.

Additions of all the organic amendments had an appreciable effect in reducing both Al_T and Al_{Mono} in soil solution (Figure 4.3). For unlimed soils, Al_T followed the order: control > household compost = grass residues \geq filter cake > poultry manure. While additions of lime reduced Al_T ,

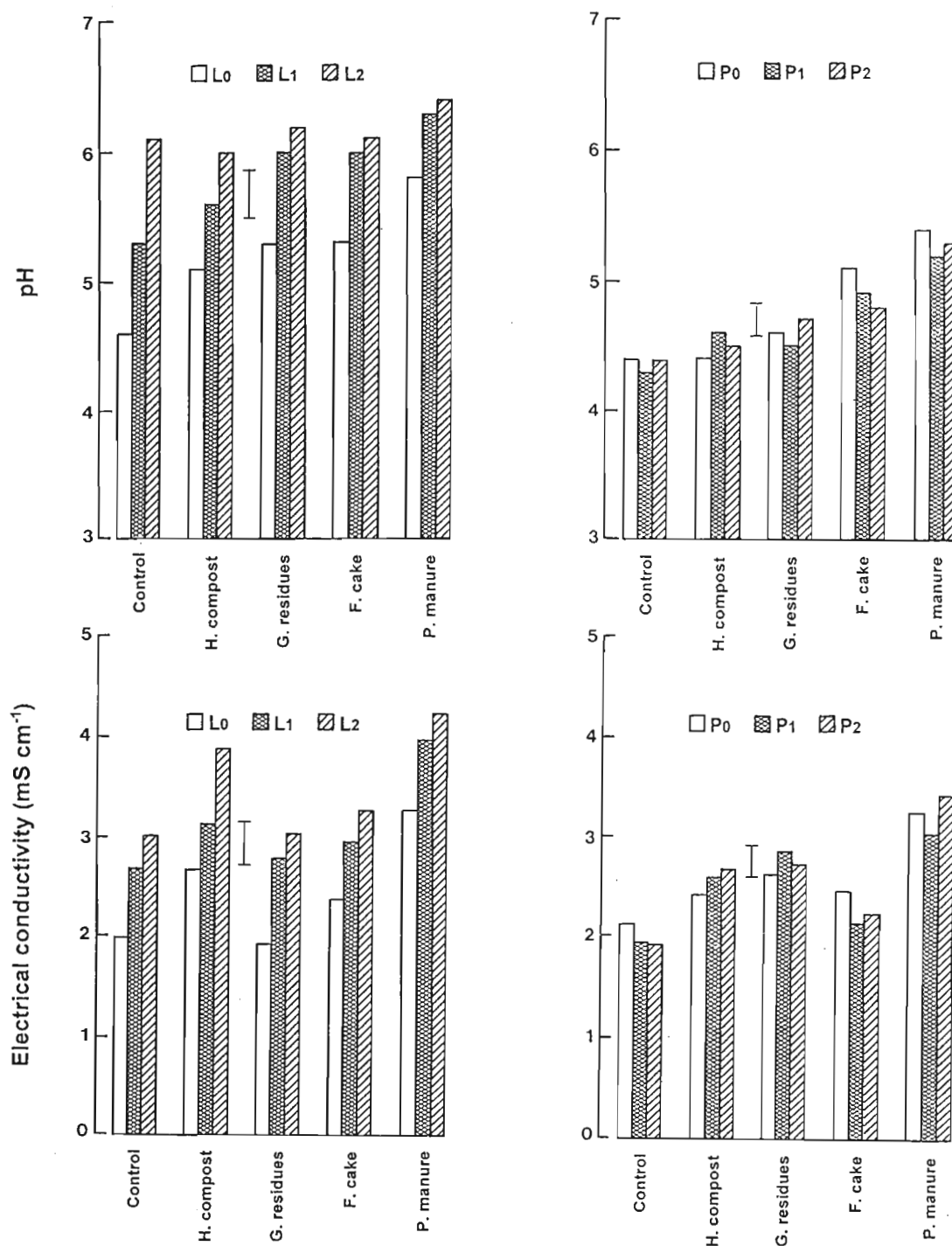


Figure 4.1 Effect of incubation of organic residues with an acid soil for 6 weeks with the addition of either lime or P at three rates on pH and electrical conductivity in soil solution. $L_0 = 0$, $L_1 = 5$, $L_2 = 10$ mg lime g^{-1} . $P_0 = 0$, $P_1 = 10$, $P_2 = 50$ μg P g^{-1} . LSD ($P \leq 0.05$) shown.

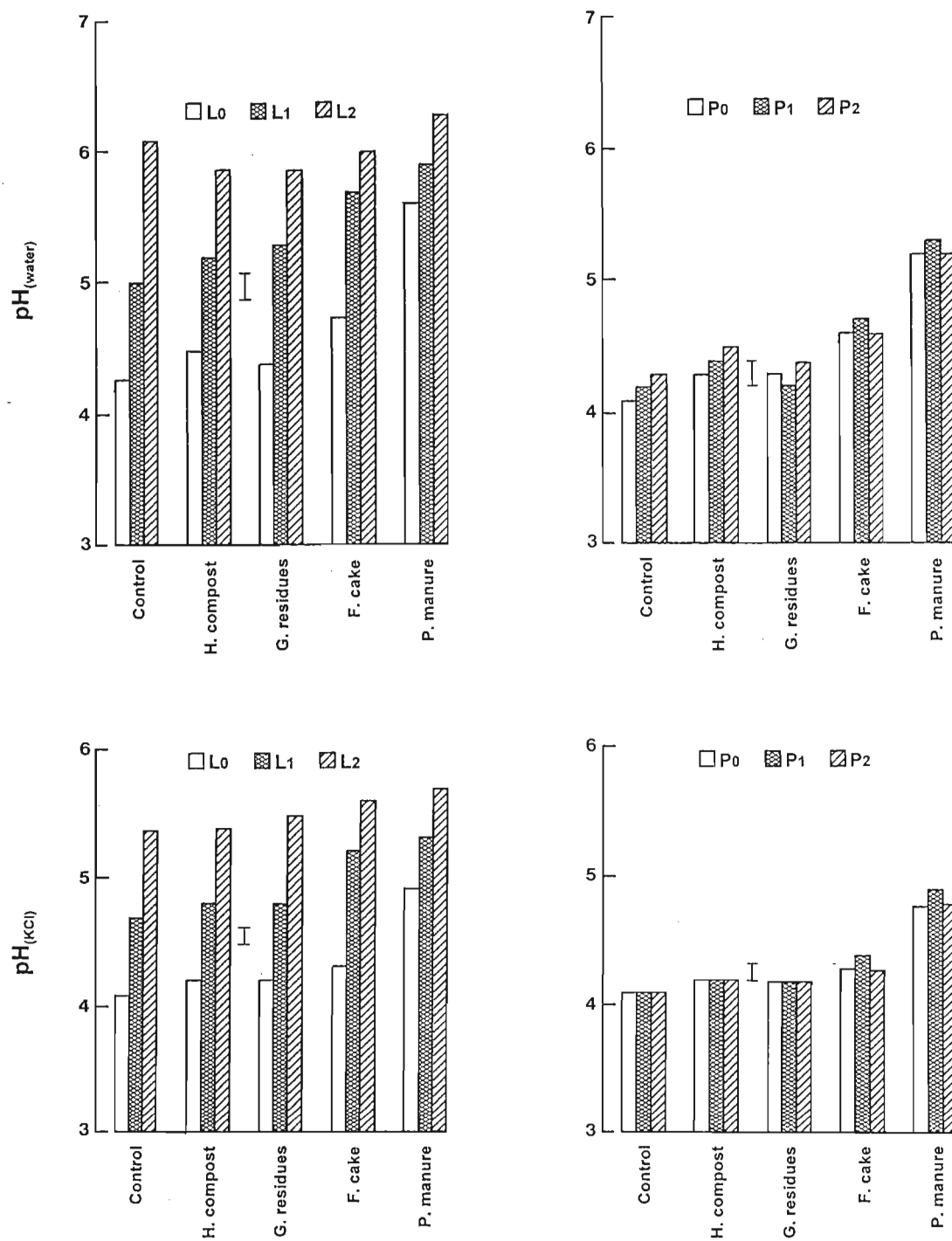


Figure 4.2 Effect of incubation of organic residues with an acid soil for 6 weeks with the addition of either lime or P at three rates on soil pH measured in water and 1M KCl. For explanation of terms, see Figure 4.1.

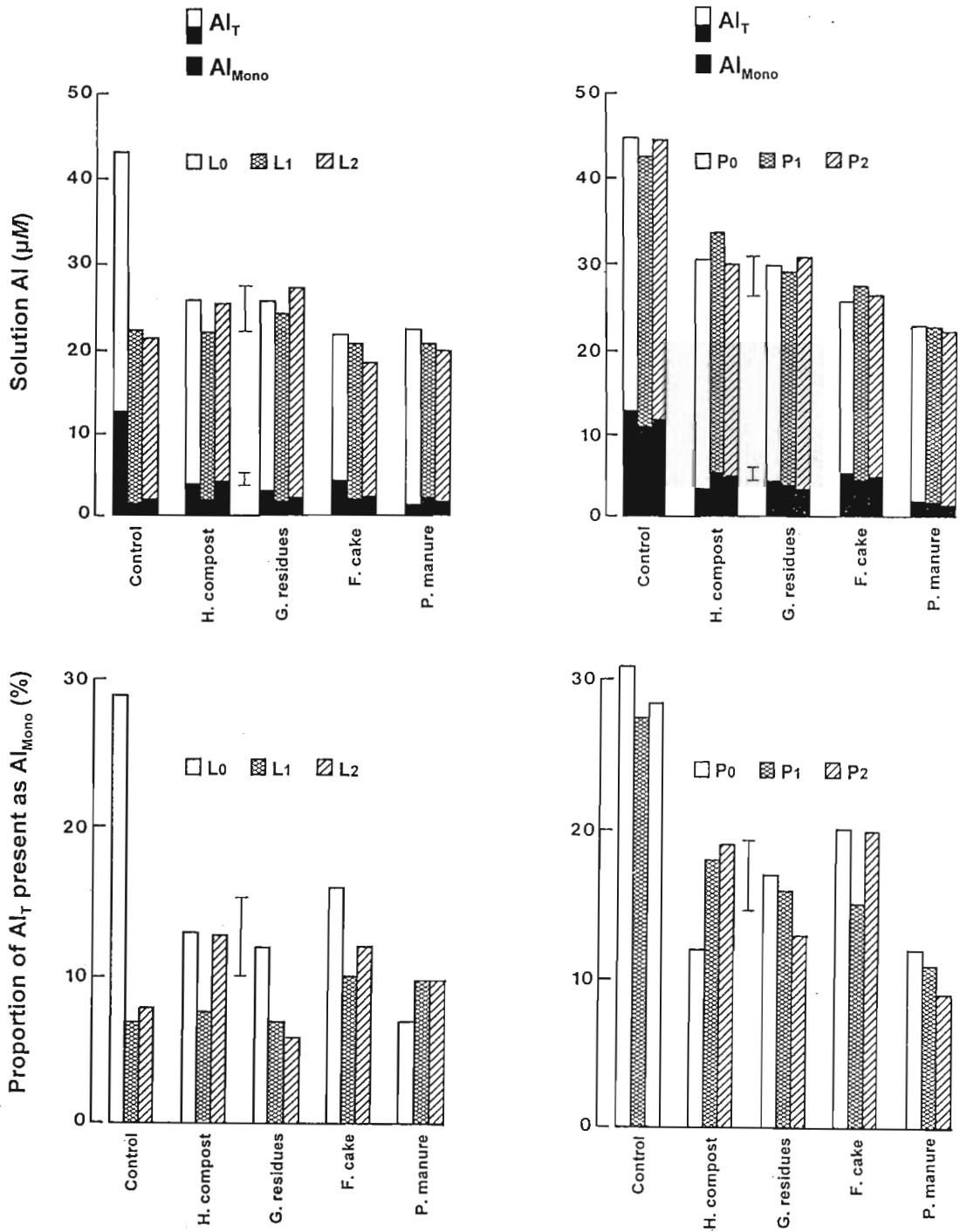


Figure 4.3 Effect of incubation of organic residues with an acid soil for 6 weeks with the addition of either lime or P at three rates on concentrations of total (Al_T) and monomeric (Al_{Mono}) Al in soil solution and the proportion of Al_T present as Al_{Mono} . For explanation of terms, see Figure 4.1)

Al_{Mono} and the proportion of Al_T present as Al_{Mono} appreciably in the control treatment, they had no appreciable effect on these parameters when any of the organic amendments had been applied (Figure 4.3). Applications of P had no consistent effect on Al_T or Al_{Mono} or the proportion of Al_T present as Al_{Mono} .

While P applications had no measurable effect on exchangeable Al concentrations, additions of lime reduced them markedly in all except the poultry manure treatment (Figure 4.4). For unlimed soils, exchangeable Al concentrations followed the order: control > grass residues \geq household compost > filter cake > poultry manure. Extractable P concentrations were increased by P applications (Figure 4.4). However, for the household compost, filter cake and poultry manure treatments lime additions tended to decrease extractable P (Figure 4.4).

As expected, lime applications increased concentrations of exchangeable Ca but had no significant effect on exchangeable Mg, K or Na (Figures 4.5 and 4.6). Applications of P had no effect on exchangeable cation concentrations. For unlimed soils, exchangeable Ca and Mg followed the order: poultry manure \geq filter cake \geq household compost \geq grass residues \geq control. Exchangeable K concentrations followed the order: poultry manure = grass residues > household compost = filter cake \geq control. Exchangeable Na concentrations were higher in the poultry manure than other treatments (Figure 4.6).

For the control treatment, there was a trend for a positive yield response to applied lime (Figure 4.7) but no response was observed for the amended treatments. For the control, household compost and grass residues treatments there was a positive yield increase to P applications but for filter cake and poultry manure treatments, no such response occurred.

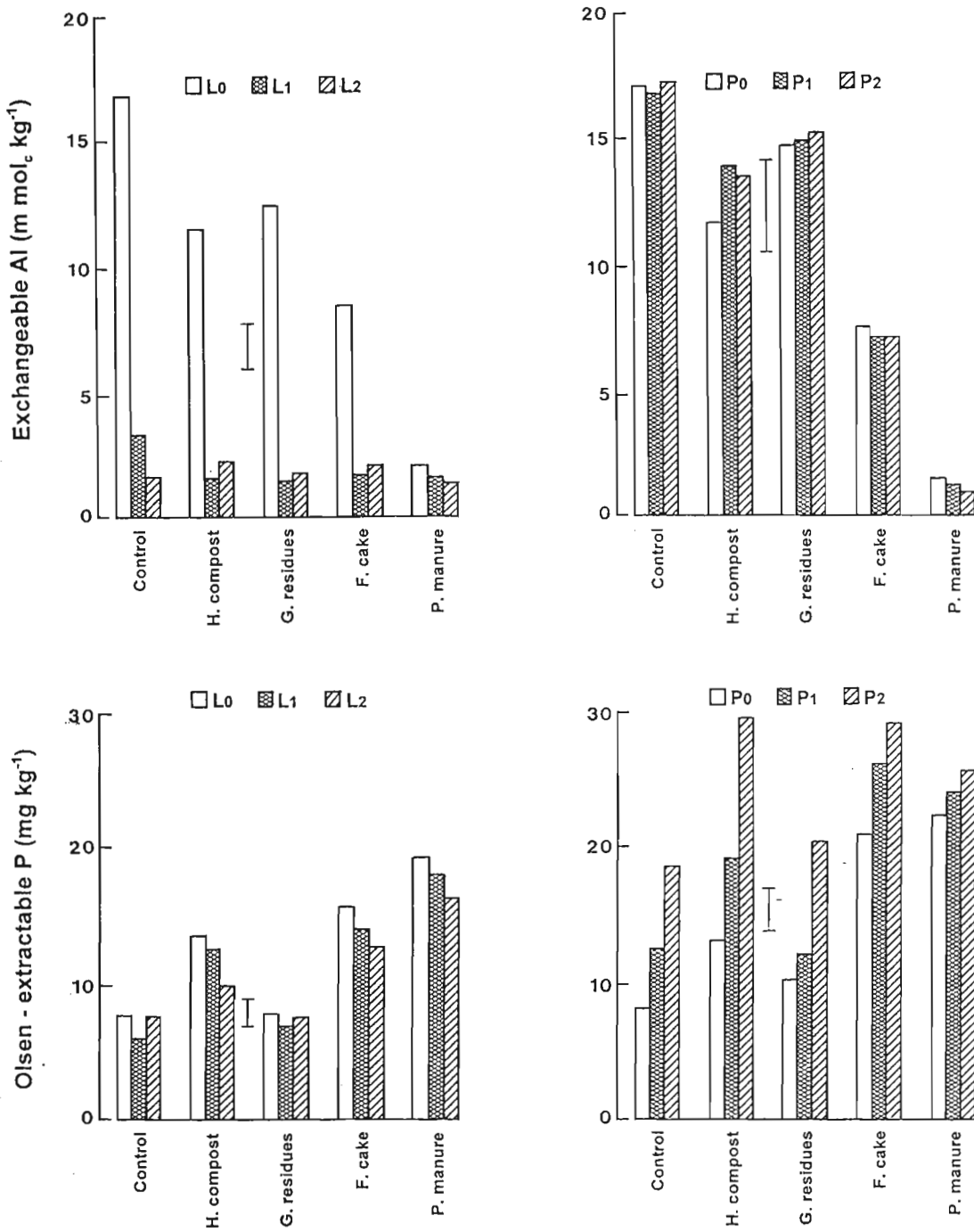


Figure 4.4 Effect of incubation of organic residues with an acid soil for 6 weeks with the addition of either lime or P at three rates on concentrations of exchangeable Al and Olsen-extractable P. For explanation of terms, see Figure 4.1.

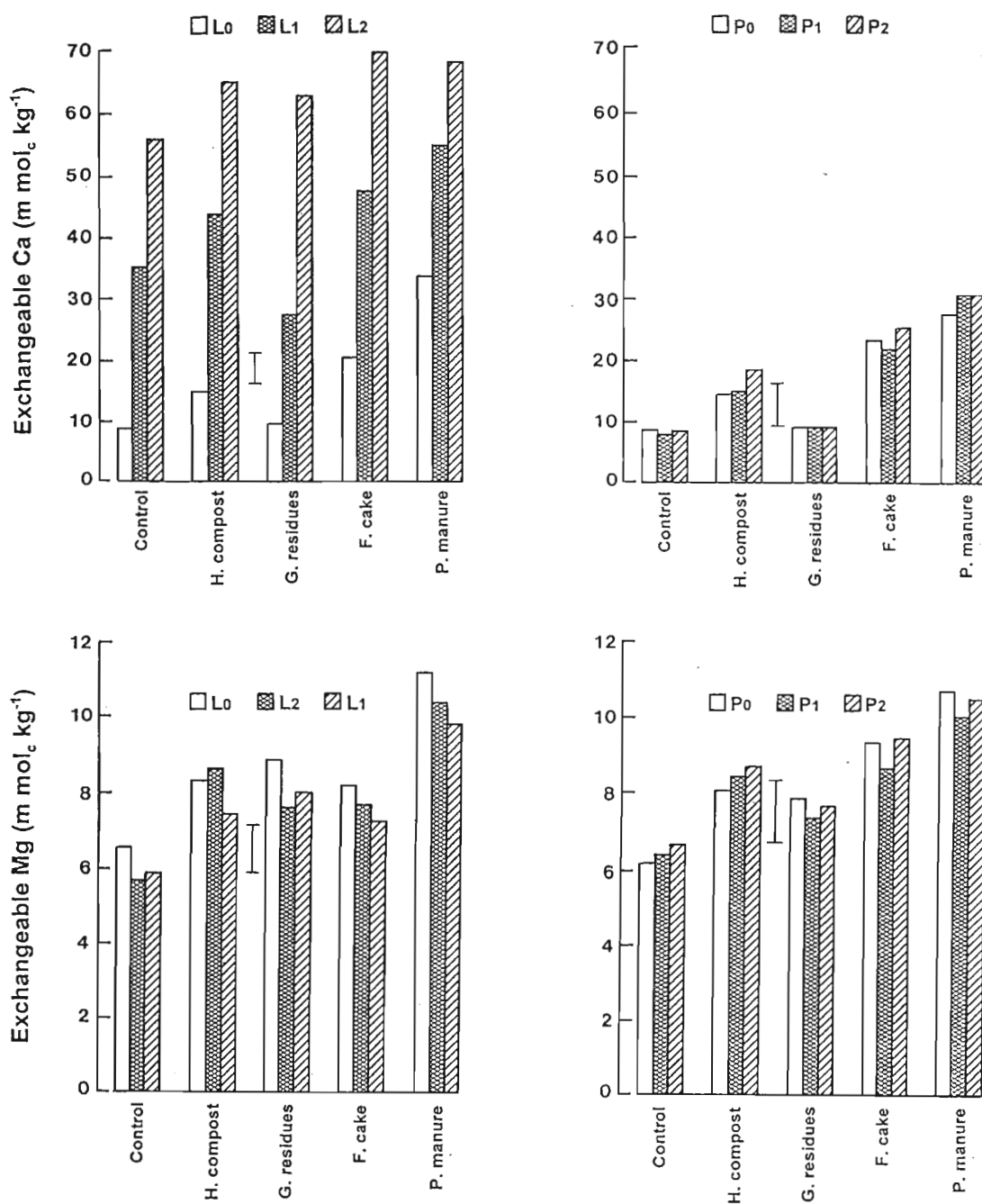


Figure 4.5 Effect of incubation of organic residues with an acid soil for 6 weeks with the addition of either lime or P at three rates on concentrations of exchangeable Ca and Mg. For explanation of terms, see Figure 4.1.

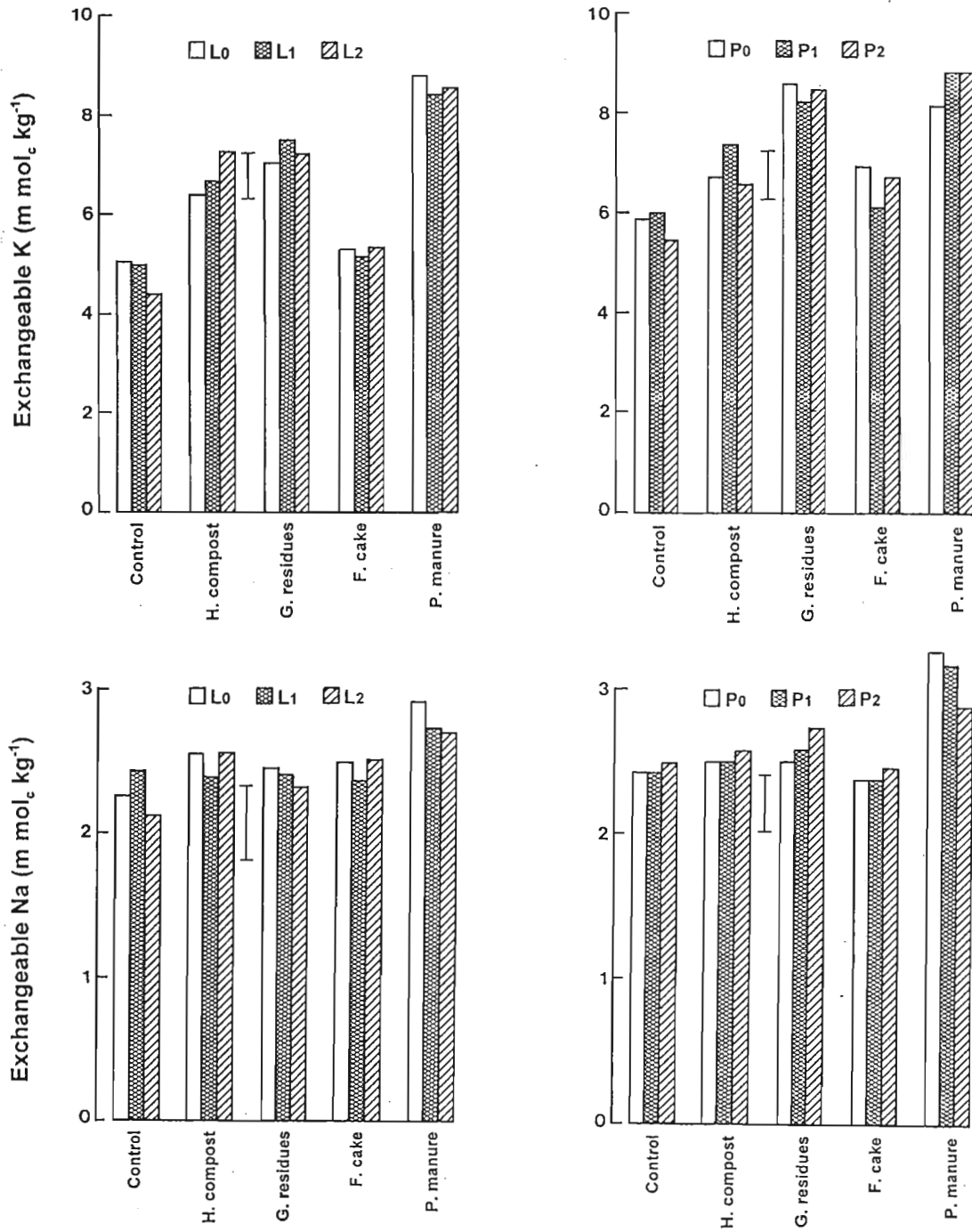


Figure 4.6 Effect of incubation of organic residues with an acid soil for 6 weeks with the addition of either lime or P at three rates on concentrations of exchangeable K and Na. For explanation of terms, see Figure 4.1.

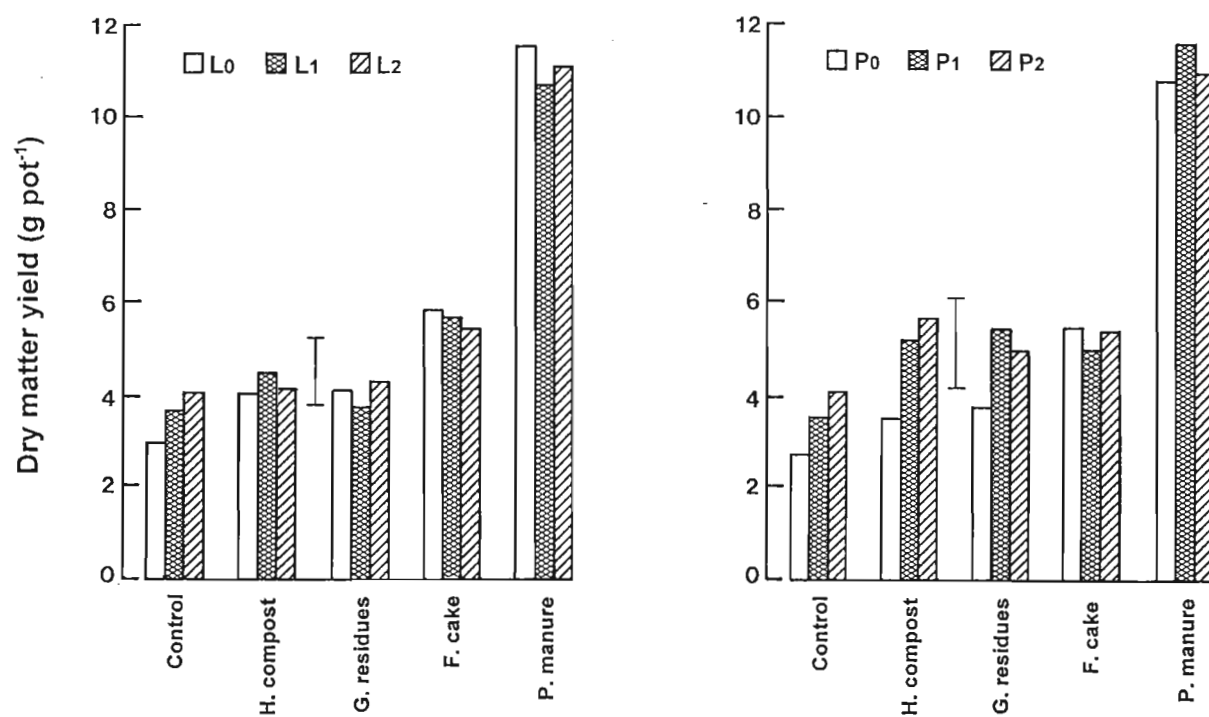


Figure 4.7 Effect of incubation of organic residues with an acid soil with the addition of either lime or P at three rates on dry matter yields of maize plants grown for 6 weeks. For explanation of terms, see Figure 4.1.

Yields were considerably higher for the poultry manure than other treatments (Figure 4.7).

The nutrient content of maize tissues is presented in Tables 4.1 and 4.2. There was no discernible trend with treatment for tissue N, P and Cu concentrations. The K content of plants from the filter cake treatment tended to be lower than those for the others. While tissue Ca concentrations were generally increased by lime applications, those of Mg were decreased. Tissue Mg concentrations were lower for the poultry manure and grass residue treatments than for the others. The Fe content of maize was generally increased by liming. Concentrations of tissue Mn and Zn showed similar broad trends being generally decreased by liming and for the unlimed treatments following the order: poultry manure < filter cake < household compost < grass residues < control.

Table 4.1 Effect of incubation of organic residues with an acid soil with the addition of three rates of P on the nutrient content of tops of maize plants grown for 6 weeks.

Treatment		N	P	K	Ca	Mg	Al	Fe	Cu	Mn	Zn
		-----(g kg^{-1})-----						-----(mg kg^{-1})-----			
Control	P ₀	11	11	40	5.6	3.4	32	165	14	339	43
	P ₁	8.9	10	39	6.5	3.8	30	171	13	361	36
	P ₂	8.6	12	35	5.5	3.0	37	180	15	309	34
Household	P ₀	9.3	13	43	6.1	3.1	31	183	13	257	27
	P ₁	9.3	14	47	7.5	3.5	46	202	18	287	30
	P ₂	9.2	14	44	6.0	3.2	26	170	13	275	29
Grass residues	P ₀	8.0	11	42	4.3	2.4	25	155	14	306	31
	P ₁	8.2	11	51	4.9	2.6	29	173	14	315	33
	P ₂	7.6	12	46	5.0	2.6	30	180	12	271	27
Filter cake	P ₀	7.7	9.2	31	7.1	3.6	23	163	12	193	21
	P ₁	10	15	31	7.0	3.5	28	156	13	213	23
	P ₂	8.8	15	34	7.5	3.7	25	182	13	203	24
Poultry Manure	P ₀	8.7	14	45	5.8	2.2	36	209	13	130	22
	P ₁	11	14	41	5.8	2.3	32	180	14	125	23
	P ₂	8.1	15	37	5.9	2.5	27	181	13	121	23
LSD (P<0.05)		3.6	4.3	8.9	1.2	0.6	9.9	52.7	2.7	50.6	4.2

Rates of P applied were P₀ = 0, P₁ = 10, P₂ = 50 $\mu\text{g P g}^{-1}$

Table 4.2 Effect of incubation of organic residues with an acid soil with the addition of three rates of lime on nutrient content of tops of maize plants grown for 6 weeks.

Treatment		N	P	K	Ca	Mg	Al	Fe	Cu	Mn	Zn
		-----(g kg^{-1})-----					-----(mg kg^{-1})-----				
Control	L ₀	9.1	11	36	5.9	3.1	46	182	11	292	31
	L ₁	6.6	8.7	35	11	3.1	42	228	12	108	24
	L ₂	6.5	8.8	34	13	2.9	37	145	11	98	17
Household	L ₀	5.9	12	42	5.9	2.2	67	178	10	229	30
	L ₁	6.8	12	41	10	2.6	65	175	12	93	20
	L ₂	6.8	10	36	11	2.5	43	211	9.7	82	17
Grass residues	L ₀	6.4	13	44	5.6	2.5	44	148	12	258	28
	L ₁	7.0	9.4	44	8.0	2.3	42	158	9.7	99	21
	L ₂	7.3	8.6	36	10	2.0	44	176	11	85	17
Filter cake	L ₀	5.2	14	29	7.9	3.4	37	166	9.8	185	22
	L ₁	7.3	13	31	10	3.0	41	168	10	109	17
	L ₂	5.5	11	29	13	2.8	48	207	11	90	14
Poultry Manure	L ₀	8.4	9.3	37	6.3	2.3	38	149	9.6	118	24
	L ₁	7.7	13	33	7.5	2.0	42	147	9.3	74	16
	L ₂	7.6	13	33	6.9	1.9	45	190	12	73	14
LSD (P<0.05)		2.5	4.1	5.9	2.4	0.6	10.4	59.8	2.2	33.7	4.2

Rates of lime applied were L₀ = 0, L₁ = 5, L₂ = 10mg lime g⁻¹

4.4 DISCUSSION

4.4.1 Soil Properties

An increase in pH induced by additions of organic residues was clearly evident in unlimed soils. Soil solution pH and $\text{pH}_{(\text{water})}$ followed the order: control < grass residues \leq household compost < filter cake < poultry manure while the trend for concentrations of exchangeable Al, Al_T , and to a lesser extent Al_{Mono} , was the reverse. Thus, as expected, as soil pH increased, concentrations of exchangeable and soluble Al decreased. The reasons for the increase in pH were discussed in detail in chapter 3. The dominant mechanisms were thought to be decarboxylation of organic acid anions during decomposition of plant material (Yan *et al.*, 1996; Tang *et al.*, 1999) for the grass residues, the high proton consumption capacity of the humic material present in the household compost (Wong *et al.*, 1998a) and the high CaCO_3 content of filter cake and poultry manure (see section 3.4.2). Increases in soil pH following applications of poultry manure (Hue, 1992; Cooper and Warman, 1997), composts (Mays *et al.*, 1973; Terman *et al.*, 1973) and crop residues (Hue and Amien, 1989; Tang *et al.*, 1999) have been reported previously. Although an increase in pH following additions of filter cake has not been mentioned by a number of workers (Roth, 1971; Moberly and Meyer, 1978; Ng Kee Kong and Deville, 1988) the results of this study suggest that its liming-effect is an important property.

Surprisingly, in the liming experiment, the pattern of change in Al_T and Al_{Mono} did not reflect that for exchangeable Al. That is, for the control treatment, liming greatly decreased exchangeable Al, Al_T and Al_{Mono} . By contrast, for the grass residue, household compost and

filter cake treatments, although liming markedly reduced exchangeable Al concentrations, it had no significant effect on either Al_T or Al_{Mono} (Figures 4.3 and 4.4). Thus where these organic amendments had been applied to the soil, concentrations of exchangeable Al did not appear to be the main factor determining concentrations of Al in soil solution. The most likely explanation for this is that Al is being complexed by the added organic matter and its decomposition products in both the solid and solution phases. That is, soil solution concentrations are more influenced by the presence of both soluble and insoluble organic ligands than by the buffering background levels of exchangeable Al.

Several workers have demonstrated that additions of decomposing organic residues to soils can reduce Al_{Mono} and/or Al_T in soil solution (Kretzschmar *et al.*, 1991; Bessho and Bell, 1992; Wong *et al.*, 1995). Soluble organic molecules such as organic acids (e.g., citric, oxalic, succinic, tartaric acids) and phenolic, humic substances produced during the decomposition of residues can complex with monomeric Al and reduce the proportion of A_T present as Al_{Mono} (Haynes and Mokolobate, 2000). Formation of soluble Al complexes with both humic molecules (Suthipradit *et al.*, 1990; Harper *et al.*, 1995) and organic acid anions (Hue *et al.* 1986) is well documented. In this regard, it is interesting to note that Tan *et al.* (1971) showed that the water extract of poultry litter exhibited a chelating effect on multivalent cations such as Al^{3+} . The compounds identified as being responsible for this effect were polysaccharides.

The relative importance of specific biochemical compounds such as organic acids and polysaccharides versus soluble humic materials in complexing soluble Al in this study is unknown. However relatively simple compounds such as organic acids and polysaccharides are likely to be present in soil solution for relatively short periods of time since they are highly

susceptible to microbial degradation. It can therefore be argued that a regular supply of these compounds into soil solution would be required for Al complexation to be sustained (Ritchie, 1994). By contrast, soluble humic substances are likely to be much more recalcitrant and also are generally more effective at complexing Al (Ritchie, *et al.*, 1982; Suthipradit *et al.*, 1990).

For limed soil samples, both the household compost and grass residue treatments tended to maintain higher concentrations of Al_T in soil solution than the control treatment (Figure 4.3). Several other workers have noted that Al_T in soil solution can be unaffected or even increased during the decomposition of organic residues (Berek *et al.*, 1995; Slattery and Morrison, 1995). In such cases it is thought that the large amounts of soluble organic matter present in solution complex with Al and maintain it in the solution phase. Indeed, a decrease in the Al^{3+} activity in soil solution due to complexation by soluble organic matter would result in movement of exchangeable Al^{3+} into soil solution through exchange reactions and, in the long term, to more dissolution of Al-containing minerals (e.g., gibbsite and amorphous hydroxy-Al oxides) and thus an increase in Al_T in soil solution.

In the main experiment reported in chapter 3, it was observed that the increased salinity caused by additions of organic amendments, and particularly that of poultry manure, resulted in relatively large values for Al_T and generally a high proportion of Al_T being present as Al_{Mono} . However, in this study, no such phenomenon was observed and additions of amendments generally reduced Al_T , Al_{Mono} and the proportion of Al_T present as Al_{Mono} . The greatest reduction was for poultry manure which had the highest pH. Certainly, both $pH_{(water)}$ and $pH_{(KCl)}$ were higher for the poultry manure than filter cake treatment while in chapter 3 it was found that although $pH_{(KCl)}$ was higher, $pH_{(water)}$ was in fact lower due to an accumulation of soluble salts.

The reason for this difference is presumably that in the present experiment, the high rates of basal fertilizer application applied to all treatments (including control), resulted in a significant accumulation of soluble salts in all the treatments. Thus, no specific effect of poultry manure was observed.

Surprisingly, there was no decrease in exchangeable or soluble Al with increasing P applications. Such a decrease in Al solubility with increasing P additions has been observed by a number of workers (Awad *et al.*, 1976; Bache and Crooke, 1981; Haynes and Ludecke, 1981) and had been attributed to the formation and precipitation of insoluble Al phosphate compounds. This can sometimes result in high rates of P reducing Al toxicity in crops (Bache and Crooke, 1981). Presumably in this study the solubility product of the Al phosphate was not exceeded. The added P may well have been rapidly removed from soil solution by adsorption onto metal hydrous oxide surfaces.

Where applications of organic amendments increased Olsen-extractable P concentrations appreciably (household compost, filter cake and poultry manure), additions of lime tended to cause a decrease in P extractability (Figure 4.4). Decreases in the extractability of applied P induced by lime applications have been observed by a number of other workers (Haynes, 1982; White, 1983). Decreases in NaHCO_3 -extractable P in limed soils have been attributed to an artifact during extraction (Sorn-Srivichai *et al.*, 1984; Naidu *et al.*, 1987). That is, the high Ca concentrations that occurs during the extraction of P from limed soils can result in the precipitation of P as calcium phosphates. Other explanations for a lime-induced decrease in P extractability include precipitation of insoluble calcium phosphate compounds in the soil (White and Taylor, 1977; Naidu *et al.*, 1987) and increased P adsorption onto newly formed hydroxy-Al

surfaces arising from precipitation of exchangeable Al (Haynes and Swift, 1989; Anjos and Rowell, 1987).

4.4.2 Maize Yield and Nutrient Content

The positive yield response of maize to applied lime in the control treatment was accompanied by a large decrease in exchangeable Al, Al_T and Al_{Mono} in soil solution and the proportion of Al_T present as Al_{Mono} . Thus, as expected, liming caused precipitation of exchangeable and soluble Al^{3+} as hydroxy-Al species (Haynes, 1984). As a result, Al toxicity was alleviated and crop growth was increased. The lack of yield response to applied lime in any of the soils amended with organic materials reflects the fact that in these treatments liming had no effect on concentrations of Al_T or Al_{Mono} in soil solution. These results show clearly that it is the concentration of Al in soil solution rather than exchangeable Al that limits crop growth. That is, for the household compost, grass residue and filter cake treatments liming greatly decreased exchangeable Al concentrations, however, concentrations of Al_T and Al_{Mono} were not greatly affected and neither was crop yield.

The Al_T concentration in soil solution ranged from 20 to $50\mu M$ which is in the range of 10 to $350\mu M$ typically found in soil solutions extracted from acid soils (Bruce *et al.*, 1988; Ritchie, 1989; Parfitt *et al.*, 1995). The proportion of Al_T present as Al_{Mono} in the unlimed soil was about 30% (Figure 4.3) which is also in agreement with the results of others. Berek *et al.* (1995), for example, recorded values of 38% for an acid podzol from Indonesia while Slattery and Morrison (1995) reported values of 16 to 41% for an Australian podzol. As noted in chapter 3, the pyrocatechol violet 60 sec. method measures monomeric Al plus some Al present in soluble Al-

organic matter complexes (Parfitt *et al.*, 1995). Measured values of Al_{Mono} of about 12 to 15 μM in the control treatment were reduced to below 5 μM in soils limed and/or amended with organic residues (Figure 4.3) and these latter concentrations are low and unlikely to limit maize growth. For example, in soil solution culture experiments Harper *et al.* (1995) showed that 19 μM Al_{Mono} inhibited root growth of maize while 3 μM did not; Diatloff *et al.* (1998) showed that 24 to 27 μM inhibited maize root growth while 8 μM did not. Thus it is concluded that additions of both organic matter and lime reduced Al_{Mono} to non phytotoxic concentrations.

Responses to applied P were recorded in the control, household compost and grass residue treatments whilst the other two treatments (filter cake and poultry manure) had much higher initial P levels (>20 mg kg⁻¹) and as a result no response occurred.

The pH dependence of Mn and Zn availability in soils is demonstrated by the lower tissue Mn and Zn concentrations in the poultry manure and to a lesser extent filter cake treatments than in the others (Table 4.2) and their decreasing concentrations with increasing lime rates (Table 4.1). These decreases in availability with increasing pH are attributable to precipitation of Mn²⁺ as Mn oxides and to increased specific adsorption of Zn onto metal hydrous oxides surfaces (Knezek and Ellis, 1980). The availability of Fe and Cu is generally less pH-dependent due to their ability to form strong complexes with soluble organic matter (Knezek and Ellis, 1980; Haynes and Swift, 1989). Indeed, liming had no effect on tissue Cu concentrations and actually tended to increase those of Fe.

The decrease in Mg concentrations in maize tissues with increasing lime rates (and increasing uptake of Ca) is attributable to competition between Ca²⁺ and Mg²⁺ during ion uptake and

translocation in the plant (Marschner, 1995). Competition between these two cations during active ion uptake across the plasma membrane of plant cells is well documented (Clarkson and Hanson, 1980; Marschner, 1995).

Surprisingly, differences in Al concentrations in maize tissue with treatment were not great. Root growth and root Al concentrations were, however, not measured. The main effect of Al toxicity in acid soils is generally on the root system which becomes short and stubby as a result of inhibition of elongation of the main axis and lateral roots (Kochian, 1995). This root system is ineffective at exploring the soil volume for water and nutrients and, in addition, active uptake of other nutrients across the plasma membrane is inhibited (Fageria *et al.*, 1988; Sasaki *et al.*, 1995). Thus concentrations of Al in plant tops are not necessarily an indicator of Al toxicity or its amelioration.

The nutrient content of compost can vary greatly depending upon the nature of organic materials used in its creation. Positive yield responses to applied compost are commonly reported (Mays *et al.*, 1973; Terman *et al.*, 1973; Moustafa, 1978) and generally its application increases the availability of most nutrients and, often also has a liming effect. In agreement with these general findings, compost application increased levels of exchangeable Ca, Mg and K, available soil P and pH and increased plant yields.

Residues of plant material (e.g., crop residues or in this case cut grassveld) can be an important source of organic matter and nutrients in small-scale farming enterprises. The grassveld residues used in this study were rather low in P (Table 3.1) and as a result, a yield response to applied P was recorded even with an application of residue equivalent to 20 Mg ha⁻¹.

Exchangeable Mg, and particularly K, were elevated in the grass residue-amended treatments reflecting the inputs of these nutrients in the residue. The liming effect of plant residues is now well known and the reduction in Al toxicity following their addition can (as in this case) greatly increase crop yields (Berek *et al.*, 1995; Wong *et al.*, 1995). As suggested by Hue and Amien (1989), the Al detoxification effect is twofold; the increased pH causes a reduction in Al solubility while soluble organic matter complexes with Al thus reducing the concentration of Al_{Mono} in soil solution.

The yield response to applied filter cake was not unexpected since it contained a significant amount of lime and P and N are the main nutrients of importance in relation to its use as a soil amendment (Alexander, 1971; Moberly and Meyer, 1978; Ng Kee Kwong and Deville, 1988). Indeed, crop yield responses in sugarcane to application of filter cake have been reported by many workers (Prasad, 1976; Moberly and Meyer, 1978; Cooper and Idris, 1980; Ng Kee Kwong and Deville, 1988). A yield response in this acidic, P-fixing soil from the KwaZulu-Natal midlands is not surprising since Moberly and Meyer (1978) showed that sugarcane yield responses to filter cake were much greater on these soils than on recent sandy soils from the coast. The high P supplying capacity of filter cake is of particular importance. The high Si content of filter cake (Alexander, 1971) may well be another important factor since silicate can be specifically adsorbed onto hydrous oxide surfaces thus decreasing the adsorption of added P (Obihara and Russell, 1972; Smyth and Sanchez, 1980).

The large effect that filter cake applications can have on P availability (Moberly and Meyer, 1978) is demonstrated in this study by the fact that the P content of compost and filter cake was similar (Table 3.1) yet concentrations of Olsen-extractable P were considerably higher in soils

amended with filter cake than compost (Figure 4.4). The competitive effect of added silicate on P adsorption may well have contributed to this effect and the higher soil pH under filter cake may have also favoured desorption of P (Barrow, 1984).

In this study, the most pronounced yield increase was to the application of poultry manure (Figure 4.7) which occurred irrespective of whether lime or P was applied or not. Indeed, yields in the poultry manure treatment were much higher than in any of the other treatments. Analysis of the nutrient concentration of maize tissues did not, however, give any indication of the reason for this large response. That is, none of the nutrients were present in notably higher concentrations in plants from poultry manure than from other treatments (concentrations of tissue Mn, Zn and Mg were, in fact lower).

Concentrations of Al_T and Al_{Mono} in soil solution, and exchangeable Al in the poultry manure treatments were similar to those in the limed control treatments (Figure 4.3 and 4.4) and concentrations of extractable P in soils were no greater in the poultry manure than household compost or filter cake treatments where the high rate of P had been applied (Figure 4.4). Thus, the response to poultry manure was not a simple response to applied lime or P. The filter cake treatments had similar Al_T and Al_{Mono} concentrations to those of poultry manure and Olsen-extractable P concentrations were slightly lower but well above 20 mg kg^{-1} . Thus a simple lime/P interaction does not explain the massive response to poultry manure either.

Visual observations suggested that the yield response to poultry manure became obvious only in the last few weeks of maize growth. A more prolonged release of nutrients in this treatment (particularly N) may have enabled plants to continue growing at a greater rate than for the other

treatments. Indeed, the fact that tissue nutrient concentrations were similar in the poultry manure to other treatments indicates that nutrient uptake was, in fact much greater (since yields were so much higher in the poultry manure treatment). Certainly a large release of nutrients from poultry manure is well known and where salinity problems are not encountered substantial crop yield responses to applications of poultry manure are often recorded (Sims and Wolf, 1994). The main yield response is usually to applied N but additions of P and K can also be important (Moberly and Stevenson, 1971; Liebhardt, 1976; Agbim, 1985; Bitzer and Sims, 1988). The release of substantial amounts of N and P from poultry manure is well-known and repeated high rates can represent a potential pollution problem (Sims and Wolf, 1994). Accumulation of large amounts of mineral N in the soil with subsequent leaching of nitrate into ground water can occur (Dudzinsky *et al.*, 1983; Bitzer and Sims, 1988; Sharpley *et al.*, 1993) while accumulation of available P in the surface soil layers can substantially increase runoff losses of P (Westerman *et al.*, 1983; Magette, 1988; Sharpley *et al.*, 1993).

The liming-effect of poultry manure has also been reported previously. Hue (1992), for example, showed that poultry manure was an effective liming material and 10g of poultry manure had a liming-effect equivalent to 6.7 cmol_c of Ca (OH)₂. Nevertheless, Hue (1992) suggested that crop yield response to poultry manure in an acid soil was not only related to increased soil pH but also to detoxification of soluble Al by organic complexation and to enhanced Ca uptake by the crop.

4.5 CONCLUSIONS

That trends with treatment for Al_T and Al_{Mono} in soil solution did not follow those for

exchangeable Al is of particular interest. It suggests that measurement of exchangeable Al and/or exchangeable Al saturation will not necessarily give a good indication of the potential for Al toxicity in crops and the need for lime. Where any of the organic amendments had been applied, there was a significant decrease in both Al_T and Al_{Mono} in soil solution and as a result, no positive yield response to lime was recorded. Increases in pH with the addition of two of the organic residues (household compost and grass residues) were small and the formation of both solid and liquid phase complexes with organic matter was suspected to contribute significantly to the depressions in soil solution Al concentrations. The results certainly suggest that the application of organic amendments to acid soils in the field situation could potentially increase crop yields where Al toxicity limits plant growth. Such a practice could be used by small-scale farmers who often cannot afford lime.

The P content of organic residues is another important aspect of their use. Whilst crop responses to applied P were observed for grass residue and household compost additions, no such responses were recorded for the filter cake and poultry manure treatments. Thus for the former two amendments, application of some fertilizer P was required in order to take full advantage of their liming effect.

The reason for the extremely large yield response to applied poultry manure was not clear but did not seem to be attributable to an effect of liming or P addition. It was possibly due to a prolonged release of nutrients (such as N) allowing for continued rapid growth of maize plants during the latter part of the glasshouse experiment. The reason for this response does, however require further study.

CHAPTER 5

GENERAL CONCLUSIONS

All of the organic amendments used in this study had a liming effect in that they raised soil pH significantly and, in the presence of a basal fertilizer-dressing, they also reduced both Al_T and Al_{Mono} in soil solution to low, non-phytotoxic, concentrations when applied at a rate equivalent to 20 Mg ha^{-1} . This effect in depressing Al concentrations in soil solution did not appear to be linked only to an effect on soil pH. Indeed, in Chapter 4, in amended soils, the background levels of exchangeable Al did not seem to be the main factor controlling Al concentrations in soil solution. Complexation of Al in both the solid and solution phase by organic matter was probably an important mechanism. It is important to note here that the measurement of exchangeable Al or Al saturation, would not be an appropriate method of estimating the potential for Al toxicity, or the need for lime, in acid soils which had been recently amended with organic materials.

The addition of organic amendments was also shown to improve soil fertility; particularly the Ca, Mg, K and P status of the soil. Concentrations of extractable P were increased and the P adsorption capacity of the soil was decreased following additions of amendments. When a basal fertilizer dressing was not applied, the relatively large input of cations from the amendments resulted in an accumulation of soluble salts in the soil. The effect was particularly pronounced for poultry manure but was also evident for the other amendments. This accumulation of cations resulted in displacement of exchangeable Al^{3+} into soil solutions with a consequent increase in the concentration of Al_{Mono} and it partially counteracted the effect of organic

materials in both increasing pH and complexing Al. When a basal fertilizer application was applied to all treatments (including the unamended control) no such effect was, however, observed.

In the case of two of the residues used, even at an application rate of 20 Mg ha⁻¹, there was a need to apply a low rate of P (equivalent to 10 kg P ha⁻¹) in order to avoid P being a limiting factor to crop yield. Thus additional inputs of P will sometimes be required when organic residues are applied. The magnitude of the requirement will depend upon factors such as the P content of the residue and the P status and P adsorption capacity of the soil; these effects need to be quantified and understood. Even so, the rates of P needed are likely to be substantially less than those required when no organic residues are applied. In this study the reason for the very high yields with the poultry manure treatment was unclear and deserves further study.

From the results of this study, it is evident that additions of organic residues can have a liming effect and markedly reduce concentrations of exchangeable and soil solution Al in an acid soil. Their addition can also improve the P status of the soil. Since soil acidity (Al toxicity) and P deficiency are usually the two most limiting factors to crop production on the underdeveloped soils of much of KwaZulu-Natal, the use of organic residues to help correct these problems is an intriguing alternative to the use of lime and P fertilizer. This is particularly so because for the resource-poor, semi-subsistence farmers in rural areas, the regular use of organic residues such as animal manures, crop and grass residues and composts is practicable whilst lime and fertilizer P are very expensive commodities.

The next step in this research is to extend it into the field in order to investigate the feasibility

of using organic residues in the small-scale farming situation. A large amount of information is still required. In this study, only one soil was used and there is an obvious need to extend the study onto a range of undeveloped acid soils representative of those currently being used by small-scale farmers. The relative effects of various types of residue, methods to predict their potential benefits, the most appropriate timing of their application and the best techniques for applying them are all important practical considerations requiring further research. Techniques such as banding may well be appropriate. For example, a rate of application of 20 Mg ha⁻¹ of residue used in this study would be exceptionally high if it were applied over an entire field but it may well be practicable to apply such a rate in a 60 cm wide band down the planting rows. Additional fertilizer P could also be applied in a band at sowing.

The purpose of such research would be to develop integrated soil fertility management programmes using organic residues available to small-scale farmers in order to minimize the need for costly manufactured fertilizer inputs while still producing high crop yields. Such programmes would greatly benefit resource-poor farmers who are currently struggling to produce crops on acidic, P-deficient soils.

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