

**USE OF ORGANIC AMENDMENTS AS AMELIORANTS FOR SOIL
ACIDITY IN LABORATORY AND FIELD EXPERIMENTS**

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ABSTRACT

Laboratory studies and field trials were carried out to investigate the effect of addition of some organic residues to acid soils on soil pH, exchangeable and soluble Al, nutrient status, microbiological and biochemical indices and maize response.

The organic wastes used in the first laboratory study included plant materials (maize, sorghum, kikuyu grass, soybean, red clover residues and acacia prunings), animal manures (kraal, pasture-fed and feedlot cattle manure, layer and broiler poultry manure and pig manure), household compost, sewage sludge, and filter cake. The poultry manure, pig manure and leguminous plant residues had the highest content of basic cations while sewage sludge had the highest N content. Poultry manure had very high values for proton consumption capacity, CaCO_3 content and ash alkalinity. Proton consumption capacity, ash alkalinity, total basic cation content and CaCO_3 content were closely correlated with one another. Soil pH was increased and exchangeable Al and total (Al_T) and monomeric (Al_{Mono}) Al in solution were decreased by addition of all the organic wastes: the effect was greater at the higher rate of application. Strong correlations were recorded between the rise in soil pH and proton consumption capacity, ash alkalinity, CaCO_3 content and basic cation content of the residues. The major mechanisms responsible for the elevations in pH were suggested to be the substantial CaCO_3 content of poultry and pig manures, and filter cake, the proton consumption capacity of humic material present in household compost and manures and decarboxylation of organic acid anions during the decomposition of plant residues and manures. It was proposed that ash alkalinity is a suitable laboratory test for predicting the potential liming effect of organic residues since it is strongly correlated with the rise in pH that occurs, it is relatively simple to measure and the values reflect the initial content of organic acid anions, humic materials and CaCO_3 in the residues.

A preliminary field experiment was set up to investigate the effectiveness of kraal manure as a liming material in an acid soil ($\text{pH}_{\text{water}} = 4.1$) at a site close to a Zulu village. The experiment consisted of two rates of lime ($L1 = 2.5$ and $L2 = 5.0 \text{ t ha}^{-1}$) and two rates of kraal manure ($K1 = 10$ and $K2 = 20 \text{ t ha}^{-1}$) which were banded and incorporated in a 30 cm wide strip down the plant rows. Treatments were arranged in a randomized block design with three replicates. A commercial maize cultivar PAN 6710 and a traditional variety EMBO, used by the farmers in the locality, were grown. Soils in the plant row were sampled at tasselling and at harvest. The addition of kraal manure significantly raised soil pH and reduced concentrations of exchangeable Al and those of both total and monomeric Al in soil solution. Lime raised pH and the pH continued to increase between tasselling and harvest. Maize yields for control, kraal manure (K1 and K2) and lime (L1 and L2) for PAN 6710 were 2.5, 3.7, 5.1, 5.3 and 6.3 t ha^{-1} ; respectively and for EMBO they were 3.0, 5.4, 5.8, 5.9 and 8.2 t ha^{-1} , respectively. These results demonstrate the high yield potential of the traditional maize variety under small scale farming conditions, and show that large yield increases can be obtained by applying kraal manure.

The long-term effects (24 weeks) of incubation of organic wastes (soybean residues, poultry, pig and kraal manures and sewage sludge) with an acid soil were investigated in a laboratory study. After incubation for six weeks incubation, soil pH was raised and exchangeable Al and Al_T and Al_{Mono} in soil solution were decreased by addition of the wastes. Soil pH generally declined and exchangeable and soluble Al increased over the remainder of the incubation period. The decline in pH was attributed mainly to nitrification of NH_4^+ originating from mineralization of wastes-derived organic N. Addition of organic materials generally resulted in a decrease in the proportion of solution Al_T present as Al_{Mono} . That is, the effects of addition of organic materials was two-fold; an increase in pH in the short term and complexation of Al by organic matter. Since these effects occur simultaneously, it would be desirable to separate them.

For this reason, short-term equilibration experiments (3 days) were conducted to study the solubility of Al in aqueous solution or in an Oxisol when in equilibrium with 3 manures (kraal, pig and poultry) at pH values of 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5. Addition of manures tended to reduce the concentrations of total Al in solution (Al_T) in the lower pH range (i.e. pH 4.0 and 4.5) but increased Al_T concentrations compared to the control, at higher pH values (i.e. at pH 5.5 and above). This was explained in terms of the complexing ability of both the solid and solution phases. At lower pH, where Al is highly soluble, complexation by added solid phase manure-organic matter results in a reduction of Al solubility. However, at high pH, where Al solubility is limited, the most important mechanism is complexation of Al by soluble organic matter and this increased Al solubility. Additions of manure reduced the proportion of Al_T present in monomeric form (Al_{Mono}). This effect was more pronounced in aqueous solution but was also clearly evident above pH 5.0 in the Oxisol. This reflects the fact that a large concentration of soluble C in solution can maintain relatively high concentrations of complexed Al in solution but at the same time maintain low concentrations of Al_{Mono} . It was concluded that formation of Al-organic matter complexes caused by additions of organic manures can alter the solubility of Al and reduce the amount of phytotoxic Al_{Mono} present in soil solution.

A second field trial was conducted to compare the effects of additions of kraal manure, grass residues, lime and fertilizer (N-P-K) under field conditions, on soil pH, Al solubility and maize response and, at the same time follow concomitant changes in the size and activity of the soil microbial biomass and enzyme activity. The greatest effects of kraal manure in increasing soil pH and decreasing Al toxicity were recorded six weeks after planting whereas those of lime and grass residues were recorded at harvest. Kraal manure and fertilizer increased significantly AMBIC extractable P and exchangeable K and Zn. In

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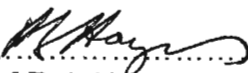
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DECLARATION

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

Signed.....
Francois-Xavier Naramabuye

Signed.....
Prof R.J. Haynes

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CHAPTER ONE

1. General introduction

Soil acidity is an underlying problem in many agricultural areas and it is increasingly becoming a yield-limiting factor in other areas (Frey *et al.*, 1984). Weathering and leaching are the important sources of natural soil acidification. In industrialized regions, anthropogenic sources of acidity are also becoming a serious problem. As reported by Wild (1988), acid rain and nitrification of ammonium originating from nitrogenous fertilizers release protons into the soil causing acidification. The reason for low crop productivity in acid soils is mainly Al toxicity but, nutrient deficiencies can also be a problem (Wild, 1993).

According to McLean (1973) and Lindsay (1979), Al is the most abundant metal cation present in the earth's crust (7.5% by mass). Aluminium was implicated for the first time in retarding the growth of some plants, approximately 86 years ago by Hartwell *et al.* (1918). Thereafter, the mechanisms involved in Al toxicity were uncovered and explained (Foy and Fleming, 1978; Hecht-Bucholz, 1983; Stegel and Haug, 1983; Wallace and Anderson, 1984).

In intensive agriculture, soil acidity is routinely ameliorated by the application of lime and sometimes gypsum (Thompson and Troeh, 1978). These materials are, however, expensive and often, both logistic and economic constraints limit their use by resource-poor, small-scale farmers. Sustainable alternative strategies need to be found. An interesting alternative to lime is the use of organic amendments (organic residues and animal manures), which can be available at low cost to most semi-subsistence farmers (Haynes and Mokolobate, 2001). Not only are the organic materials able to increase the soil pH and decrease Al toxicity (Hue, 1992; Berek *et al.*, 1995), but they also play an important role in improving soil physical properties (Johnson, 1991) and during their

decomposition nutrients are released thus, improving soil fertility (Johnson, 1991).

The mechanisms by which the addition of organic amendments increase soil pH and/or detoxify phytotoxic soil Al are still unclear (Hue and Amien, 1989) and a number of different mechanisms have been suggested (Haynes and Mokolobate, 2001). It has been suggested that detoxification of Al due to addition of organic amendments to an acid soil, is explained by both an increase in pH and Al complexation by the added organic matter (Haynes and Mokolobate, 2001). Short and long-term reactions are suggested to control the increase in pH and the solubility of Al. These reactions include immediate chemical reactions (Tang *et al.*, 1999; Yan *et al.*, 1996) and a number of reactions related with the decomposition of organic materials (Hue *et al.*, 1986; Iyamuremye and Dick, 1996).

In addition to the multiple soil constraints (nutrient deficiency, Al toxicity) to crop production, acid soils have been reported to have a poor biological activity Doran (1987). It is believed that the amelioration of soil acidity results in improving the soil microbial activity. Many workers including Doran (1987) suggested that the application of organic materials on an acid soil, not only increases soil pH, but also increases soil nutrient status and the size and activity of the soil microbial community. Up until now very few studies have focused on the interaction between soil pH and microbiological and biochemical properties and results from previous studies have been somewhat inconclusive (Haynes and Swift, 1988; Neale *et al.*, 1997).

This study was carried out to further investigate the use of organic amendments to ameliorate soil acidity. It consists of both field experiments to investigate the applicability of using such materials under field conditions and laboratory studies investigating how to predict the liming effect of such residues and to further

elucidate the mechanisms by which these materials have a liming / Al detoxifying effect.

The main objectives of this study were:

- 1) to review and discuss the mechanisms involved in the liming effect of organic residues;
- 2) to evaluate the effectiveness of a number of proposed laboratory indices for predicting the liming effect of different organic materials;
- 3) to investigate the effect of kraal manure in ameliorating Al toxicity under small scale farming conditions and compare the productivity of an indigenous and commercial cultivar of maize under such conditions;
- 4) to investigate the short and long-term effects of the addition of organic manures on Al solubility under laboratory conditions; and
- 5) to compare the effects of application of kraal manure, grass residues, lime and fertilizer to an acid soil, on soil pH, Al solubility, maize response and microbiological and biochemical properties under field conditions.

The thesis is organized into five chapters: (1) a review of the nature of soil acidity and the use of organic amendments to ameliorate aluminium toxicity (CHAPTER 2); the use of laboratory indices to predict the effect of addition of a range of organic wastes on soil pH and Al solubility (CHAPTER 3); the response of maize to kraal manure and lime as ameliorants for soil acidity in a field trial on a small scale farm in KwaZulu-Natal (CHAPTER 4); laboratory studies on the mechanisms controlling the solubility of Al when organic manures are added to an acid soil in short and long-term experiments (CHAPTER 5); and lastly, comparison of the effects of kraal manure, grass residues, lime and fertilizer on

soil acidity indices and microbiological and biochemical indices and maize yields under field conditions (CHAPTER 6). For additional information on the thesis, detailed data collected during experiments as well as photography of the field experiments are provided in appendices

CHAPTER TWO

2 Literature review: The nature of soil acidity and the use of amendments to ameliorate aluminium toxicity.

2.1 Introduction

The purpose of this review firstly is to summarize and discuss the central role of Al in the chemistry of soil acidity and the role of Al toxicity as the major limitation to crop production in acid soils. In the second part of the review, the role of organic amendments as ameliorants for soil acidity is discussed. Particular attention is paid to the various mechanisms that have been proposed to explain such amelioration.

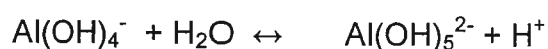
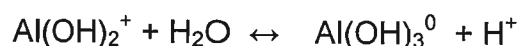
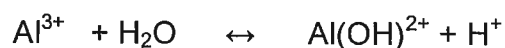
2.2 Nature of soil acidity.

Soil pH is probably the single most important chemical characteristic of a soil. It has a major influence on most soil chemical processes as well as soil biological activity and plant growth. The relative proportion of exchangeable cations held on the exchange site of negatively charged soil colloids largely controls soil pH. Exchangeable Al^{3+} and H^+ increase soil acidity whereas exchangeable base-forming cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) increase alkalinity. The term, pH, is a way of representing the H^+ or OH^- concentrations in aqueous solutions and is defined as the negative logarithm, base 10, of H^+ activity [$-\log(\text{H}^+)$]. Soil pH is measured in a water or salt solution in equilibrium with the soil. In a strict sense, any soil with a pH of below 7 could be considered as acidic but soils with a pH (water) between 5.5 and 7 are, in fact, generally not referred to as "acidic" (Thompson and Troeh, 1978). From the viewpoint of soil fertility, soils with a pH_{water} of below 5.5 are usually considered as acidic (Thompson and Troeh, 1978). In such soils, Al invariably occupies a substantial proportion of the cation

exchange capacity and Al toxicity can be a major growth-limiting factor for crop production (Thompson and Troeh, 1978)

2.2.1 Chemistry of Al.

Aluminium is an inorganic element found in aluminosilicates and oxide minerals (Lindsay, 1979), where it is present in soils in greater quantity than Ca^{2+} , K^+ and Mg^{2+} (Clarkson and Hanson, 1980) but aluminium also occurs in exchangeable form. The chemistry of Al in acid soils is extremely important and its hydrolysis, speciation and ionic charge are mainly controlling Al reactions in soil. The hydrolysis reaction can be explained as an electrical interaction between the ion and water molecules. This is influenced by the ionic charge and the charge density. The Al ion has an ionic radius of 0.5 Å, a hydrated radius of 4.75 Å and a charge density of 4.75 (Nightingale, 1959). The intensity of hydration of an ion increases with increasing ionic charge and decreasing ionic radius. Under acidic conditions Al is hydrated as $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Hydrolysis occurs when the charge/size ratio is so great as to cause rupture of H-O bonds and H^+ ions are released. In this way protons can be dissociated from the water molecules on the Al hexahydrate ion: $[\text{Al}(\text{H}_2\text{O})_6^{3+} \leftrightarrow \text{Al}(\text{H}_2\text{O})_5^{2+} + \text{H}^+]$. Hydrolysis proceeds with increasing pH, and equations presented below show the sequence of hydrolysis reactions that can occur (McLean, 1976) and Lindsay (1979). For simplicity, the water of hydration is omitted.



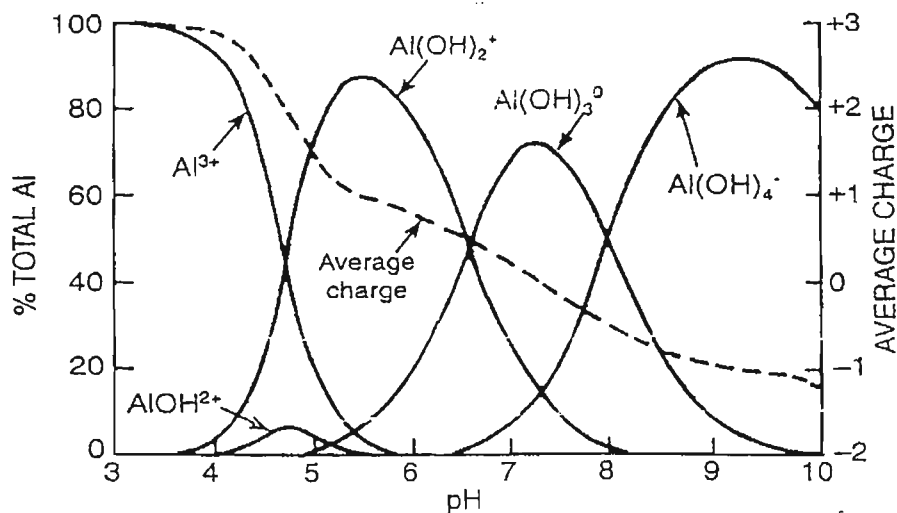


FIGURE 2.1 Relationship between pH and the distribution and average charge of soluble Al species. (after Havlin *et al.*, 1999).

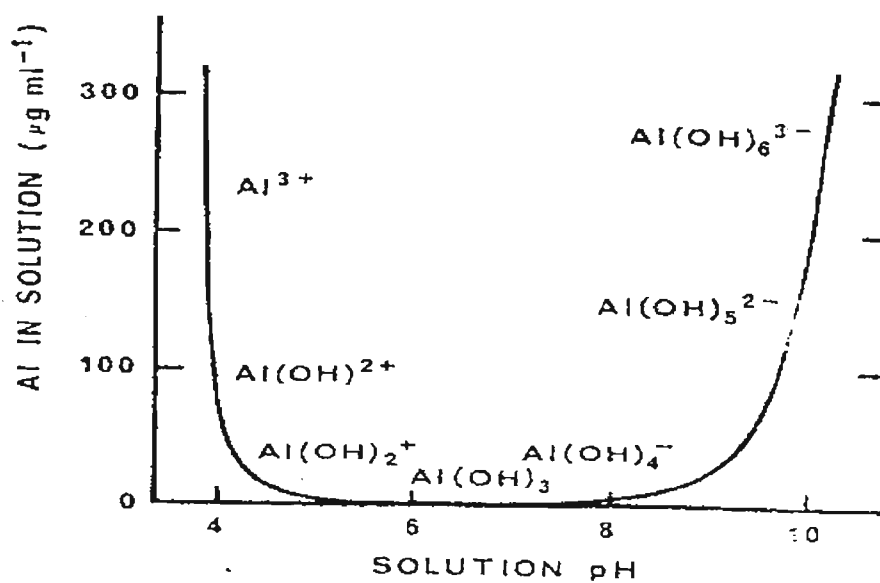
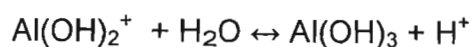


FIGURE 2.2 Effect of pH on the solubility of Al in solution. (Redrawn from McLean, 1996).

The relationship existing between pH and the distribution and average charge of soluble Al is shown in FIGURE 2.1 whilst the solubility of these Al species in equilibrium with gibbsite is illustrated in FIGURE 2.2. It is evident that at pH 4.0 and below, Al^{3+} predominates and that Al solubility decreases with increasing pH until at about pH 6, insoluble $\text{Al}(\text{OH})_3$ (e.g. gibbsite) is the dominant species. At higher pH values increasingly soluble, negatively charged, aluminate ions form.

An important property of positively charged monomeric Al species is that they can polymerize to form both large and small positively-charged poly-nuclear complexes. As the pH and the OH/Al ratio in solution rise, polymers of increasing complexity are formed (Lindsay, 1979). Aluminium can function as an acid or a base either donating or consuming protons. For example:



Thus protons are released if base is added to Al ions and by the reverse reaction protons are removed from solution when acid is added. The practical significance of the above reactions is that when a soil is acidified, soil Al becomes increasingly soluble while when an acid soil is limed (i.e., the pH is raised), exchangeable and soluble Al precipitate as hydroxy-Al polymerizes.

2.2.2 Measurement of soil acidity

Several forms of soil acidity may be defined and measured. These include active, exchangeable and non-exchangeable acidity. Active acidity is measured by taking account of protons in soil solution. It is estimated by measuring pH in soil solution or in a soil/water suspension or a soil suspended in a solution of about

the same ionic composition as the soil solution (e.g., 0.01M CaCl₂) (Thompson and Troeh, 1978).

Exchangeable acidity is measured by extraction with unbuffered 1 M KCl (Wild, 1988). This extracts exchangeable H⁺ and Al³⁺ along with other cations (predominantly Ca²⁺ and Mg²⁺) at the natural soil pH. The exchangeable acidity (H⁺+Al³⁺) is determined in the extract by titration with NaOH using phenolphthalein as indicator. Exchangeable Al in the extract may also be determined separately. The nature of exchangeable Al has not been examined in detail but the average charge per Al ion is between 2 and 3 decreasing as pH rises, (Wild, 1993). This presumably reflects the fact that this Al is a mixture of monomeric species [Al³⁺, Al(OH)²⁺ and Al(OH)₂⁺] and polymeric forms.

Non-exchangeable acidity contributes to total or titratable acidity. Total acidity is usually measured by titrating a soil suspension up to a pH of 8 with NaOH. The amount of acidity in the soil is equivalent to the NaOH used (Wild, 1988). Non-exchangeable acidity is present in soils in the form of protons or as non-exchangeable Al that can be released from surfaces as the pH rises. The main sources of protons that can be released are (i) the reactive OH⁻ groups on the surfaces of hydrated Fe and Al oxides and/or the edges of clay minerals (particularly 1:1 clay minerals) and (ii) carboxyl, hydroxyl and amino groups on organic matter which can dissociate as pH rises (Wild, 1988).

Non-exchangeable Al is a buffering reserve of the reactive Al in soils and levels of exchangeable Al are partially controlled by this reserve (Haynes, 1984). Non-exchangeable Al includes polymeric hydroxy Al which can be present on exchange sites, as coatings on soil colloids and in the interlayers of 2:1 clay minerals plus monomeric and polymeric hydroxy Al in forms complexed with soil organic matter (Wild, 1988)

2.2.3 Processes of Soil Acidification.

2.2.3.1 Natural factors.

Soil acidification is a natural process that occurs slowly (Wild, 1994). For acidification to occur there needs to be a source of protons. Rainwater, in the absence of oxides of S and N is a dilute carbonic acid solution with a pH of 5.65 (Wild, 1988). Dissolution of CO₂ produced by soil respiration (originating from respiration from living plant roots, soil microorganisms and soil fauna) lowers the pH of percolating rainwater further. The processes involved are that the CO₂ dissolves to give H₂CO₃ with dissociation to H⁺ and HCO₃⁻. The HCO₃⁻ is leached along with exchanged Ca²⁺ and Mg²⁺ leaving most of the H⁺ behind in the soil (Wild, 1988):

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$$

Organic acids can also be an important natural source of acidification (Wild, 1994). These may originate directly from plant litter or may be synthesized by microorganisms during decomposition processes. Oxidation processes such as nitrification may also contribute to acidification. The major sources of soil acidity (and alkalinity) are listed in TABLE 2.1.

As water percolates down the soil profile, an acidic soil solution is moved downward. Over time, the soil pH begins to fall, the more total cation exchange sites occupied by Al) and a low base components of clay minerals are removed and Al present in the residues begins to dissolve. As a result, basic cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺) become replaced on the cation exchange sites by protons and Al ions. The basic cations are then slowly leached down the soil profile. As a result, acid soils have a high Al saturation (percentage of total cation exchange sites occupied by exchangeable Al). A generalized relationship between Al saturation and soil pH is demonstrated in FIGURE 2.3.

TABLE 2.1 Sources of acidity and alkalinity in soil (after Wild, 1993).

Acidity	
1.	Addition of acids and acid-forming chemicals from the atmosphere
2.	Uptake of $(\text{cations})_c > (\text{anions})_c$ by plants ^a
3.	Removal of basic cations in plant harvest and by leaching
4.	Oxidation processes such as nitrification
5.	Microbial production of organic acids
6.	Increase of soil organic matter content
7.	Volatilization of ammonia from ammonium compounds
Alkalinity	
1.	Addition from the atmosphere of carbonates and weatherable minerals in dust
2.	Uptake of $(\text{anions})_c > (\text{cations})_c$ by plants
3.	Reduction processes
4.	Weathering of primary minerals
5.	Hydrolysis of exchangeable sodium ions, which may be present in high concentrations after irrigation with saline water

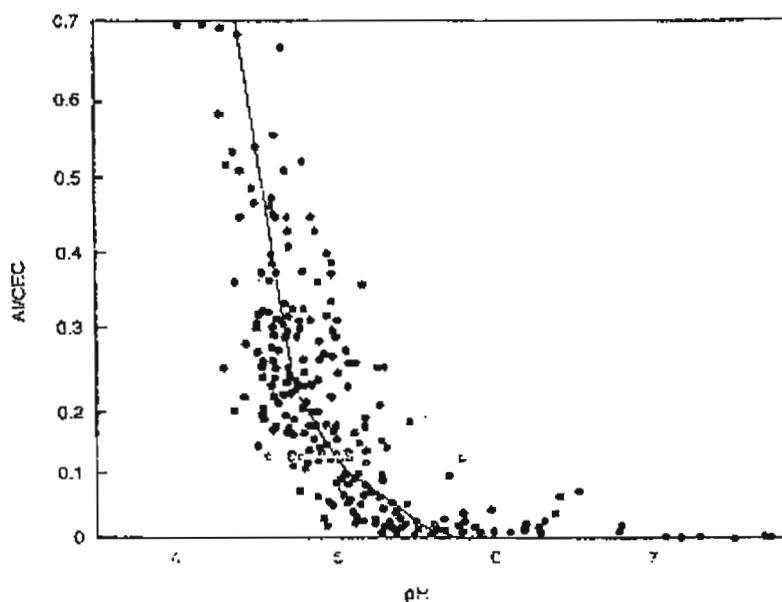


FIGURE 2.3 Relationship between pH and Al saturation (after Havlin *et al.*, 1999).

2.2.3.2 Anthropogenic factors

In recent times there has been increasing concern regarding the possibility of soil acidification being accelerated by the activities of man. The two most important anthropogenic acidifying effects are generally considered to be acid rainfall and the use of N fertilizers in agriculture (Wild, 1993).

Acid rainfall.

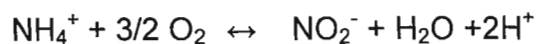
The most important acids contained in precipitation are HNO_2 , HNO_3 and H_2SO_4 formed in the atmosphere. Areas where liming and heavy fertilization practices are used, acid precipitations are not likely to cause soil acidity. However, soils having a very low CEC, low organic matter content, and low clay content and are very shallow, have a high risk of acidification due to acid precipitation (Cowling, 1980; McFee and Kelly, 1977)

Until recently, soil acidification induced by acid rain had not been clearly demonstrated.. However, some research does confirm a relationship between acid rain and a decrease in soil pH. According to Van Breemen *et al.* (1984), acid depositions far exceed soil sources of acidity in the northeastern United States. It has been shown that since industrialization, large amount of basic cations have been lost from arable soil and there has been a concomitant increase in Al solubility.

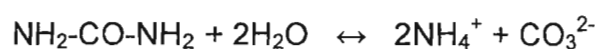
Nitrogenous fertilizers

Ammoniacal fertilizers are often the most important anthropogenic factor of soil acidification. Their acidifying effects are illustrated in TABLE 2.2. Urea, anhydrous ammonia, ammonium nitrate, ammonium phosphates and ammonium sulfates constitute 95% of the world fertilizer nitrogen use and are distributed into two groups (i) the fertilizers which release consumers of protons (i.e., OH^- and/or CO_3^{2-}) and (ii) those which do not (Bolt *et al.*, 1986).

Nitrification of NH_4^+ is a two-stage oxidation process carried out by autotrophic bacteria such as *Nitrobacter* and *Nitrosomonas* which transform NH_4^+ into NO_3^- releasing two protons (H^+) into the soil:



The above reaction shows that per mole of NH_4^+ oxidized, two moles of protons are produced. For urea and anhydrous NH_3 this acidifying effect is partially neutralized by the formation of CO_3^{2-} and OH^- respectively during their initial reactions in the soil:



Thus, the acidifying effect of urea and anhydrous ammonia is less than that of ammonium sulfate and ammonium phosphates.

TABLE 2.2 Source of acidity and alkalinity in soil (after Wild, 1993)

N Source	Nitrification Reaction	Residual soil acidity				
		Maximum		Minimum		Official Value
		Acid Residue	CaCO3 Equip	Acid Residue	CaCO3 Equip	
Anhydrous ammonia	$\text{NH}_3(\text{g}) + 2\text{O}_2 \rightarrow \text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O}$	H^+	kg CaCO ₃ /kg of N		— kg CaCO ₃ /kg of N—	
Urea	$(\text{NH}_2)_2\text{CO} + 4\text{O}_2 \rightarrow 2\text{H}^+ + 2\text{NO}_3^- + \text{CO}_2 + \text{H}_2\text{O}$	NO_3^- 2H^+ 2NO_3^-	$50/14 = 3.6$	None	0	1.8
Ammonium nitrate	$\text{NH}_4\text{NO}_3 + 2\text{O}_2 \rightarrow 2\text{H}^+ + 2\text{NO}_3^- + \text{H}_2\text{O}$	2H^+ 2NO_3^-	$100/28 = 3.6$	None	0	1.8
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4 + 4\text{O}_2 \rightarrow 4\text{H}^+ + 2\text{NO}_3^- + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	4H^+ 2NO_3^- SO_4^{2-}	$200/28 = 7.2$	2H^+ SO_4^{2-}	$100/28 = 3.6$	5.4
Monoammonium phosphate	$\text{NH}_4\text{H}_2\text{PO}_4 + \text{O}_2 \rightarrow 2\text{H}^+ + \text{NO}_3^- + \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	2H^+ NO_3^- H_2PO_4^-	$100/14 = 7.2$	H^+ H_2PO_4^-	$50/14 = 3.6$	5.4
Diammonium phosphate	$(\text{NH}_4)_2\text{HPO}_4 + \text{O}_2 \rightarrow 3\text{H}^+ + 2\text{NO}_3^- + \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	3H^+ 2NO_3^- H_2PO_4^-	$150/28 = 5.4$	H^+ H_2PO_4^-	$50/28 = 1.8$	3.6

2.2.4 Al Toxicity and Soil Acidity.

2.2.4.1 Effect on plant growth

Many workers have documented the relationship existing between Al toxicity and inhibition of the physiological functions of plant growth and nutrition. Investigations carried out by Kamprath (1970), Pearson (1975) and Saigusa *et al.* (1980) confirmed that inhibition of plant growth in acid soils and concentrations of exchangeable Al are closely related. Due to differences in CEC caused by differences in mineralogy, surface charge and organic matter content, there is often a stronger relationship between growth inhibition in acid soils and Al saturation than with exchangeable Al (McCray and Sumner, 1990). The range of 20 to 70 % Al saturation has been estimated as the growth limiting range depending on soil and crop type (Kamprath, 1970; Sartain and Kamprath, 1977; Farina *et al.* 1980; Abruna-Rodriguez *et al.*, 1982). It has, however, been demonstrated that Al concentrations in soil solution are more closely related to growth inhibition than either exchangeable Al or Al saturation (Pearson, 1975; McCray and Sumner, 1990).

It is not only the quantity of Al present in soil solution that is important but also the Al species that are present. The monomeric species Al^{3+} , $\text{Al}(\text{OH})_2^{2+}$ and $\text{Al}(\text{OH})_2^+$ have all been implicated in inhibition of root growth (Moore, 1974; Blamey *et al.* 1983; Farina *et al.*, 1980). Even the negatively charged aluminate ions (e.g., $\text{Al}(\text{OH})_4^-$) have been reported to inhibit root growth at pH values of about 8.8 (McCain and Davies, 1983). Both Alva *et al.* (1986) and Kinraide and Parker (1990) found that plants are more sensitive to $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^{2+}$ than Al^{3+} . The reason for this is thought to be that at very low pH (where Al^{3+} predominates) the presence of H^+ partially alleviates the phytotoxic effect of Al^{3+} at the root plasma membrane (Kochian, 1995). A possible method of detoxifying monomeric Al present in soil solution is to complex it with ligands such as F^- , SO_4^{2-} , organic acid anions or soluble humic material. In general, Al complexed

with such ligands has been found to be non-toxic to plants (Ritchie, 1989; Kochian, 1995).

Aluminium toxicity is known to inhibit the availability and uptake of macro-nutrients as well as micronutrients (Foy and Brown, 1963; Clarkson, 1967; Foy *et al.* 1972; Andrew and Vanden Berg, 1973; Foy, 1974, Clark, 1977, Foy *et al.*, 1978; Wright, 1989 and Kochian, 1995). For instance, inhibition of Ca and P uptake have been reported by both Mugwira (1980) and Huang *et al.* (1992). Foy *et al.* (1978) observed foliar symptom on aluminium-treated plants which resembled those of P deficiency. However the initial, and most important, symptom of Al toxicity is the inhibition of root growth due to impedance of both cell elongation and cell division (Foy, 1988; Kochian, 1995). Indirect effects can also be important. For example, Al toxicity can result in poor nodulation and N₂ fixation in legume (Munns, 1965a).

2.2.4.2 Mechanisms of Al toxicity

A number of different mechanisms have been proposed to explain Al toxicity in plants. These include Al interactions within the cell wall, the plasma membrane or the root symplasm (Kochian, 1995). Ryan *et al.* (1993) suggested that the root apex is the site that is most affected by aluminium toxicity. Important mechanisms of Al toxicity include inactivation of DNA, interference with P metabolism and inhibition of Ca uptake. These are summarized below.

Inactivation of DNA

Toxic concentrations of aluminium are known to interfere with DNA synthesis (Matsumoto *et al.*, 1976; Naidoo *et al.*, 1978; Wallace and Anderson, 1984). Aluminium treatment has been reported to cause a decline in the frequency of transmission of mitotic figures in the root meristem which causes inhibition of onion root elongation (Clarkson, 1965). The inactivation of DNA could be due to

Al binding with polyphosphates or phosphoxylated proteins associated with DNA (Kochian, 1995). Aluminium, not only inhibits DNA synthesis (Matsumoto, 1976), but also decreases DNA activity (Morimura *et al.* 1978). Although inhibition of root growth has been linked to a reduction in cell division (caused by inhibition of DNA synthesis) (Morimura *et al.*, 1978), at least in the early stages of Al toxicity, inhibition of cell elongation appears more important (Wallace and Anderson, 1984; Kochian, 1995).

Interference with Phosphorus metabolism

Phosphorus is involved in electron transfer reactions and influences activators (other ions) of enzyme systems (Hanson, 1980). As a conclusion of their works, both Clarksons, (1967) and Andrew and Vander Berg (1973) suggested that Al and phosphorus coincidentally concentrate predominantly in the plant root. This supports the idea that one of the first mechanisms of Al toxicity is the precipitation of phosphorus within the plant root as insoluble aluminium phosphates. In general, in acid soils, Al toxicity and phosphorus deficiency cannot be treated separately. Indeed a major effect of aluminium toxicity is that the plant is unable to use available soil phosphorus effectively (Haynes, 1984; Sumner and Farina, 1986).

Inhibition of Ca uptake.

Antagonistic effects of Ca and Al in soil or nutrient solution have been demonstrated in numerous studies (Huang *et al.* 1992, 1994). The interactions between these two elements include reduced uptake and translocation of Ca as solution Al concentration is increased, and decrease a susceptibility to Al toxicity at increasing solution Ca concentrations (Kochian, 1995). According to Kochian (1995) several workers have noted that Al inhibition of root apical Ca influx is closely associated with inhibition of root growth (Huang *et al.*, 1992) and it has been proposed that Al^{3+} blocks Ca^{2+} channels in the root cell plasma membrane (Huang *et al.* 1994; Huang *et al.*, 1992). It is of interest to note that many acid

soils contain very low levels of exchangeable and soil solution Ca so that inhibition of its uptake is a potential problem.

2.2.4.3 *Tolerance to Al toxicity.*

The variability of several crop species in their responses to Al toxicity has been useful to plant breeders for the production of Al resistant crops (Kochian, 1995). Aluminium resistance can be divided into two types. These are: Al exclusion mechanisms and Al tolerance mechanisms (Kochian, 1995).

Al exclusion mechanisms.

One of the most important mechanisms of Al exclusion is the Al-induced release of organic acids from the root apex (Rincon and Gonzalez, 1992). Delhaize *et al.* (1993a, 1993b) argued that the malate released is able to protect the root apex of wheat plants by chelating Al^{3+} . This has also been demonstrated by Ryan *et al.* (1994) and Basu *et al.* (1994) who showed that malate efflux was triggered only by Al^{3+} , the efflux was localized solely to the root apex, and addition of malate to Al-toxic solutions protected roots from Al toxicity. They also showed that high rates of malate efflux were related with Al resistance. Similarly it has been shown that Al exposure triggers a rapid release of citrate in Al-resistant maize genotypes (Pellet *et al.* 1994).

Aluminium-exclusion via a plant-induced rise in rhizosphere pH has also been suggested as a mechanism of resistance (Taylor, 1991). However, little convincing evidence has been forwarded in support of this mechanism. Most studies that support of this model have measured changes in bulk solution pH, which is influenced mainly by mature root regions and not the root apex, which is the site of Al toxicity (Kochian, 1995). Other mechanisms that have been proposed include the existence of an active Al efflux at the root plasma

membrane (Taylor, 1991) and reduced fixation of Al in the root cell walls (Blamey *et al.* 1990)

Al tolerance mechanisms

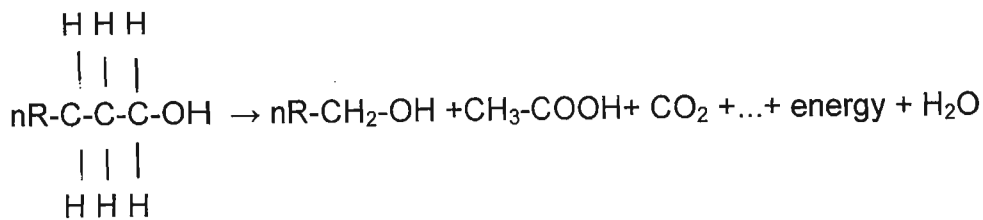
The induction of synthesis of low-molecular-weight binding peptides may play a role in metal-tolerance (Kochian, 1995). In this mechanism, heavy metals activate synthesis of metal-binding ligands at the gene or enzyme level. For example, Basu *et al.* (1994) found in the root apex of an Al-resistant cultivar of wheat, two 51-kDa microsomal proteins were induced by exposure to Al for 24 to 96 hours. These proteins were not found in the root apex of an Al-sensitive cultivar. Other workers have also noted Al-induction of the synthesis of a number of proteins in the root apex. However, Kochian (1995) considered there was little evidence to support Al induction of tolerance.

2.3 Role of organic amendments in Al detoxification.

An organic amendment can be defined as a material originating from animals, plant or microorganism, which is more or less decomposed. Typical examples include animal manures, plant residues, industrial and municipal wastes. In this section the nature of organic compounds originating from the application of these materials is summarized and their possible roles in ameliorating Al toxicity are discussed.

2.3.1 Nature of soil organic matter

After physical breakdown of organic materials by earthworms and other soil mesofauna, soil microorganisms carry out further decomposition. As shown below, the decomposition of organic material is effectively an oxidation reaction and results in the release of small organic molecules, CO₂, water and energy :



Organic materials provide a source of C and energy for heterotrophic microorganisms. Generally speaking, the different compounds present in organic materials are decomposed at different rates depending on their relative resistance to microbial attack. Stevenson (1981) reported that the final stage of decomposition of organic material is characterized by gradual decomposition of the more resistant plant parts such as lignin, which is attacked mainly by actinomycetes and fungi.

2.3.1.1 *Non-humic substances.*

Non-humic substances can be divided into light fraction organic matter and specific classes of biochemical compounds (Stevenson, 1994). The light fraction consists of decaying plant and animal products and their partial decomposition products that occur within the soil (Stevenson, 1994). This fraction is recovered by flotation with a liquid of high density (e.g., 1.2 to 2.0 g.cm⁻³). Plant-derived substances such as lignin, cellulose polyphenols and proteins will be released from the light fraction (Tale and Theng, 1980). Other compounds belonging to specific biochemical classes such as carbohydrates, fats, waxes, resins and organic acids are also present. The compounds can be of plant origin but most are thought to have been synthesized by the decomposer microbial community (Rovira and McDougall, 1967).

In relation to detoxification of Al in soils, the low molecular weight organic acids, such as formic, acetic, propionic, oxalic, *a*-crotonic, succinic, fumaric, tartaric and citric, are considered of particular importance (Stevenson 1967). These are

added to soils in decomposing plant material and, in addition, a wide range of organic acids, are synthesized by the microbial biomass (Rovira and McDougall, 1967). Organic acids generally occur in soils at low concentration (about 1-5 mM) (Stevenson and Vance, 1989) but substantially higher concentration, are found in the rhizosphere and in soils amended with organic manures (Iyamuremye and Dick, 1996). Organic acids can form stable chelate complexes with Al^{3+} and other polyvalent cations (Stevenson and Vance, 1989). Hydroxy-acids such as citric acid form stronger complexes than those containing a single COOH group (Stevenson and Vance, 1989). The chelate structure of an Al-citrate complex is shown in FIGURE 2.4.

2.3.1.2 Humic substances.

Seventy to 80 % of the soil organic matter is normally made up of humic substances. These substances are formed from the products of biological degradation of plant and animal residues and the synthetic activity of microorganisms (Stevenson, 1981). Humic materials or humic substances are defined as a complex mixture of high molecular weight macromolecules. Alken *et al.* (1985) define humic substances as a "general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight and refractory."

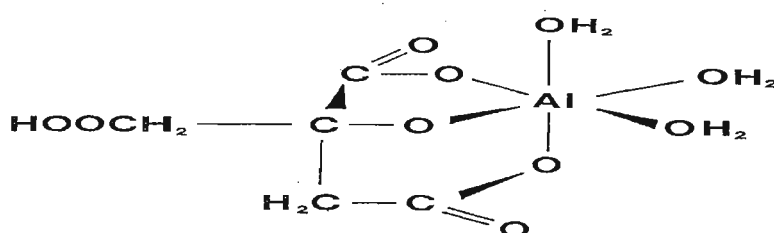


FIGURE 2.4 The chelate structure of an Al-citrate complex (after Stevenson and Vance, 1989).

The above definition is important because it refers to molecular size, shape and charge considered by Hayes and Swift (1978) as the most useful characteristics involved in the physico-chemistry of humic substances. Humic substances are classically fractionated into humic acid and fulvic acid. The extraction of fulvic and humic acid is commonly performed according the IHSS (International Humic Substances Society) method (Kumada, 1987). The humic acid is extracted from soil with an alkaline solution and precipitated upon acidification while the fulvic acid is the yellow fraction that remains in solution.

Aluminium can be adsorbed or complexed by humic substances because they contain a large number of functional groups which include COOH, phenolic, enolic, alcoholic OH and C=O (Stevenson and Vance, 1989). The total binding capacity of humic acids for metal ions is estimated as 200 to 600 $\mu\text{mol/g}$ (Thompson and Troeh, (1978). According to the same author, the cation exchange sites adsorb one-third while metal complexing sites adsorb two-thirds of the total metal cations. The adsorption power of humic acids is explained by their high surface area (estimated to $2000 \text{ m}^2 \text{ g}^{-1}$), which is much greater than that of clay minerals (Frimel and Christman, 1987). Stevenson and Vance (1989) stated that the complexation reactions between humic substances and Al occur differently according to the type of bondings, which range from weak ionic bonds to strong coordinate linkages. Haynes (1984) underlined the complexity of the mechanisms involved in the reactions between Al and organic matter and stated that simultaneous chelation, complex formation, adsorption and coprecipitation occur. 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.

2.3.2 Relative role in Al detoxification.

A number of workers have observed that when monomeric Al becomes complexed with soluble humic material it is no longer toxic to plants (Suthipradit

et al. 1990). Harper *et al.* 1995), for example, demonstrated that addition of fulvic acid to solution cultures containing 30 μ M Al complexed virtually all the Al and alleviated the phytotoxic effect of Al on the growth of maize roots. The addition of organic acids (e.g., citric, oxalic acids) to solution cultures containing phytotoxic concentrations of monomeric Al can also complex Al and greatly promote plant growth (Bartlett and Riego, 1972; Hue *et al.*, 1986). In general, Hue *et al.* (1986) showed that citric, oxalic and tartaric acids were more effective than malic malonic and salicylic acids. It is interesting to note that malic and citric acids are synthesized and excreted by plant roots as a method of detoxifying Al in some Al tolerant crop cultivars (Miyasaka *et al.* 1991; Delhaise and Ryan, 1995).

A number of workers have, however, questioned the role of organic acids in detoxification of Al (Ritchie, 1994; Suthipradit *et al.*, 1990). It has been suggested that their characteristically low concentration in soil and their susceptibility to rapid biodegradation by soil microorganisms may limit their effectiveness (Ritchie, 1994; Wong and Swift, 1995). Ritchie (1994) suggested that a regular supply of organic acids into soil solution would be required to sustain Al detoxification. In addition some researchers have demonstrated that fulvic acid (Suthipradit *et al.*, 1982) and humic acid (Ritchie *et al.* 1982) are more effective at complexing and detoxifying Al than simple organic acids.

2.3.3 Mechanisms of detoxification.

Many authors have observed that during decomposition of organic residues in soils there is a decrease in exchangeable and soluble Al (Hoyt and Turner, 1975; Besho and Bell, 1992; Noble *et al.*, 1996; Wong *et al.*, 1998). Several different mechanisms have been proposed to explain this. These include a rise in soil pH and/or complexation of Al by organic matter in both the solid and soil solution phases. These mechanisms are discussed below.

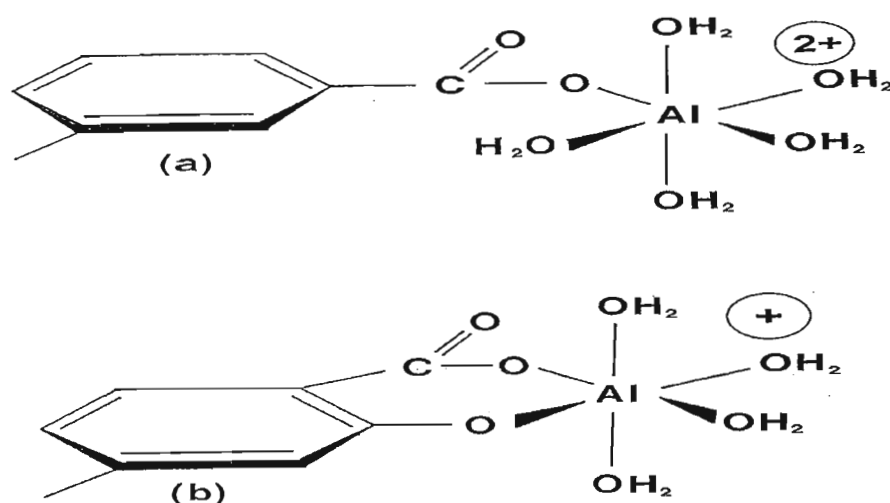


FIGURE 2.5 Binding of Al to humic substances by coordinate linkage with (a) a single donor group and (b) the formation of a chelate complex (redrawn from Stevenson and Vance, 1989).

2.3.3.1 Increase in pH.

Initial pH and buffering capacity of the organic amendments.

The initial pH and buffering capacity of organic amendments will obviously be important factors influencing their effects on soil pH. For example, when plant material is added to soil there is an initial small increase in pH followed by a more marked increase as the material begins to decompose (Tang *et al.*, 1999) and this is generally followed by a decrease in soil pH (FIGURE 2.6).

A rise in soil pH at day 0 which was most pronounced for lupin leaves, when legume residues were mixed with a sandy loam is evident in FIGURE 2.6. The degree of consumption of H^+ by plant material will be dependent on the dissociation constants (pK_a) of the weak organic acids in the material and the actual percent decomposition of organic acids as they are released into the soil

(Ritchie and Dolling, 1995). If soil pH is less than the pKa of the weak acid groups and added organic matter there will be an increase in soil pH due to association of H^+ from the soil with some of the organic anions (Ritchie and Dolling, 1995).

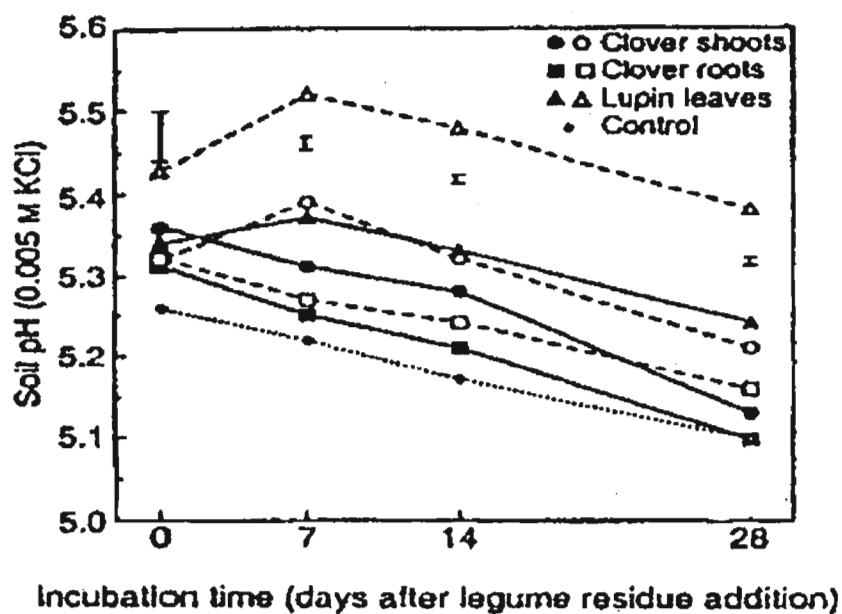


FIGURE 2.6 Change in soil pH over time following addition of 0 (dotted lines), 1.54 (solid lines), 3.08 (dashed lines) g/kg soil of ground legume residues to Kojonup sandy loam. Bars represent the least significant difference ($P=0.05$) between means at a given time (after Tang *et al.*, 1999).

Similarly Wong *et al.* (1998) found that addition of compost and peat to acid soils increased soil pH and ameliorated soil acidity. They attributed this effect primarily to the proton consumptive ability of the added organic materials. Composts, manure and peats contain humic type substances with many functional groups such as carboxyl and phenolic groups that are able to consume protons at their natural pH values (Stevenson and Vance, 1989). These substances are formed during the decomposition process and are relatively stable against further decomposition. Their capacity to consume protons therefore controls the buffer characteristics of these materials and therefore their ability to neutralize soil acidity. For this reason, Wong *et al.* (1998) proposed the measurement of the proton consumption capacity of such materials by titration with 0.05 M H₂SO₄. They showed that the magnitude of the increase in pH when composts, manure and peats were added to a spodosol and incubated for two weeks was directly proportional to the proton consumptive capacity of the materials.

Calcium carbonate content of amendments.

Some organic amendments have a relatively high (e.g., 10-20%) CaCO₃ content. For example, filter cake (a byproduct of the sugar milling industry) has a relatively high CaCO₃ content and therefore has a liming effect when applied to acid soils (Mokolobate and Haynes, 2002a).

Animal manures can also contain CaCO₃. This can be due to limestone being added to animal's diets as a Ca source and much of this is excreted in the manure. For example, the recommended CaCO₃ level for feedlot beef cattle diets is about 15 g kg⁻¹ of feed while growing pig diets contain about 9 g kg⁻¹ (Reece *et al.*, 1995; Klemesrud *et al.*, 1998). The CaCO₃ content of broiler poultry diets is about 11 g kg⁻¹ while diets for layer hens and breeders contain about 77g kg⁻¹ (Cleaves *et al.*, 1991). Reports of increased soil pH induced by application of feedlot cattle manure (Eghball, 1999; Whalen *et al.*, 2000) and poultry manure (Hue, 1992; Cooper and Warman, 1997; Mokolobate and Haynes, 2002b) are widespread and are generally attributable to the CaCO₃ content of the manure.

When animals have not been fed limestone, the influence that animal manure applications have on soil pH will depend greatly on the proportion of dung and urine present in the manure. The feces are then main excretory pathway for Ca, Mg and P, K is mainly excreted in urine, whilst N and S are voided in both dung and urine (Haynes and Williams, 1999). The high Ca and Mg content of dung results in excess content of nutrient cations over anions. This imbalance is made up for by carbonate (Barrow, 1987). Thus much of the Ca and Mg in dung is present as CaCO_3 and MgCO_3 . As a result, the soil pH rises below dung patches on grazed pastures (Haynes and Williams, 1993) and the greater the proportion of dung compounds relative urine present in a manure, the more will be the tendency for soil pH to rise following its application to soils.

Decomposition of organic acids anions.

During organic residue decomposition, OH^- anions are produced from the microbial oxidation of organic acid anions originating from the organic materials. According to De Wit *et al.* (1963), organic acids anions such as citrate, malate and oxalate are synthesized in plants in order to maintain the balance between inorganic cations and inorganic anions. There is normally an inorganic cation excess in plant materials, which is balanced by the organic acids anions. The organic acid anion content of plant material can be calculated based on the difference between the sum of cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and anions (SO_4^{2-} , H_2PO_4^- , NO_3^- , Cl^-) present. It can also be determined by ashing plant material and measuring ash alkalinity (Pierre and Banwart, 1973). A close linear relationship between ash alkalinity of legume residues and alkalinity created in the soil following applications of the residues is shown in FIGURE 2.7. It has also been demonstrated by several authors that a relationship exists between the rise in pH value during decomposition of plant material and the cation content of the decomposing organic material (Besho and Bell, 1992; Wong *et al.*, 1998). This is to be expected since the higher the cation content, the greater will be the cation excess and thus the higher will be the content of organic acids anions.

Microbial degradation of organic acid anions leads to an increase in soil pH through decarboxylation (Yan *et al.*, 1996; Tang *et al.*, 1999) according to the following equation. $R-CO-COO^- + H^+ \leftrightarrow R-CHO + CO_2^{\uparrow}$.

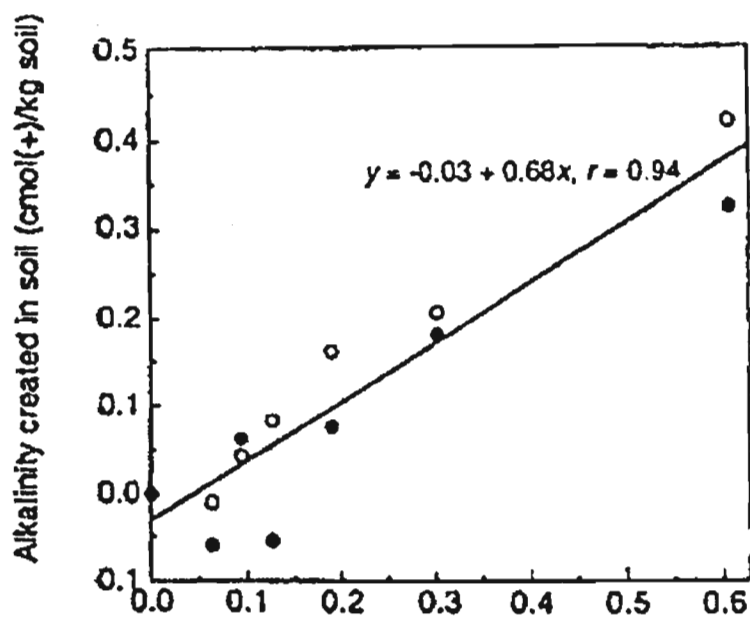
From the above equation it can be assumed that the pH increase will be correlated with CO₂ evolution. Indeed Yan *et al.* (1996a) showed that increases in soil pH following addition of malate and citrate were highly correlated with CO₂ evolution during the decomposition of these two anions. It is now generally accepted that during decomposition of plant materials there is a rise in soil pH which is positively correlated with ash alkalinity in the material (Noble *et al.*, 1996; Tang *et al.*, 1999) and primarily attributable to decarboxylation of organic acid anions.

Transformations of Nitrogen.

Ammonification is the microbial oxidation of nitrogenous organic compounds with the release of ammoniacal nitrogen: $N\text{-organic} \leftrightarrow NH_4^+ + OH^-$. The OH⁻ anions released cause a rise in pH. Hoyt and Turner (1975), in their study on the effects of organic materials on soil pH, showed that ammonification was accompanied by a rise in soil pH. In addition, both Hoyt and Turner (1975) and Yan *et al.* (1996) suggested that organic acid anions and ammonification act together to increase pH during decomposition of organic residues.

The effect of ammonification is, however, counteracted by the acidifying influence of nitrification. In fact, when the soil presents favorable conditions for nitrification (well aerated, moist, warm and well supplied with nutrients), the oxidation of ammonium is rapid and there is a release of two H⁺ ions. Thus, where ammonification and nitrification occur simultaneously, there is a decrease in soil pH, whereas where nitrification is inhibited, there is a rise in pH (Pocknee and Sumner, 1997). Yan *et al.* (1996b) showed that although soil pH may initially increase when legume crop residues are added to soils, the long-term (e.g., 300

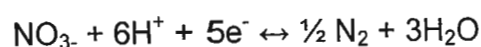
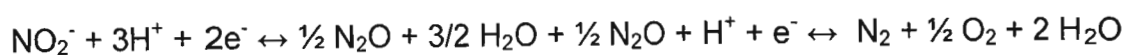
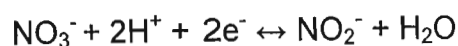
days) effect can be acidification because of nitrification of N originating from the residues.



Amount of ash alkalinity added as legume residue (cmol(+)/kg soil).

FIGURE 2.7 Relationship between the amount of ash alkalinity added and the amount of alkalinity in soil calculated according to soil pH change following application of legume residues in Kojonup and Moora soils after 28 days incubation (after Tang *et al.*, 1999).

Denitrification can result in an increase in soil pH since protons are consumed during the process. In fact, anaerobic microorganisms are very active in some localized micro-sites where the oxygen partial pressure is low (Sumner, 1986) and there can be a rise in pH in these localities:

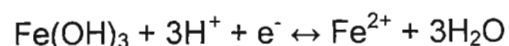
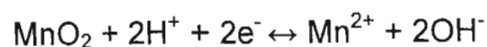


According to Sumner (1986), complete denitrification consumes three times the amount of protons per unit mass of N as nitrification produces. Therefore, one can conclude that the denitrification reaction is potentially important for correcting soil acidity. It can occur even in well-aerated soils (Leffelaar, 1979). Indeed, denitrification is likely to occur in any anaerobic site of the soil containing denitrifying bacteria, water, nitrate and a source of energy (Leffelaar, 1986).

Reduction reactions.

It has been suggested that intense microbial activity in localized micro-sites where organic residues are decomposing in the soil can lead to localized O₂ depletion which can promote reduction reactions and a rise in pH (Hue and Amien, 1989). It is well known that several high valence metal-oxides and hydroxides are reduced under wet soil conditions and protons are consumed thus raising soil pH. Hoyt and Turner (1975) and Hue (1992) suggested that an increase in soil pH when organic residues are added to soil could be partially due

to reduction reactions of Mn oxides-hydroxides and Fe oxides-hydroxides as illustrated by the following reactions:



Although these reactions raise pH, they also release metal cations into soil solution and at high concentrations these may be toxic to plants.

Specific adsorption of organic molecules.

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). Negatively charged, high molecular weight humic substances can form strong bonds with metal hydrous oxide surfaces through both anion exchange and specific adsorption (ligand exchange) (Stevenson, 1992). Ligand exchange occurs through displacement of $\text{OH}_2^{0.5+}$ and $\text{OH}^{0.5-}$ groups at the oxide surface by OH and COOH groups on the humic molecules (Stevenson, 1992). Parfitt *et al.* (1977), for example, demonstrated that adsorption of fulvic acid onto oxide surfaces was accompanied by displacement of OH^- groups by COO^- ions indicating ligand exchange. Low molecular weight organic acids such as citrate, malate and oxalate can also be specifically adsorbed to oxides surfaces by ligand exchange (Stevenson, 1992). Specific adsorption of oxalate onto on Al hydrous oxide surface with the release of OH ions (and thus a rise in solution pH) is shown in FIGURE 2.8.

2.3.3.2 Complexation in the solid phase.

Aluminium could be complexed by organic compounds present in the solid phase of the organic residues and/or by those produced during residue decomposition. In particular, composts, manure and decomposing residues contain humic and fulvic-type materials with functional groups such as carboxyl and phenolic groups that are able to complex Al (Wong *et al.*, 1998).

Hoyt and Turner (1975), for example, found that the solid phase of decomposing organic materials complexed exchangeable and soluble Al resulting in the formation of Al-organic matter complexes that were insoluble in water. Similarly, during the initial phase of decomposition of farmyard manure, Patiram (1996) found there was a decrease in exchangeable and soluble Al without a corresponding increase in soil pH. This suggests that solid phase complexation of Al was occurring.

Other evidence also suggests that the building of soil organic matter through additions of organic amendments will tend to reduce exchangeable and soluble Al concentrations through Al complexations. Thomas (1975) for example, investigated the relationship between soil organic matter and exchangeable Al. He showed there was an inverse relationship between soil organic matter content and exchangeable Al levels. The depressing effect of organic matter content on exchangeable Al concentrations was greater at lower pH values and at pH 3.5 an increase from 1 to 2% organic matter lowered exchangeable Al from 60 to 42 mmole kg⁻¹.

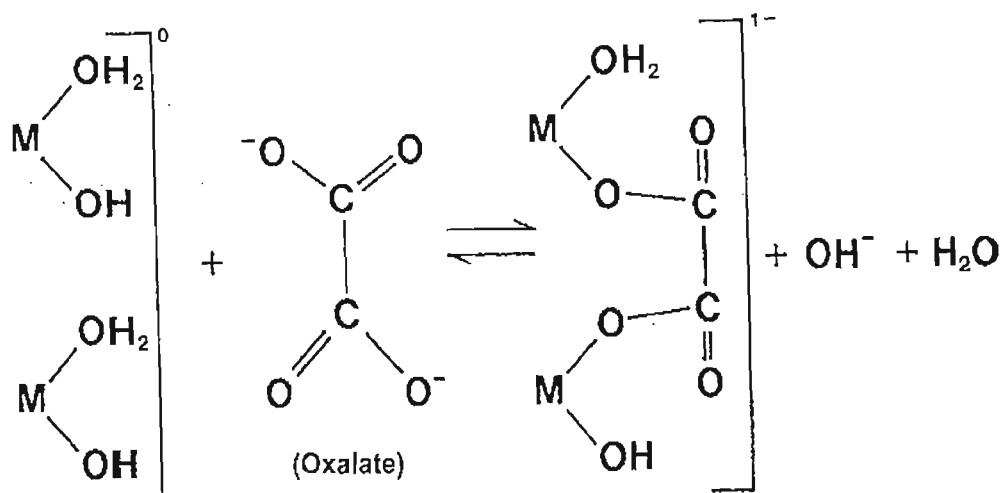


FIGURE 2.8 Specific adsorption of oxalate to an Al or Fe (M) hydroxide surface (after Hue, 1992).

2.3.3.3 Complexation in solution.

Both soluble humic material and organic acid anions can complex with monomeric Al in soil solution and thus render it non-phytotoxic. Such soluble organic compounds are released during decomposition of organic residues. Several studies have demonstrated that when organic residues are added to soils the proportion of total Al in solution present in monomeric form is drastically reduced often regardless of whether soil pH is reduced or not (Kretzschman *et al.*, 1991; Besho and Bell, 1992; Berek *et al.*, 1995; Mokolobate and Haynes, 2002a). Indeed in greenhouse studies, the growth promoting-effects of adding organic residues to acid soils are often closely related to the magnitude of the reduction in monomeric Al present in soil solution (Mokolobate and Haynes, 2002a). The reduction in monomeric Al generally coincides with an increase in

the concentration of complexed forms of Al present in solution (i.e. Al complexed to soluble organic compound) (Mokolobate and Haynes, 2002a).

2.3.3.4 Practical implications.

A number of greenhouse studies have demonstrated that adding organic residues to acid soils has a growth-promoting effect on crops primarily through decreasing the concentration of total Al (Hue and Amien, 1989; Hue, 1992) or more particularly of monomeric Al (Kretzschman *et al.*, 1991; Besho and Bell, 1992; Berek *et al.*, 1995; Mokolobate and Haynes 2002a) present in soil solution.

In a series of glasshouse experiments, Mokolobate and Haynes (2002a; 2002b) compared poultry manure, filter cake, household compost and grass residues as amendments to an acid soil. These four amendments were applied at 20 mg kg⁻¹ with or without lime at rates equivalent to 0, 10 and 50 Mg ha⁻¹. Lime applications to the control (unamended) treatment resulted in a marked reduction in exchangeable Al and in the concentrations of total and monomeric Al in soil solution. Increasing applications of lime resulted in increased maize yields. The addition of organic amendments increased soil pH and reduced the total and monomeric Al concentrations in soil solution to low level regardless of whether lime was applied or not. Results presented in FIGURE 2.88 illustrate that the addition of these amendments to an acid soil increased soil pH and decreased concentrations of exchangeable Al and total and monomeric Al in soil solution. Mokolobate and Haynes (2002a) concluded that addition of organic amendments to acid soils is a practicable way of liming them and reducing the potential for Al toxicity. They suggested that the effect of organic residues was primarily through an increase in soil pH and the complexing ability of organic matter.

Berek *et al.* (1995), however suggested that the complexing ability of organic matter was the most important factor. They found that incubation of the residues of six plants species at increasing rates with Indonesian red-yellow podzolic soil

resulted in marked reductions in monomeric Al in soil solution even though there were no significant changes in soil pH. Leguminous residues were more effective than non-leguminous ones, possibly due to their more rapid rate of decomposition. Growth of soybean in the residue-amended soils was greater than that in unamended soil and growth was generally better for legume than non-legume amended treatments.

Only a few field experiments have been conducted on the use of organic amendments to ameliorate soil acidity (Haynes and Mokolobate, 2001). Lungu *et al.* (1993) conducted field experiments in Zambia over a two-year period using farmyard manure applied at 30 Mg ha⁻¹. Large reduction in exchangeable Al were recorded which were associated with an increase in soil pH and a large increase in yields of maize. In a field experiment on an Oxisol in Burundi, Wong *et al.* (1995) applied prunings of three tree species and farmyard manure at 3 and 6 Mg ha⁻¹. Applications of these organic residues resulted in small increases in soil pH and substantial decreases in exchangeable Al saturation and in the concentration of monomeric Al in soil solution. Grain yields of both maize and beans were increased by applications of residues and yields were inversely related to percent Al saturation. Yield improvements were attributable to the ameliorative effects of organic matter on Al toxicity.

The above discussion demonstrates that there is limited evidence that organic amendments can be used as effective liming materials to increase crop yields in acid soils. There is, however, a need of more definitive research in this area, particularly in the field situation.

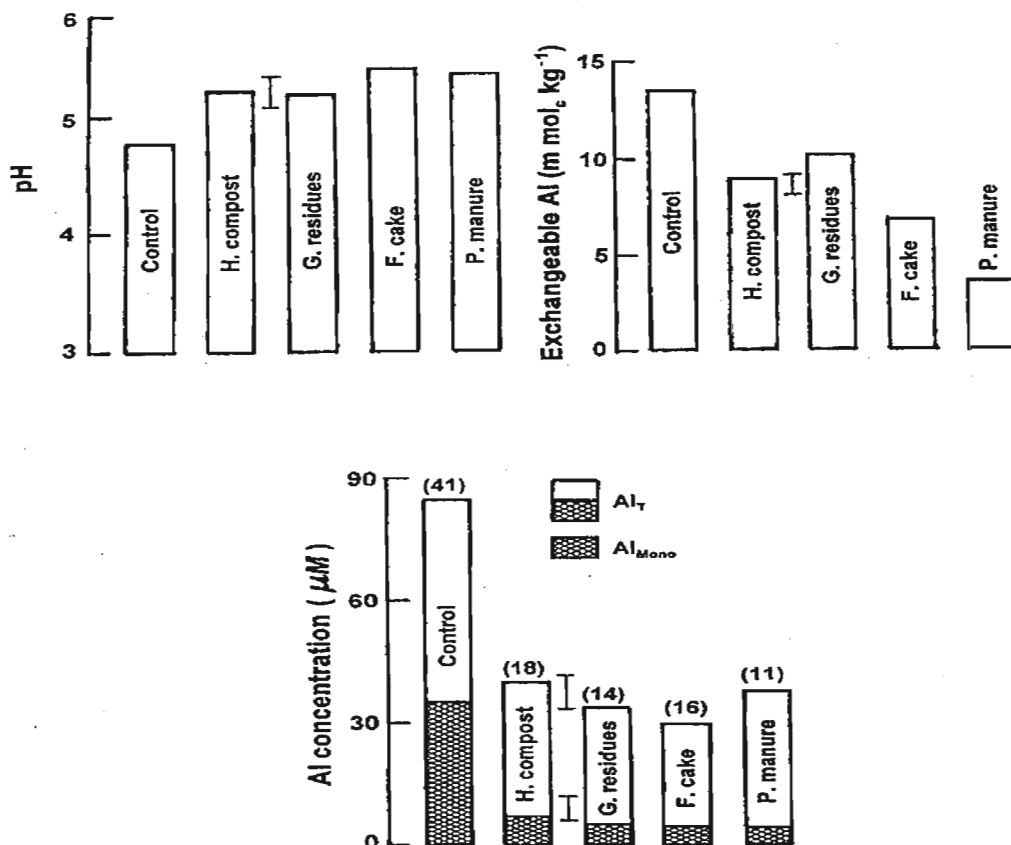


FIGURE 2.9 Effect of incubation of organic amendments with an acid soil for 6 weeks on solution pH, exchangeable Al and concentrations of total soluble (Al_T) and monomeric (Al_{mono}) Al in soil solution. The proportion of Al_T present as Al_{mono} is shown in brackets. Organic amendments used were household compost (H. compost), grass residues (G. residues), filter cake (F. cake) and poultry manure (P. manure). LSD ($P < 0.05$) shown (redrawn from Mokolobate and Haynes, 2002a).

2.4 Conclusions and recommendations.

As briefly discussed in this review, it is evident that the addition of organic amendments to acid soil causes an increase in soil pH and a decrease in Al toxicity. Mechanisms such as precipitation reactions of soluble and exchangeable Al due to the increase in soil pH and complexation reactions of Al by newly decomposed organic matter compounds (soluble humic compounds, specific biochemical compounds and/or soluble organic acids), are responsible for this reduction in Al phytotoxicity. It may well be that the relative importance of the mechanisms responsible for this amelioration differs for different organic residues and in different conditions of their use. This aspect certainly deserves further study.

The rise in soil pH may be the most important reason for the decrease in Al toxicity. Therefore, it would be interesting to investigate the factors involved in maintaining the pH at a high value, for instance by regular additions of organic amendments. Methods for predicting the effects of various organic amendments on soil pH also need to be developed.

Very few studies have investigated the role of organic amendments as liming materials under field conditions. There is an obvious need to do this since soil acidity is a major limitation to resource-poor, semi-subsistence farmers in South East Asia, central and South America and Africa. The regular use of organic residues is a practical alternative to lime for many such farmers.

CHAPTER THREE

3 Use of laboratory indices to predict the effect of addition of a range of organic wastes on soil pH and Al solubility

3.1 Introduction.

Amelioration of soil acidity is commonly achieved by applying lime and/or gypsum (Thompson and Troeh, 1978). The relatively high cost of lime often limits its use by small scale, semi-subsistence farmers in developing countries. For this reason, increasing interest to being focused on the use of alternative liming materials such as organic wastes and manures (Haynes and Mokolobate, 2001). Organic waste applications have been shown to raise soil pH, reduce exchangeable and soluble Al and increase plant growth in acid soils (Hue, 1992; Haynes and Mokolobate, 2001). A number of different organic materials have been used for this purpose including plant materials (Asghar and Kanehiro, 1980; Berek *et al.*, 1995; Noble *et al.*, 1996; Yan *et al.*, 1996; Tang *et al.*, 1999; Berek *et al.*, 1995), animal manure (Hue, 1992; Eghball, 1999; Whalen *et al.*, 2000), compost (Mbagwa, 1985; Mokolobate and Haynes, 2002a), sewage sludge (Hue, 1992) and industrial wastes (Mokolobate and Haynes, 2002a).

The mechanisms by which organic materials raise soil pH can apparently differ appreciably depending upon the material being considered (Mokolobate and Haynes, 2002b). Suggested mechanisms include the significant CaCO_3 content of some residues such as poultry manure (Robinson, 1961; Sims and Wolf, 1994), oxidation of organic acid anions during the decomposition of plant tissues (Barekzai and Mengel, 1993; Helyar and Porter, 1989; Noble *et al.*, 1996; Ritchie and Dolling, 1985; Tang *et al.*, 1999), rapid ammonification without accompanying nitrification following application of residues with a high N content (Hoyt and Turner, 1975) and the proton consumption capacity of humic materials present in

composts and decomposing manures (Wong *et al.*, 1998). In addition, the application of organic materials to acid soils can result in complexation of Al in the solid phase and soluble organic materials can complex with monomeric Al in soil solution thus rendering it non-phytotoxic (Hoyt and Turner, 1975; Hue *et al.*, 1986; Tan and Binger, 1986; Suthipradith *et al.*, 1990; Mokolobate and Haynes, 2002b).

In order to use organic materials effectively as liming agents it will be necessary to predict their liming effect prior to application. If a predictive laboratory test were available then recommendations could be made as to the rate required in the same way that lime recommendations are currently made. However, different measurements have been recommended for different materials (Mokolobate and Haynes, 2002b). For example, for compost and manures the proton consumption capacity has been proposed (Wong *et al.*, 1998), for plant materials, ash alkalinity is often used (Noble *et al.*, 1996) while for some animal manures and industrial wastes the CaCO_3 content can be a good predictor (Mokolobate and Haynes, 2002a). The purpose of this study was to try and develop one predictive test, which would serve effectively for a range of organic wastes. Hence, the effects of addition of 15 different organic materials to an acid soil on pH, exchangeable and soil solution Al were investigated and related to various measures of their potential liming ability.

3.2 Material and methods

Topsoil samples were collected from areas under undisturbed grassland in the upper Tongat area on the coastal lowland of KwaZulu-Natal. The soil was of Cartref form (Gleyic Luvisol, FAO; Inceptisol, USDA). It had a clay content of 13 % and its mineralogy was dominated by kaolinite and some accessory vermiculite. The soil had the following properties: $\text{pH}_{(\text{water})}$ 4.0, organic C = 11 g kg⁻¹, Truog P = 9 mg kg⁻¹, and exchangeable Ca^{2+} = 2.2, Mg^{2+} = 1.8, K^+ = 2.4, Na^+ = 0.52 and Al^{3+} = 13 mmol_c kg⁻¹. The 15 types of

organic residues used included the above-ground portion of non-leguminous (maize, sorghum and kikuyu grass) and leguminous (red clover, soybean and acacia pruning) plants, cattle manure (collected from a commercial feedlot, a pasture and a kraal on a small scale farm), poultry manure (collected from a commercial layer and commercial broiler producer) and pig manure (from a commercial pig producer). In addition, household compost, sewage sludge (from Hammarsdale Sewage Works, Durban) and filter cake (an organic waste from a commercial sugar mill) were also used. The Maize, sorghum and soybean residues were chopped from the standing crop at flouring while fresh kikuyu grass and clover residues were cut from the field. The determination of the lime equivalence of organic materials was carried out by investigating the changes in soil pH after two weeks incubation of lime $[\text{Ca}(\text{OH})_2]$ using the same acid soil. Seven rates of lime were used (L0= control, L2.5= 2.5 mg g^{-1} , L5= 5 mg g^{-1} , L7.5= 7.5 mg g^{-1} , L10= 10 mg g^{-1} , L15= 15 mg g^{-1} and L20= 20 mg g^{-1}). A standard curve was displayed using the regression analysis between the amounts of $\text{Ca}(\text{OH})_2$ and the induced pH. The lime equivalence of organic materials was determined by plotting the pH values (FIGURE 3.2, a) (induced by 20 mg of organic materials used for incubation) against the standard curve (FIGURE 3.6).

The pH of organic amendments was determined in 2mM CaCl_2 and the proton consumption capacities were measured by slowly titrating them from their natural pH values down to pH 4 with 0.05 M H_2SO_4 (Wong *et al.*, 1998). The CaCO_3 content of organic materials was measured by the titrimetric method of Bundy and Bremner (1972) and ash alkalinity was determined as described by Slattery *et al.* (1991). Samples were digested in nitric and perchloric acids, and the P content was measured by the molybdenum blue method (Blakemore *et al.*, 1972) and the Ca, Mg, K, Na, Zn, Cu, Mn, Fe and Al content by atomic absorption spectrophotometry. The C, N and S content were measured using a LECO C/N/S Analyser.

For the incubation experiment, the 15 organic materials were added to the soil (two replicates per treatment) at two rates: 10 mg g^{-1} and 20 mg g^{-1} , which are equivalent to about 10 and 20 Mg ha^{-1} (dry matter basis)

respectively based on a hectare to a depth of 10 cm. Residues were thoroughly mixed with the soil samples (1 kg air-dried, sieved < 2mm) and placed in plastic containers (fitted with perforated lids). Samples were wetted to 70 % water holding capacity and incubated at room temperature for 6 weeks. The water content of samples was adjusted weekly. At the end of incubation, samples were split in three. One subsample was air dried for analysis of exchangeable Al and pH, one was stored at 1⁰C for subsequent analysis of mineral N. The third was wetted to 100 % water holding capacity and the soil solution was extracted 48 h later by centrifugation (Elkhatib *et al.*, 1987).

Soil pH was measured in 1:2.5 soil: solution ratio (in both water and 1 M KCl) using a glass electrode. Exchangeable Al was extracted with 1 M KCl (1:20 soil: extractant ratio) and determined by the pyrocatechol violet (PCV) method (Mosquera and Mombiela, 1986). Exchangeable NH₄⁺ and NO₃⁻-N were extracted from soil with 2 M KCl (1:5 soil:extractant ratio) before and after incubation and determined by distillation (Keeney and Nelson, 1982). The amount of NH₄⁺ and NO₃⁻ accumulated during incubation were determined by difference. Total Al (Al_T) in soil solution was measured by a PCV method using LaCl₃-Fe reagent after passing the solution through a 0.22 μm filter (Menzies *et al.*, 1992). Monomeric Al (Al_{Mono}) was measured in the filtrate (0.05 μm) by the PCV method of Kerven *et al.* (1989). It is accepted, that the PCV method used here for measuring Al_{Mono} measures monomeric Al plus a small amount of Al present in soluble Al-organic matter complexes (Parfitt *et al.*, 1995)

The data was subjected to analysis of variance analysis using the Genstat 5 computer package. The relationship between various chemical properties of the organic residues, various chemical properties of the amended soils and the relationship between soil pH and the various chemical properties of the residues was investigated by fitting the data to linear, quadratic, cubic and exponential functions using the above package.

3.3 Results

3.3.1 *Nutrient content of organic amendments*

The nutrient content of the organic amendments used is shown in TABLE 3.1. The poultry manure, pig manure and leguminous plant residues had the highest content of basic cations (Ca, Mg, K and Na). Layer poultry manure had the highest content in Ca and K, pig manure had the highest P, broiler poultry manure the highest Mg and sewage sludge the highest N. The organic C content of plant residues was relatively high while that of filter cake, compost, kraal and feedlot cattle manure was low (< 15 %), The C/N ratio of materials ranged from 32:1 for maize to 6:1 for sewage sludge and broiler manure. Animal manures generally had a relatively high micronutrient contents. The micronutrient content of pig manure was exceptionally high (reflecting the large amounts of micronutrients added as feed supplements). Kraal manure and compost had high Al due to a significant amount of soil being present in those materials

3.3.2 *Key properties of organic amendments.*

As shown in FIGURE 3.1, the initial pH of amendments followed the order animal manures > wastes > plant residues. Feedlot cattle manure had the highest pH value (8.6), while maize residues had the lowest pH (5.3). The initial pH of all the organic amendments was higher than that of soil ($\text{pH}_{\text{water}} = 4.0$). The proton consumption capacity, calcium carbonate content and ash alkalinity of amendments followed the same order: animal manures > wastes > leguminous \geq non-leguminous. Poultry manure, and to a lesser extent filter cake, had very high values for proton consumption capacity, CaCO_3 content and ash alkalinity. Broiler and pig manure also had a significant CaCO_3 content. Ash alkalinity values for leguminous residues were in general close to those for animal manures and approximately double those for non-

leguminous residues. Total N content and the initial pH of amendments were not closely correlated with each other or with other chemical properties (TABLE 3.2). By contrast, proton consumption capacity, ash alkalinity, total basic cation content and CaCO_3 content were closely correlated with one another.

3.3.3 *Changes in NH_4^+ , NO_3^- , pH, exchangeable Al, Al_T and Al_{Mono} after 6 weeks incubation*

Soil pH was increased significantly by application of all the amendments and the effect was greater at the higher rate of addition (FIGURE 3.2). Changes in pH were more marked when measured in water rather than 1 M KCl. The increase in pH_{KCl} and pH_{water} measured in layer poultry manure-amended soil was at least 2.5 pH units at both rates of addition. In sewage sludge, filter cake and broiler poultry manure treatments the increase in pH was at least 1 unit. The general trend for pH_{water} at the high rate of addition was: poultry manures > wastes > leguminous > pig manure > non-leguminous > cattle manures > control. For pH_{KCl} (at high rate) trends were similar. During incubation, NH_4^+ was the predominant form of N accumulated (FIGURE 3.2). For example, at the higher rate of addition, only the control, compost and filter cake contained more NO_3^- than NH_4^+ -N. The amounts of mineral N produced were generally greater at the higher rate of addition, and tended to be larger for animal manures than plant residues. Amounts produced were notably high for broiler poultry manure and sewage sludge.

Addition of organic amendments significantly decreased the concentration of exchangeable Al and the effect was greater at the higher rate (FIGURE 3.3). For the lower rate, values followed the general order: layer poultry and pig manures < leguminous < wastes = non-leguminous < cattle and broiler poultry manures < control. For the higher rate, the trends were similar. Both Al_T and Al_{Mono} were decreased by additions of amendments and the effect was more pronounced at the higher rate of addition (FIGURE. 3.3). At the

lower rate of addition, the most effective treatments at reducing Al_T and Al_{Mono} were clover residues, layer poultry manure, pig manure and sewage sludge. At both rates, cattle manure, non-leguminous plant residues and compost were least effective at reducing both A_T and Al_{Mono} . At the higher rate of addition, the proportion of Al_T present as Al_{Mono} was increased by additions of plant residues (other than clover), wastes and pig manure.

Addition of $Ca(OH)_2$ resulted in increasing the soil pH proportionally to the amount of lime added (FIGURE 3.6) The estimation of lime equivalence of organic materials used are shown on TABLE 3.4. In the mentioned table, the values given are equivalent to 20 mg of organic materials. The lime equivalence followed the trend order: layer poultry manure > Sewage sludge > filter cake > Broiler poultry manure > clover > soybean. Maize, sorghum, kikuyu grass, acacia pruning, cattle manures and compost had a relatively low liming ability.

3.3.4 *Relationship between the chemical properties of organic amendments, pH, exchangeable Al and soluble Al.*

Correlation coefficients between chemical properties of organic wastes and soil pH measured in 1 M KCl or water are presented above in TABLE 3.3. Correlations were similar whichever medium pH was measured in. Regression equations and lines of best fit for the relationships between chemical properties of the wastes and pH_{KCl} are shown in FIGURE 3.4. Whilst initial pH and total N content of wastes were poorly correlated with soil pH, strong linear correlations were found with proton consumption capacity, ash alkalinity, total basic cation content and $CaCO_3$ content (TABLE 3.3, FIGURE 3.4). As expected, concentrations of exchangeable Al and both Al_T and Al_{Mono} in soil solution were negatively related to pH_{KCl} (FIGURE 3.5) and pH_{water} (data not shown). In addition, concentrations of Al_{Mono} and Al_T in soil solution were positively related to each other and to exchangeable Al (FIGURE 3.5). These relationships were best described by exponential equations.

TABLE 3.1 Nutrients content of organic amendments.

Amendments ¹	C/N ratio	Macronutrient content								Micronutrient content				
		(g kg ⁻¹)								(mg kg ⁻¹)				
		C	N	S	P	Ca	Mg	K	Na	Zn	Cu	Mn	Fe	Al
maize	32	400	12.5	1.20	1.8	3.40	2.10	14.30	0.30	27	16	69	494	254
sorghum	31	415	13.3	1.20	2.2	3.90	3.40	11.20	0.20	35	67	99	315	188
kikuyu	16	344	22.0	2.80	3.8	5.00	2.80	22.20	0.40	78	17	153	12,158	7,925
soybean	12	410	33.4	2.20	2.9	12.70	7.60	22.50	0.40	43	17	80	307	153
clover	11	421	38.0	2.20	2.8	17.40	6.30	15.40	0.60	45	24	69	1,330	944
acacia pr	15	461	31.5	2.60	1.8	13.00	3.60	9.20	0.60	34	32	368	690	449
cattle past	18	382	21.5	3.10	5.3	6.10	6.70	8.60	0.20	91	24	322	7,975	5,106
cattle kra	11	114	10.3	1.90	1.8	0.30	0.10	0.60	0.10	12	2	33	2,445	32,612
cattle fdl	10	130	13.4	2.30	7.9	10.60	5.40	11.50	2.60	13	4	130	3,674	16,747
poultry lay	7	252	38.5	5.40	20.5	110.70	11.00	26.90	5.40	593	136	684	5,204	1,571
poultry bro	6	340	53.4	4.60	18.8	34.80	17.00	19.00	3.50	639	143	657	1,826	454
pig manu	13	340	25.4	5.20	34.5	50.90	11.50	12.40	4.00	1,185	1,382	1,052	2,893	246
sewage sl	6	380	63.3	13.00	21.4	10.10	2.90	6.80	7.00	488	147	160	4,584	16,937
compost	10	101	10.0	1.80	2.3	6.50	3.20	6.50	0.70	17	4	46	2,734	36,508
filter cake	21	73	3.4	2.60	5.8	39.60	4.30	4.70	0.30	53	25	816	2,245	8,226

¹ Maize residues = maize, sorghum residues = sorghum, kikuyu gross = kikuyu, soybean residues = soybean, clover residues = clover, acacia pruning = acacia pr, pasture cattle manure = cattle past, kraal cattle manure = cattle kra, feedlot cattle manure = cattle fdl, layer poultry manure = poultry lay, broiler poultry manure = poultry bro, pig manure = pig manu, sewage sludge = sewage sl,

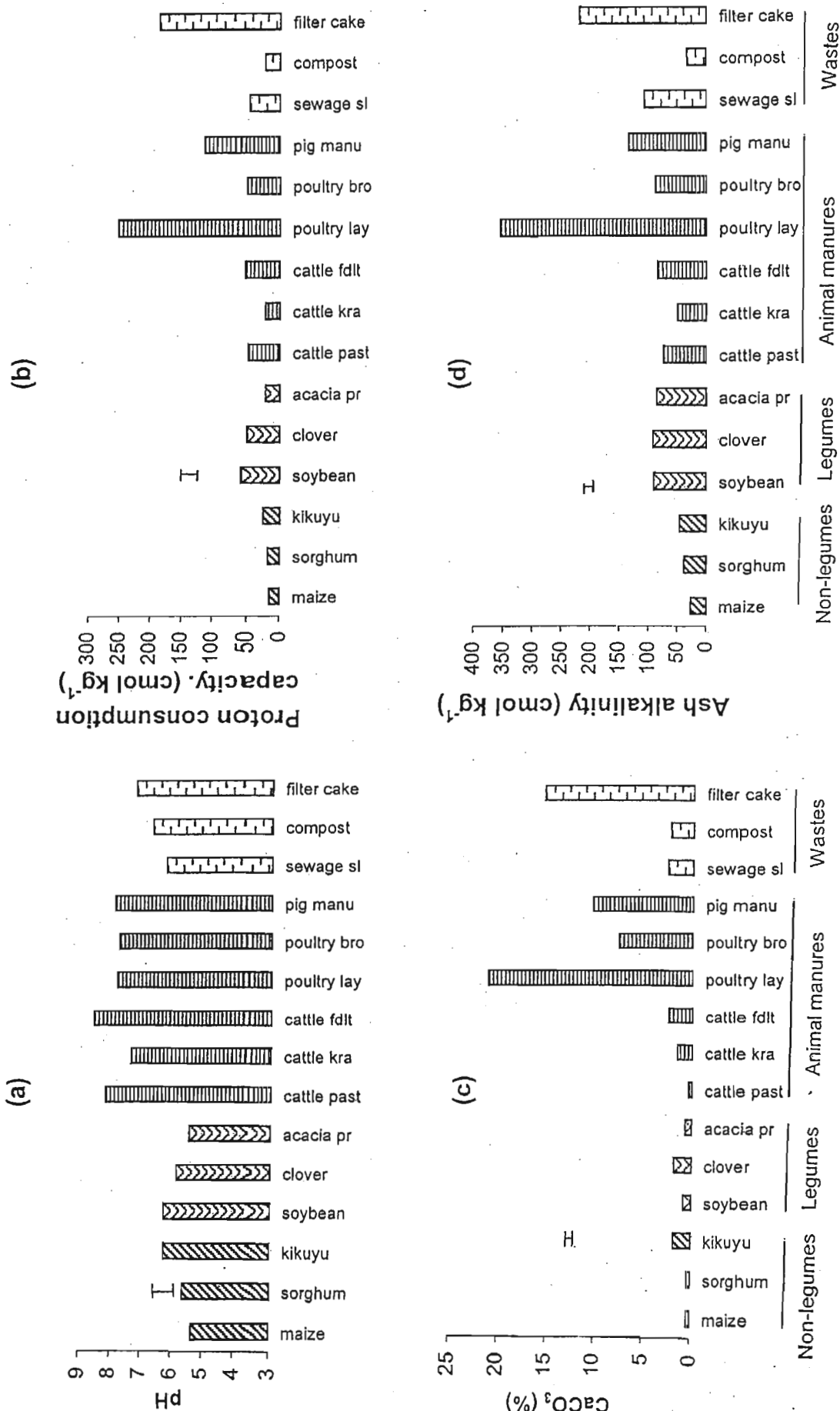


FIGURE 3.1 Residue pH (a), Proton consumption capacity (b), CaCO₃ content (c) and Ash alkalinity of fifteen organic amendments. LSD ($P \leq 0.05$) shown (For explanation of the terms, see TABLE 3.1).

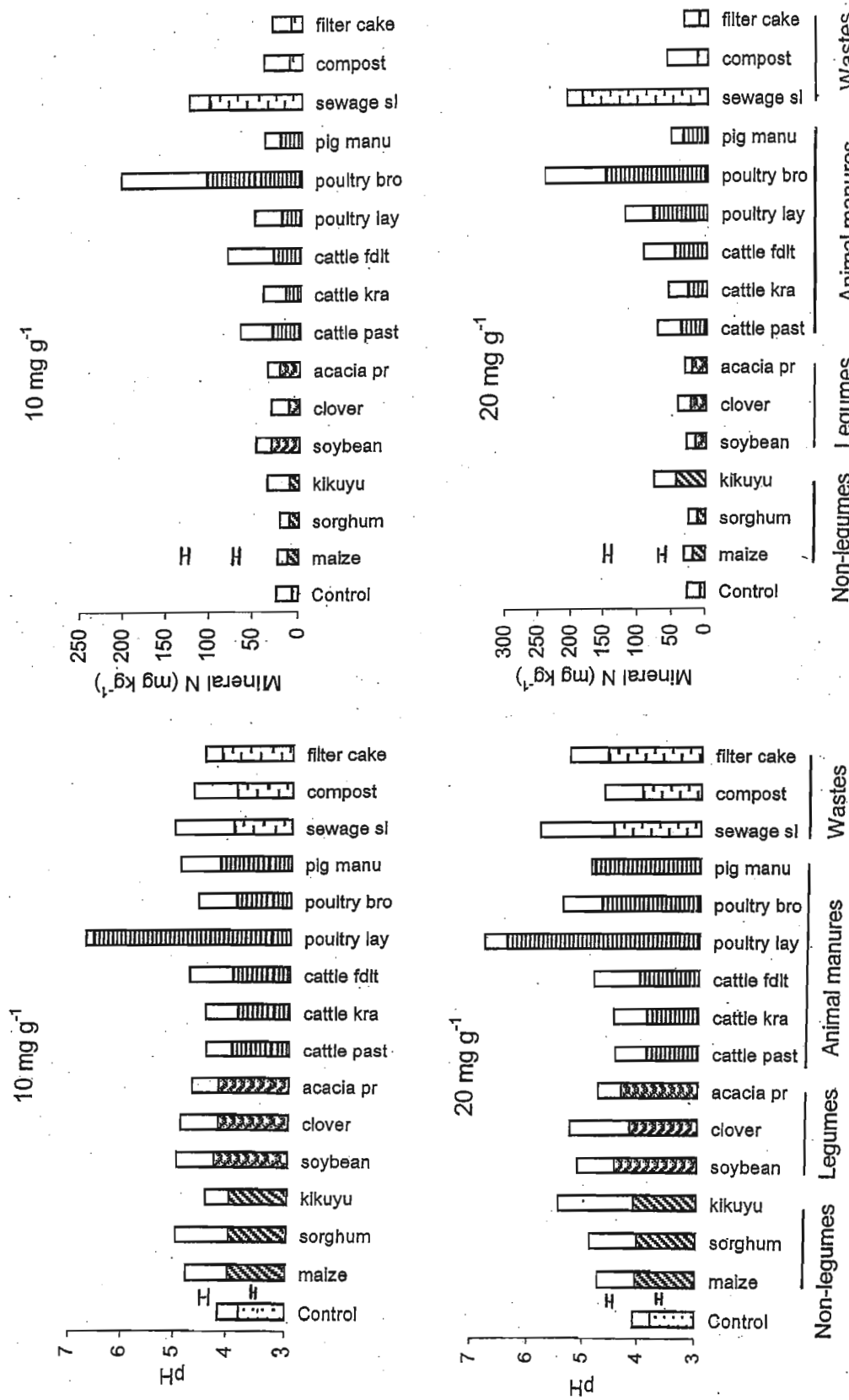


FIGURE 3.2 Effect of incubating fifteen organic amendments with an acid soil for six weeks at 10 and 20 mg g⁻¹ on soil pH (height of histogram = pH_{water}, shaded area = pH_{KCl}) and mineralized NH₄⁺ = shaded area, exchangeable NO₃⁻ = unshaded area). LSD (P ≤ 0.05) shown. (For explanation of the terms, see TABLE 3.1).

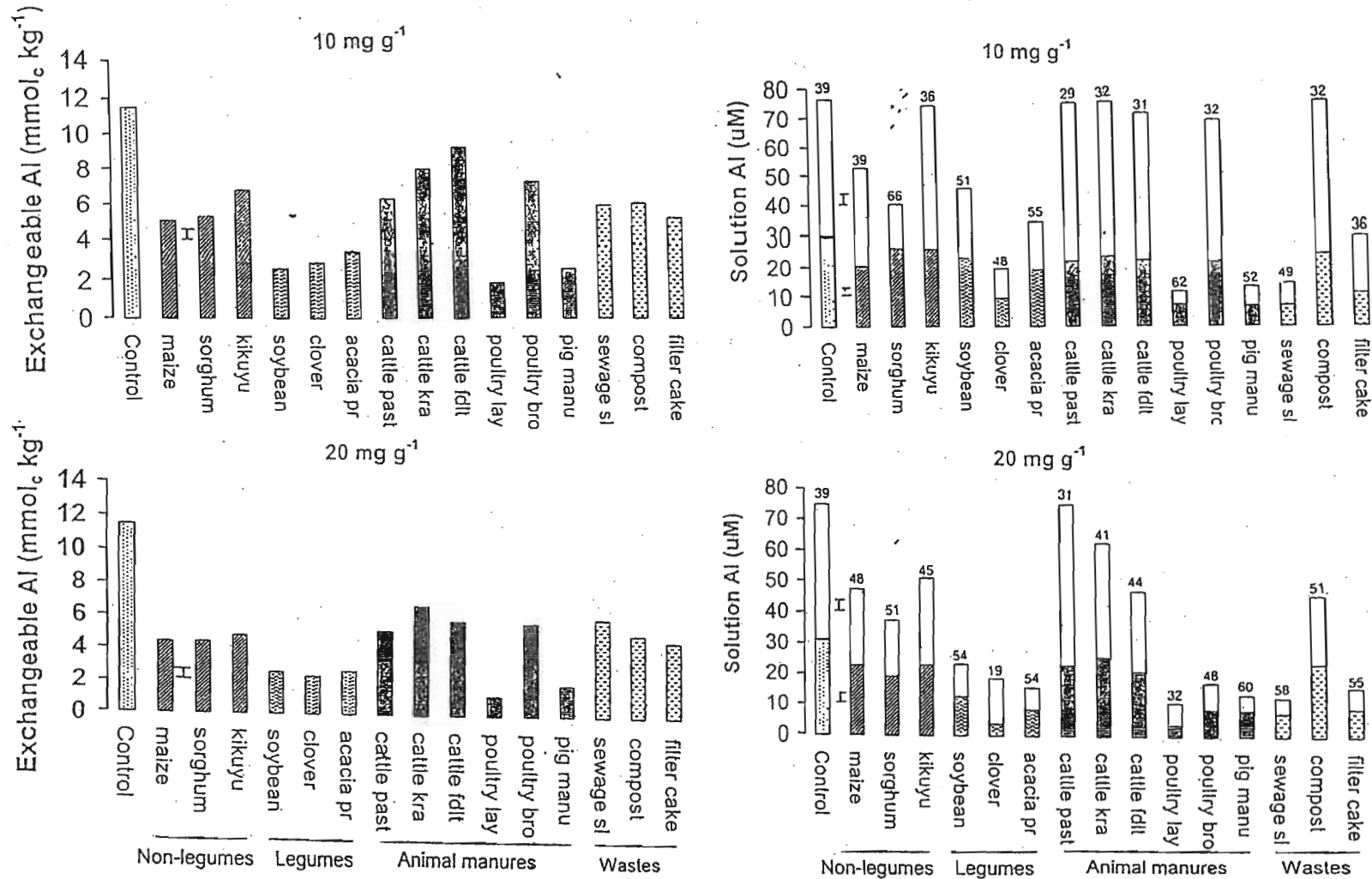


FIGURE 3.3

Effect of incubating fifteen organic amendments with an acid soil for six weeks at 10 and 20 mg g⁻¹ on the concentration of total (Al_T = height of histogram) and monomeric (Al_{Mono} = shaded area) Al in solution and exchangeable Al. Percentage of Al_T present as Al_{Mono} shown above histograms. LSD (P < 0.05) shown. (For explanation of the terms, see TABLE 4.1).

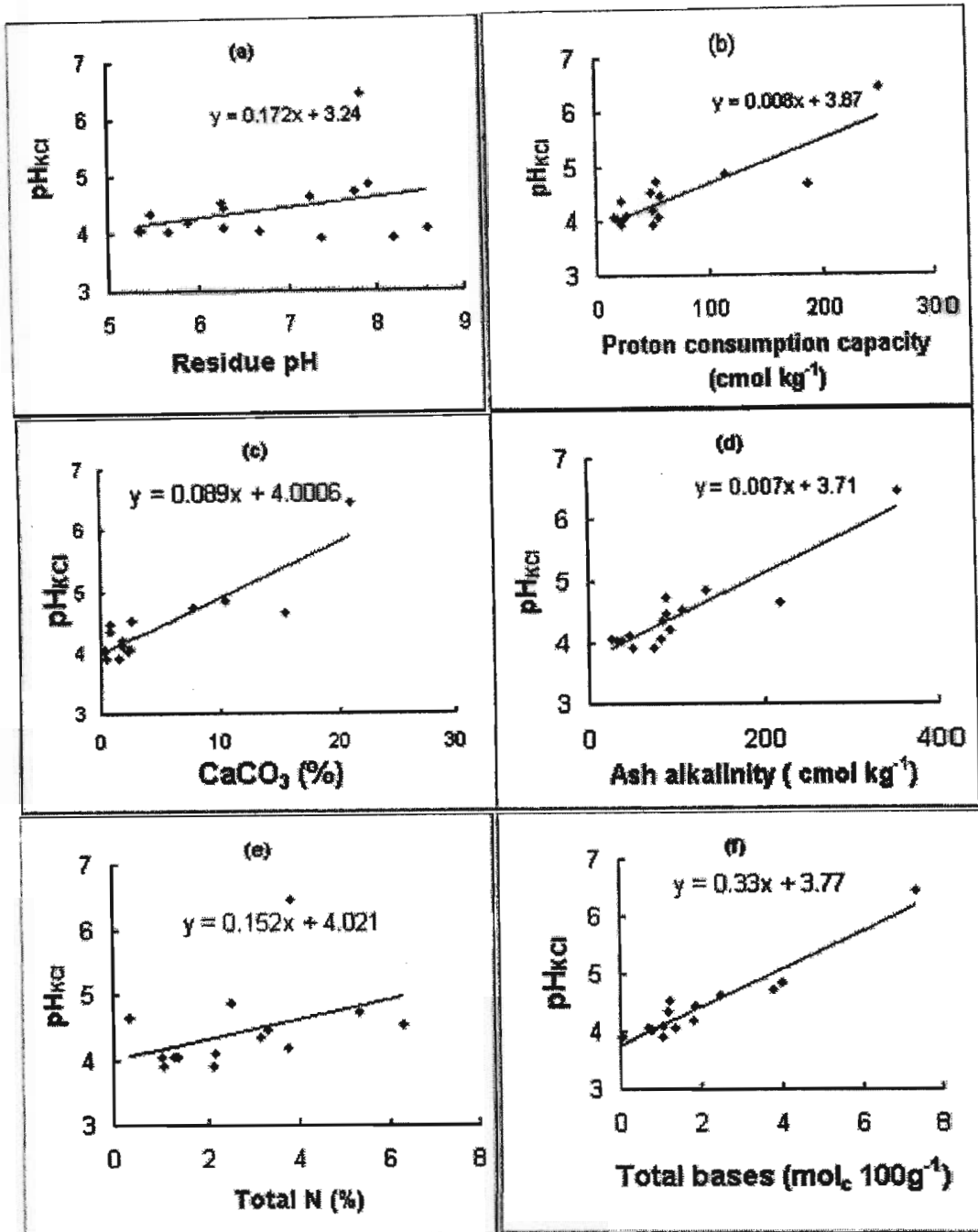


FIGURE 3.4

Relationship between soil pH_{KCL} and (a) residue pH, (b) proton consumption capacity, (c) CaCO_3 content, (d) ash alkalinity, (e) total N and (f) total basic cation content of the organic amendments when added at 20 mg g^{-1} . Regression equation and line of best fit are shown.

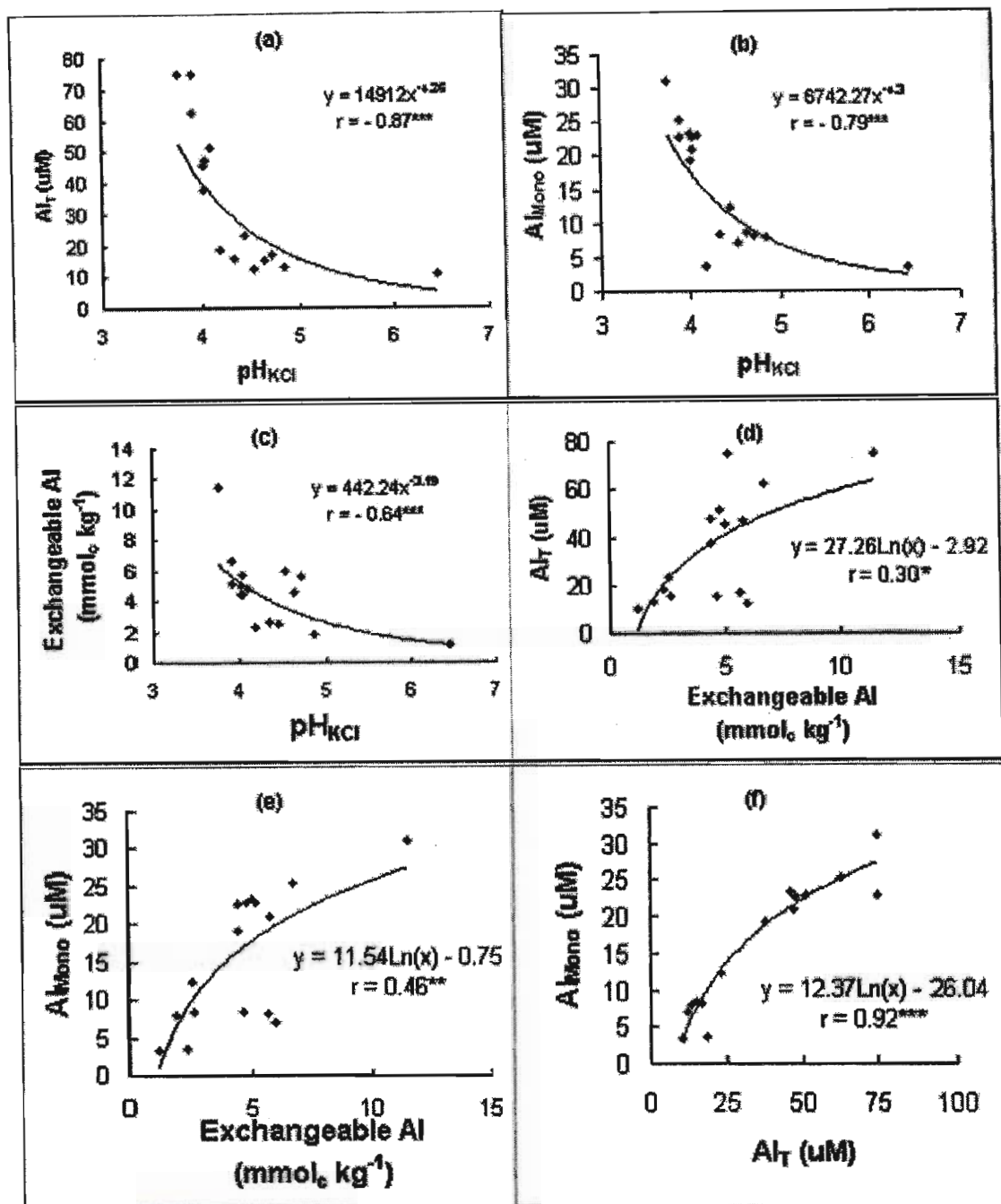


FIGURE 3.5 Relationship between soil pH_{KCL} and (a) Al_T , (b) Al_{Mono} and exchangeable Al and relationship between exchangeable Al and (d) Al_T , (e) Al_{Mono} and relationship between Al_T and Al_{Mono} when organic amendments are added at $20 mg g^{-1}$ to an acid soil. Regression equation, line of best fit, correlation coefficient and level of significance (** $P < 0.01$; *** $P < 0.001$) shown.

TABLE 3.2 Correlation coefficients (r) between properties of the amendments known to affect their liming ability¹.

	Total N content	Proton consumption capacity	Ash alkalinity	CaCO ₃ content	Total basic cation content
Proton consumption capacity	0.01 ^{NS}				
Ash alkalinity	0.01 ^{NS}	0.95***			
CaCO ₃ content	0.01 ^{NS}	0.91***	0.85***		
Total basic cation content	0.07 ^{NS}	0.70***	0.74***	0.76***	
Initial pH	0.01 ^{NS}	0.14 ^{NS}	0.08 ^{NS}	0.15 ^{NS}	0.12 ^{NS}

¹Level of significance shown (* p ≤ 0.05; ** p ≤ 0.01; *** p ≤ 0.001)

TABLE 3.3 Correlation coefficients (r) between chemical properties of the amendments and soil pH measured in 1M KCl or water.

Property	pH _{KCl}	pH _{water}
Initial pH	0.01 ^{NS}	0.01 ^{NS}
Proton consumption capacity	0.73***	0.45*
Ash alkalinity	0.83***	0.58***
Total basic cation content	0.91***	0.56***
CaCO ₃ content	0.75***	0.46**
Total N content	0.27*	0.1 ^{NS}

¹Level of significance shown (* p ≤ 0.05; ** p ≤ 0.01; *** p ≤ 0.001)

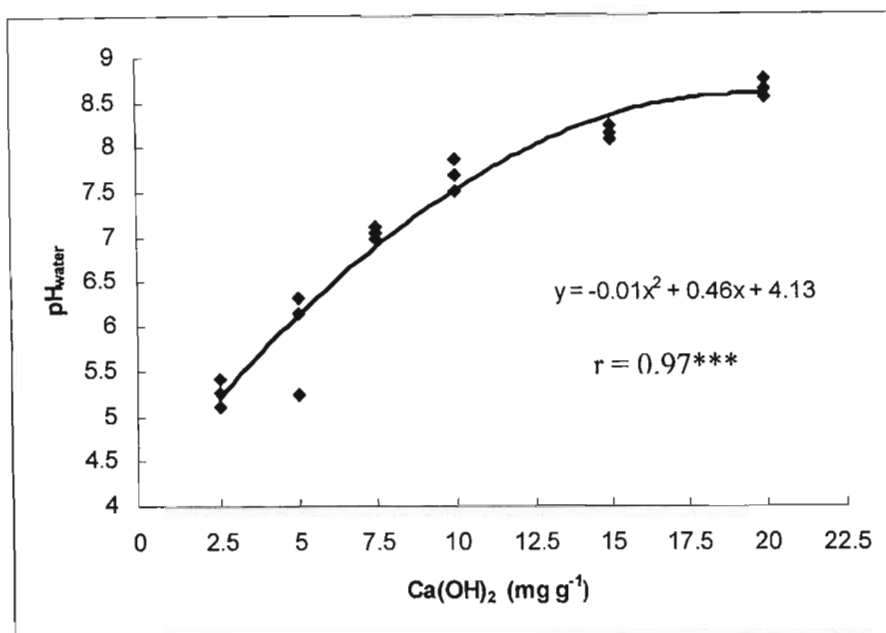


FIGURE 3.6 Effect of 2 weeks incubation of $\text{Ca}(\text{OH})_2$ with an acid soil on soil pH (Used as a standard curve for estimation of lime equivalence of organic materials).

TABLE 3.4 Estimation of lime equivalence of organic materials.

20 mg of material g ⁻¹ of soil	Equivalent $\text{Ca}(\text{OH})_2$ mg g ⁻¹
maize	1.5
sorghum	1.7
kikuyu	-
soybean	2.2
clover	3.1
acacia pr	1.6
cattle pasture	1
cattle kraal	1.1
cattle feedlot	1.9
poultry layer	7.5
poultry broiler	3.5
pig manure	2
sewage sudge	5.1
compost	1.5
filter cake	4

3.4 Discussion

3.4.1 Changes in pH

The large pH increases observed in this study at the higher rate of waste addition (2.5 units for layer poultry manure and more than 1 unit for pig manure, sewage sludge and filter cake) are presumably attributable to the sandy nature of the study soil and thus its low buffering capacity. Comparable studies using a range of organic materials applied to soils at similar rates have generally recorded pH increases of only 0.2- 0.6 units (Berek *et al.*, 1995; Iyamuremye *et al.*, 1996; Noble *et al.*, 1996). As expected, values for pH_{water} were higher than those for pH_{KCl} but the difference was least for layer poultry and pig manure. This is attributable to the high cation (especially Ca) content of these materials. The addition of large quantities of cations to a soil results in accumulation of cations in soil solution with a consequent displacement of H^+ from exchangeable sites into solution (Samuel *et al.*, 1985). Such a "salt effect" results in a depression of pH_{water} values.

Although addition of all the amendments raised soil pH, the mechanisms responsible are likely to have differed depending on the nature of the residue being considered. For plant residues, their organic acid anion content is of particular importance (De Wit *et al.*, 1963). Organic acid anion content is commonly estimated by measuring ash alkalinity (Pierre and Banwart, 1973). Oxidation of organic acid anions during decomposition of plant materials produces OH^- ions and/or consumes protons and this results in an increase in soil pH (Berekzai and Mengel, 1993; Helyar and Porter, 1989; Noble *et al.*, 1996; Ritchie and Dolling, 1985; Tang *et al.*, 1999). Since organic acid anions are synthesized in plants to balance the excess in inorganic cations (De Wit *et al.*, 1963), the greater the content in inorganic cations, the greater will be the organic acid anion content. Indeed, this is probably the reason why leguminous residue-amended (clover, soybean and acacia pruning) soils had higher pH values than

those amended with other plant materials such as maize, sorghum and kikuyu grass. That is, the leguminous residues had a higher basic cation and thus organic acid anion content than non-leguminous ones.

The proton consumption capacity of humic materials is another important factor contributing to a rise in soil pH when organic wastes are added to acid soils. Indeed, microbial decomposition of organic materials produces a large number of humic substances containing functional groups such as carboxylic, phenolic and alcoholic, which can consume protons (Stevenson and Vance 1989). Research by Wong *et al.* (1998) showed that the increase in pH in a compost and manure-amended Spodosol was positively correlated to the proton consumption capacity of these organic materials. Thus, for the manures, and in particular the compost, the proton consumption capacity of humic materials will be of importance. The release of OH^- from humic molecules during complexation of Al species may also contribute to increase the soil pH, as previously demonstrated by Hue *et al.* (1986).

The substantial CaCO_3 content of layer and broiler poultry manure, feedlot cattle manure, pig manure and filter cake will have played an important role in raising soil pH. For the manures, the CaCO_3 content originates principally from CaCO_3 that is provided to poultry, pigs and cattle in their feed rations. For layer poultry, the CaCO_3 content in rations is very high because of the high Ca requirement for eggshell formation (Sims and Wolf, 1994). This explains why poultry manure was the most effective amendment for raising soil pH and decreasing exchangeable and soluble Al. In sugar mills CaCO_3 is added to the juice produced following milling sugarcane in order to flocculate organic material and the residue produced (organic matter plus CaCO_3) constitutes the filter cake.

Upon addition to the soil, the CaCO_3 is dissociated in solution, releasing CO_3^{2-} that combines with protons forming H_2CO_3 and the pH rises. The important role of residual CaCO_3 in animal manure and filter cake has been noted previously by

a number of workers (Sims and Wolf, 1994; Mokolobate and Haynes, 2002a).

During ammonification, one OH^- ion is produced per mole of organic N converted to NH_4^+ while during nitrification two H^+ ions are produced per mole of NH_4^+ converted to NO_3^- (Yan *et al.*, 1996). Thus, ammonification and the accumulation of NH_4^+ can cause a rise in soil pH but the production of NO_3^- from organic N is acidifying. The only treatment where nitrification was markedly inhibited was sewage sludge. Among the amendments, sewage sludge had a high N content, and nitrification proceeded more rapidly. The accumulation of NH_4^+ (and consequently OH^-) probably explains the surprisingly high pH of sewage sludge treatment. For example, sewage sludge had a considerably During ammonification, one OH^- ion is produced per mole of organic N converted to NH_4^+ while during nitrification two H^+ ions are produced per mole of NH_4^+ converted to NO_3^- (Yan *et al.*, 1996). Thus, ammonification and the accumulation of NH_4^+ can cause a rise in soil pH but the production of NO_3^- from organic N is acidifying. The only treatment where nitrification was markedly inhibited was sewage sludge. Among the amendments, sewage sludge had the highest total N content and consequently large quantities of mineral N were produced during incubation. Accumulation of high concentrations of NH_4^+ may have inhibited nitrification (Pocknee and Sumner, 1997). This did not, however, occur for broiler poultry manure, which also lower ash alkalinity and proton consumption capacity than pig manure yet the pH was similar or higher for sewage sludge amended soil. Hoyt and Turner (1975) also suggested that ammonification of N from organic residues without nitrification, was partially responsible for a rise in soil pH.

3.4.2 Changes in Al solubility

The general decrease in exchangeable and soluble Al following addition of organic amendments to the acid soil was presumably related to the increase in

soil pH. That is, with increasing pH, exchangeable and soluble Al precipitate as insoluble hydroxy-Al species (Noble *et al.*, 1996; Pocknee and Sumner, 1997)). Thus, exchangeable Al, Al_T and Al_{Mono} were negatively correlated with soil pH and positively correlated with each other. It is the activity of Al^{3+} and/or monomeric hydroxy-Al species in soil solution that is most negatively correlated with depressed plant growth due to Al toxicity (Tan and Binger, 1986; Suthipradith *et al.*, 1990; Hue *et al.*, 1986). Thus, it is the effect of organic residues on Al_{Mono} concentrations in soil solution that is of particular interest. The fact that there was a highly significant negative correlation between Al_{Mono} and pH demonstrates the importance of the rise in pH in depressing Al_{Mono} concentrations. Other factors such as complexation of Al in the solid phase or in solution by organic matter are of lesser importance but presumably explain much of the remaining variability in Al_{Mono} concentrations not explained by pH.

Indeed there were specific effects of various amendments on soil Al concentrations evident which did not appear to be directly related to changes in pH. For example, in comparison with sewage sludge and broiler poultry manure, relatively low concentrations of exchangeable Al were encountered at the high rate of compost addition. This is likely to be attributable to complexation of Al in the solid phase by humic substances contained in the compost. Indeed compost is predominantly humified organic matter (Sinesi and Brunetti, 1996), and due to the large number of functional groups present on humic substances they are able to complex Al^{3+} strongly (Stevenson and Vance, 1989). The reactions between Al and humic substances are complex and involve simultaneous chelation, complexation, adsorption and co-precipitation (Haynes, 1984)

At the lower rate of addition, the proportion of Al_T present as Al_{Mono} in soil solution was decreased by the addition of cattle manures, broiler poultry manure and compost. This increase in the proportion of complexed Al in soil solution is presumably attributable to the complexation of Al by soluble organic compounds originating from the added wastes. Soluble organic molecules such as organic

acids (e.g. citric, malic, succinic, tartaric acids) and phenolic, humic substances produced during the decomposition of residues can complex with Al_{Mono} and reduce the proportion of Al_T present as Al_{Mono} (Hue *et al.*, 1986; Harper *et al.*, 1995).

3.4.3 Prediction of liming effects

It is important to note that the measurements used here were developed to estimate the relative liming effect of a specific type of organic residue. The wide range of residues used in the study confounds their interpretation. For example both ash alkalinity and proton consumption capacity are measured by acid titration and this will include the $CaCO_3$ content of the residue or ash. Thus, the relatively large values for ash alkalinity and proton consumption capacity for layer poultry manure, pig manure and filter cake are likely to be primarily because of their substantial $CaCO_3$ content and this was demonstrated by the lime equivalence determination (TABLE 3.4).

The two properties of organic wastes best correlated with the increase in soil pH during incubation were basic cation content and ash alkalinity. Ash alkalinity measures the alkalinity resulting from the loss of organic matter, which occurs during ashing. Prior to ashing this alkalinity will have been balanced by negatively charged organic molecules. This may have been principally through low-molecular weight organic acids such as oxalate, malate and citrate (as in fresh plant material), more stable negatively charged high-molecular-weight polymers in humified materials (as in compost) or a mixture of both types of materials (as in the case of manures in various stages of decomposition). When these organic molecules are added to soils they may consume protons from the soil and/or release OH^- ions during their decomposition. In either case, the molecules contribute to the increase in pH that occurs when organic wastes are applied to soils. As already noted, any $CaCO_3$ in the organic waste will remain in the ashed residue (mainly as CaO) and this will also contribute to ash alkalinity

values. Thus ash alkalinity represents a robust measure of the ability of the waste to increase pH when it is added to soil.

The negatively charged organic molecules and any residual CO_3^{2-} present in organic materials is balanced by inorganic cations (mainly Ca, Mg, K and Na), so that the basic cation content of materials is also strongly correlated with their ability to raise soil pH. Similarly, other workers have found that the increase in soil pH during decomposition of plant materials is closely related to basic cation content of the material (Bessho and Bell, 1997; Wong *et al.*, 1998). Ash alkalinity is a relatively simple single measurement while total cation content involves digesting the sample and measuring individual cation contents. Thus, ash alkalinity seems the most appropriate measurement that should be pursued in the future. It is interesting to note that Slattery *et al.* (1991) determined the ash alkalinity of a wide range of animal and plant products for the opposite reason to that proposed here. That is they used the values as an indicator of the soil acidifying effect of the removal of products for farming systems in harvested crops. They then estimated this in terms of lime replacement values.

In addition, lime equivalence of organic materials was calculated using the regression equation presented in FIGURE 3.6. The differences in lime equivalence of different organic materials are explained by the various factors controlling the increase in pH depending on the material being considered, as discussed above. The lime equivalence presented in TABLE 3.4 can be used to determine the amount of organic material to be added to the soil based on the lime requirement calculated in terms of amount of $\text{Ca}(\text{OH})_2$.

3.5 Conclusions

It is evident that the effect of organic residues in ameliorating soil acidity (reducing concentrations of exchangeable Al and more particularly Al_{Mono} in soil solution) occurs mainly through soil pH. Although ash alkalinity was originally

developed as a measure of the organic acid anion content of plant tissues, it is apparent that it can also be used as an effective index of the ability of organic residues to raise pH following their incubation with soils. The use of ash alkalinity as a laboratory test for the liming-effect of organic residues deserves further investigation.

CHAPTER FOUR

4 Response of maize to kraal manure and lime as ameliorant for soil acidity

4.1 Introduction

Soil acidity is a major limitation to crop production in many areas of the world including South Africa. Because Al toxicity is usually the major limitation to crop production in such soils, lime rates are usually calculated based on exchangeable Al and/or Al saturation (Kamprath, 1970; Moschler *et al.*, 1960; Reeve and Sumner, 1970, Farina *et al.*, 1980). Poor, small-scale farmers are often unable to afford the high cost of lime required to ameliorate soil acidity. It has, however, been reported that organic wastes amendment can be used as soil acidity ameliorants for overcoming acid soil infertility and increasing crop yields when applied to some tropical acid soils (Lungu *et al.*, 1993; Haynes and Mokolobate 2001).

Various animal manures have been found to raise soil pH, decrease soluble and exchangeable Al and increase plant yield (Hue, 1992; Eghball 1999; Whalen *et al.*, 2000). Cattle manure for example, increased soil pH and also supplied significant amounts of plant-available nutrients (Joann *et al.*, 2000). In many African small scale-farming systems, cattle are left to graze native grassland during the day but are brought back close to the houses at night where they are penned in kraals in which manure accumulates. Kraal manure is widely used in semi subsistence arable farming. It is often applied to the soil in the row area before sowing or planting the crop. Based on the above results, it seems possible that applications of kraal manure also raise soil pH in the root zone so that farmers are inadvertently liming their soils. However this aspect of the current use of kraal manure in small-scale farming has yet to be investigated.

Most of research on the use of organic wastes as liming materials has been conducted in the laboratory and/or greenhouse and very few have investigated the effects under field conditions. The purpose of this preliminary study was to investigate under field conditions, on small scale farming plots, whether kraal manure does indeed, have a liming effect. The study was carried out on an integrated small scale farming study at Ogogwini (KwaZulu-Natal South Coast). The field trial had two rates of lime, two rates of kraal manure and had two cultivars of maize (an indigenous line "EMBO" and a commercial cultivar "PAN 6710").

4.2 Materials and Methods.

The field experiment was conducted in a small scale farming area at Ogogwini (EMBO Traditional Authority) on the KwaZulu-Natal south coast. The mean annual rainfall is 939 mm and mean monthly temperatures range from a maximum of 22 °C in January to a minimum of 16 °C in June. The soil was classified as Inanda form, Glenariff family (Soil Classification Working Group, 1991) or a Humic ferralsol (FAO). The soil had the following properties: organic C = 30 g kg⁻¹, pH_{water} = 4.1, AMBIC P, Mn and Zn = 2, 7 and 3 mg kg⁻¹ respectively, exchangeable Ca, Mg, K and Al = 25, 12.5, 2.6, and 32 mmol_c kg⁻¹. Six months prior to the experiment the site had been cropped with maize. The cattle manure used was collected from a kraal situated closeby. It had a total element content of organic C = 273, N = 14, S = 2.5, P = 1.4, Ca = 8, Mg = 5, and Na = 0.8 g kg⁻¹ and Zn = 91, Cu = 21, Mn = 537 and Fe = 18266 mg kg⁻¹ respectively. It had a pH_{water} of 8, and a CaCO₃ content of 1.5 %.

Maize was planted in rows 50 cm apart with an intrarow spacing of 50 cm. Plots were 4 m long and 2 m wide and each plot was separated from adjoining ones by two guard rows. The experiment consisted of three rates of kraal manure (0, 10, and 20 t ha⁻¹), three rates of dolomitic lime (0, 2.5 and 5.0 t ha⁻¹) and two cultivars of maize (an indigenous selection, EMBO and commercial cultivar, PAN 6710). Manure and lime were applied in a

band 15 cm wide down the rows and were incorporated to a depth of 10 cm using a hand hoe. Seeds were then sown into the center of these bands. Treatments were arranged in a randomised block design with three replicates. Fertilizer rates recommended for maize by the KwaZulu-Natal Department of Agriculture Fertilizer Advisory service, based on soil test results for the soil were 75 kg N ha⁻¹, 112 kg P ha⁻¹ and 75 kg K ha⁻¹. These were applied in the 15 cm wide band to the control and limed plots. The lime rate recommended was 5.0 t ha⁻¹ of dolomitic lime (15 % Ca, 15 % Mg) and a lower rate (2.5 t ha⁻¹) was also used as this was considered more affordable for small-scale farmers.

Soil sampling was carried out at tasseling and harvest, 3 and 5 months respectively after planting. Soil was randomly sampled in the plant row to a depth of 10 cm using a tube sampler (4 samples per plot) and samples from each plot were bulked. Field-moist soil was sieved (< 2 mm), thoroughly mixed, and a sub sample was air-dried for measurement of pH and exchangeable Al. The water content of another subsample was adjusted to 100 % field capacity, incubated for 24 hours and soil solution was then extracted by centrifugation (Elkhatib *et al.*, 1987).

Both soil pH_{water} and pH_{KCl} were measured in 1:2.5 soil: solution (distilled water and 1M KCl) ratio using a glass electrode. Exchangeable Al was extracted with 1M KCl 1:20 soil:extract ratio and determined by a pyrocatechol violet (PCV) method (Mosquera and Mombiela, 1986). Monomeric Al (Al_{Mono}) in solution was measured by the PCV method of Kerven *et al.* (1989) while total soluble Al (Al_T) was measured by a modified PCV method of Menzies *et al.* (1992) using LaCl₃-Fe reagent.

Soil samples were analysed using routine soil testing methods at KwaZulu-Natal Department of Agriculture Cedara laboratory as described by Manson *et al.*, (1993). Exchangeable Ca and Mg were extracted with 1 M KCl (1:10; soil : solution ratio for 10 minutes). Exchangeable K and extractable P, Zn and Mn were extracted with AMBIC reagent (0.025 M NH₄HCO₃, 0.01 M NH₄Fe, 0.01 M ethalinediaminetetraacetic acid at pH 8.0) using a 1:10 soil: solution ratio for 10 minutes. In the extract, Ca, Mg, K, Mn and Zn were

analysed by atomic absorption spectrophotometry and P by the molybdenum blue method. Organic C content were measured by near infrared spectroscopy using an NIR analyzer.

All amended rows were harvested and corn cobs were removed by hand, grains were removed from cobs and grain mass was recorded for each plot. Yield data were analysed by Analysis of Variance using the Genstat V package. Least significance differences (LSD) were calculated at the 5% level. The relationship between pH and extractable Al and crop yield and pH or extractable Al was investigated by regression analysis. The data were fitted with linear, quadratic, cubic and exponential functions and regression equations and lines of best fit are presented.

4.3 Results

4.3.1 Changes in soil pH and exchangeable Al

The results for soil pH and exchangeable Al recorded at tasselling and harvest are presented in FIGURE 4.1. Soil pH_{water} and pH_{KCl} were increased significantly by addition of both lime and kraal manure. Increases in pH_{water} and pH_{KCl} were greater at the higher rate of application for both kraal manure and lime. At harvest, the order of increasing in soil pH generally followed the trend: control < kraal manure (R1) < kraal manure (R2) \leq lime (R1) < lime (R2). The pH of kraal manure treatment tended to decrease between tasselling and harvest while the reverse was the case for limed plots. As a result, the effect of kraal manure in increasing soil pH was greater at tasselling than that of lime while at harvest the pH induced by lime was greater than that of kraal manure. At harvest, the rate of kraal manure had no significant effect on pH_{KCl} .

The concentration of exchangeable Al measured at tasselling and harvest, was significantly reduced by both kraal manure and lime additions. Concentrations decreased between tasselling and harvest for limed plots.

The effect of lime in decreasing the concentration of exchangeable Al was very marked at harvest. The effect of kraal manure in reducing exchangeable Al was greater than that of lime at tasselling but this was reversed at harvest.

4.3.2 *Changes in soluble Al (Al_T and Al_{Mono}).*

Soluble Al (Al_T and Al_{Mono}) was significantly reduced by both kraal manure and lime at both rates of addition (FIGURE 4.2). At tasselling, the effect of kraal manure was greater than that of lime while at harvest the reverse was observed. At harvest, the following trend was observed: lime (R2) < lime (R1) \leq kraal manure (R2) < kraal manure (R1) < control. The decrease in Al_{Mono} induced by the addition of kraal manure and lime followed the similar trend order as that of Al_T . The lime had a limited effect in reducing soluble Al at tasselling but the effect was much more marked at harvest. Strongly negative exponential relationships between pH_{water} and pH_{KCl} and exchangeable and soluble Al (Al_T and Al_{Mono}) for limed plots were observed and these are shown in FIGURE 4.3 and 4.4. The relationships between pH and exchangeable and soluble Al in kraal manure treatments were, however, not significant (FIGURES 4.3 and 4.4).

4.3.3 *Nutrients status*

The macro and micronutrient status of the soil measured at tasselling is shown in TABLE 4.1. Exchangeable K levels were generally increased in the kraal manure treatments compared with the control. In contrast, levels of exchangeable Ca were not significantly elevated in the amended plots. AMBIC (ammonium bicarbonate) P was, however, markedly decreased in both the limed and kraal manure-treated plots and this effect was more pronounced at the higher rate of application. The recommended ranges of exchangeable K ($0.22 - 0.33 \text{ cmol}_c \text{ kg}^{-1}$) exchangeable Ca ($2 - 6 \text{ cmol}_c \text{ kg}^{-1}$)

¹).exchangeable Mg ($0.68 - 1.02 \text{ cmol}_c \text{ kg}^{-1}$) and extractable P ($15 - 25 \text{ mg kg}^{-1}$) (Manson *et al.*, 1993) so soil levels of Ca, P and K are generally low whilst those of Mg are adequate.

4.3.4 Maize yield

The maize yield was calculated using the grain mass basis (moisture content: 12 %). Addition of kraal manure or lime had a generally significant effect in increasing the yield of both cultivars of maize compared with the control (FIGURE 4.5). The effect was more pronounced for lime than kraal manure and greater at the higher rate of addition of both amendments. For both cultivars, the general trend for yield was: lime (R2) > lime (R1) = kraal manure (R2) > kraal manure (R1) > control. For all treatments the traditional maize variety (EMBO) had a higher yield than the commercial cultivar (PAN 6710).

Regression equations, lines of best fit and correlation coefficients between indices of acid soil infertility (pH, exchangeable Al, Al_T , Al_{Mono}) measured at tasselling and harvest and final maize yield are shown in FIGURES 4.6 and 4.7. The correlation coefficient between maize yield and pH_{KCl} was 0.65^{***} (regression line not shown). A strong linear relationship was found between maize yield and both pH and exchangeable Al while strong negative logarithmic relationships were recorded between Al_T and Al_{Mono} (measured at harvest) and maize yield. Maize yield was not significantly correlated with pH, exchangeable or soluble Al measured at tasselling (FIGURE 4.6).

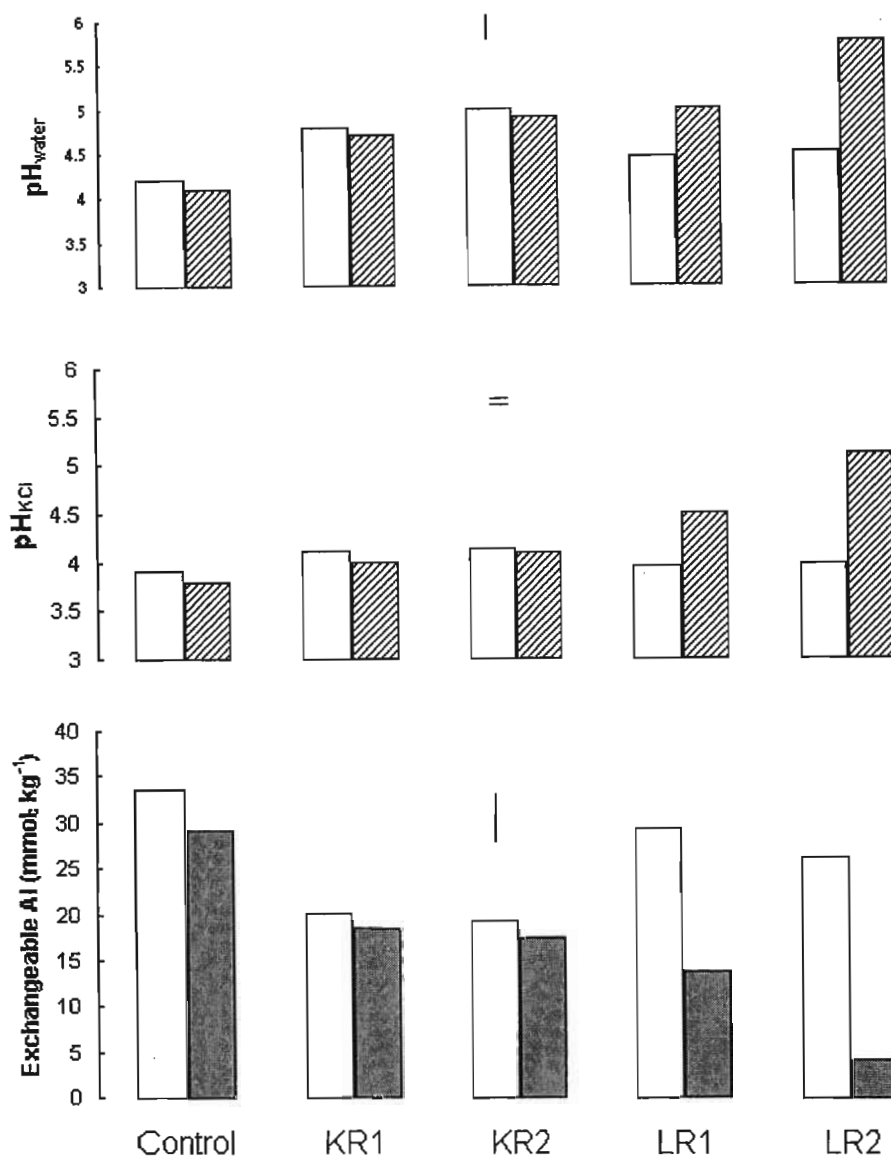


FIGURE 4.1: Changes in soil pH and exchangeable Al measured at tasselling (non-shaded area) and harvesting (shaded area) following application of cattle kraal manure and lime at 2 rates¹. LSD ($P \leq 0.05$) shown.

¹ KR1 = cattle manure added at the rate of 10 t ha^{-1} ; KR2 = cattle kraal manure added at the rate of 20 t ha^{-1} ; LR1 = Lime added at the rate of 2.5 t ha^{-1} and LR2 = Lime added at the rate of 5 t ha^{-1} .

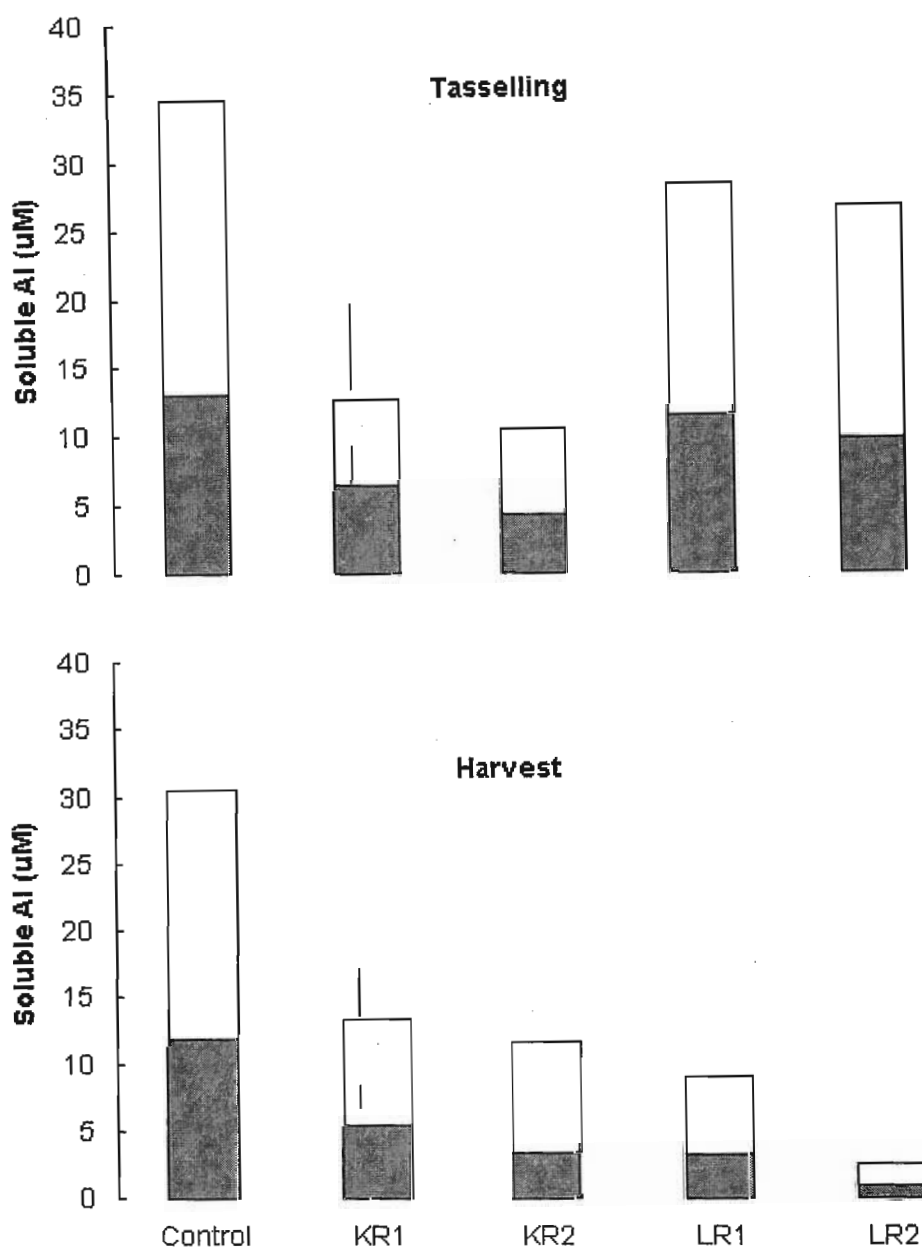


FIGURE 4.2 Changes in total soluble Al (height of histogram) and monomeric Al (shaded area), when cattle kraal manure and lime are added to an acid soil. LSD ($P \leq 0.05$). For explanation of the treatments see FIGURE 4.1.

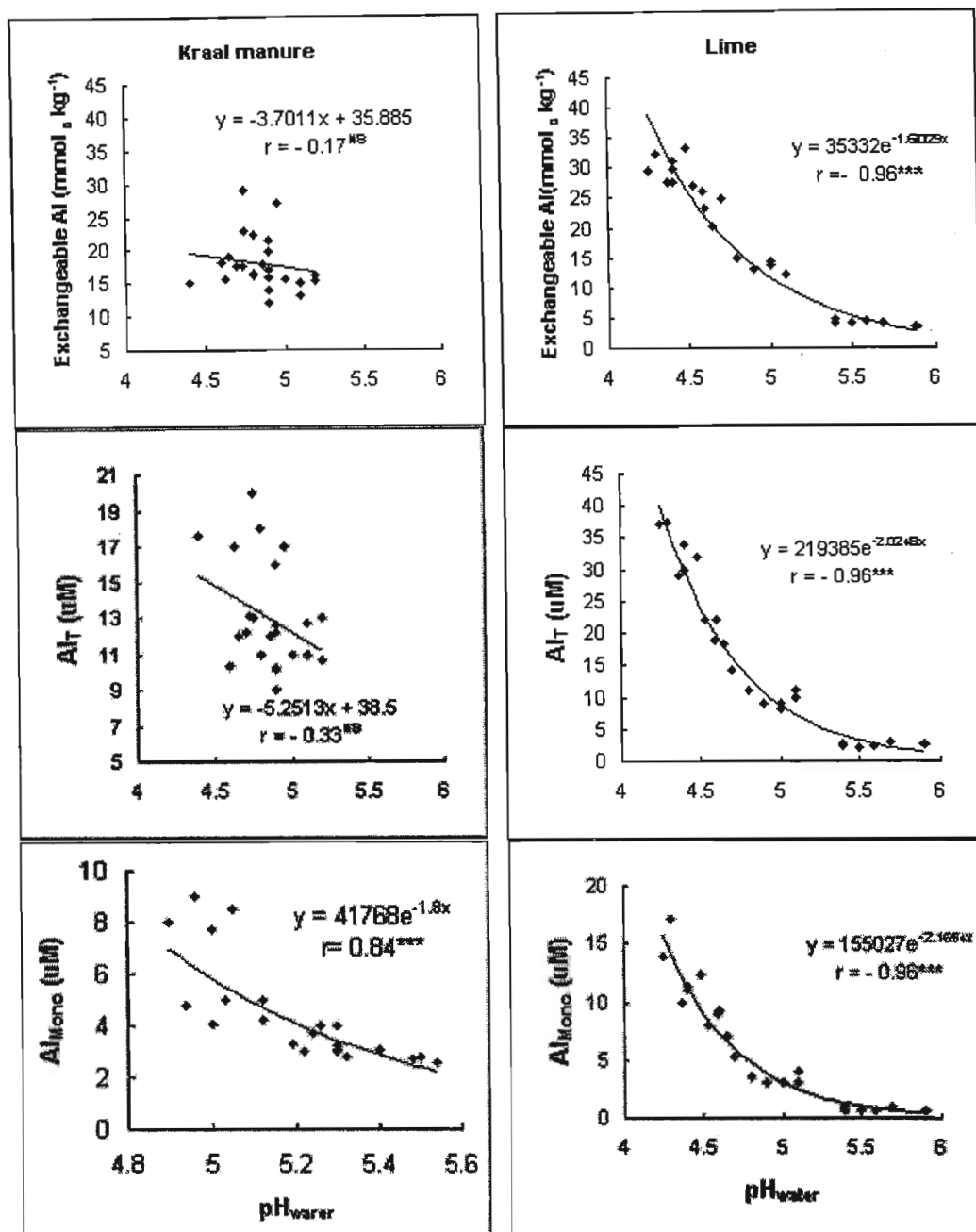


FIGURE 4.3 Relationships between pH_{water} and soluble Al (Al_T and Al_{Mono}) when cattle kraal manure and lime are added to an acid soil (samples collected at tasselling). Regression equations, lines of best fit, correlation coefficients and level of significance (NS P > 0.05, ** P ≤ 0.01; *** P ≤ 0.001) shown.

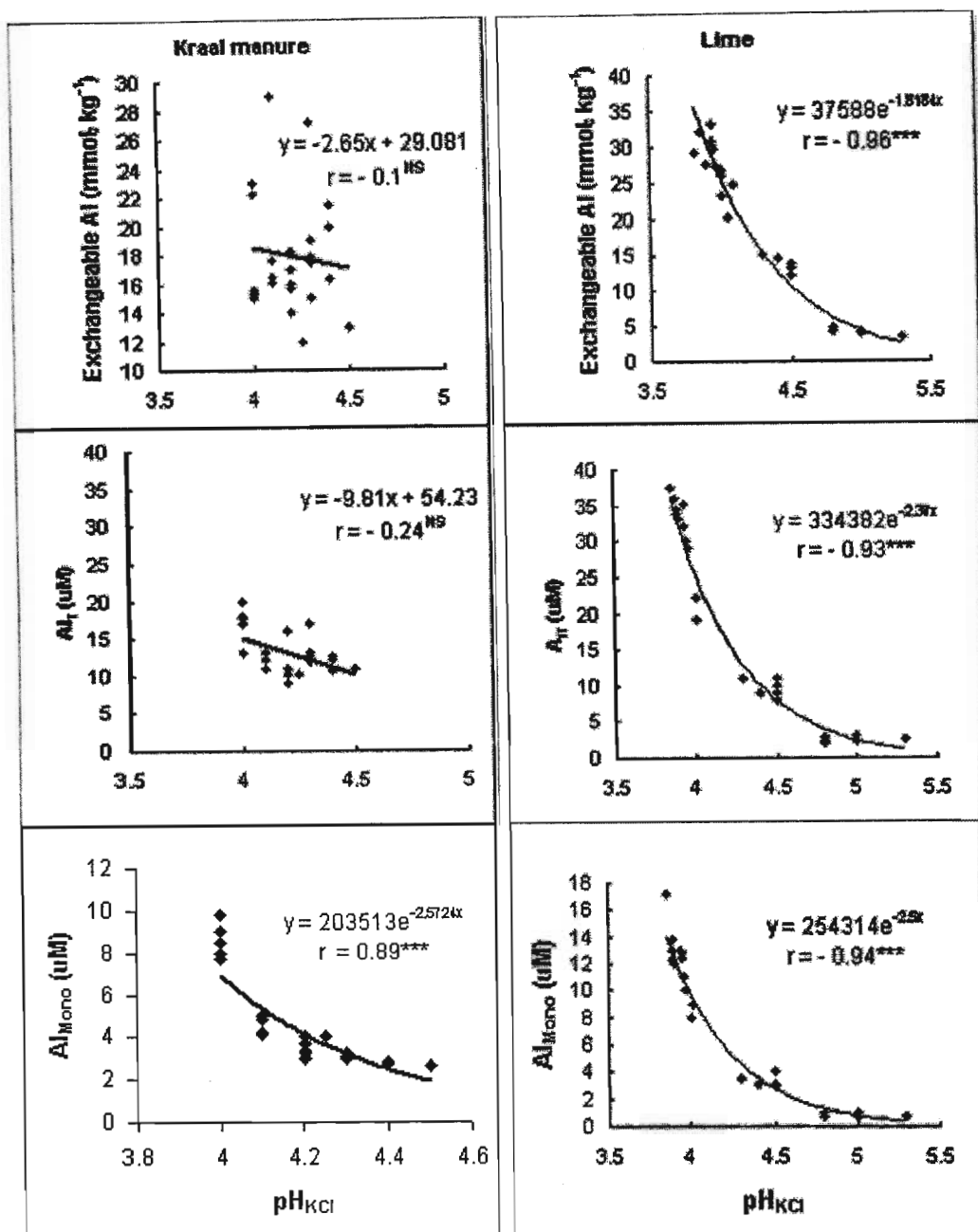


FIGURE 4.4 Relationships between pH_{KCl} and exchangeable and soluble Al (Al_T and Al_{Mono}) when cattle kraal manure and lime were added to an acid soil (soil analysis data from sampling at tasselling and harvest combined). Regression equations, lines of best fit, correlation coefficients and level of significance (^{NS} = Not significant, * P ≤ 0.05 ** P ≤ 0.01; *** P ≤ 0.001) shown

TABLE 4.1 Nutrient status of the soil measured at tasselling following addition of lime and kraal manure ¹.

	Exchangeable cations			AMBIC	Extractable		Organic C
	K	Ca	Mg	P	Zn	Mn	%
	(cmol _c kg ⁻¹)			(mg kg ⁻¹)			
Control	0.17	1.7	0.70	7.00	3.33	6.33	2.4
KR1	0.25	1.7	2.13	5.83	3.25	3.83	2.3
KR2	0.26	1.78	1.6	4.33	3.08	4.67	2.3
LR1	0.19	1.66	0.77	5.50	2.58	6.33	2.3
LR2	0.20	1.76	0.69	3.58	2.83	7.33	2.3

¹ For explanation of the terms see Figure 3)

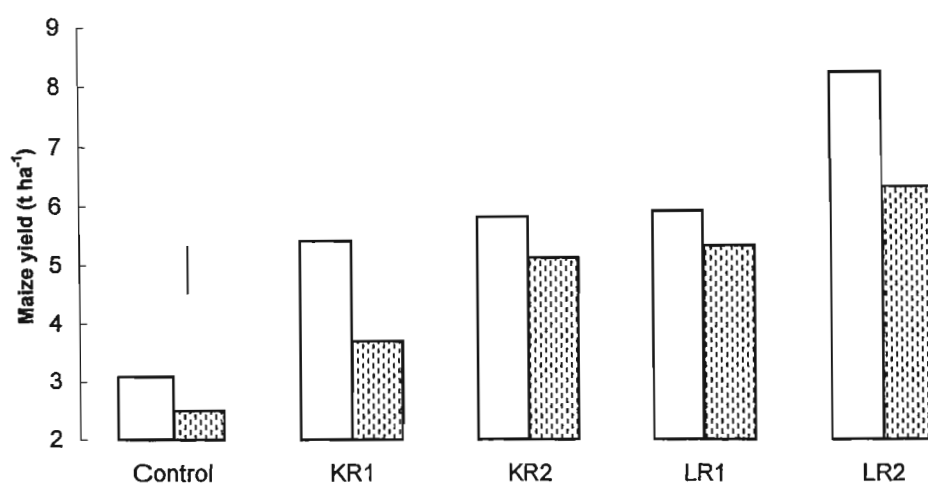


FIGURE 4.5 Maize yield of two cultivars: EMBO (non-shaded area) and PAN 6710 (shaded area) when cattle kraal manure and lime are added to an acid soil. LSD ($P \leq 0.05$) shown. For explanation of the treatments see FIGURE 4.1.

TASSELLING SAMPLING

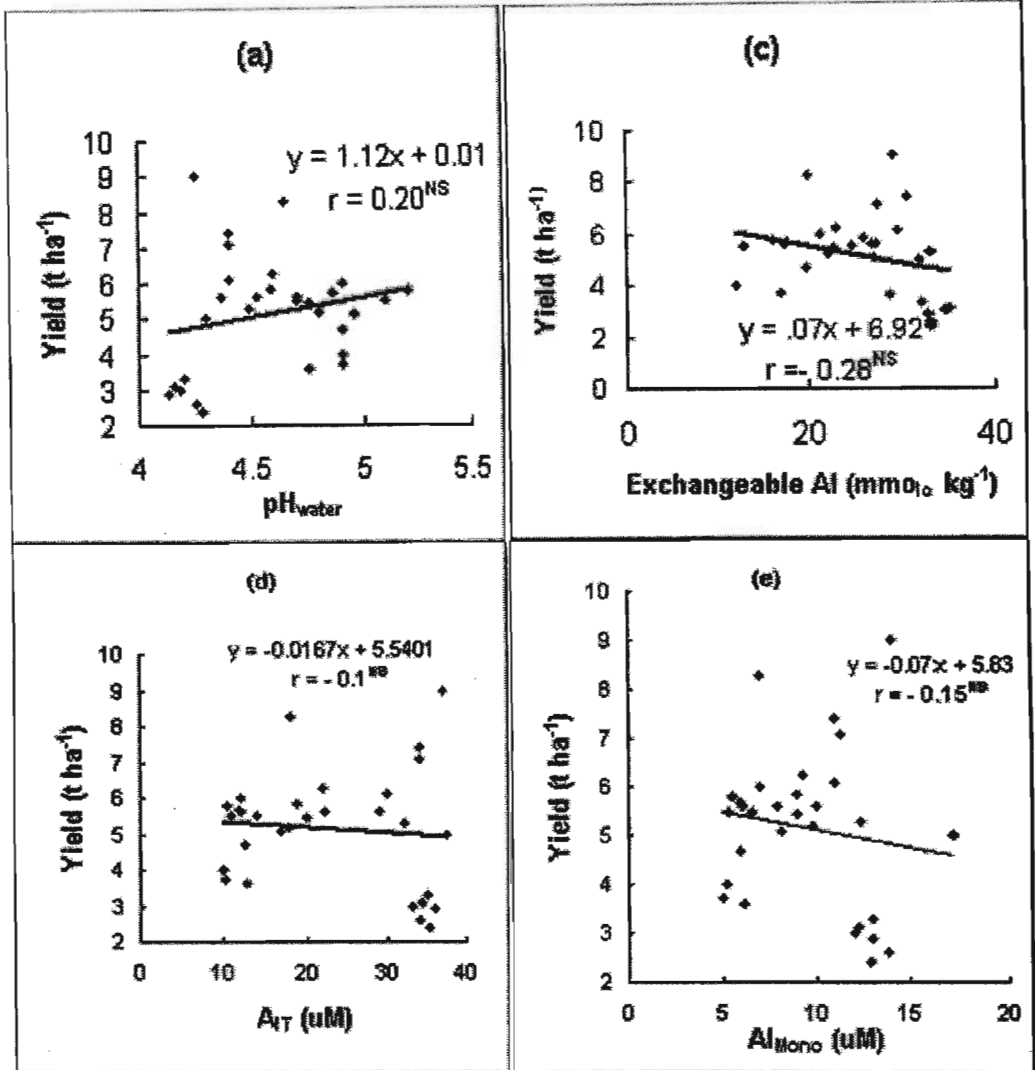


FIGURE 4.6 Overall relationships between approximately maize yield and (a) soil pH_{KCl}, (b) exchangeable Al, (c) total soluble Al and (d) monomeric Al when cattle kraal manure or lime are added to an acid soil. Regression equations, lines of best fit, correlation coefficients and level of significance (** P ≤ 0.01; *** P ≤ 0.001) shown.

HARVEST SAMPLING

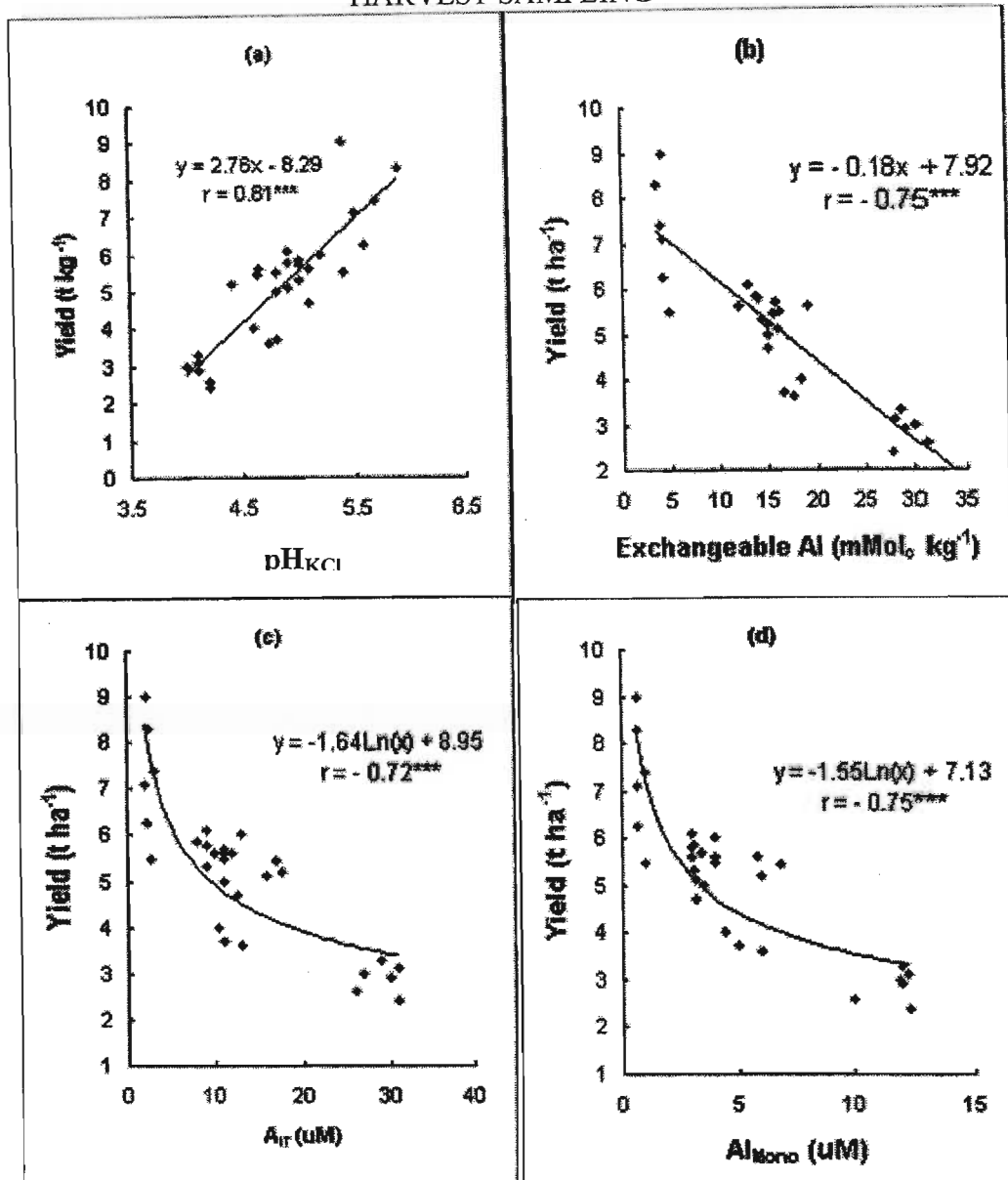


FIGURE 4.7 Overall relationships between approximately maize yield and (a) soil pH_{KCl}, (b) exchangeable Al, (c) total soluble Al and (d) monomeric Al when cattle kraal manure or lime are added to an acid soil. Regression equations, lines of best fit, correlation coefficients and level of significance (** P_≤ 0.01; *** P_≤ 0.001) shown.

4.4 Discussion

4.4.1 Changes in soil pH

The ability of kraal manure to increase the soil pH when added to an acid soil has been reported from an earlier laboratory study (CHAPTER 3). The relatively large elevation in soil pH recorded in the present study is attributable to the high concentration of animal dung in the kraal manure used. The increase in soil pH was less marked in the laboratory study reported in the previous chapter. The reason for this is believed to be that the previous sample of kraal manure contained a considerably high proportion of soil mixed with the dung.

Whilst most of the K, N and S are excreted by cattle in urine, faeces are the main excretory pathway for Ca and Mg (Hutton *et al.*, 1967; Hogg, 1981). The high concentration of faecal Ca and Mg results in an excess content of nutrient cations over anions in dung and this imbalance is made up by carbonates (Barrow, 1987). Barrow (1975) for example, showed that Merino sheep faeces had a CaCO_3 content of about 1.3 % and it seems probable that much of the Mg is also present as MgCO_3 . As a result of the presence of Ca and Mg carbonates, animal faeces usually, as shown here, have a pH in the range 7.0 – 8.0 (Barrow, 1987). Many studies have shown that on grazed pastures, increases in exchangeable Ca and Mg and pH occur in the surface 2.5 – 5.0 cm of soil below dung patches (During *et al.*, 1973; Weeda, 1977). Similarly, the addition of farmyard manure as an amendment to acid soils has been shown to raise soil pH (Lungu *et al.*, 1993). Thus, it is not surprising that application of kraal manure (which is mainly cattle dung) had a liming effect and raised soil pH appreciably. Cattle manure from feedlots has also been reported to have a substantial liming effect although this is partially as a result of the fact that such cattle are routinely fed CaCO_3 in their diet (Egball, 1999; Whalen *et al.*, 2000)

Other mechanisms may have also contributed to the liming effect of kraal manure (Haynes and Mokolobate, 2000). These could include the proton consumption capacity of humic materials formed during decomposition of the

manure (Wong *et al.*, 1998), oxidation of organic acid anions present in the dung (Yang *et al.*, 1996), specific adsorption of organic molecules originating from the dung onto hydrous oxide surfaces (Hue *et al.*, 1986) and ammonification of organic manure-N (Hoyt and Turner, 1975). Nonetheless, the high initial pH and substantial CaCO_3 content of the manure are likely to have been the main reasons for its liming effect.

It is interesting that whilst the pH of limed plots increased between taseing and harvest, due to continued dissolution of the applied dolomitic lime that of the plots receiving kraal manure tended to decline over that same period. It is possible that this tendency for a decline in pH in the manure plots is due to nitrification of NH_4^+ derived from continued ammonification of manure N during its decomposition. Unfortunately, levels of soil NH_4^+ and NO_3^- were not monitored in this field study. The reason for the decline does, however, deserve further detailed study. The results suggest that the liming effect of kraal manure could be transitory.

4.4.2 Al detoxification.

The decrease in exchangeable and soluble Al (Al_T and Al_{Mono}) noted for the kraal manure and lime treatments is primarily attributable to an increase in soil pH. Many workers demonstrated that the increase in soil pH is accompanied by precipitation reactions of Al^{3+} as hydroxy-Al compounds (Noble *et al.*, 1996; Pocknee and Sumner, 1997). Indeed the concentration of exchangeable and soluble Al in the limed treatments decreased between tasselling and harvest, concomitant with the increase in soil pH and there was a strong negative relationship between soil pH and exchangeable and soluble Al (Al_T and Al_{Mono}) in limed treatments. However, the poor relationship between soil pH and exchangeable and soluble Al for kraal manure treatments suggests that, factors other than soil pH are contributing to Al solubility in these treatments.

It seems likely that complexation of Al in the solid and solution phase by organic matter played an important role in affecting Al solubility in these treatments. As kraal manure is a decomposing material, it is likely to contain humic substances. Such substances are able to complex with Al^{3+} due to their numerous functional groups (Stevenson and Vance, 1989). Other investigators (Thomas, 1988; Hue and Amien, 1989) have noted that soluble Al can be complexed by organic molecules especially organic acids. Complexation of Al by solid phase organic matter is presumably the reason for the decline in exchangeable Al levels in kraal manure plots between tasselling and harvest. The tendency for a decrease in pH over this period would be expected to cause an elevation in exchangeable Al concentrations. The relatively slow effect of lime additions in reducing exchangeable Al, may be related to a slow dissolution rate of lime.

4.4.3 Soil nutrient status

Clearly, liming is by no means the only benefit of applying kraal manure since both macro and micronutrients are added to the soil. Thus there was a tendency for exchangeable K concentrations to be increased by manure application.

Surprisingly, concentrations of exchangeable Ca were not elevated by additions of either amendment and neither were those of exchangeable Mg in limed plots. This is presumably because of slow dissociation of lime and nutrient uptake by the crop, which occurred during the period between application of amendments and tasselling when soils were sampled.

Addition of both lime and kraal manure had the surprising effect of reducing AMBIC P levels appreciably; the effect being greater at the higher rate of both materials. Part of this effect could be attributable to plant uptake of P. However, decreases in the extractability of P induced by lime applications (i.e. raising soil pH) have been observed by a number of workers (Haynes, 1982, 1984; Haynes *et al.*, 2001). It has been suggested (Haynes, 1984) that liming results in precipitation of exchangeable and soluble Al in the form of amorphous hydroxy-Al compounds. These positively charged materials have

a significant P-adsorption capacity so that following liming the availability of P is reduced. Precipitation of insoluble Al-phosphates is another possibility (White and Taylor, 1977; Naidu *et al.*, 1987). Other possible explanations include precipitation of insoluble Ca-phosphates in the soil (White and Taylor, 1977; Naidu *et al.*, 1987) and/or Ca-phosphates precipitating during extraction particularly when the Olsen extractant (0.5 M NaHCO₃, pH 8.5) is used (Sorn-Srwichai *et al.*, 1984; Naidu, 1987). This is also a possibility when the AMBIC extractant (NH₄HCO₃, pH 8) is used. However results presented in Table 1 show that exchangeable Ca levels were not elevated appreciably in the lime or kraal manure treatments. Thus, the former explanation of increased P adsorption and/or precipitation of Al-phosphates seem more likely. Whatever the mechanisms, the decline in available P seems to be of some significance since the critical AMBIC P level for maize is about 15 mg kg⁻¹ (Manson *et al.*, 1993). In amended plots the AMBIC P levels, were all below 6 mg kg⁻¹. The reason for this needs further investigation. Another possible reason of the reduction of AMBIC P could have been the microbial immobilization of P.

4.4.4 *Maize yield*

The relatively high yield recorded for the EMBO variety compared with PAN 6710 may be related to a difference in Al tolerance. Plant species and cultivars can tolerate high concentrations of soluble Al through several strategies including both Al exclusion and Al tolerance mechanisms (Kochian, 1995). In this connection, it has been shown that Al exposure triggers a rapid release of citrate in some Al-resistant maize genotypes (Pellet *et al.*, 1994). In addition, Kochian, (1995) noted that the induction of synthesis of low-molecular-weight binding peptides may play a role in metal-tolerance.

The reason for the substantially higher yields in the limed compared to kraal manure plots is unclear since the experiment was not primarily designed to compare the liming effects of the two materials on yield. That is, the trial was

a participatory demonstration experiment for small-scale farmers to demonstrate the positive effects of both kraal manure and lime. Application rates and release characteristic of various nutrients were not identical even though a basal application was applied to the limed treatments. For example, a substantial portion of nutrients in manure is only slowly available because they are in organic forms and are released via mineralization over time.

Certainly both materials increased soil pH and lowered Al_{Mono} concentrations markedly. Indeed it is the activity of Al^{3+} and/or monomeric hydroxy-Al species (e.g. $AlOH^{2+}$ and $Al(OH)_2^+$) that are most negatively correlated with depressed yields due to Al toxicity (Haynes and Mokolobate, 2001). Measured values of Al_{Mono} were reduced from 12 μM in the control soil to below 6 μM in amended soils (FIGURE 4.2). Such a reduction is of considerable significance since the critical soil solution Al_{Mono} concentration above which maize growth is limited by Al toxicity is in the range of 3 - 8 μM (Harper *et al.*, 1995; Diatloff *et al.*, 1998). Thus a reduction in Al toxicity is likely to have been a major contributory factor to the yields of all amended plots being greater than the control.

4.5 Conclusions

When added to an acid soil, cattle kraal manure can ameliorate acid soil infertility by providing plant nutrients, increasing soil pH and reducing the concentration of exchangeable and soluble Al. The effect of cattle kraal manure in decreasing exchangeable and soluble Al is likely to be partially attributable to the increase in soil pH but also to be related to the ability of organic matter to complex with Al. The amelioration of soil acidity by additions of cattle kraal manure can increase maize yield.

Dolomitic lime remains a very important soil acidity ameliorant and its effects on increasing soil pH, decreasing Al toxicity and increasing maize yield were shown to be greater than that of cattle kraal manure. Surprisingly when cropped on an acid soil, the indigenous maize variety (EMBO) had a higher

yield than that of the commercial cultivar (PAN 6710) regardless of whether the soil is amended with dolomitic lime or cattle kraal manure. This phenomenon is of considerable practical significance and deserves further study.

More investigations are recommended in order to establish the mechanisms involved in the liming effect of kraal manures (particularly the poor relationship between pH and Al solubility) and to draw up practical and technical guidelines for a sustainable agricultural production in acid soils by small-scale farmers. In addition, the decrease in extractable soil P induced by applications of both lime and manure is puzzlin

CHAPTER FIVE

5 Short and long-term effects of the addition of organic manures on Al solubility.

5.1 Introduction

A growing interest is being directed toward to the investigation of the liming ability of organic residues. An important reason for this is the development of an alternative to mineral lime for poor, small scale farmers from developing countries (Hue, 1992; Haynes and Mokolobate, 2001) and thus a sustainable agricultural system on acid soils (Parr and Hornick, 1992). However, a lack of knowledge about the mechanisms involved in the liming effects of organic residues makes it difficult to methodically maximize the beneficial effects and minimize any deleterious ones (Pocknee and Sumner, 1997).

It is clear that the liming of acid soils aims mainly at Al detoxification and it has been suggested that Al detoxification occurring when organic residues were added to an acid soil, is due to both an increase in pH and Al complexation by the added organic matter. The increase in soil pH recorded when organic amendments are added to acid soils is considered to occur through two main steps. Firstly, a range of immediate chemical reactions occurs (Tang *et al.*, 1999; Yan *et al.*, 1996). These include the complexation of protons by organic acid anions found in the organic residues (Ritchie and Dolling, 1985) and the dissolution of CaCO_3 contained at relatively high concentration in some organic wastes such as animal manures (Robinson, 1961; Sims and Wolf, 1994; Mokolobate and Haynes, 2002a). Secondly, a number of reactions occur during residue decomposition. Those include the specific adsorption of organic molecules (humic material and organic acid anions) produced during decomposition onto Al and Fe hydrous oxides (Hue *et al.*, 1986; Iyamuremye and Dick, 1996) and the decarboxylation of organic acid anions released in the soil from the decomposing material and/or

synthesised by microorganisms (Berekzai and Mengel, 1993; Mengel, 1994; Tang *et al.*, 1999; Yan *et al.*, 1996). Other important mechanisms include ammonification of organic N during decomposition of organic amendments (Hoyt and Turner, 1975; Pocknee and Sumner, 1997) and reduction reactions occurring in localised sites (Hoyt and Turner, 1975; Hue and Amien, 1989; Hue, 1992)

In addition, it has been observed that the complexation of Al by organic matter can be another important factor controlling the solubility of Al in acid soils (Bloom *et al.*, 1979; Haynes, 1984; Stevenson and Vance, 1989; Sinesi and Brunetti, 1996). Some workers, including Kretsman *et al.* (1991), Besho and Bell (1992), Berek *et al.* (1995), Patiram (1996) and Mokolobate and Haynes (2002a) observed that changes in Al solubility when organic residues were added to an acid soil were not necessarily correlated with changes in pH. They therefore suggested that complexation of Al by the added organic matter was strongly influencing Al solubility.

It is likely that the two mechanisms (increased pH and Al-complexation by organic matter) are time-dependent and are mediated by a number of chemical and biochemical reactions, whose intensity and importance depend upon the type and the amount of material being used. In this study, short-term (3 days) equilibration experiments were carried out to determine the effects of addition of animal manures to soils on Al solubility over the pH range 4 – 6.5. To further explain the results, the effects of animal manures on Al solubility in $AlCl_3$ solutions were studied. The effects of longer-term incubation (6 – 24 weeks) of manures with soil were also investigated. In particular, the role of N transformations (ammonification and nitrification) in influencing pH was studied. In this latter study the range of organic materials was extended to include sewage sludge and plant residues.

5.2 Materials and Methods

5.2.1 Materials

Topsoil samples were collected on the coastal lowlands of KwaZulu-Natal and were air dried and sieved (< 2mm). The soil was of Shortlands form (chromic Luvisol, FAO) and it had the following properties: $\text{pH}_{\text{water}} = 4.1$, organic C = 18 g kg^{-1} , Truog extractable P = 14 mg kg^{-1} , exchangeable $\text{Ca}^{2+} = 15$, $\text{Mg}^{2+} = 9.3$, $\text{K}^{+} = 2.9$, $\text{Na}^{+} = 1.7$ and $\text{Al}^{3+} = 13 \text{ mmol}_c \text{ kg}^{-1}$, exchangeable acidity = $14 \text{ mmol}_c \text{ kg}^{-1}$ and acid saturation = 33 %. It had a clay content of 36 % and its mineralogy was dominated by kaolinite with some accessory vermiculite and some smectite were also present.

Three animal manures used for the short-term equilibration experiments were cattle manure (collected from a small scale farm of KwaZulu-Natal), poultry manure (collected from a commercial layer producer) and pig manure (from a commercial pig producer). The pig and poultry manures had the same properties as those used in CHAPTER 3. The kraal manure used in the short-term equilibration experiment had the following properties: organic C = 273 g kg^{-1} , N = 14 g kg^{-1} , S = 2.5 g kg^{-1} , P = 1.4 g kg^{-1} , Ca = 8 g kg^{-1} , Mg = 5 g kg^{-1} , and Na = 0.8 g kg^{-1} and Zn = 91 mg kg^{-1} , Cu = 21 mg kg^{-1} , Mn = 537 mg kg^{-1} and Fe = 18266 mg kg^{-1} respectively. It had a pH_{water} of 8, and a CaCO_3 content of 1.7 %. The pig, poultry and kraal manures used in the long-term experiment had the same properties as those used in CHAPTER 3. In addition to the animal manures, a leguminous (soybean from Cedara Research Station) plant residue and sewage sludge (from a Hammarsdale Sewage Works, Durban) were used as amendments for the long-term incubation experiment and their properties are given in TABLE 3.1.. The organic amendments were oven dried (at $70 \text{ }^{\circ}\text{C}$) and ground to pass a $500 \text{ }\mu\text{m}$ sieve.

5.2.2 Experimental design.

The short-term equilibration experiment involved 3 parts. Firstly the soil was amended with the three animal manures (three replicates per treatment) at 0.02 g g^{-1} , which is equivalent to a rate of about 20 Mg ha^{-1} based on a hectare to a depth of 10 cm. Manures (0.2g), were mixed with the soil samples (10g), placed in polyethylene centrifuge tubes and 25 mL of 0.01 M CaCl_3 was added to each tube. The samples were shaken for three days after which the pH was measured. Samples were centrifuged at 10,000 RPM for 5 minutes and soil solutions were filtered through a filter paper number 42 for the analysis of Al_T , Al_{Mono} and soluble C.

The first experiment (experiment 1) showed that the pH of equilibration differed for the different manures. Therefore in the second part (experiment 2), pH of equilibration (0.2 g manures, 10 g soil, 25 mL of 0.01 M CaCl_3) was adjusted to 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5 with HCl or NaOH. The pH was readjusted after every 12 hours equilibration. The samples were shaken in triplicates for three days after which the final pH was measured and soil solution extracted (as described above) for the analysis of Al_T , Al_{Mono} and soluble C.

A third experiment (experiment 3) was carried out in order to further examine the effects of animal manure on Al solubility at different pH values, 0.2 g of the three manures were equilibrated. with 25 mL of $40 \mu\text{M AlCl}_3$ (in 0.01M CaCl_3) for three days. The pH was adjusted to each of the same values as outlined above (in triplicate) and following equilibration. The solution was extracted for the measurement of Al_T , Al_{Mono} and soluble C.

For the long-term incubation experiment, the five organic amendments were thoroughly mixed with soil (9 replicates per treatment) at two rates (0.1 and 0.2 g g^{-1}) and placed in 2-L plastic containers fitted with perforated lids to allow aeration. Samples were wetted with distilled water at 70 % water holding capacity. Samples were incubated for 18 weeks and were rewetted

every week when necessary to maintain the moisture content at 70 %. Three replicates of each treatment were removed after 6, 12, 18 and 24 weeks. Soil samples were split in three. One sub-sample was immediately wetted to a 100 % water holding capacity. The soil solution was extracted 48 hours later by centrifugation (Elkhatib et al., 1987) and Al_T and Al_{Mono} were measured. Another was stored at 1^oC for subsequent analysis of mineral N. The third was air-dried for analysis of exchangeable Al and pH.

5.2.3 Analyses

Soil pH was determined with a glass electrode using 1:2.5 soil:solution (water and 1 M KCl) ratio. Exchangeable Al was extracted with 1M KCl (1:2.5 soil:solution ratio and determined by the pyrocatechol violet (PCV) method (Mosquera and Mombiela, 1986). Total soluble Al was determined by a modified PCV method using $LaCl_3$ -Fe reagents after the solution had been passed through a 0.22 μ m filter (Menzies et al., 1992). The inorganic monomeric Al was measured in soil solution passed through 0.22 μ m filter using the short-term PCV method (Kerven et al., 1989). Soluble C in equilibration extractants was measured using a Shimadzu 5000 A soluble C analyser. Exchangeable NH_4^+ and NO_3^- were extracted from soil at the beginning and at the end of each period of incubation using 2 M KCl (1:5 soil:extractant) ratio and determined by distillation (Keeney and Nelson, 1982).

5.2.4 Data analysis

All experiments were arranged in completely randomized designs and data analysis were performed by ANOVA using Genstat V computer package and LSDs were computed at the 5 % level.

5.3 Results

5.3.1 Experiment 1

The addition of animal manures to an acid soil had a significant effect in increasing soil pH and decreasing both total soluble aluminium (Al_T) and monomeric aluminium (Al_{Mono}) (FIGURE 5.1). The increase in soil pH and decrease in Al_{Mono} followed the trend: poultry manure > pig manure > kraal manure > control. Poultry manure reduced Al_{Mono} concentrations to less than 10 % of those present in the control while the equivalent values for pig and kraal manures were 25 and 40 % respectively. No difference was recorded between the effects of pig manure and poultry manure in decreasing Al_T , but the soil pH values induced by these two animal manures were significantly different. However, pig and poultry manures had a relatively greater effect in increasing pH and reducing both Al_T and Al_{Mono} concentrations than kraal manure.

5.3.2 Experiment 2

At low pH (i.e. 4), the concentration of Al_T was reduced by the addition of all three amendments and the effects was most marked for kraal and pig manures. The solubility of Al was highly pH-dependent in all treatments and it decreased exponentially with increasing pH. The concentration of Al_T for the layer poultry manure-amended soil remained relatively high with increasing pH compared with that in the pig manure, kraal manure and control treatments. At high pH (> 5.5), the concentration of Al_T followed the order: layer poultry manure > pig manure > kraal manure > control (FIGURE 5.2).

At pH = 4, the concentration of Al_{Mono} was not greatly decreased by application of animal manures. By contrast, Al_{Mono} concentrations were reduced substantially as the pH was increased and at high pH, the concentrations of Al_{Mono} followed the trend: control > kraal manure \geq pig

manure > poultry manure. The percentage of Al_T present in the soil solution as Al_{Mono} followed a similar trend to that for Al_{Mono} .

The concentration of soluble organic C followed the trend: poultry manure > pig manure > kraal manure > control and markedly higher values were recorded at all pH values for the poultry manure samples (FIGURE 5.3). Soluble C concentrations were not greatly influenced by increasing pH, although for the control, kraal and pig manures lower values were recorded at pH 4.

5.3.3 Experiment 3.

At low pH (i.e. 4) the concentrations of Al_T were drastically reduced in animal manure treatments (FIGURE 5.4). The kraal manure amendment was most effective in decreasing the concentration of Al_T . Concentrations of Al_T were decreased with increasing pH; this effect was extremely marked in the control and much less obvious in the animal manure treatments. As a result, at pH = 5.5 and above, Al_T tended to be higher in the pig and poultry manure treatments than in the control and the same was true for the kraal manure treatments at pH 6 and above.

The concentrations of Al_{Mono} were decreased by the addition of animal manures (FIGURE 5.4). This effect followed the trend: poultry manure > pig manure > kraal manure. Concentrations of Al_{Mono} were highly pH-dependant in the control treatment but this trend was much less clear in the animal manure treatments. Indeed, very low concentrations of Al_{Mono} were detected in poultry manure samples, regardless of the pH value being considered.

The percentage of Al_T present as Al_{Mono} in samples followed the general order: control > kraal manure > pig manure > poultry manure and it clearly decreased with increasing pH for the control and kraal manure treatments. The concentrations of soluble organic C followed the order: poultry manure > pig manure > kraal manure (FIGURE 5.5). The values of soluble C were

approximately double of those measured in experiment 2. The concentrations of soluble organic C tended to increase with increasing pH for the pig and poultry manure treatments.

5.3.4 *Relationship between Al solubility and soluble C*

Correlations between Al_{Mono} , Al_{T} and soluble C for the soil and solution Al equilibration experiments, were not significant when values for all pH values were included (data not shown). However, when values for pH = 5.5, 6.0 and 6.5 were used (the pH range where largest differences in trends for Al_{T} and Al_{Mono} were noted) soluble C was positively correlated with Al_{T} and negatively correlated with Al_{Mono} (FIGURE 5.6). In fact over that pH range there was a negative correlation between Al_{T} and Al_{Mono} ($r = -0.55^{**}$ for soil and $r = -0.64^{**}$ for solution Al equilibration).

5.3.5 *Long-term incubation experiment*

Soil pH.

After 6 weeks of incubation, the soil pH (measured in water and KCl) was significantly increased by the addition of all organic wastes excluding kraal manure (FIGURE 5.7 and 5.8). The high rate of application generally raised soil pH a little more than the lower rate. For both rates of application and for the whole period of incubation, poultry manure samples had the highest pH values. Soil pH generally declined over the incubation period for all treatments. Except for poultry manure, soil pH tended to stabilize after about 18 weeks incubation. At the lower rate of addition, soil pH at 6 weeks incubation followed the order: poultry manure > sewage sludge \geq pig manure = soybean residues > kraal manure > control.

Al concentrations.

Concentrations of exchangeable Al were significantly decreased after 6 weeks incubation with the organic amendments (FIGURE 5.10). The magnitude of the decrease followed the order: poultry manure > pig manure \geq soybean residues > sewage sludge > kraal manure. Exchangeable Al concentrations were greater after 24 than 6 weeks incubation for all of the treatments. After 24 weeks incubation, poultry and pig manure were considerably more effective than the other amendments at depressing exchangeable Al levels.

For both rates of amendment, the concentrations of Al_T and Al_{Mono} were reduced following 6 weeks incubation. The pattern of change in Al_T and Al_{Mono} with incubation period was broadly similar to that for exchangeable Al (FIGURES 5.9 and 5.10). After 6 weeks incubation, lowest values of Al_T and Al_{Mono} were measured in poultry and pig manure and sewage sludge treatments. After 24 weeks, concentrations were lowest in the poultry manure treatment. For the pig manure and sewage sludge treatments concentrations of Al_T and Al_{Mono} increased greatly between 6 and 24 weeks of incubation. By contrast, for the kraal manure treatment Al_T concentrations decreased between 6 and 24 weeks even though exchangeable Al concentrations increased.

The proportions of Al_T present as Al_{Mono} were generally decreased by additions of organic manures (FIGURE 5.10). In general, kraal manure was most effective at depressing this percentage. For amended soils, highest proportions were observed at the lower rate of poultry manure and lowest proportions were measured at the high rate of the same treatment.

N mineralization.

After six weeks incubation of animal manures with an acid soil, the accumulation of NH_4^+ in amended samples was significantly higher (FIGURES 5.11 and 5.12) than the control. The high rate application of

organic wastes generally resulted in a greater accumulation of NH_4^+ . Greatest concentrations of NH_4^+ after 6 and 12 weeks incubation were measured in the poultry manure and sewage sludge-amended soils. Concentrations of NH_4^+ in sewage sludge treatments remained higher than those in the other treatments after 18 and 24 weeks incubation. The major period of accumulation of NO_3^- in soils occurs between 6 and 12 weeks of incubation (FIGURE 5.11 and 5.12) and this coincided with the period when the pH fell most markedly in the amended soils (FIGURE 5.7 and 5.8).

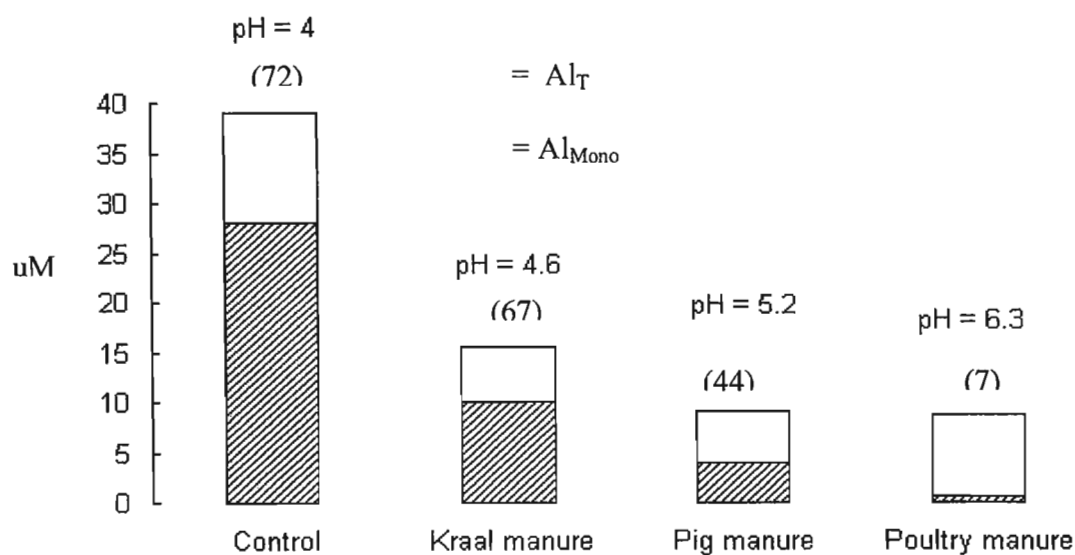


FIGURE 5.1 Changes in Al_T (height of histogram) and Al_{Mono} (shaded area) following equilibration of 10 g of an acid soil with 0.2 g animal manures for 3 days. The percentage of Al_T present as Al_{Mono} is shown in parenthesis and the final pH of the equilibration is also shown. LSD ($P \geq 0.05$) is shown for Al_T and Al_{Mono}

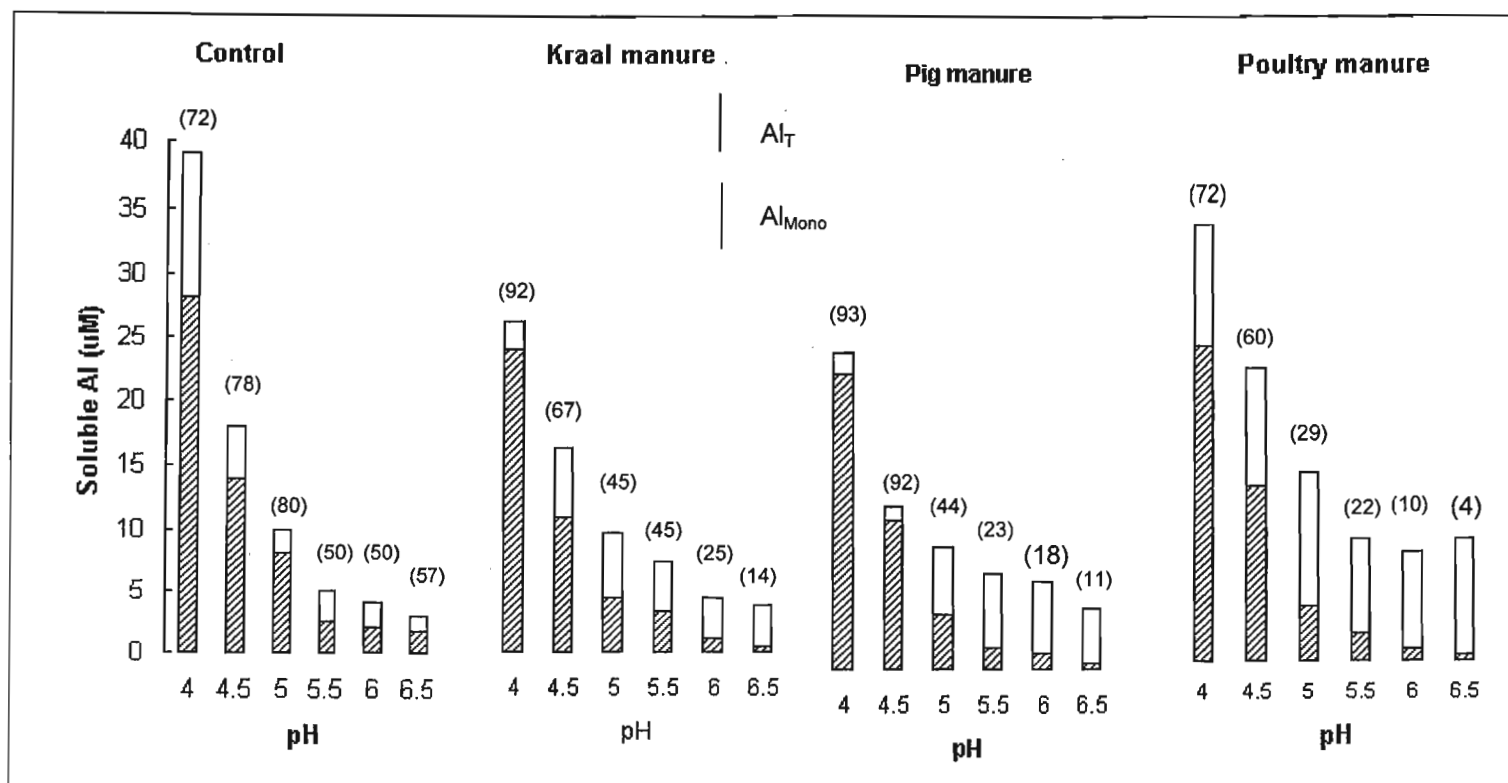


FIGURE 5.2 Changes in Al_T (height of histogram) and Al_{Mono} (shaded area) following equilibration of 10 g of an acid soil with 0.2 g animal manures in 0.01 M $CaCl_2$ for 3 days (experiment 2), LSD ($P \leq 5\%$) and percentage of Al_T present as Al_{Mono} shown

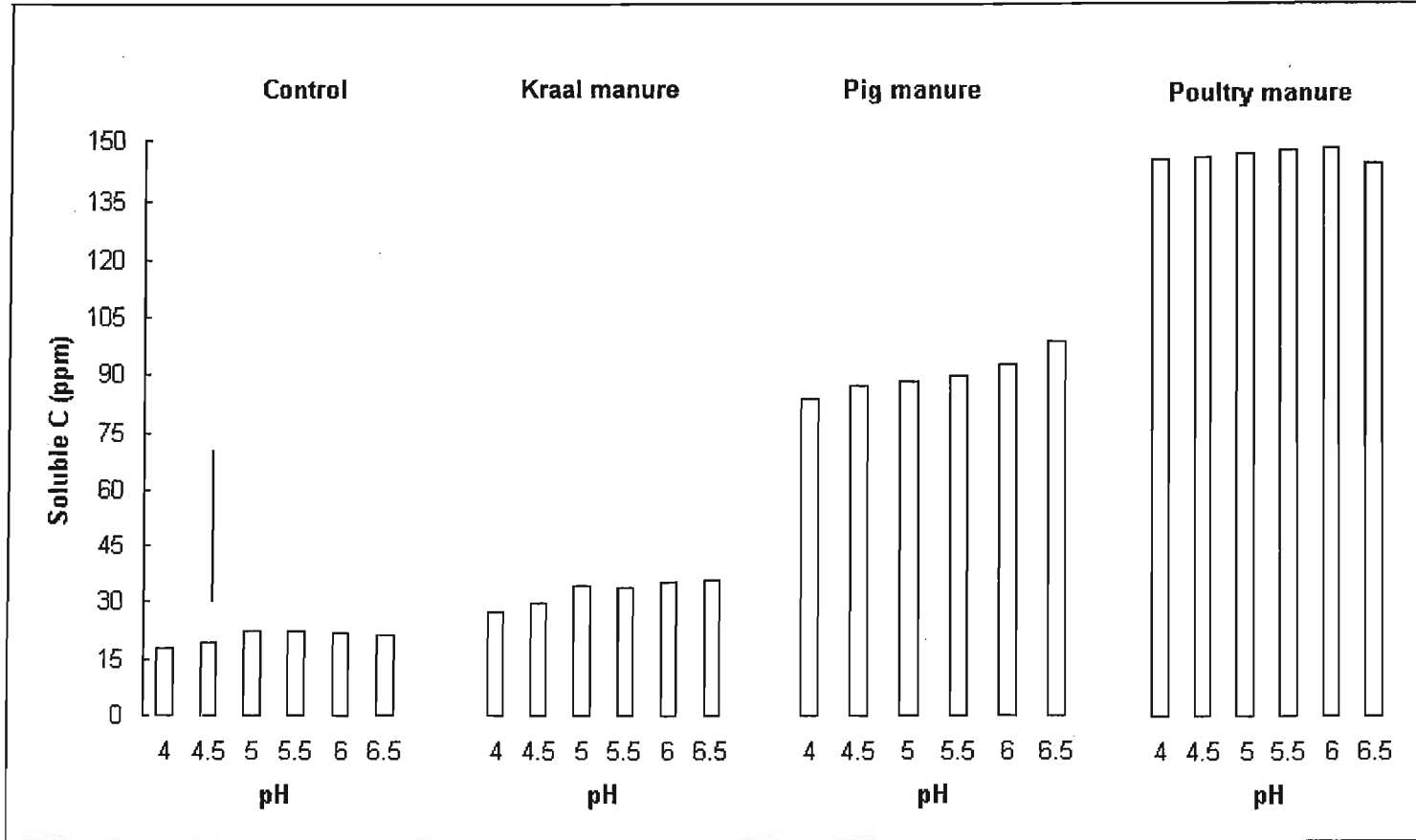


FIGURE 5.3 Soluble C concentrations measured after 3 days equilibration of 10 g of an acid soil with 0.2 g animal manures in 0.01 M CaCl₂ (experiment 2). LSD ($P \leq 5\%$) shown.

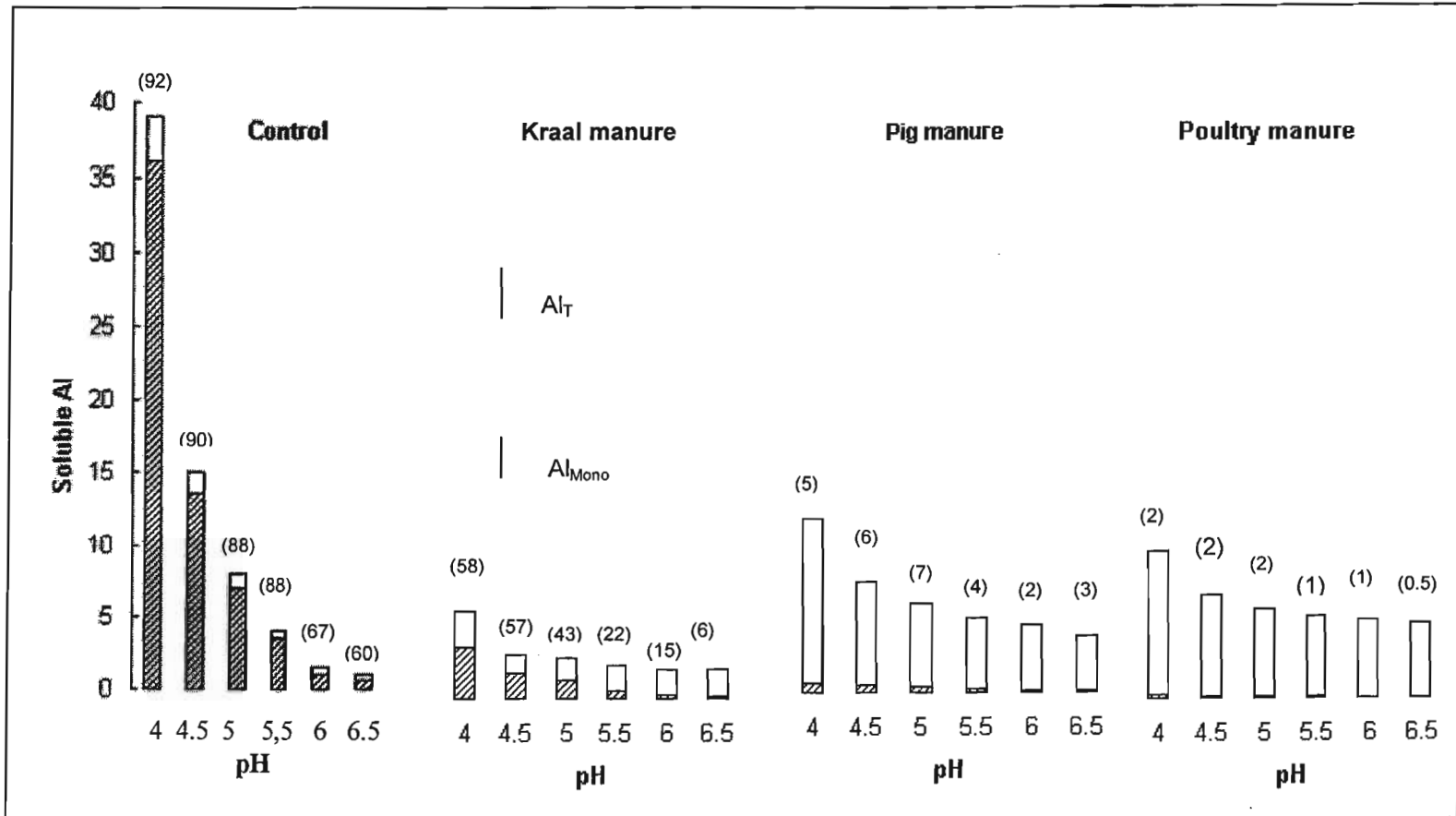


FIGURE 5.4 Changes in Al_T (height of histogram) and Al_{Mono} (shaded area) following equilibration of 0.2 g of animal manures with 25 ml of 40 µM AlCl₃ in 0.01 M CaCl₂ for 3 days (experiment 3). LSD ($P \leq 0.05$ and percentage of Al_T present as Al_{Mono}) shown. The soluble Al is expressed in µM.

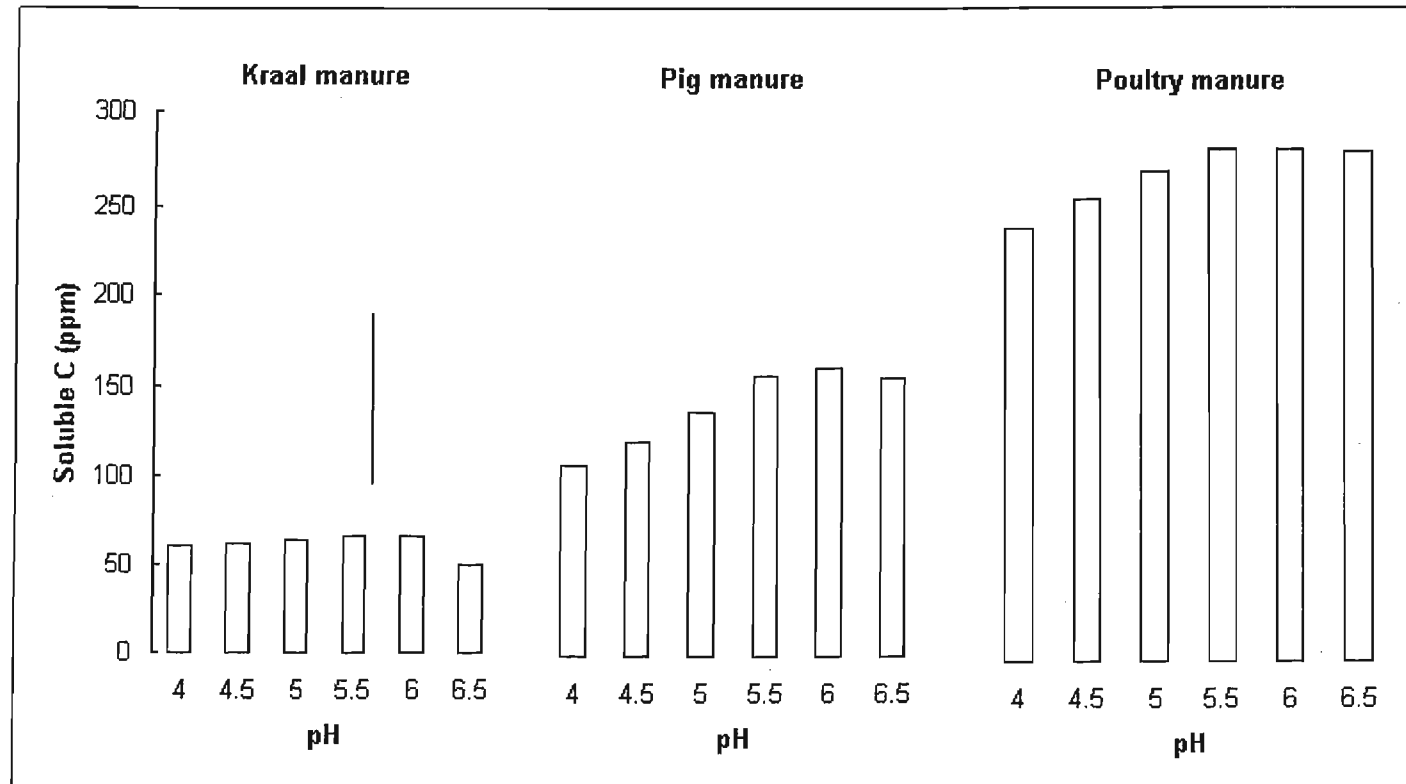


FIGURE 5.5 Soluble C concentrations measured after 3 days equilibration of 0.2 g of animal manures with 25 ml of 40 μM AlCl_3 in 0.01 M CaCl_2 (experiment 3). LSD ($P \leq 0.05$) shown.

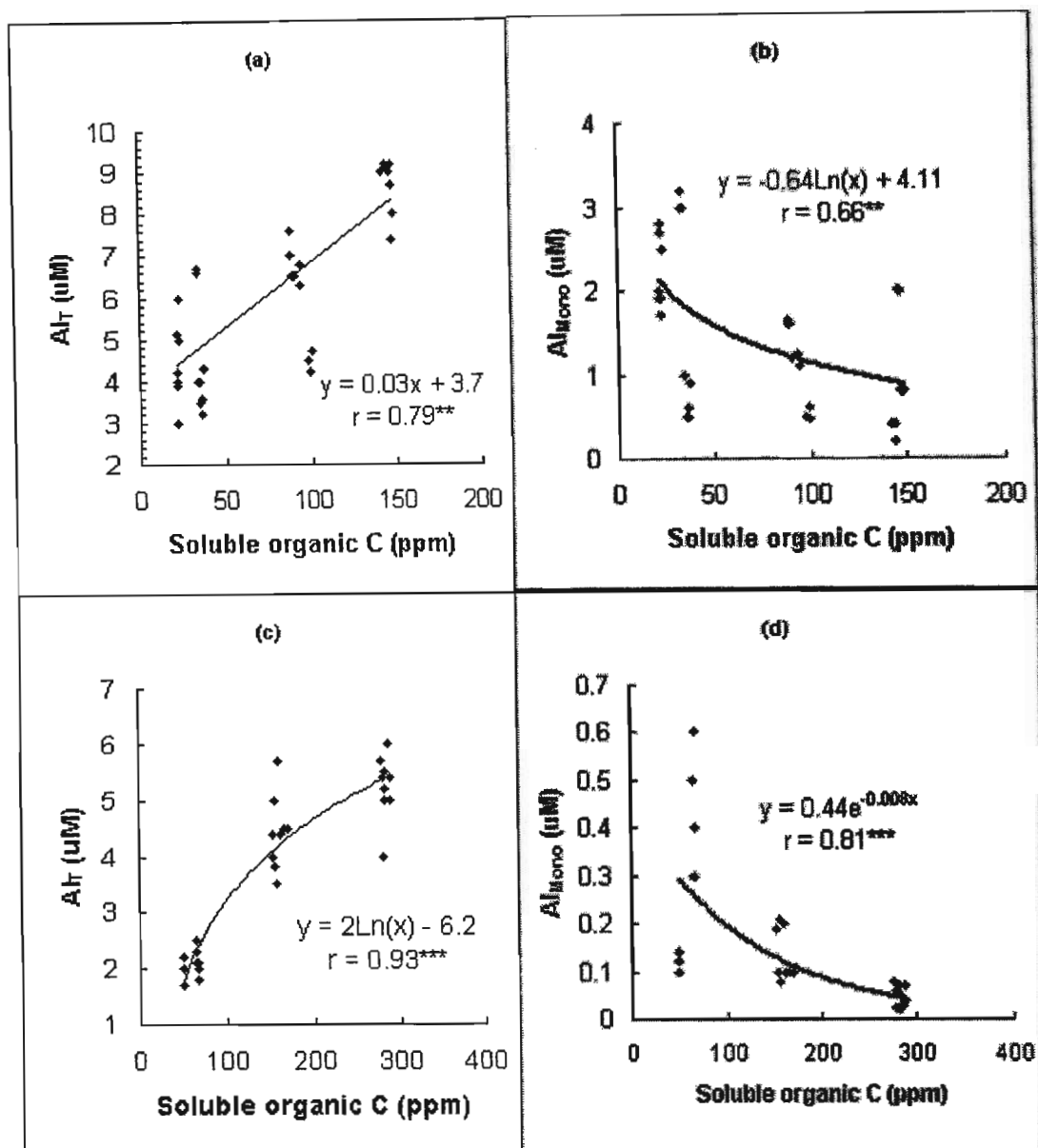


FIGURE 5.6

Relationship between Soluble organic C and Al_T and Al_{Mono} measured in soil samples equilibrated with animal manures [(a) and (b)] and Al_T and Al_{Mono} measured in samples where 40 μM AlCl₃ were equilibrated with animal manures [(c) and (d)] for high pH (5.5; 6; 6.5).

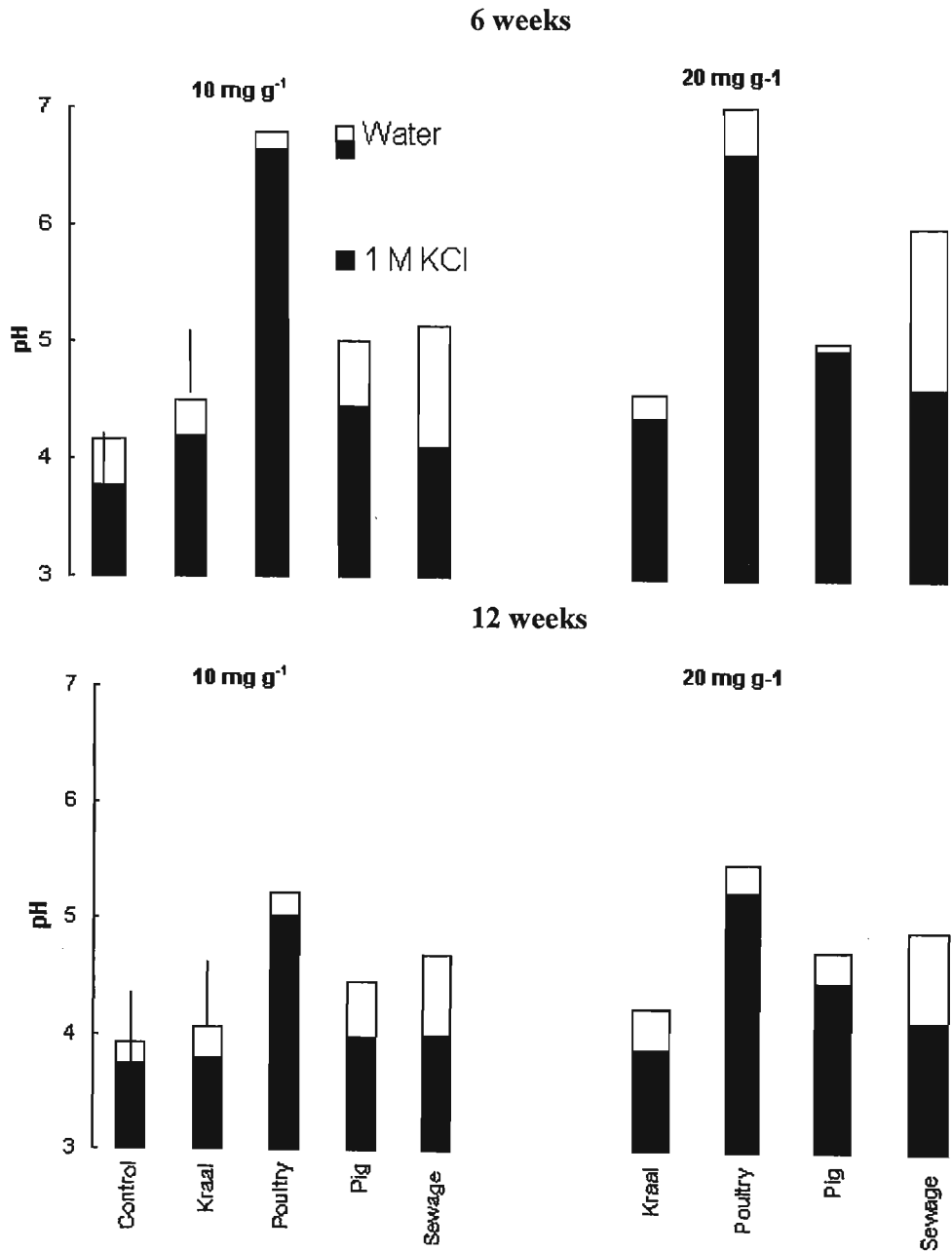


FIGURE 5.7 Changes in pH_{water} and pH_{KCl} following incubation of kraal manure (kraal), pig manure (Pig), layer poultry manure (Poultry), and sewage sludge (Sewage) with an acid soil at two rates (10 and 20 mg g^{-1}) for 6 and 12 weeks. LSD ($P \leq 0.05$) shown.

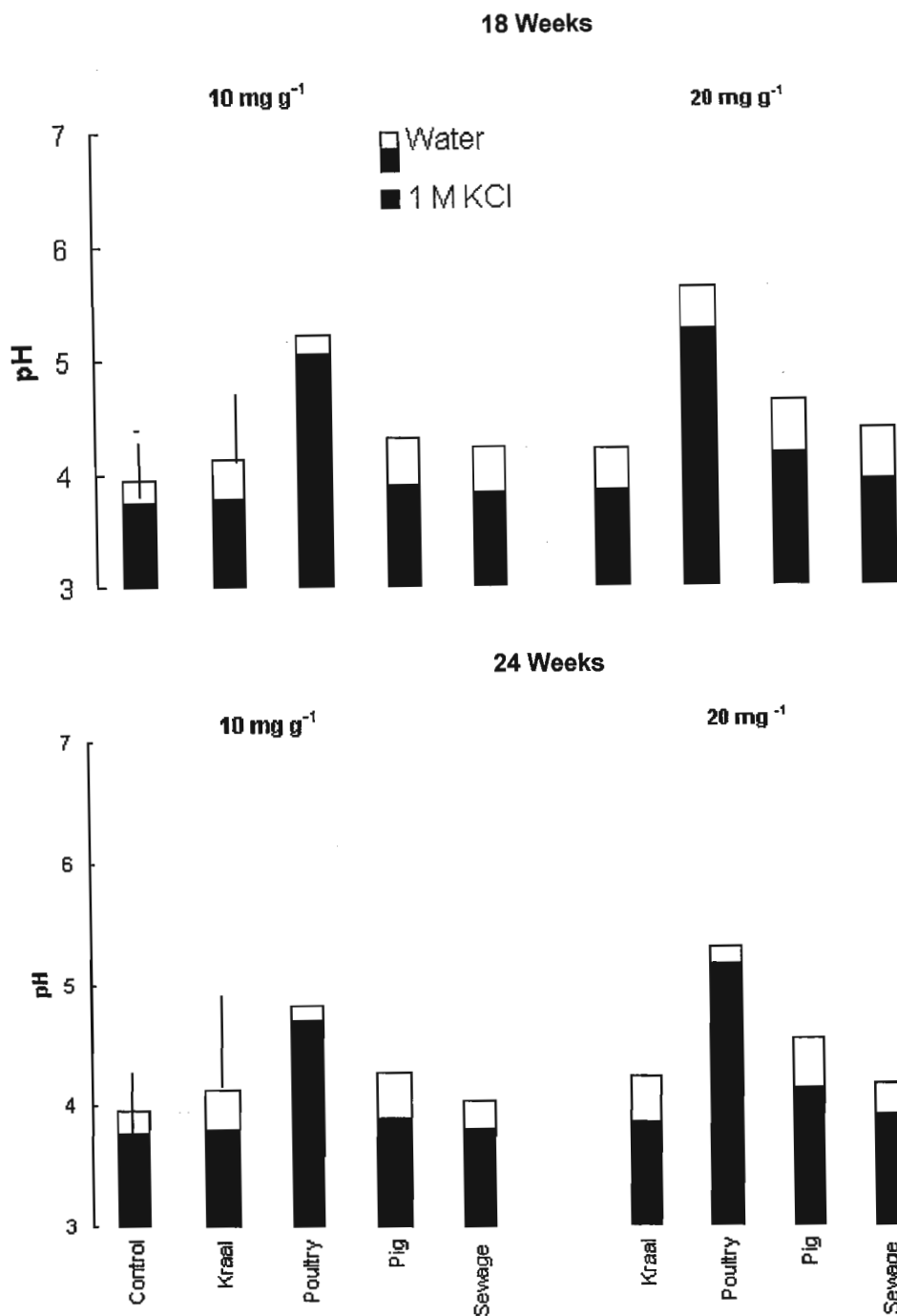


FIGURE 5.8 Changes in pH_{water} and pH_{KCl} following incubation of kraal manure (kraal), pig manure (Pig), layer poultry manure (Poultry), and sewage sludge (Sewage) with an acid soil at two rates (10 and 20 mg g^{-1}) for 18 and 24 weeks. LSD ($P \leq 0.05$) shown.

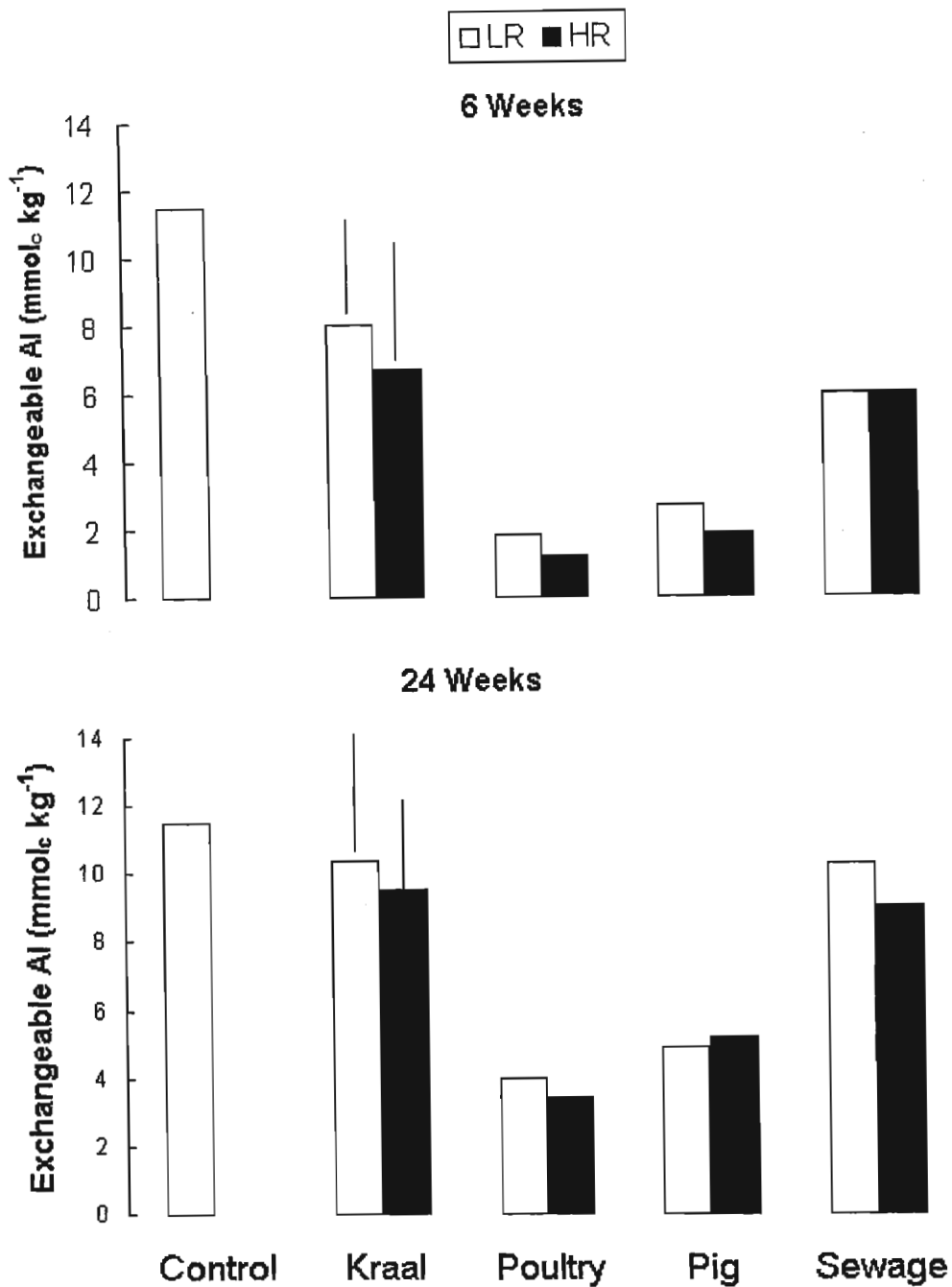
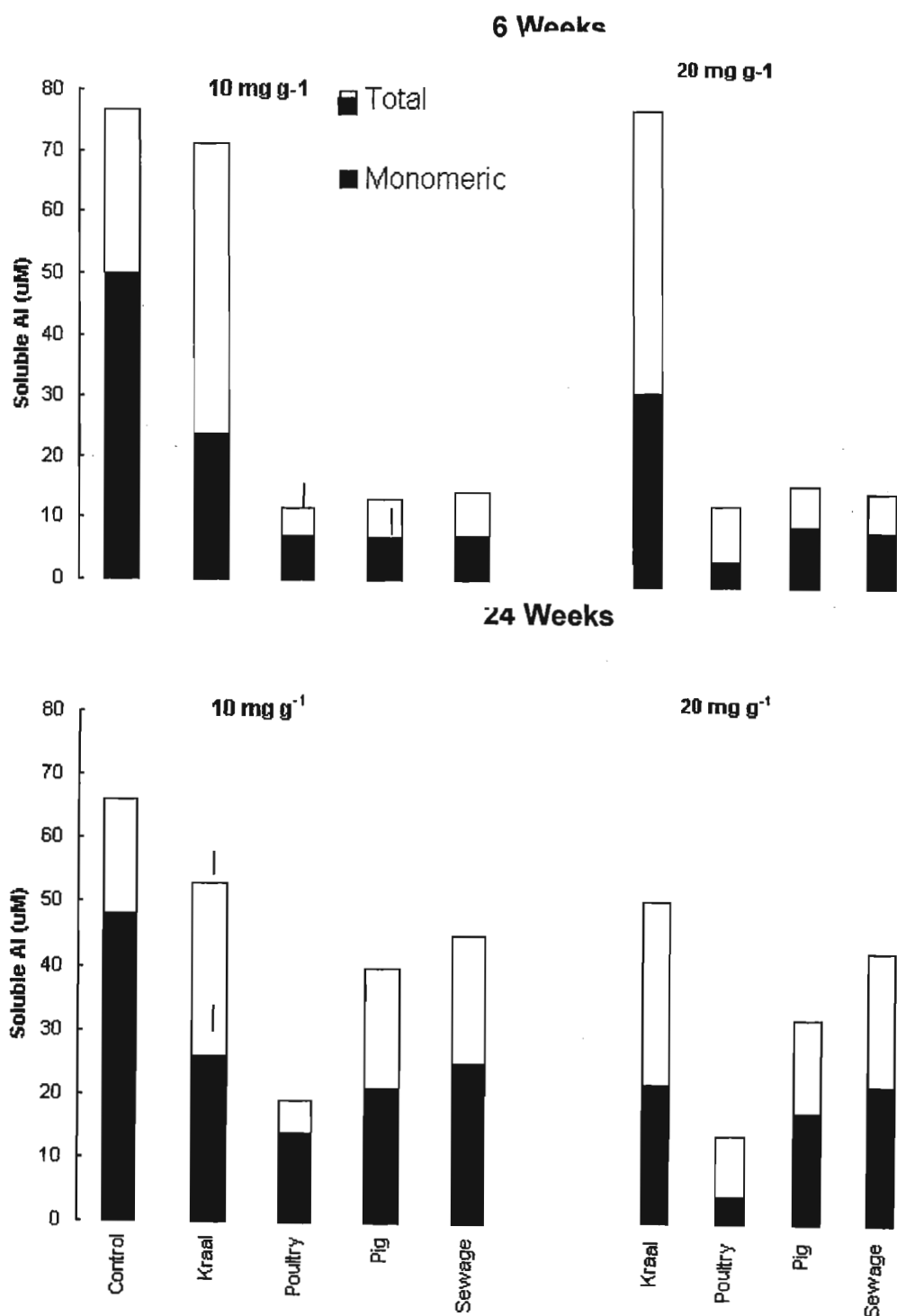


FIGURE 5.9 Changes in Exchangeable Al following incubation of kraal manure (kraal), pig manure (Pig), layer poultry manure (Poultry), and sewage sludge (Sewage) with an acid soil at two rates (LR =10 mg g⁻¹ and HR=20 mg g⁻¹) for 6 and 24 weeks. LSD ($P \leq 0.05$) shown.

**FIGURE 5.10**

Changes in soluble Al following incubation of kraal manure (Kraal), pig manure (Pig), layer poultry manure (Poultry), and sewage sludge (Sewage) with an acid soil at two rates (10 and 20 mg g⁻¹) for 6 and 24 weeks. LSD (P < 0.05) shown.

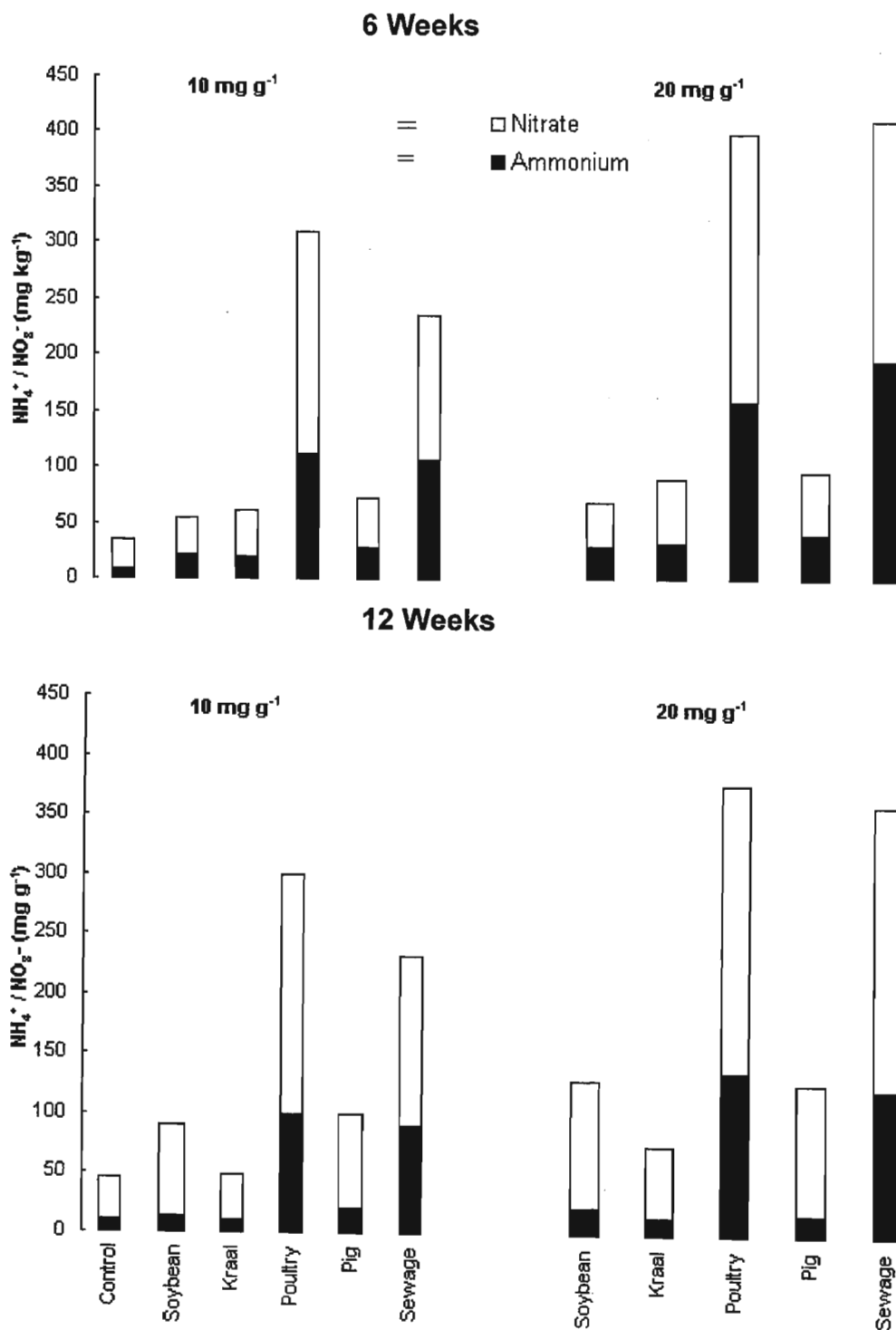


FIGURE 5.11 Changes in NH_4^+ , NO_3^- following incubation of kraal manure (Kraal), pig manure (Pig), layer poultry manure (Poultry), soybean residues (Soybean) and sewage sludge (Sewage) with an acid soil at two rates (10 and 20 mg g^{-1}) for 6 and 12 weeks. LSD ($P \leq 0.05$) shown.

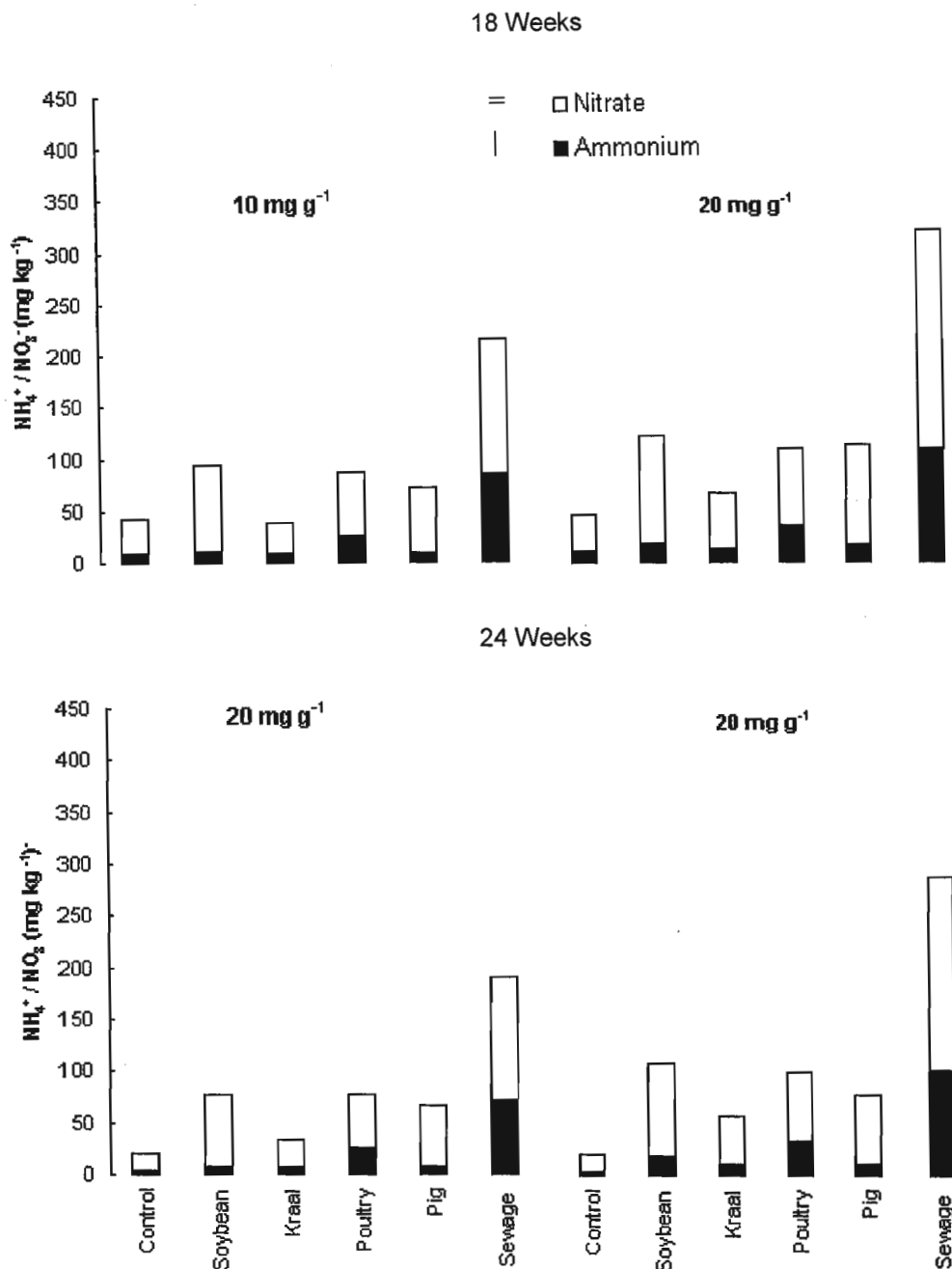


FIGURE 5.12 Changes in NH₄⁺, NO₃⁻ following incubation of kraal manure, pig manure, poultry manure, soybean residues and sewage sludge with an acid soil at two rates (10 and 20 mg g⁻¹) for 18 and 24 weeks. LSD (P < 0.05) shown.

5.4 Discussion

In order to understand the interrelations and interactions between the various chemical and biochemical mechanisms affecting the solubility of Al when organic amendments are added to an acid soil, the overall results of this study are discussed in three main sections. Firstly, the various mechanisms thought to have influenced the changes in soil pH are discussed, secondly, the role of pH as the main factor controlling Al solubility is outlined and lastly, the role played by the complexation of Al by organic matter is considered.

5.4.1 Changes in soil pH.

Mechanisms affecting the increase in pH.

The increases in pH observed in experiment 1 (FIGURE 5.1), are mainly attributable to immediate chemical reactions, since the extent of microbiological decomposition of manures was small after only 3 days equilibration. The chemical reactions likely to be involved include: (i) the proton consumption by added organic acid anions and humic-like materials (Ritchie and Dolling, 1985; Wong *et al.*, 1998; Tang *et al.*, 1999), (ii) the dissolution of CaCO_3 releasing CO_3^{2-} anions which consume protons and (iii) the specific adsorption of organic acid anions and/or humic materials onto Al-Fe hydrous oxides with a consequent release of OH^- (Hue *et al.*, 1986; Iyamuremye and Dick, 1996).

Haynes and Mokolobate (2001) suggested that association of protons from the soil with some of the organic acid anions (e.g. simple aliphatic organic acid anions and humic substances) occurs if the pH is less than the dissociation constant (pKa) for the weak organic acid from the added residue. Elsewhere, the same authors observed that this was a major mechanism involved in the increase in soil pH when relatively stable composted wastes are added to an acid soil. The measurement of the proton

consumption capacity (Wong *et al.*, 1998) provided an index for the immediate capability of the organic material to consume protons from the surrounding soil. Indeed, results from CHAPTER 3 showed that pig- and layer poultry manures have relatively high proton consumption capacities.

Nevertheless, the relatively high CaCO_3 content of layer poultry manure and to a lesser extent pig manure (CHAPTER 3) (originating from limestone added to their feed) is likely to have been a major factor leading to their ability to raise soil pH in both the short and long-terms (Robinson, 1961; Sims and Wolf, 1999; Mokolobate and Haynes, 2002 a).

Ligands exchange between hydroxyl groups on the surfaces of Al and Fe hydrous oxides and low molecular weight organic acids and/or humic substances are another possible mechanism, which could have raised the pH (Hue *et al.*, 1986; Iyamuremye and Dick, 1996). Such a mechanism is suspected to be of minor importance because ligand exchange reactions are only likely to cause small increases in soil pH (e.g. 0.1 to .2 unit) (McCray and Sumner, 1990). In addition, the concentration of these organic acid anions and humic materials in soluble form is not likely to be high in the short-term but will increase during the decomposition of organic residues.

For the long-term incubation experiment, the general increase in soil pH after 6 weeks incubation with the five organic residues was probably attributable to both short-term chemical reactions and reactions occurring during the decomposition of the added residues. In this connection, Tang *et al.*, (1999) and Yan *et al.*, (1996) observed that there appear to be two mechanisms operative in the organic acid anion-induced increase in soil pH; an immediate chemical reaction followed by a more marked increase associated with the decomposition process. It was, however, evident that for the five amendments tested, the rise in pH occurred during the initial 6 weeks period, after which soil pH began to decline.

The effect of soybean residues in increasing the soil pH is likely to have been related to the release of organic acid anions contained in the residue

and the microbial synthesis of new organic acid anions during residue decomposition. Many other investigations have shown that the decarboxylation of organic acid anions is responsible for most rises in pH when plant residues decompose in soils (Barekzai and Mengel, 1993; Mengel, 1994, Tang *et al.*, 1999 and Yan *et al.*, 1996). Other investigators demonstrated that addition of calcium oxalate and calcium gluconate to soils had identical effects on final pH as addition of CaCO_3 where added in equimolar rates of Ca (Pocknee and Sumner, 1997). Because of the narrow C/N ratio of soybean residues, decomposition occurs rapidly and as a result the rise in soil pH occurred during the first 6 weeks of incubation.

The decarboxylation of organic acid anions may have also played a role in increasing the soil pH when animal manures (Pig and layer poultry manure) were added to soil. The period of incubation would also have allowed time for dissolution of CaCO_3 present in the animal manures. This is also likely to have contributed to the increase in pH after 6 weeks incubation.

Ammonification of organic N contained in organic residues is also considered as a relatively important factor involved in the increase in soil pH (Hoyt, 1975; Pocknee and Sumner, 1997). Some of the organic residues used in this study such as soybean, layer poultry manure and sewage sludge had a relatively high organic N content. The oxidation of organic N results in a production of NH_4^+ and OH^- (responsible of pH increase). This is however counteracted by the production of 2 H^+ per mole of NH_4^+ nitrified to NO_3^- . Thus, if nitrification is temporarily inhibited then the pH will tend to rise, while when nitrification proceeds rapidly the pH will decline.

The only treatments where substantial amount of NH_4^+ accumulated in the soil were sewage sludge and poultry manure and ammonification early in the incubation may well have contributed to the rise in pH measured after 6 weeks incubation. The effect of soybean (leaves) in increasing soil pH, was also observed by Pocknee and Sumner (1997). They reported that the addition of soybean leaves to an acid soil was related to both basic cation content (reflecting the amount of organic acid anions containing in the

residue) and N content (reflecting the effect of ammonification). In this study, however, there was no substantial accumulation of NH_4^+ in the soybean treatment.

It has also been suggested that during decomposition, anaerobic conditions could develop thus promoting reduction reactions which result in a rise in pH (Hue and Amien, 1989; Hue, 1992). However, anaerobic conditions did not predominate during the incubation, so it is not likely to have been an important mechanism.

Throughout the long-term incubation pH_{KCl} values were almost as high as those for pH_{water} in the poultry manure treatment. Poultry manure has a large content of base cations and its application can induce salinity (Sims and Wolf, 1994; Mokolobate and Haynes, 2002a). The high salt content tends to depress pH_{water} values through displacement of exchangeable Al^{3+} and H^+ back into solution. As a result pH_{water} values are close to those measured in KCl.

Mechanisms affecting the decrease in pH

The general decrease in pH observed in the long-term incubation experiment could be caused by various mechanisms including; (i) the nitrification of NH_4^+ (Hoyt and Turner, 1975; Haynes and Swift, 1993; Yan *et al.*, 1996), (ii) the microbial decomposition of Al-organic acid anion complexes (Ritchie, 1994; Wong *et al.*, 1995) and (iii) the increase in exchangeable H^+ and Al^{3+} induced by an increase in cation exchange capacity (Donald and Williams, 1954; William and Donald, 1957; Brenes and Pearson, 1973; Manson and Fey, 1989; Mokolobate and Haynes, 2002a).

The substantial increase in NO_3^- concentration after 12 weeks incubation for all the treatments reflects the fact that considerable nitrification occurred in the period between 6 weeks and 12 weeks. Concomitant with the accumulation of NO_3^- was a decrease in soil pH. This strongly suggests that

production of H^+ ions during nitrification was a major contributor to the decline in pH.

Largest amounts of NO_3^- were produced in sewage sludge and poultry manure treatments yet the final pH attained for poultry manure was, in fact, highest for all treatments. This is attributable to the large amount of $CaCO_3$ present in layer poultry manure, which maintained a higher final pH than the other treatments.

It was also possible that, Al and protons complexed by some organic acid anions during the early chemical reactions are released following decomposition of the complexing organic acid anions. This could have also contributed to decrease the pH. In relation to that, it has been shown that the organic acid anions (involved in complexing protons and Al^{3+}) may be present in soil solution at high concentrations for relatively short periods of time since they are highly susceptible to microbial degradation (Ritchie, 1994; Wong *et al.*, 1995; Porter *et al.*, 1980; Helyar, 1976).

The release of basic cations contained in the organic amendments could be another factor contributing to decrease the soil pH in the long-term incubation experiment. The release of cations in the soil system tends to increase the competition of cations for the cation exchange sites. This may result in displacement of some H^+ ions from the exchange sites and increase the concentration of H^+ in soil solution (Mokolobate and Haynes, 2002a). Bloom *et al.*, (1979), for example, showed that exchangeable cations were involved in controlling H^+ and Al^{3+} exchange on organic matter. Similarly, Manson and Fey (1989) observed that addition of Na, K, Ca and Mg at increasing ionic strengths resulted in a lower solution pH and a higher Al solubility. However trends in pH measured in water and 1 M KCl (which would have negated any such soluble salt effect) were similar suggesting that such an effect was of little importance in the present study.

In long-term field experiments where there has been an appreciable increase in soil organic matter content, it has been observed that a corresponding

increase in cation exchange capacity is correlated with a decrease in soil pH and an increase in exchangeable H^+ and Al^{3+} (Donald and Williams, 1954; Williams and Donald, 1957). Such an effect occurs because the cation exchange capacity increases due to an accumulation of humic materials while balancing exchangeable cations (e.g. Ca^{2+} , Mg^{2+} and K^+) are leached predominantly with NO_3^- . In this study, leaching was precluded so such an effect is unlikely. However such an effect could well occur when organic amendments are applied repeatedly under field conditions.

5.4.2 *The role of pH in controlling Al solubility.*

The dominant effect of pH in controlling Al solubility (Lindsay, 1979) is well documented. When kraal, pig and layer poultry manures were equilibrated with an acid soil (FIGURE 5.1), the general decrease in Al_{Mono} was related to a concomitant increase in pH. Similarly, the equilibration experiment 2 (FIGURE 5.2) showed that the decrease in concentrations of Al_{Mono} was closely related to the increase in soil pH. Indeed, research by many workers including Noble *et al.* (1996) and Pocknee and Sumner (1997) demonstrated that exchangeable and soluble Al precipitate as insoluble hydroxy-Al following an increase in pH. Although the concentration of Al_{Mono} in experiment 3 (FIGURE 5.4) was generally low for the samples amended with animal manures, a negative correlation between pH and Al_{Mono} concentrations was still observed.

The increase in pH had also played an important role in decreasing the solubility of Al in the long-term experiment after 6 weeks of incubation. The soil pH measured was found to be strongly, negatively correlated to exchangeable Al, Al_T and Al_{Mono} (CHAPTER 3). The general increase in Al solubility concomitant to a general decrease in soil pH observed in the long-term incubation experiment was another indication that soil pH was a major factor controlling the solubility of Al.

5.4.3 *The effect of Al-organic matter complexes on Al solubility.*

In the two short-term equilibration experiments, concentrations of Al_T and Al_{Mono} could only be partially explained by the changes in pH. For instance, no significant relationship was recorded between pH and Al_T concentrations in either equilibration experiment. This indicates that other mechanisms such as complexation of exchangeable and soluble Al by the solid and solution phases of organic matter were involved in controlling the solubility of Al. In this connection, many workers (Bloom *et al.*, 1979; Haynes, 1984; Stevenson and Vance, 1989; Sinesi and Brunetti, 1996; Mokolobate and Haynes, 2002b) have observed that organic matter is strongly involved in controlling Al solubility in acid soils through complexation reactions.

In general, the effect of addition of organic manures on Al solubility in equilibrium with $AlCl_3$ or soil differed in the lower pH range (pH 4-5) to that in the higher range (pH 5-6.5). That is in the lower pH range addition of manures tended to reduce Al solubility (both Al_T and Al_{Mono} concentrations) but in the higher range concentrations of Al_T were elevated while those of Al_{Mono} were depressed. This can be explained in terms of the strong complexing ability of organic matter for Al (Stevenson and Vance, 1989). Complexation of Al by organic matter occurs in both the solid and solution phases (Haynes and Mokolobate, 2001). However, the relative importance of these reactions to Al solubility may well differ at the lower and higher pH ranges because the solubility of Al changes greatly with increasing pH. At lower pH where Al is highly soluble, complexation by added solid phase manure-organic matter results in a reduction in Al solubility. However, at higher pH, where Al solubility is limited, the most important mechanism is complexation of Al by soluble organic matter and this increases Al solubility.

The reduction in Al solubility at low pH was very much more marked for the equilibration with $AlCl_3$ compared with that with soil (FIGURES 5.2 and 5.4). This is attributable to the large buffering reserve of Al that is present in acid soils. The buffering reserve includes (1) positively charged hydroxy-Al polymers of various sizes and degrees of hydration, (2) interlayer hydroxy-Al

in vermiculite and montmorillonite, (3) Al^{3+} and hydroxy-Al in forms complexed to soil organic matter (McLean, 1976;). At low pH, these potentially reactive forms of Al can be solubilized as Al is removed from solution by complexation to solid phase manure-organic matter. The concentration of dissolved organic carbon generally increases with pH which could also be related to the increase in the amount of soluble Al with pH.

In the soil equilibration experiment (experiment 2), in the higher pH range, there was a tendency with increasing pH for Al_T to be above that of control and for Al_{Mono} to be below that of control (FIGURE 5.2). This trend followed the order: poultry manure > pig manure > kraal manure; the same order that concentrations of soluble C in solution followed. Similarly, in the equilibration using AlCl_3 , with increasing pH (i.e. above pH 5.5) Al_T concentrations in manure treatments were above those of control (FIGURE 5.4). This effect was notably greater for pig and poultry than kraal manure and the former two treatments also maintained notably greater soluble C concentrations and exceptionally low Al_{Mono} concentrations.

Such results reflect the fact that a large concentration of soluble C in solution can maintain relatively high concentrations of complexed Al in solution but at the same time, maintain very low concentrations of Al_{Mono} . Thus in this study at pH values above 5.5, there was a positive correlation between Al_T and soluble C, but a negative correlation between Al_{Mono} and soluble C (FIGURE 5.6). When organic residues are added to soils, organic matter in soil solution, including simple aliphatic organic acid anions, phenols and humic molecules, is able to complex with Al_{Mono} in solution (Slattery and Morison, 1995; Wong *et al.*, 1995; Mokolobate and Haynes, 2002b). Whilst concentrations of Al_{Mono} are greatly reduced, concentrations of Al_T in solution can remain unaffected or even increased (Berek *et al.*, 1995; Slattery and Morison, 1995; Mokolobate and Haynes, 2002b). Slattery and Morison (1995), for example, found that additions of crop stubble to an acid soil tended to increase Al_T but markedly reduced Al_{Mono} .

In the long-term incubation experiment, addition of organic residues generally reduced the proportion of Al_T present as Al_{Mono} suggesting that complexation of Al_{Mono} in solution by soluble organic matter originating from the manures was influencing Al solubility. The addition of kraal manure generally resulted in the lowest proportion of Al_T present as Al_{Mono} . Between 6 weeks and 24 weeks incubation, there was a decrease in pH and increase in exchangeable Al in the kraal manure treatments yet Al_T values declined over that period. This may have been due to microbial decomposition of soluble organic matter over time, thus inducing a decrease in Al_T in solution

Soils amended with poultry manure at the low rate had the greatest proportion of Al_T present as Al_{Mono} whilst those amended with the high rate had the lowest proportion. The high proportion of Al_{Mono} present may reflect a salt effect (originating from the high cation content of poultry manure) displacing exchangeable Al^{3+} into solution. At the higher rate, however, the high pH (highest of all the treatments) presumably greatly limited Al solubility thus reducing the proportion of Al_{Mono} present. Indeed, exchangeable Al concentrations were lowest of all the treatments at the higher rate of addition of poultry manure.

5.5 Conclusions.

From the results of short and long-term experiments carried out in this chapter, a number of conclusions can be drawn:

- a) The increase in soil pH in the first few days after addition of organic materials can be ascribed to a combination of chemical reactions including proton consumption by simple organic acid anions and humic-like materials and dissolution of $CaCO_3$ present in manures.
- b) The solubility of Al in acid soils amended with organic materials is largely dependant on soil pH.

- c) The formation of organic matter complexes in both the solid and solution phases can modify this pH-dependant solubility compared to unamended soils.
- d) At low pH values (< 5), the formation of solid phase complexes tends to lower Al_T concentrations whilst at higher pH values (> 5), formation of soluble Al-organic matter complexes tends to raise Al_T concentrations. Nevertheless, Al_{Mono} concentrations are greatly reduced over the whole pH range because Al_{Mono} complexes with soluble organic matter.
- e) In the longer-term, the effect of organic materials in raising soil pH and reduce Al solubility is partly transient. The effect generally tends to decline after 6 weeks incubation.
- f) The decrease in pH in longer-term incubations (e.g. 6-24 weeks) is strongly related to nitrification of NH_4^+ originating from ammonification of organic N added in the organic materials.

It seems that addition of organic residues to acid soils can cause an increase in pH and decrease in Al solubility at least in the short-term. This potentially provides a window of opportunity for establishment and early growth of acid-intolerant crops in acid soils. The residues could be added in the band down a plant row in the volume of soil most exploited by crop roots. The addition of such residues to soils will not only modify soil pH and Al solubility but also greatly influence soil biochemical and microbial activity. This aspect will be investigated in the following cha

CHAPTER SIX

6 Effects of addition of kraal manure, grass residues, lime and fertilizer to an acid soil on soil pH, Al solubility, maize response, microbiological and biochemical indices in field conditions.

6.1 Introduction.

As already shown by many researchers (Chapter two) and the results in the previous chapters, the application of organic amendments can ameliorate soil acidity. In addition, the application of such materials increases soil nutrients status and the size and activity of the soil microbial community (Doran, 1987) as well as improve soil physical conditions (Martens et al. 1992; Pascual et al. 1997). Thus, their application can concurrently change soil chemical, biochemical and physical properties.

The effects of organic amendments in stimulating soil microbial activity do not necessarily occur only through the addition of C substrate. For example, the increase in pH, which occurs during their decomposition, could also help in stimulating microbial activity (Hue *et al.*, 2001). Furthermore; the increase in pH is, to a large extent mediated by the microbial decomposition of the organic residues. Thus, the effects of organic amendments in increasing soil pH and stimulating microbial activity are likely to be interrelated and interdependent.

Indeed, the increase in soil pH following addition of organic materials has been principally attributed to the microbial decomposition of the materials themselves (Tang *et al.*, 1999 and Yan *et al.*, 1996). The decarboxylation of organic acid anions released or synthesized by microorganisms during the microbial decomposition of plant residues has been shown to be the major factor influencing the rise in pH (Barekzai and Mengel, 1993; Mengel, 1994, Tang *et al.*, 1999 and Yan *et al.*, 1996). When animal manures are added to an acid soil, the concentrations of organic acid anions and humic substances

in soil solution will increase with time, as the manures are microbially decomposed. These organic substances are involved in various reactions leading to the increase in soil pH. Such reactions include complexation of protons (Ritchie and Dolling, 1985; Wong et al., 1998; Tang *et al.*, 1999), adsorption onto Al-Fe hydrous-oxides (Hue *et al.*, 1986; Iyamuremye and Dick, 1996) and ligand exchange (Hue *et al.*, 1986; Iyamuremye and Dick, 1996).

In addition, soil pH exerts an important influence on the incorporation of organic matter into the microbial biomass, and can be as an important factor as soil C and N (Wardle, 1992). Acidification of a soil often results in a reduction in the microbial biomass values (Wardle, 1992). Many investigations have confirmed the important role played by soil pH in controlling biochemical and microbial activities. Adams and Adams (1983); Badalucco *et al.* (1992) and Neale *et al.* (1997) all found a marked increase in the size of microbial biomass following liming.

Long-term addition of fertilizers to soils have generally been shown to increase microbial biomass since there is an increase in yields and therefore in plant residues returned to the soil (Roper and Gupta, 1995). However, in some cases fertilizer applications have resulted in a decline in microbial biomass and this has generally been related to fertilizer N-induced acidification (Roper and Gupta, 1995). Soil bacteria are very sensitive to pH levels below pH 4.5 and some grow poorly in acid soils (<http://www.agric.nsw.gov.au/reader/soil-sense/ss392-soil-ph.htm> - 11k). In general fungi are more tolerant and soil acidification can cause an increase in fungal:bacterial ratio (<http://www.agric.nsw.gov.au/reader/soil-sense/ss392-soil-ph.htm> - 11k).

The effect of pH on enzyme-catalyzed reactions is even greater than temperature (Tabatabai, 1994), since changes in H^+ concentrations influence enzymes, substrates and cofactors by altering their ionisation and solubility (Tabatabai, 1994). Characteristically, each enzyme has a pH value at which the catalysed reaction rate is optimal. Enzymes can be irreversibly denatured with extremes in acidity and alkalinity (Tabatabai, 1994). Extreme changes in pH may irreversibly inactivate enzymes that play an essential role in nutrient cycling and humus formation (Tabatabai, 1994). Thus studies have revealed that different mechanisms are operative in raising pH when different organic amendments are added to soils. In addition complexing of phytotoxic monomeric Al in solution can be another important factor. It was also shown (CHAPTER FOUR) that the addition of kraal manure to soils under field conditions resulted in a substantial increase in pH and reduction in Al solubility. The aim of this study was to compare the effects of additions of kraal manure, grass residues and lime, under field conditions, on soil pH, Al solubility and crop response and, at the same time follow concomitant changes in the size and activity of the soil microbial biomass.

6.2 Materials and Methods.

6.2.1 Site and experimental design

A field experiment was carried out in a small scale farming area at Odogwini (EMBO Traditional Authority) on the KwaZulu-Natal south coast. The mean annual rainfall is 939 mm and mean monthly temperatures range from a maximum of 22 °C in January to a minimum of 16 °C in June. The soil was classified as Inanda form, Glenariff family (Soil Classification Working Group, 1991) or a Humic ferralsol (FAO). The soil had the following properties: organic C = 40 g kg⁻¹, pH_{water} = 5.0, AMBIC P, Mn and Zn = 3, 6 and 3 mg kg⁻¹ respectively, exchangeable Ca, Mg, K and Al = 28, 12.8, 2.7, and 33 mmol_c kg⁻¹. Six months prior to the experiment the site had been cropped with maize.

The kraal manure used as amendment was collected from a kraal-situated close by. It had a total element content of organic C = 273 g kg⁻¹, N = 14 g kg⁻¹, S = 2.5 g kg⁻¹, P = 1.4 g kg⁻¹, Ca = 8 g kg⁻¹, Mg = 5 g kg⁻¹, and Na = 0.8 g kg⁻¹ and Zn = 91 mg kg⁻¹, Cu = 21 mg kg⁻¹, Mn = 537 mg kg⁻¹ and Fe = 18266 mg kg⁻¹ respectively. It had a pH_{water} of 8, and a CaCO₃ content of 1.7 %. Grass residues were also used as an organic amendment. They were collected from Ukulinga farm (University of Kwazulu-Natal) and they contained 4.15, 8, 1.5 and 1.0 g kg⁻¹ of C, N, S and P respectively and Zn = 21 mg kg⁻¹, Cu = 3.2 mg kg⁻¹, Mn = 377 mg kg⁻¹ and Fe = 218 mg kg⁻¹. Their basic cation content were 3.8, 1.3, 5.4 and 1.2 g kg⁻¹ of Ca, Mg, K and Na respectively.

Maize (PAN 6710 cultivar) was planted in rows 50 cm apart with an inter row spacing of 40 cm. Plots were 4 m long and 2 m wide and each plot was separated from adjoining ones by 1 m distance. The experiment was a split plot design with three replicates per treatment. The experiment consisted of 3 rates of kraal manure [0 (Control), 10 (Kraal 1), and 20 t ha⁻¹ (Kraal 2)], 3 rates of grass residues [0 (Control), 10 (Grass 1), and 20 t ha⁻¹ (Grass 2)]. Half of the experimental plots were fertilized and the others were not and fertilizer rates for maize were recommended by the KwaZulu-Natal Department of Agriculture Fertilizer Advisory service, based on soil test results. They were 75 kg N ha⁻¹, 112 kg P ha⁻¹ and 75 K kg ha⁻¹. The lime rate [Lime 2 = 5.0 t ha⁻¹ of dolomitic lime (15 % Ca, 15 % Mg) was also recommended by the above Department and a lower rate (Lime 1 = 2.5 t ha⁻¹) was also used as this was considered affordable for small scale farmers. Kraal manure, grass residues, lime and fertilizer were applied in a band 15 cm wide down the rows. The amendments were incorporated to a depth of 20 cm using a hand hoe. Seeds were then sown (plant population = 50 000 plants ha⁻¹) into the center of these bands.

Soil sampling was carried out 6 weeks following planting, at tasseling and harvest. Soil was randomly sampled in the plant row and inter-row to a depth of 20 cm. Four samples randomly collected from each plot were bulked. Forty-eight hours after sampling field moist samples were thoroughly mixed

and split into two sub-samples. One sub-sample was air-dried, sieved (< 2mm) for analysis of exchangeable Al, pH and nutrient status. The second one was wetted to 100 % water holding capacity and the soil solution was extracted 48 h later by centrifugation (Elkhatib *et al.*, 1987) for the measurement of total soluble Al and inorganic monomeric Al. At harvest, the samples were split into four and the third subsample was air-dried, ground and sieved (< 0.5 mm) for organic C analysis. The fourth was stored at 2°C for subsequent analysis of microbial biomass size and activities and enzyme activities. Samples were also collected at 20 cm depth from an undisturbed pasture situated close by the experimental site. Those samples were treated exactly like those from the experimental site.

6.2.2 Laboratory analysis

Soil acidity indices

Soil pH was measured in 1:2.5 soil : solution ratio (in both water and 1 M KCl) using a glass electrode. Exchangeable Al was extracted with 1 M KCl (1:20 soil: extractant ratio) and determined by the pyrocatechol violet (PCV) method (Mosquera and Mombiela, 1986). Total Al (Al_T) in soil solution was measured by a PCV method using $LaCl_3$ -Fe reagent after passing the solution through a 0.22 μm filter (Menzies *et al.*, 1992). Monomeric Al (Al_{Mono}) was measured in the filtrate (0.05 μm) by the PCV method of Kerven *et al.* (1989). It is accepted that the PCV method used here for measuring Al_{Mono} measures monomeric Al plus a small amount of Al present in soluble Al-organic matter complexes (Parfitt *et al.*, 1995).

Microbiological and biochemical indices

Organic C was measured by a dichromate wet oxidation method (Yeomans and Bremner, 1988). Microbial biomass C (C_{mic}) was measured using the method of Vance *et al.* (1987). The C_{mic} was calculated as the difference between the organic C extracted by with 0.05 M K_2SO_4 from chloroform-fumigated and unfumigated soil samples using a K_c factor of 0.38 (Brookes

et al., 1985). The microbial quotient (C_{mic}/C_{org}) ratio was calculated by expressing microbial biomass C as a percentage of total soil organic C.

Basal respiration was measured placing 50 ml beakers containing 30 g of soil (field-moist content) in an airtight sealed jar. The samples were incubated in the dark at room temperature for 10 days along with 10 ml of 0.5 M NaOH. The CO_2 -C evolved was determined by titration (Anderson, 1982). The metabolic quotient (g CO_2) was calculated by expressing basal respiration per unit of microbial biomass ($qCO_2 = CO_2-C/C_{mic}$). Arginine ammonification rate was determined as described by Franzluebbers *et al.* (1995). Prior to measurement, the samples were incubated for 3 hours at a temperature of 25°C.

The determination of enzyme activities was performed as follows: soil samples were incubated with appropriate substrate and suitable buffer solution and the assays of enzyme activities were based on the release and quantitative determination of the product in a reaction mixture. The activity of arylsulphatase, and acid and alkaline phosphomonoesterase were determined using the methods described by Tabatabai (1994) and casein hydrolysing protease was assayed using the method of Ladd and Butler (1972).

6.2.3 Data analysis

Statistical analyses of data were performed using the Genstat 5 computer package. The least significant differences (LSD) between treatments were determined at 5% by subjecting the data to Analysis of Variance (ANOVA). The relationships between soil pH, microbiological and biochemical indices were investigated by the determination of correlation coefficients using the above package.

6.3 Results

6.3.1 Nutrient status

The nutrient status of soil from the various treatments is shown in TABLE 6.1. The concentration of exchangeable Ca and Mg were significantly increased by the addition of kraal manure and (TABLE 6.1). AMBIC extractable P and exchangeable K and Zn were increased by the addition of fertilizer and kraal manure. In comparison with inter row and control samples, undisturbed samples had relatively high concentrations in exchangeable cations but had the lowest concentrations of AMBIC extractable P, Zn and Mn (TABLE 6.1).

6.3.2 Maize yields

The addition of all treatments tended to increase maize yields (FIGURE 6.1). In general, yields were greater at the high rate of addition of kraal manure, grass residues and lime. In the absence of fertilizer, yields for kraal manure were markedly greater than those for the grass residue and lime treatments. Addition of fertilizer increased yields greatly particularly in the control, grass residue and lime treatments. A combination of the recommended rate of lime and fertilizer (Lime 2 + F) gave the greatest yields but kraal 2 + F gave a statistically similar yield.

6.3.3 Soil acidity indices

Soil pH

Soil pH measured in the undisturbed site was greater than that of the control and inter-row samples of the experimental site (FIGURE 6.2). The soil pH in the unfertilized kraal manure treatments was greatly increased 6 weeks after planting. At that time, the highest pH_{water} and pH_{KCl} were recorded in the high

rate kraal manure. Values of pH in these manure treatments declined with time. By contrast there was a progressive increase in pH over time in the experimental grass residue and lime treatments. By harvest, the highest pH_{water} and pH_{KCl} values in unfertilized treatments were recorded in the lime 2 treatments.

At the first sampling (6 weeks after planting), addition of fertilizer lowered the measured pH_{water} in all treatments and it also lowered the pH_{KCl} in the kraal manure treatments. This fertilizer effect was less evident at tasselling and by harvest, there were no significant differences between the fertilized and unfertilized plots in terms of increasing pH. Because. The pH tended to increase over time in all the fertilized plots.

Exchangeable Al.

Concentrations of exchangeable Al in kraal manure treatments were greatly decreased 6 weeks after planting. Concentrations increased with time in these treatments. For the grass residues and lime treatments exchangeable Al levels decreased with time. At harvest, the lime treatments were most effective at depressing exchangeable Al concentrations.

At 6 weeks after planting and at tasselling, exchangeable Al concentrations were generally greater in the fertilized than in unfertilized treatments. By harvest, all treatments were effective in decreasing exchangeable Al concentration compared with unfertilized and fertilized control samples. At each sampling time, the high rate of addition of each amendment tended to have a greater effect in decreasing exchangeable Al concentrations. Due to the high pH, exchangeable Al concentrations were lower in the undisturbed than at the experimental sites (FIGURE 6.2 and 6.3).

Total soluble and monomeric Al

Changes in concentrations of total soluble and monomeric Al in soil solution are shown in FIGURE 6.4. Both fertilized and unfertilized kraal manure

treatments significantly decreased concentrations of soluble Al (Al_T and Al_{Mono}), 6 weeks after planting, at tasselling as well as at harvest. The concentrations of Al_{Mono} measured at tasselling were significantly decreased by unfertilized and fertilized lime treatments.

At harvest, all treatments were effective in decreasing Al_{Mono} concentrations. Except at the low rates of grass residue addition, additions of amendments also decreased Al_T concentrations (FIGURE 6.4). At harvest, the lime treatments tended to have the greatest effect at decreasing the concentrations of soluble Al followed by kraal manure and grass residues.

Concentrations of soluble Al measured in samples collected from the undisturbed site were lower than that of the control and inter row samples collected from the experimental site.

6.3.4 Microbiological and biochemical indices

Organic C, microbial biomass C and microbial quotient

As shown in FIGURE 6.5, organic C contents measured at the undisturbed site were markedly greater than those on experimental sites. No significant differences in organic C contents were found between various treatments used in this experiment. Microbial biomass C content measured followed the trend: undisturbed site samples > grass residues > kraal manure = lime > control > inter row samples. The microbial biomass C content in inter row samples was markedly lower than that of all other treatments. The microbial quotient generally followed the same trend as microbial biomass C except there was a trend for values to be lower for kraal manure than limed treatments.

Basal respiration, microbial metabolic quotient and arginine ammonification

The rate of basal respiration, the microbial metabolic quotient and arginine ammonification are shown in FIGURE 6.6. The basal respiration rate was significantly increased by addition of all treatments. The addition of fertilizer tended to have the effect (although not statistically significant) of increasing basal respiration rates. The basal respiration rates induced by fertilized and unfertilized lime treatments were significantly greater than those of fertilized and unfertilized grass residue treatments respectively. Samples collected from the undisturbed site had significantly higher basal respiration rates than that of experimental site.

The metabolic quotient measured in fertilized lime treatments and inter row samples were significantly greater than that of fertilized and unfertilized control and grass residue treatments (FIGURE 6.6). The low values for metabolic quotient in the grass residue treatments were associated with high values for microbial biomass in these treatments (FIGURES 6.5 and 6.6) Addition of fertilizer to lime, kraal manure and grass residues tended to increase the metabolic quotient.

The arginine ammonification rates measured in unfertilized and fertilized kraal manure, grass residue and lime treatments were significantly higher than those measured in fertilized and unfertilized control and inter row samples (FIGURE 6.6). The levels of arginine ammonification activity induced by unfertilized and fertilized lime were significantly higher than that of unfertilized and fertilized grass residues. It was also evident that samples from the undisturbed site had the highest arginine ammonification rates.

Enzymes activities

Enzyme activities measured in different treatments are shown in FIGURES 6.7 and 6.8. It was observed that enzyme activities measured in samples from the undisturbed site were distinctly higher than those from the experimental site. Fertilizer addition generally increased protease, aryl sulphatase and acid phosphatase activities. Unfertilized lime treatments had a significantly higher protease, aryl sulphatase and alkaline phosphatase

activity than unfertilized kraal manure and grass residue treatments. Levels of enzyme activity measured in fertilized lime treatments were significantly greater than that of fertilized kraal manure treatments.

Levels of acid phosphatase activity measured in the fertilized control were significantly higher than that of the unfertilized control. Alkaline phosphatase activities recorded in this study were markedly lower than those for acid phosphatase. Among all treatments, only fertilized and unfertilized lime and kraal manure treatments had a significant effect in increasing alkaline phosphatase activities compared with the control.

6.3.5 Interaction between soil acidity and microbial and biochemical indices.

The results of the regression analysis showed that soil acidity and microbial and biochemical indices were generally significantly correlated (TABLE 6.2). As expected, high negative correlations were found between soil Al indices (exchangeable and soluble Al) and soil pH (measured in water and in 1 M KCl). Both pH_{water} and pH_{KCl} were generally highly positively correlated with microbial biomass C, microbial and enzyme activity levels whereas soil Al indices were negatively correlated to microbial biomass C and microbial and enzyme activity levels. In addition, Microbial and enzymes activity indices were positively correlated with one another (TABLE 6.2).

TABLE 6.1 Effect of addition of amendments¹ on nutrients status of the soil measured at harvest

	Exchangeable cations			AMBIC extractable		
	K	Ca	Mg	P	Zn	Mn
	Cmol _c kg ⁻¹			mg kg ⁻¹		
Inter row	0.18	1.98	0.77	3	1.2	4
Control	0.14	2.05	0.99	4	2.5	6
Kraal 1	0.92	2.97	1.63	7	4	5
Kraal 2	1.01	4.59	2.54	8	4.5	9
Grass 1	0.24	2.1	1.14	4	2.3	5
Grass 2	0.25	2.15	1.22	4.2	2.8	5
Lime 1	0.26	3.17	1.35	5	1.9	4
Lime2	0.23	3.89	1.46	5.3	2.2	5
Control + F	0.49	2.07	0.81	27	5	7
Kraal 1 + F	0.99	3.91	1.74	36	8	9
Kraal 2 + F	1.02	5.34	2.10	22	6	8
Grass 1+ F	0.64	1.99	1.28	16	6.5	7
Grass 2 + F	0.49	2.10	1.56	15	4.8	7
Lime 1 + F	0.51	3.1	1.60	11	4.3	4
Lime2 + F	0.74	3.56	2.17	9	5.4	3
Undisturbed samples	0.67	2.61	2.71	3	0.94	0.6
LSD (P ≤ 0.05)	0.3	0.46	0.36	2.2	0.36	1.6

¹ Control = 0 t ha⁻¹, Kraal 1 = 10 t ha⁻¹, Kraal 2 = 20 t ha⁻¹, Grass 1 = 10 t ha⁻¹, Grass 2 = 20 t ha⁻¹, Lime 1 = 2.5 t ha⁻¹ and Lime 2 = 5 t ha⁻¹.

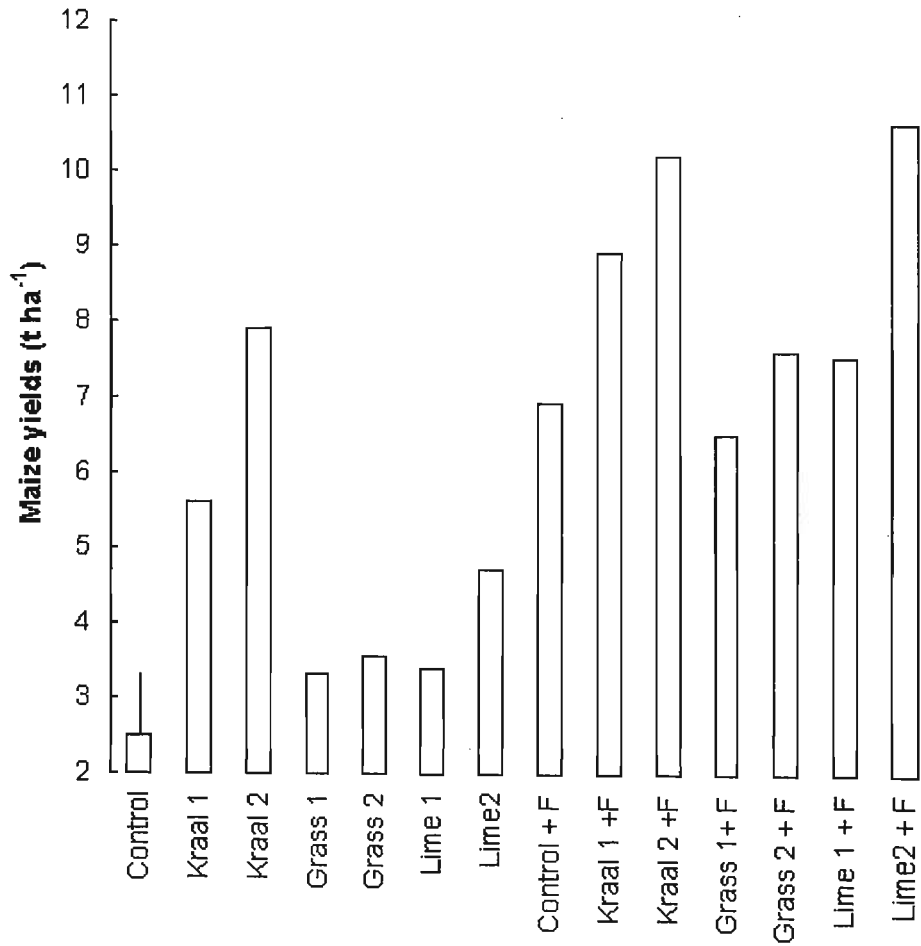


FIGURE 6.1

Effect of addition of kraal manure (Kraal 1 = 10 t ha⁻¹ and kraal 2 = 20 t ha⁻¹); grass residues (grass 1 = 10 t ha⁻¹ and grass 2 = 20 t ha⁻¹); lime (lime 1 = 2.5 t ha⁻¹ and lime 2 = 5 t ha⁻¹) and fertilizer (F) to an acid soil on maize yields. LSD ($P < 0.05$) shown.

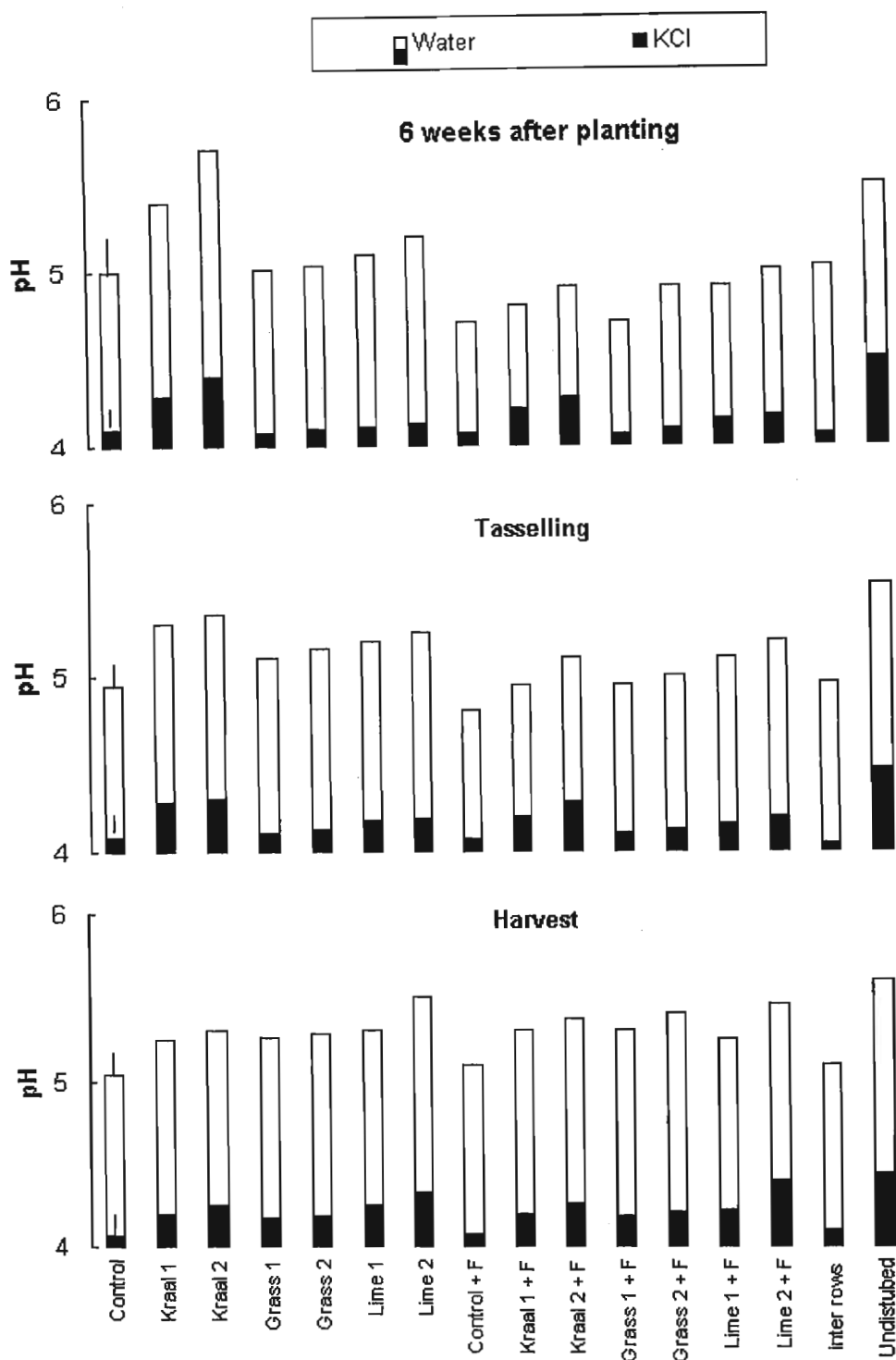
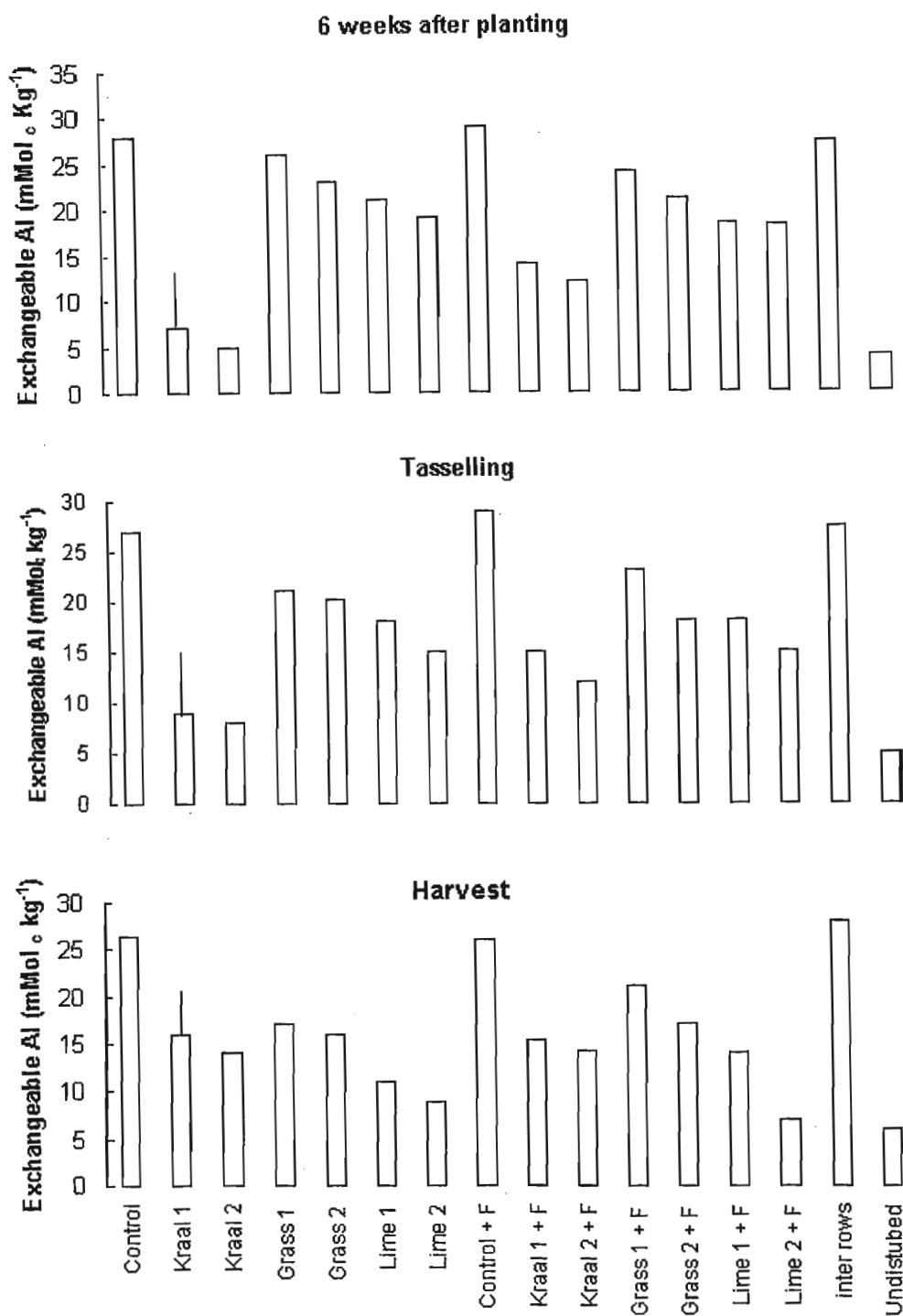


FIGURE 6.2

Effect of addition of kraal manure (Kraal 1 = 10 t ha⁻¹ and kraal 2 = 20 t ha⁻¹); grass residues (grass 1 = 10 t ha⁻¹ and grass 2 = 20 t ha⁻¹); lime (lime 1 = 2.5 t ha⁻¹ and lime 2 = 5 t ha⁻¹) and fertilizer (F) to an acid soil on pH (measured in water and 1 M KC), LSD (P ≤ 0.05) shown.

**FIGURE 6.3**

Effect of addition of kraal manure (Kraal 1 = 10 t ha⁻¹ and kraal 2 = 20 t ha⁻¹); grass residues (grass 1 = 10 t ha⁻¹ and grass 2 = 20 t ha⁻¹); lime (lime 1 = 2.5 t ha⁻¹ and lime 2 = 5 t ha⁻¹) and fertilizer (F) to an acid soil on exchangeable Al, LSD ($P \leq 0.05$) shown.

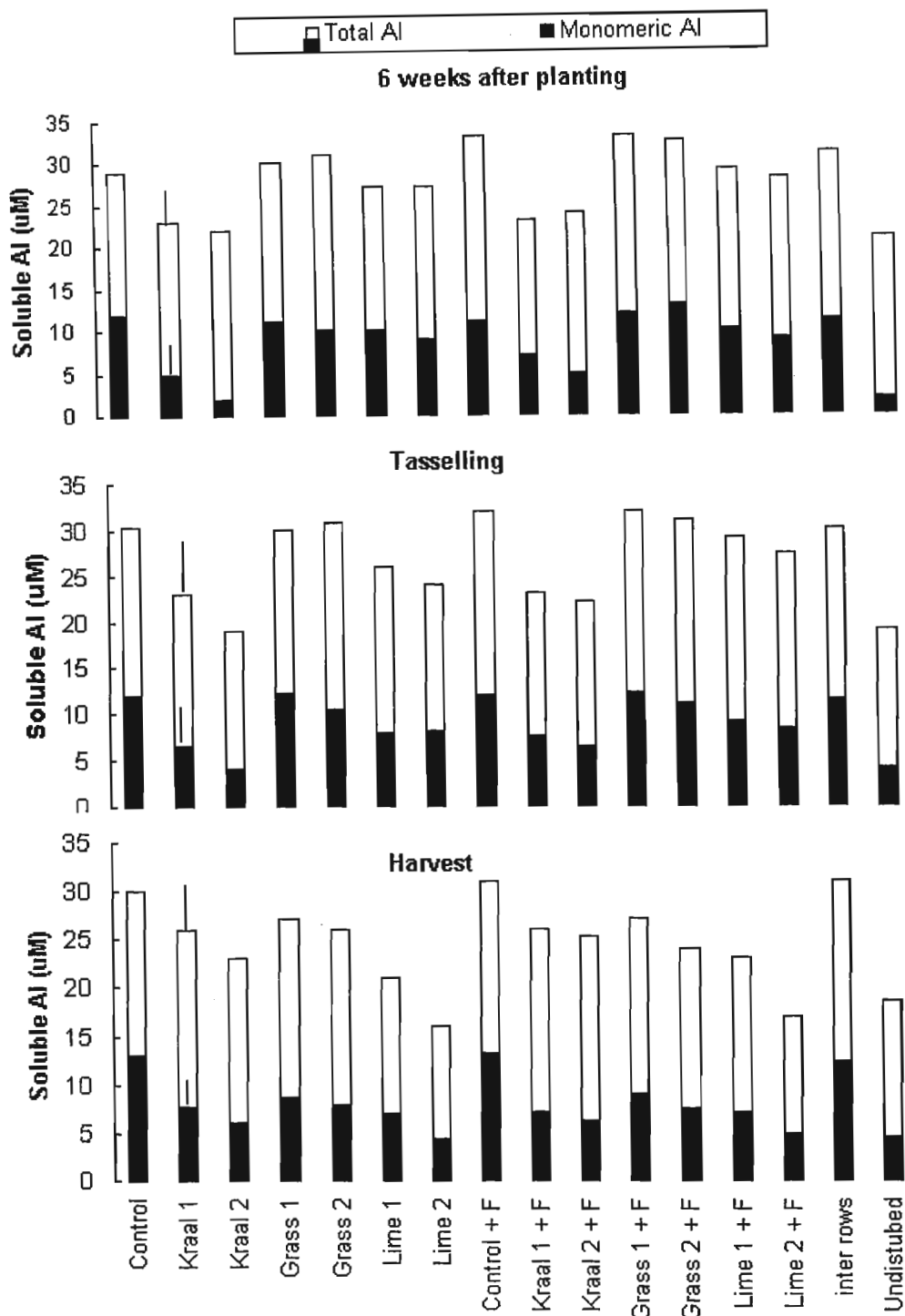


FIGURE 6.4

Effect of kraal manure (Kraal 1 = 10 t ha⁻¹ and kraal 2 = 20 t ha⁻¹); grass residues (grass 1 = 10 t ha⁻¹ and grass 2 = 20 t ha⁻¹); lime (lime 1 = 2.5 t ha⁻¹ and lime 2 = 5 t ha⁻¹) and fertilizer (F) on soluble Al in an acid soil where maize was cropped, LSD (P ≤ 0.05) shown.

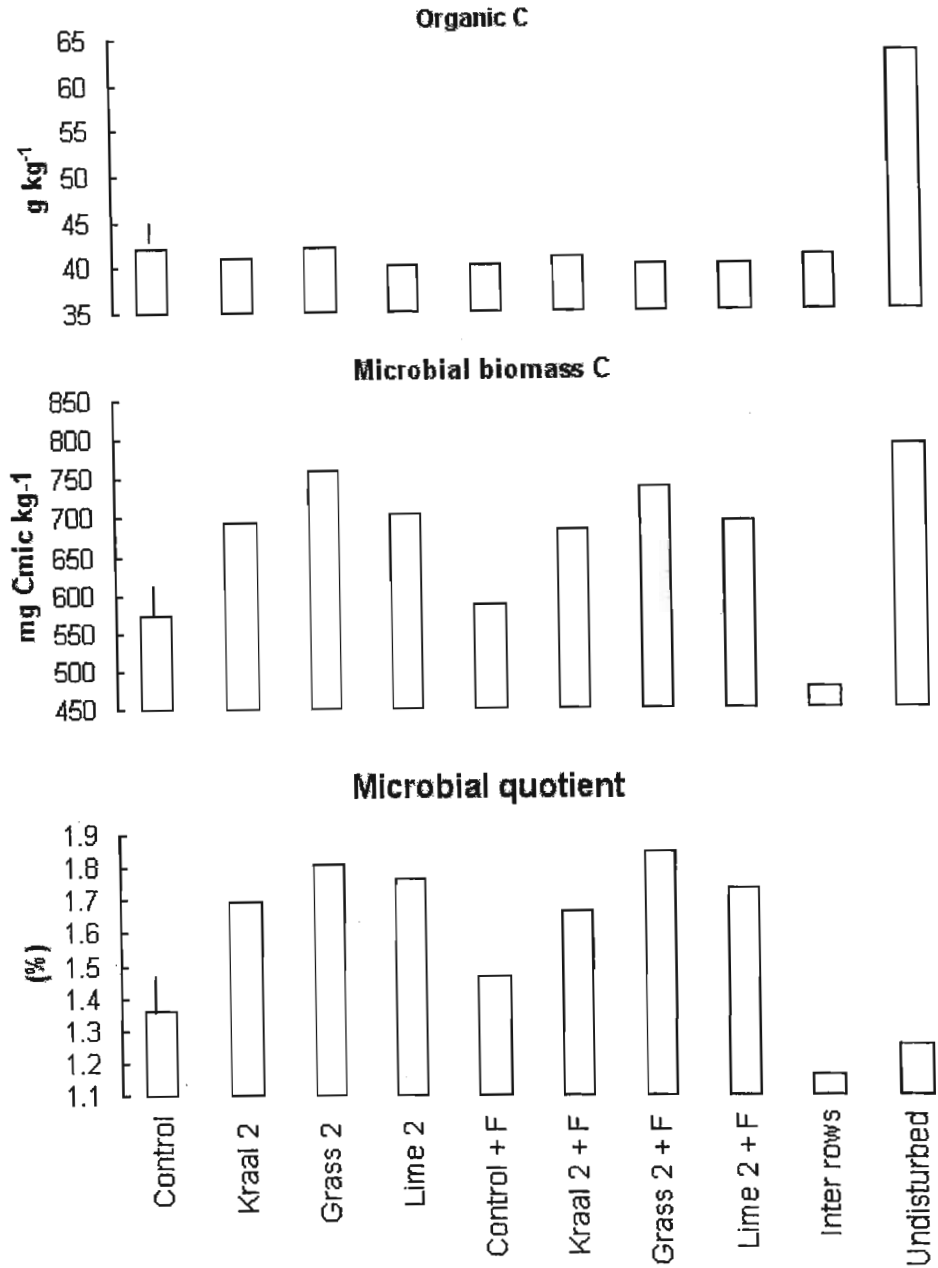


FIGURE 6.6

Effect of kraal manure (kraal 2 = 20 t ha⁻¹), grass residues (grass 2 = 20 t ha⁻¹), lime (lime 2 = 5 t ha⁻¹), and fertilizer (F) on organic C, microbial biomass C and microbial quotient in an acid soil where maize was cropped., LSD (P ≤ 0.05) shown

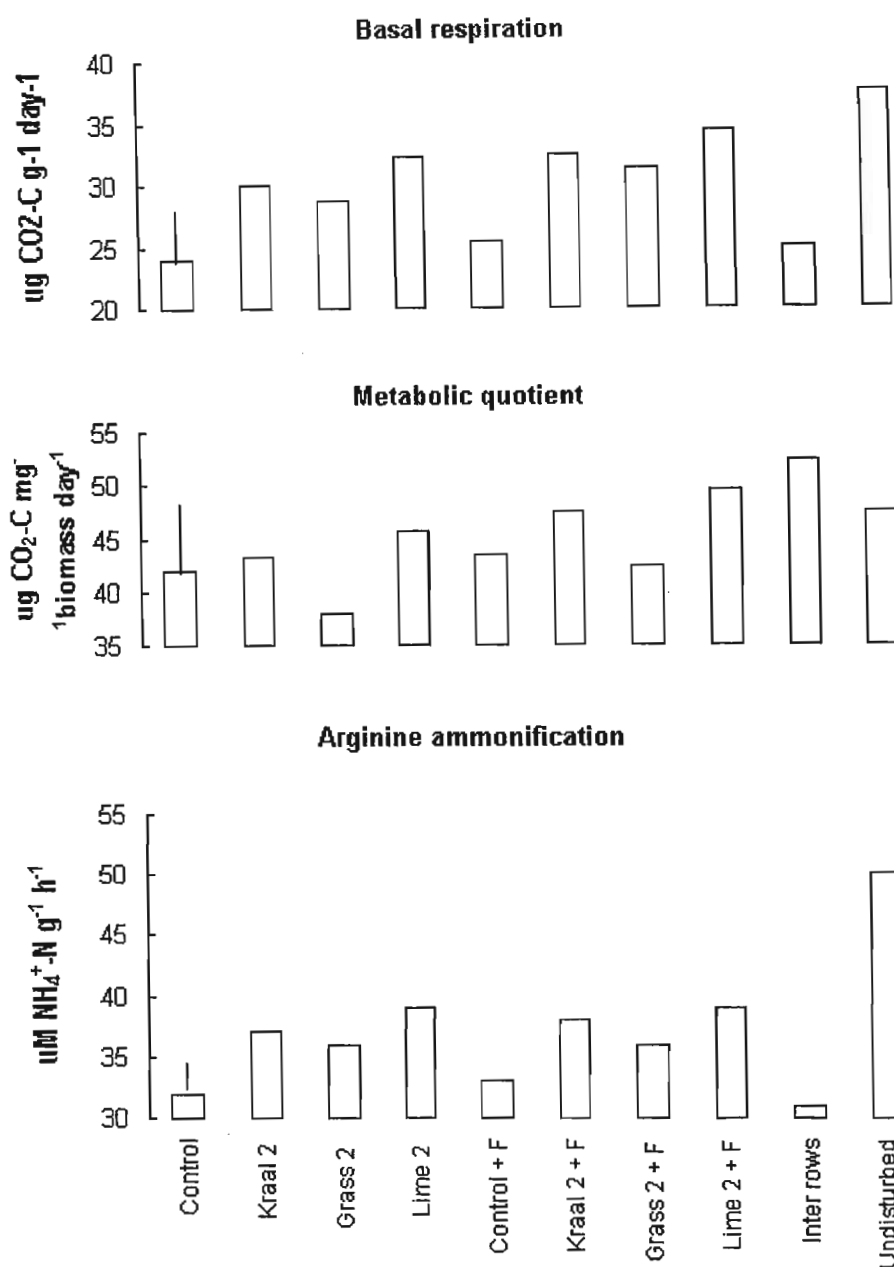
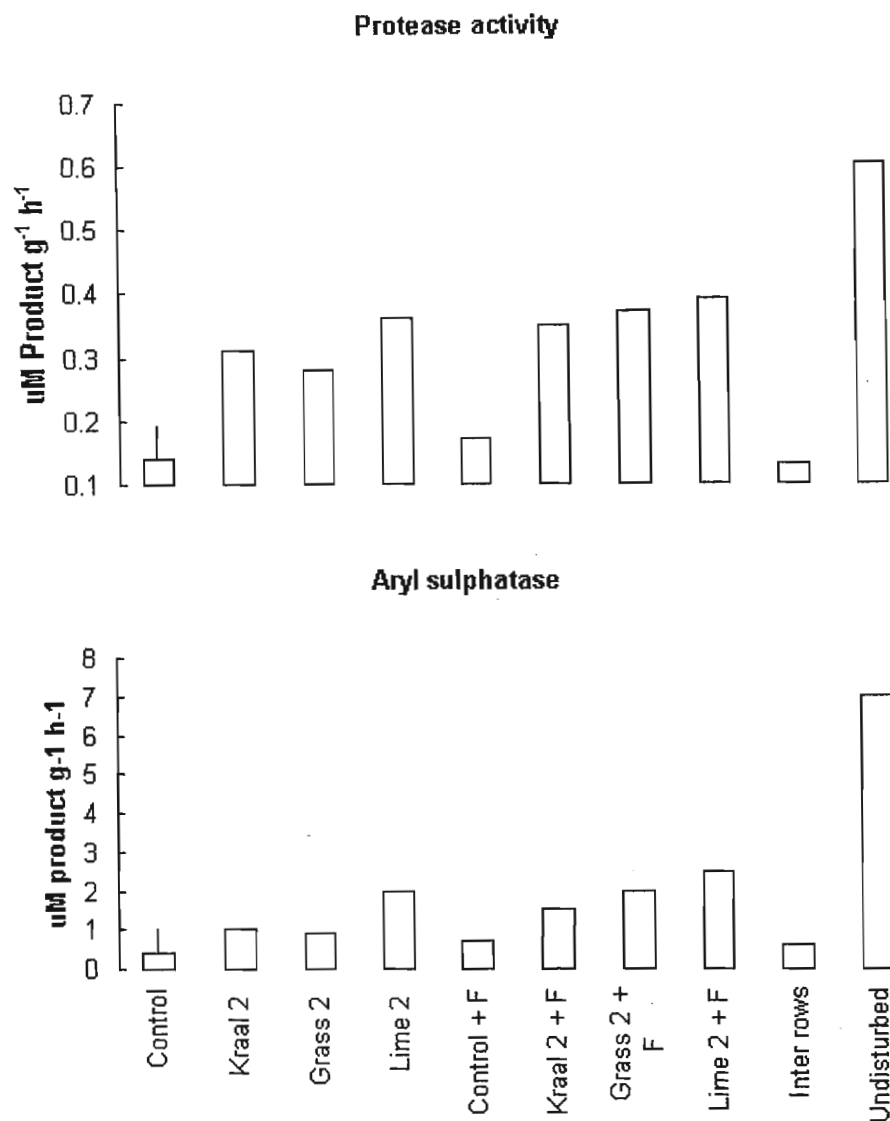


FIGURE 6.6

Effect of kraal manure (kraal 2 = 20 t ha⁻¹), grass residues (grass 2 = 20 t ha⁻¹), lime (lime 2 = 5 t ha⁻¹), and fertilizer (F) on basal respiration, metabolic quotient and arginine ammonification in an acid soil where maize was cropped., LSD ($P \leq 0.05$) shown

**FIGURE 6.7**

Effect of kraal manure (kraal 2 = 20 t ha⁻¹), grass residues (grass 2 = 20 t ha⁻¹), lime (lime 2 = 5 t ha⁻¹), and fertilizers (F) on protease and aryl sulphatase activity levels in an acid soil where maize was cropped., LSD ($P \leq 0.05$) shown.

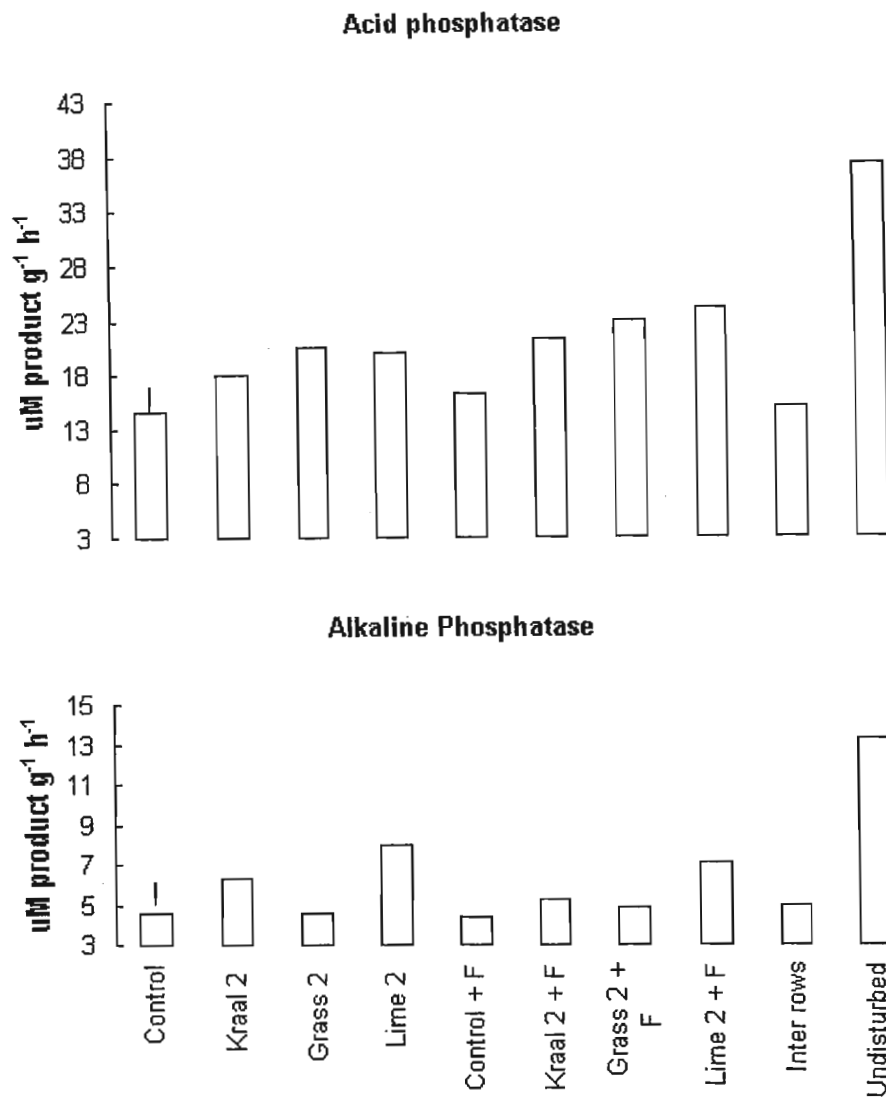


FIGURE 6.8

Effect of kraal manure (kraal 2 = 20 t ha⁻¹), grass residues (grass 2 = 20 t ha⁻¹), lime (lime 2 = 5 t ha⁻¹), and fertilizer (F) on acid and alkaline phosphatase activity levels in an acid soil where maize was cropped, LSD ($P \leq 0.05$) shown.

TABLE 6.2 Linear correlation coefficients (r) between measures of selected soil acidity indices and microbiological and biochemical indices.

	pH _{water}	pH _{KCl}	Exchangeable Al	Al _T	Al _{Mono}	C _{mic}	Basal respiration	Arginine ammonification	Protease	Aryl sulphatase	Acid phosphatase
pH _{KCl}	0.92***										
Exchangeable Al	-0.90***	-0.94***									
Al _T	-0.88***	-0.94***	0.95***								
Al _{Mono}	-0.88***	-0.80***	0.85***	0.80***							
C _{mic}	0.70**	0.58**	-0.71**	-0.62**	-0.71**						
Basal respiration	0.85***	0.80***	-0.83***	-0.76**	-0.77***	0.62**					
Arginine ammonification	0.90***	0.86***	-0.84***	-0.77***	-0.79***	0.81***	0.77***				
Protease	0.96***	0.89***	-0.89***	-0.85***	-0.85***	0.77***	0.85***	0.95***			
Aryl Sulphatase	0.83***	0.80***	-0.72**	-0.69**	-0.61**	0.61**	0.71**	0.92***	0.89***		
Acid phosphatase	0.87***	0.81***	-0.79***	-0.73**	-0.70**	0.69**	0.76**	0.94***	0.93***	0.96***	
Alkaline phosphatase	0.78***	0.77***	-0.67**	-0.67**	-0.59**	0.61**	0.66**	0.88***	0.82***	0.94***	0.87***

Statistical significance shown: ** $P \leq 0.01$, *** $P \leq 0.001$.

6.4 Discussion

6.4.1 Changes in, soil pH, Al solubility and nutrient status

Soil pH

The effect of kraal manure in increasing soil pH recorded in this study has been demonstrated previously in laboratory (CHAPTERS 3 and 5) and in the field (CHAPTER 4). As previously noted, kraal manure is essentially made of more, or, less decomposed cattle dung mixed with soil. As suggested previously, the ability of kraal manure to increase pH depends on the proportion of dung contained in the manure. The higher the proportion of dung, the larger will be the increase in pH (CHAPTERS 3 and 5). Indeed, Ca and Mg carbonates are found in cattle dung (Barrow, 1975; Barrow 1987) resulting in it having a relatively high pH (7.0 – 8.0) (Barrow, 1987). Likewise, several workers have shown that animal dung deposited on the soil surface by grazing animals (During *et al.*, 1973) or applied to the soil as a farmyard manure (Weeda, 1977) cause an increase in soil pH.

The early (6 weeks after planting) effect of kraal manure in increasing the soil pH was attributable to the dissociation of CaCO_3 releasing CO_3^{2-} anions which consume protons. As suggested by Haynes and Mokolobate (2000), it is also possible that a proton consumption capacity of humic materials formed during decomposition of the manure (Wong *et al.*, 1998), oxidation of organic acid anions present in the dung (Yang *et al.*, 1996), specific adsorption of organic molecules originating from the dung onto hydrous oxide surfaces (Hue *et al.*, 1986) and ammonification of organic manure-N (Hoyt and Turner, 1975) could have made minor contributions to the increase in soil pH in kraal manure treatments.

The general decrease in soil pH recorded in kraal manure treatments between the first sampling (6 weeks after planting) and harvest can be attributed to a number of mechanisms as already reported in CHAPTER 5. The most important mechanism involved is believed to be the nitrification of

NH_4^+ which releases H^+ into the soil and decreases pH (Hoyt and Turner, 1975; Haynes and Swift, 1993; Yan *et al.*, 1996), The kraal manure used had a relatively high concentration of N (14 g kg^{-1}). Other mechanisms such as an increase in exchangeable H^+ and Al^{3+} induced by an increase in cation exchange capacity (Donald and Williams, 1954; William and Donald, 1957; Brenes and Pearson, 1973; Mason and Fey, 1989; Mokolobate and Haynes, 2002a) could have also contributed to the pH decline.

The progressive increase in soil pH measured in lime and grass residue treatments is attributable to progressive dissolution of dolomitic lime and the slow decomposition of grass residues. Since grass residues had a relatively high C/N ratio, N immobilization during the decomposition presumably delayed the mineralization process. This would have delayed ammonification process, which induces a pH increase. The oxidation of organic acid anions contained in the grass residues (De Wit *et al.*, 1963), during residue decomposition, is probably the main mechanism of proton consumption during decomposition of plant material (Berekzai and Mengel, 1993; Helyar and Porter, 1989; Noble *et al.*, 1996; Ritchie and Dolling, 1985; Tang *et al.*, 1999). It therefore occurs progressively as the plant material decomposes.

The pH of the undisturbed site represents that which would have existed on the experimental site prior to agricultural activity. Soil acidification under small scale farming systems (where N fertilizers are used sparingly or not at all) is mainly attributable to mineralization and nitrification of organic N and subsequent NO_3^- leaching. A massive loss of soil organic matter content was evident at the site under small scale farming (FIGURE 6.5). The reason for this is discussed in a following section. Soil organic matter degradation and concomitant N mineralization and nitrification resulted in a substantial decrease in soil pH (FIGURE 6.2).

The lower pH values in fertilized than unfertilized plots measured at 6 weeks after planting and to a lesser extent at tasselling were not evident at harvest. The effect was most noticeable in pH_{water} values and is likely to have been due to a high soluble salt concentration in soil solution following fertilizer

application. The high concentration of cations in solution results in a depression in pH_{water} values due to displacement of Al^{3+} and H^+ from cation exchange sites into soil solution. By harvest, soluble salts concentrations will have been much reduced due to plant uptake and/or leaching and as a result the effect was no longer evident.

Al solubility

The decrease in exchangeable and soluble (total and monomeric) Al recorded when kraal manure, grass residues and lime were added to the soil was attributable to the concomitant increase in soil pH. The highly significant negative correlations found between soil pH and exchangeable and soluble Al demonstrates that soil pH was the major factor controlling Al solubility. In fact, the increase in soil pH causes precipitation reactions of Al^{3+} as hydroxy-Al compounds (Noble *et al.*, 1996; Pocknee and Sumner, 1997). As a result, the decrease in exchangeable and soluble Al followed the same trend order as the increase in soil pH (Lime > Kraal manure > grass residues). The close relationship between soil pH and exchangeable and soluble Al was also demonstrated by the progressive increase in soil pH recorded in lime and grass residues treatments being accompanied by a progressive decrease in exchangeable and soluble Al.

As already observed in the preliminary field trial (CHAPTER 4) and by many other authors (Juo and Kamprath, 1979; Lungu *et al.* 1993), the delay following lime applications in decreasing exchangeable Al concentrations is mainly explained by the progressive dissolution of lime. The buffering reserve of potentially reactive Al and non-exchangeable acidity present in acid soils, including negatively charged Fe and Al hydrous oxides, also tends to buffer the liming effect and maintain exchangeable Al levels.

In addition to the increase in pH the decomposition of kraal manure and grass residues was expected to produce organic compounds (CHAPTERS 3, 4 and 5) capable of complexing with Al in solid and solution phases. As already demonstrated in CHAPTER 5, and by a number of investigators (Bloom *et al.*, 1979; Haynes, 1984; Stevenson and Vance, 1989; Sinesi and

Brunetti, 1996; Mokolobate and Haynes, 2002b), complexation of Al by organic matter can be an important factor controlling Al solubility when organic materials were added to an acid soil. In particular, unfertilized and to a lesser extent fertilized, kraal manure treatments at 6 weeks after planting and to a lesser extent at tasselling contained unexpectedly high concentrations of Al_T compared to the low concentrations of exchangeable Al present (FIGURES 6.3 and 6.4). It has already been shown (CHAPTER 5) that manure addition can cause increase in soluble C and therefore maintain relatively high concentrations of Al_T in solution even though concentrations of Al_{Mono} are low.

Nutrients status

The lower concentration of exchangeable Mg, K and Ca in the control than the undisturbed soil reflects soil acidification and consequent leaching of exchangeable bases under the small scale farming system. Kraal manure was the only unfertilized treatment, which had elevated macronutrient and micronutrient contents. The marked increase in concentrations of exchangeable Ca and Mg were expected since, as already noted, kraal manure contains $CaCO_3$ and $MgCO_3$.

The increase in exchangeable K in kraal manure treatments was presumably due to the high concentration of K found in cattle urine (Hutton *et al*, 1967; Hogg, 1981). As the cattle spend the night in the kraal, they excrete urine, which becomes mixed with the dung and soil. The effect of lime in increasing the concentration of Ca, and Mg was attributable to the Ca and Mg carbonates contained in dolomitic lime. The increase in exchangeable K concentrations and extractable AMBiC P, Zn and Mn in fertilized lime, grass residue and control treatments were attributable to the addition of fertilizer..

The fertilized lime treatments had lower concentrations of AMBiC P than the other fertilized treatments. Similarly, low extractable AMBiC P concentrations were recorded in fertilized lime treatments in the preliminary field trial (CHAPTER 4) and a number of factors were proposed to explain such a situation. Plant uptake could have contributed to the low extractable AMBiC

P since those treatments had high maize yields (10.6 t ha^{-1}). A reduction in AMBIC P could also be due to other mechanisms such as P-adsorption onto positively charged amorphous hydroxy-Al compounds resulting from precipitation of exchangeable and soluble Al due to the increase in pH (Haynes, 1984), precipitation of insoluble Al-phosphates (White and Taylor, 1977; Naidu *et al.*, 1987), and/or Ca-phosphates precipitating during extraction particularly when the Olsen extractant (0.5 M NaHCO_3 , pH 8.5) is used (Sorn-Srvichai *et al.*, 1984; Naidu, 1987).

6.4.2 Maize yields.

All treatments increased maize yields compared with the control. This increase is attributable to the combination and interaction of various mechanisms (increase in nutrient status and soil pH and the decrease in Al toxicity,...) induced by the added amendments.

These mechanisms may have acted individually or together depending on the amendments being considered. For example unfertilized kraal manure treatments gave significantly higher maize yields than unfertilized lime treatments. This was because kraal manure had increased both nutrient status and soil pH while lime had mainly increased soil pH. In addition, it was clear that the marked increase in maize yields in all fertilized treatments compared with unfertilised ones was due to the increase in nutrient status induced by fertilizer addition, since fertilizer tended to decrease rather than increase the soil pH.

From a practical viewpoint, it is important to note that all amendments significantly increased yields compared to the control. In particular, kraal manure applications resulted in yields that were 5.2 % (Kraal 1) and 79 % (kraal 2) of maximum yields that were obtained in the lime 2, fertilized treatment. While lime and manufactured fertilizers are beyond the reach of

many small scale farmers, kraal manure is readily available. This is because of the traditional importance of cattle in Zulu culture. The dual role of kraal manure in rapidly raising soil pH and also adding substantial quantities of nutrients means it is particularly effective in increasing maize yields on acidic, nutrient-poor soils. A combination of kraal 2 (20 t ha⁻¹) plus fertilizer gave yields statistically similar to those of lime 2 plus fertilizer demonstrating the practical effectiveness of kraal manure as a liming material.

Although grass residues raised soil pH, the effect was much less immediate than that for kraal manure and highest pH values and lowest exchangeable and soluble Al concentrations were not reached until harvest. In order to raise soil pH sufficiently at planting and in the early stages of crop growth when yield potential is determined, it is evident that the grass residues would need to be incorporated into the soil two or three months prior to planting.

6.4.3 *Organic C content.*

It was observed in this study that the undisturbed native grassland had a markedly higher organic C (63 g kg⁻¹) content than the cultivated area amended or not by organic materials, lime or fertilizer (FIGURE 6.5). The higher organic C contents found in the undisturbed area compared with the cultivated one are in accordance with the findings of many researchers (Jonston, 1986; Gupta *et al.* 1994; Grace *et al.* 1994; Haynes and Beare, 1996 and Riezebos and Loerts, 1998). Indeed, it was expected that under permanent native grassland large amount of organic matter would accumulate due to turnover of root material, root exudates and return of dung and urine by grazing cattle (Lovell *et al.*, 1994; Haynes and Beare, 1996).

The relatively lower organic C content measured at the experimental site, compared with the undisturbed one is attributable to tillage-induced organic matter breakdown. Small scale farmers in the area rely almost exclusively on conventional tillage to prepare a seed bed. During tillage operations, organic

matter that was previously protected by aggregate structure is exposed to the attack by soil microorganisms. In addition, cultivation increases soil aeration and promotes oxidation reactions performed by soil microorganisms and this contributes to a high rate of organic matter decomposition. In comparison with native grassland, organic matter inputs to the soil are much lower under arable production. This is because crop plants are usually spaced widely apart in rows and often much of the aboveground plant material is removed from the field with, or as, the harvested crop.

In this study no significant changes in organic C content induced by various treatments were observed. Indeed although total soil organic matter content is an important agronomic attribute, it is not affected by short-term soil management (Gregorich *et al.*, 1994). That is the background levels of organic matter already present in the soil are large making small changes difficult to detect. For that reason, other indicators measuring the biological activity (e.g. microbial biomass C, enzyme activities,) have been proposed to assess the effect of short-term agronomic practices on soil organic matter status (Gregorich *et al.*, 1994).

6.4.4 *Microbial biomass C, microbial quotient and microbial activity*

Microbial biomass C and microbial quotient

The relatively high microbial biomass C measured in the undisturbed site (native permanent pasture) was expected because of the high organic C content (63 g kg^{-1}) measured in that area. Many researches have shown that microbial biomass C is closely correlated with organic C content (Anderson and Domsch, 1989; Carter, 1991; Haynes, 1999; Haynes and Tregurtha, 1999) and values are generally greatest under permanent grassland. The large ramified root system of grassland supports a substantial microbial biomass in the rhizosphere (Gregorich *et al.*, 1994).

The microbial quotient was lowest in the inter rows and significantly higher in the row area of the control. This reflects the rhizosphere-effect in the row

area where maize roots proliferated. Root turnover and exudation of carbonaceous material from roots stimulates soil microbial activity in the rhizosphere (Gregorich *et al.*, 1994). As result, microbial biomass C and the microbial quotient are characteristically higher in the rhizosphere than the bulk soil (Gregorich *et al.*, 1994). There was little proliferation of maize roots into the inter row soil, so this area effectively remained fallow. The lack of inputs of readily available organic material to the inter row soil resulted in a low microbial quotient.

The general increase in microbial biomass C observed in grass residues and kraal manure treatments compared with the control may be partially explained by the effect of readily available carbonaceous compounds originating from grass residues and kraal manure decomposition. In fact, many workers including Vaughan and Malcolm (1985) have reported that the size of soil microbial biomass increases during the decomposition of organic materials added to a soil. For example, Doran (1980), Biederbeck *et al.* (1984) and Gupta and Roper (1992) demonstrated an increase in the size of populations of total heterotrophic microorganisms in the soil in response to the retention of crop residues.

The increase in soil pH and concentrations of basic cations and the decrease in exchangeable and soluble Al (TABLE 6.1 and FIGURES 6.2; 6.3 and 6.4) following the addition of all three amendments probably contributed to the increase in microbial biomass C in those treatments. In fact, as reported by Badalucco *et al.* (1992) and Dee *et al.* (2002) an increase in soil pH ameliorates conditions of limiting microbial proliferation such as Al toxicity and Ca deficiency. Thus the increase in pH may provide more favourable conditions for microbial proliferation. Indeed, in this study both microbial biomass C and microbial activity, as estimated by basal respiration and arginine ammonification rate were positively correlated with soil pH and negatively correlated with exchangeable Al, Al_T and Al_{Mono}. (TABLE 6.2). Changes in the composition of microbial community are also likely. In an acid soil, a large proportion of the indigenous microorganisms will be acid tolerant and raising soil pH will tend to cause proliferation of acid-intolerant

species already present in the soil in relatively inactive forms (Dee *et al.*, 2002). There are therefore likely to be shift in microbial composition and possibly an increase in the proportion of bacteria relative to fungi at higher pH (Neale *et al.*, 1997).

The tendency for the microbial biomass and the microbial quotient to be greater under the grass residues than kraal manure and lime treatments probably reflect the slow but continuing decomposition of the grass residues. As already noted at harvest, soil pH was continuing to increase as the residues decomposed. At harvest, decomposing residue material was still evident in the soil and this presumably supported a large microbial community.

Microbial activity

The general increase in basal respiration and arginine ammonification recorded in kraal manure and grass residue treatments could be partially attributed to the high energy provided by particulate organic matter and soluble C produced during kraal manure and grass residue decomposition. As already noted the increased pH caused by additions of all of the amendments may well have provided conditions more favorable for microbial activity.

The high metabolic quotient values were recorded in inter row samples and these were associated with the lowest microbial biomass C values. These results are in accordance with the finding by Sparling (1997) and Graham *et al* (2001) who reported that factors limiting the size of microbial biomass C tended to increase the metabolic quotient. An increase in the metabolic quotient has been interpreted as a response by soil microflora to adverse environmental conditions (stress or disturbance) (Wardle and Ghani, 1995). That is, under stress microorganisms divert a relatively larger amount of the available energy into maintenance of various biochemical functions and there is a decrease in the efficiency with which C substrates are converted

into cellular material. As a result, there is an increase in respiration rate per unit of microbial biomass (Anderson and Domsch, 1993). In the inter row area the main stresses are likely to be a sparse supply of labile C and nutrients.

It was also observed that the lower metabolic quotient values measured in grass residue than kraal manure or lime treatments were associated with higher microbial biomass C values. The addition of grass residues probably provided a relatively large amount of readily available C and consequently favoured a development of a large and relatively unstressed microbial community (Sakamoto and Oba, 1994).

6.4.5 *Enzyme activity*

Soil enzymes are the mediators and catalysts of important soil functions that include decomposition of organic inputs, transformation of native soil organic matter, release of inorganic nutrients for plant growth, detoxification of xenobiotics, N₂ fixation, nitrification and denitrification (Dick, 1997). Enzyme activity has been widely used to study the dynamics of the microbial population in various ecosystems and to assess the effects of land management on soil biochemical activities (Dick, 1984; Deng, and Tabatabai, 1997; Perucci *et al.*, 1997; Bandick and Dick, 1999; Haynes, 1999; Acosta-Martinez and Tabatabai, 2000).

The markedly higher enzyme activities recorded at the undisturbed site compared with the experimental one is explicable in terms of the high microbial biomass C and organic C content at the undisturbed site. The high organic matter content at the undisturbed site provides a large amount of readily available C for the metabolic activity of the heterotrophic microbial community. Indeed, the influence of high organic C in sustaining high soil enzyme activities was demonstrated by Dick (1984) and Deng and Tabatabai (1997). Organic matter has a dual role in increasing the enzyme activity: it is a substrate for microbial activity and the same time it plays an

important role in protecting soil enzymes since they become immobilized by clay-humus complexes (Tabatabai, 1994).

Fertilizer addition generally increased protease, aryl sulphatase and acid phosphatase activities. Similarly, research by Dick (1997) has shown that application of NPKS fertilizers increased soil enzyme activities. This is possibly partially related to greater release of enzymes from plant roots since plant growth and crop yields were generally greater in the fertilized treatments.

The activity of all four assayed enzymes was positively correlated with soil pH and negatively correlated with exchangeable Al, Al_T and Al_{Mono} (TABLE 6.2). Similarly, other workers (Haynes and Swift, 1988; Accosta-Martinez and Tabatabai, 2000, Dee *et al* 2002), have reported that although aryl sulphatase and acid phosphatase are assayed at their optimum pH values changes in soil pH due to amendment additions can greatly affect their assayed activity. Both Deng and Tabatabai (1997) and Kang and Freeman (1999) have demonstrated a positive correlation between aryl sulphatase activity and soil pH. Indeed, soil pH is considered as one of the most important environmental factors controlling the activity and stability of soil enzymes (Tabatabai, 1994). In addition, the increase in soil pH resulted in a larger, more active microbial biomass and this would have favoured greater synthesis and release of enzymes into the soil environment.

The acid phosphatase activity levels measured in this study were markedly higher than that of alkaline phosphatase activity (FIGURE 6.8). This was expected since acid phosphates have been shown to be the dominant phosphomonoesterases present in acid soils (Accosta-Martinez 2000; Tabatabai; 2000 and Dee *et al* 2002). Nonetheless, alkaline phosphatases activities were significantly increased by lime and kraal manure applications (FIGURE 6.8). This was presumably related to the increased soil pH in these treatments.

6.5. Conclusions

The present study was designed to compare the effects of additions of kraal manure, grass residues and lime when added to an acid soil, on soil pH, Al solubility, microbiological and biochemical indices and maize response under field conditions. The results of the present investigation have shown that various treatments used had differing effects on the measured parameters and that there was a significant relationship between soil acidity indices (soil pH and Al solubility) and biochemical and biological indices.

The addition of kraal manure decreased Al toxicity and significantly increased the soil nutrient status, the soil pH, the microbial biomass C and activity, the enzyme activities and maize yields. The combination of kraal manure and N-P-K fertilizer accentuated the effect of kraal manure in increasing the soil nutrient status, microbial and enzyme activities and maize yields. Unfertilized kraal manure had a markedly greater effect in increasing soil nutrient status and maize yields than unfertilized lime and grass residue treatments.

Grass residues were less effective in increasing maize yields than kraal manure and lime and their effects in increasing soil pH and reducing Al toxicity were greater at harvest. However, grass residue addition resulted in increased microbial and enzyme activities and soil microbial biomass C was greater than that of kraal manure and lime treatments. It is, however, advised to apply grass residues to the soil some months prior to sowing a crop, since the liming effect is not immediate but is progressive over a period of several months.

It was also observed that the undisturbed site had higher pH, lower Al toxicity, higher exchangeable cation concentrations than the control treatment of the experimental site. In addition, the undisturbed site had the highest organic C, microbial biomass C contents and higher microbial and enzyme activities than those recorded on the experimental site. Considering

the importance of soil organic matter in sustaining plant growth by providing and storing essential plant nutrients and maintaining soil physical conditions, the drastic decrease in the soil organic C (from 63 g kg⁻¹ to 43 g kg⁻¹), soil pH, nutrients status microbial biomass C and microbial and enzyme activities due to continuous cultivation, under small scale farming is of concern. The addition of organic amendments, such as kraal manure or grass residues, on a regular basis is likely to increase soil organic matter content as well as having an important liming effect. Since the addition of even the low rate of grass residues, kraal manure and lime significantly increased maize yields, it is suggested that, economically disadvantaged small scale farmers can use those amendments in order to obtain reasonable maize yields.

More investigations should be conducted in order to determine the appropriate time of grass residues application to improve its efficiency to ameliorate soil acidity. The liming effect of various organic materials used in CHAPTER 3 should be investigated in field conditions to allow practical recommendations to be proposed.

CHAPTER SEVEN

7 General conclusions

Soil acidity is one of the major problems limiting soil productivity in many parts of the world. Soils affected by acidity represent approximately 30% of the ice-free land area. In developed countries, soil acidity amelioration has been undertaken during the last century while in developing countries, very little has been done in soil acidity management. The reasons for this situation are multiple, but it seems that both financial and logistic factors often limit the use of lime by small scale farmers.

Therefore, the development of new methods and/or adaptation of existing methods for the use by resource poor small scale farmers are of particular importance. The use of various organic amendments as ameliorants for soil acidity in laboratory and field conditions in this study yielded an improved understanding of how these organic amendments act to reduce Al toxicity as well as field results demonstrating their practical use for crop production in acid soils.

Among all laboratory indices tested ash alkalinity seemed the best index in predicting the liming ability of organic materials. Indeed, ash alkalinity has a dual advantage by being closely correlated to other important indices such as proton consumption capacity and CaCO_3 content as well as being easy to measure. It appears that ash alkalinity is a suitable index to predict the ability of organic residues to raise pH following their addition to soils, although it was originally designed to measure the organic acid anion content of plant tissues.

The mechanisms influencing the increase in soil pH and Al solubility when organic materials are added to an acid soil vary with time and with the type of organic material being considered. The short-term increase in soil pH following addition of organic materials can be attributed to a combination of various immediate chemical reactions such as the dissolution of CaCO_3 present in manures and the proton consumption by simple organic acid

anions and humic-like materials. In addition, decarboxylation of organic acid anions during the decomposition of plant and other organic residues also contribute to the rise in soil pH. The solubility of Al in acid soils amended with organic materials depends mainly on soil pH but can also be influenced by Al complexation by organic matter. At low pH, solid phase organic matter can complex soluble Al and reduce its solubility whereas at high pH soluble Al-organic matter complexes remain in soil solution and this tends to maintain high concentrations of Al_T in solution. Al_{Mono} is generally decreased by the addition of organic materials because it complexes with both the solid and solution phases of organic matter. The effects of organic materials in increasing soil pH tend to decline with time. This is strongly related to the nitrification of NH_4^+ originating from ammonification of organic N added in the organic materials.

Small-scale farmers in the region commonly incorporate kraal manure into the soil down the rows before planting maize. The results of this study demonstrated that such a practice has a substantial liming effect. This was attributable mainly to the high pH and significant Ca and Mg carbonate content of the manure. The addition of kraal manure decreased exchangeable Al, total soluble Al and monomeric Al and increased significantly the soil nutrients status, the soil pH, the size and activity of the soil microbial community, the activities of soil enzymes involved in mineralization of C, N, S and P and maize yields. Fertilizer addition accentuated the effect of kraal manure in increasing the soil nutrient status, microbial and enzyme activities and maize yields. Compared with lime or grass residues, kraal manure had a markedly greater effect in increasing soil nutrient status and maize yields. The effects of grass residues in increasing soil pH and decreasing Al toxicity were not immediate and were greatest at harvest. This suggests that application of grass residues to the soil should be performed some months prior to sowing a crop in order to raise soil pH sufficiently at planting and in the early stages of crop growth when yield potential is determined.

The addition of organic amendments, such as kraal manure or grass residues, on a regular basis is likely to increase soil organic matter content as well as

having an important liming effect. This will result in an increase in soil organic matter content. This is an important consideration since, as shown in this study, conventional tillage under small scale farming systems can result in a large decrease in soil organic matter content. An attendant decline in soil physical conditions is likely and this could favour runoff and erosion as well as reduced crop yield. The use of kraal manure as a soil amendment needs to be encouraged and its liming effect should be recognized and promoted by those involved in agricultural extension for small scale farming systems. Grass residues seem also useful although the optimum time for their application needs further study.

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APPENDICES

APPENDIX 3.1 Means of selected properties (Initial pH, CaCO₃ content, proton consumption capacity and ash alkalinity) of organic materials.

	Initial pH of materials	CaCO ₃ content	Proton consumption capacity Cmol _c kg ⁻¹	Ash Alkalinity
maize	5.34	0.366	15.467	26.4
sorghum	5.65	0.366	18.867	38.4
kikuyu	6.27	1.799	26.633	46.8
soybean	6.27	0.839	57.933	90.8
clover	5.86	1.800	51.400	93.2
acacia pr	5.45	0.699	22.367	85.2
cattle pasture	8.21	0.398	50.000	75.2
cattle kraal	7.37	1.540	22.667	50.0
cattle feedlot	8.60	2.490	55.133	84.4
poultry layer	7.84	21.17	252.167	355.2
poultry broiler	7.77	7.714	53.467	88.8
pig manure	7.92	10.360	114.333	134.8
sewage sudge	6.25	2.650	48.600	107.6
compost	6.69	2.370	23.267	33.6
filter cake	7.25	15.398	187.533	219.2

APPENDIX 3.2 Means of pH_{water} , pH_{KCl} , exchangeable Al and soluble Al following 6 weeks incubation of a range of organic materials at two rates R1 = 10 mg g⁻¹ and R2 = 20 mg g⁻¹) added to an acid soi.

	pH_{water} , R1	pH_{KCl} , R1	pH_{water} , R2	pH_{KCl} , R2	Exchangea ble Al, R1	Exchangea ble Al, R2	Al_{T} present as Al_{Mono} , R1	Al_{T} present as Al_{Mono} , R2	Al_{T} ,R1	Al_{T} , R2	Al_{Mono} , R1	Al_{Mono} ,R2
	mmol _c kg ⁻¹						%		uM			
Control	4.16	3.76	4.08	3.77	11.48	11.48	39.24	40.20	76.70	74.80	30.10	31.10
maize	4.77	4.00	4.72	4.05	5.07	4.44	38.79	47.84	53.10	47.45	20.60	22.70
sorghum	4.98	4.00	4.89	4.03	5.30	4.44	66.38	51.20	40.68	37.50	27.00	19.20
kikuyu	4.44	4.00	5.46	4.10	6.81	4.81	35.66	44.81	74.60	51.10	26.60	22.90
soybean	4.99	4.29	5.12	4.45	2.63	2.56	50.92	53.56	45.95	23.15	23.40	12.40
clover	4.93	4.23	5.27	4.19	2.96	2.33	48.21	19.46	19.50	18.50	9.40	3.60
acacia pr	4.73	4.23	4.75	4.34	3.48	2.63	55.44	53.55	34.45	15.50	19.10	8.30
cattle pastURE	4.47	4.00	4.46	3.91	6.30	5.15	29.39	30.53	75.20	74.85	22.10	22.85
cattle kraal	4.50	3.90	4.49	3.91	8.00	6.67	31.52	40.62	75.50	62.65	23.80	25.45
cattle feedlot	4.80	4.00	4.84	4.05	9.26	5.78	31.40	44.33	71.65	47.15	22.50	20.90
poultry layer	6.78	6.64	6.83	6.45	1.85	1.19	61.54	31.60	11.70	10.60	7.20	3.35
poultry broiler	4.65	3.95	5.43	4.72	7.30	5.67	31.88	47.95	69.00	17.10	22.00	8.20
pig manure	5.00	4.27	4.92	4.85	2.67	1.89	51.52	59.85	13.20	13.20	6.80	7.90
sewage sudge	5.12	4.02	5.86	4.53	5.96	5.96	48.95	57.72	14.30	12.30	7.00	7.10
compost	4.77	3.97	4.69	4.03	6.07	5.04	32.41	50.87	75.60	45.80	24.50	23.30
filter cake	4.56	4.26	5.33	4.64	5.22	4.63	35.55	55.19	30.66	15.40	10.90	8.50

APPENDIX 4.1 Means of soil pH_{water}, pH_{KCl}, exchangeable Al, Al_T and Al_{Mono} measured at tasselling and at harvest, following addition of two rates of kraal manure (KR1= 10 t ha⁻¹; KR2 = 20 t ha⁻¹) and two rates of lime (LR1 = 2.5 t ha⁻¹; LR2 = 20 t ha⁻¹) to an acid soil.

	pH _{water}		pH _{KCl}		Exchangeable Al mmol _c kg ⁻¹		Al _T uM		Al _{Mono}	
	Tasselling	Harvest	Tasselling	Harvest	Tasselling	Harvest	Tasselling	Harvest	Tasselling	Harvest
Control	4.2	4.1	3.91	3.8	33.61	34.3	34.6	30.5	13	11.8
KR1	4.8	4.7	4.11	4.0	20.12	29.3	12.6	13.3	6.5	5.4
KR2	5.0	4.9	4.14	4.1	19.29	27.2	10.4	11.5	4.3	3.3
LR1	4.5	5.0	3.96	4.5	29.3	30.5	28.2	8.9	11.4	3.2
LR2	4.5	5.7	3.97	5.1	26.02	30.0	26.5	2.5	9.8	0.9

APPENDIX 5.1 Means of concentrations of Al_T , Al_{Mono} , % of Al_T present as Al_{Mono} and soluble C measured after 3 days equilibration of 40 μM $AlCl_3$ with 0.2 g animal manures (cattle kraal, pig and poultry) for 3 days. LSD ($P \leq 0.05$) shown.

	pH	Al_T (μM)	Al_{Mono}	Soluble C	% of Al_T present as Al_{Mono}
Control	4.0	39.0	36.0	0.0	92.3
	4.5	15.0	14.0	0.0	90.0
	5.0	8.0	7.0	0.0	87.5
	5.5	4.0	3.5	0.0	87.5
	6.0	1.5	1.0	0.0	66.7
	6.5	1.0	0.6	0.0	60.0
Kraal	4.0	6.0	3.5	60.0	58.3
	4.5	3.0	1.7	61.6	56.7
	5.0	2.8	1.2	64.0	42.9
	5.5	2.3	0.5	65.6	21.7
	6.0	2.0	0.3	66.4	15.0
	6.5	2.0	0.12	49.6	6.0
Pig	4.0	12.0	0.6	107.2	5.0
	4.5	7.5	0.45	120.0	6.0
	5.0	6.0	0.4	136.0	6.7
	5.5	5.0	0.2	156.0	4.0
	6.0	4.5	0.1	160.0	2.2
	6.5	3.8	0.1	155.0	2.6
Poultry	4.0	10.0	0.2	240.0	2.0
	4.5	7.0	0.1	256.0	1.4
	5.0	6.0	0.1	272.0	1.7
	5.5	5.5	0.07	283.2	1.3
	6.0	5.2	0.05	284.0	1.0
	6.5	5.0	0.02	283.0	0.4
LSD ($P < 0.05$)	-	1.0	0.02	13.0	-

APPENDIX 5.2 Means of concentrations of Al_T , Al_{Mono} , % of Al_T present as Al_{Mono} and soluble C measured after equilibration of 10 g of an acid soil with 0.2 g animal manures for 3 days, LSD ($P \leq 0.05$) shown..

	pH	Al_T	Al_{Mono}	Soluble C	% of Al_T present as Al_{Mono}
Control	4.0	39.0	28.0	18.0	71.8
	4.5	18.0	14.0	19.5	77.8
	5.0	10.0	8.0	22.5	80.0
	5.5	5.0	2.5	22.5	50.0
	6.0	4.0	2.0	21.75	50.0
	6.5	3.0	1.7	21.5	56.7
Kraal	4.0	24	22.0	27.3	91.7
	4.5	15	10.0	30.0	66.7
	5.0	8.8	4.0	34.2	45.5
	5.5	6.7	3.0	33.6	44.8
	6.0	4.0	1.0	35.5	25.0
	6.5	3.5	0.5	36.0	14.3
Pig	4.0	23	21.5	84.4	93.5
	4.5	12	11.0	87.9	91.7
	5.0	9.0	4.0	88.5	44.4
	5.5	7.0	1.6	90.0	22.9
	6.0	6.5	1.2	93.3	18.5
	6.5	4.5	0.5	99.3	11.1
Poultry	4.0	32	23.0	144.4	71.9
	4.5	21.5	13.0	145.0	60.5
	5.0	14	4.0	146.1	28.6
	5.5	9.0	2.0	147	22.2
	6.0	8.0	0.8	147.7	10.0
	6.5	9.0	0.4	143.8	4.4
LSD ($P < 0.05$)	-	1.6	0.3	42.0	-

APPENDIX 5.3 Means of concentrations of NH_4^+ and NO_3^- , pH_{water} and pH_{KCl} , following incubation of organic residues with an acid soil at a rate of 10 mg g^{-1} for 24 weeks.

	Incubation period (Weeks)				
	0	6	12	18	24
	NH_4^+ (mg kg^{-1})				
Control	0.9	7.2	8.8	8.1	1.1
soybean	0.9	19.7	12.3	8.9	6.2
cattle kraal manure	0.9	18.1	9.5	7.0	5.6
Layer poultry manure	0.9	110.0	98.0	24.0	23.0
pig manure	0.9	26.4	20.7	7.0	6.0
Sewage sludge	0.9	105.7	89.3	82.0	70.0
LSD ($P \leq 0.05$)		6.2	6.2	7.2	7.2
	NO_3^- (mg kg^{-1})				
Control	18.2	26.5	36.8	33.9	18.6
soybean	18.2	34.1	78.8	84.1	71.2
cattle kraal manure	18.2	42.0	39.5	32.0	27.6
Layer poultry manure	18.2	199.0	202.0	62.0	54.0
pig manure	18.2	45.4	78.8	64.0	60.3
Sewage sludge	18.2	129	141.9	132.0	120.0
LSD ($P \leq 0.05$)		10.3	10.3	13	13
	pH_{water}				
Control	4.1	4.2	3.9	3.9	4.0
cattle kraal manure	4.8	4.5	4.1	4.1	4.1
Layer poultry manure	6.2	6.8	5.2	5.2	4.8
pig manure	5.3	5.0	4.5	4.3	4.3
Sewage sludge	5.6	5.1	4.7	4.2	4.0
LSD ($P \leq 0.05$)		0.6	0.6	0.7	0.7
	pH_{KCl}				
Control	3.8	3.8	3.8	3.7	3.8
cattle kraal manure	4.5	4.2	3.8	3.8	3.8
Layer poultry manure	6.0	6.6	5.0	5.1	4.7
pig manure	4.8	4.5	4.0	3.9	3.9
Sewage sludge	4.2	4.1	4.0	3.8	3.8
LSD ($P \leq 0.05$)		0.5	0.5	0.4	0.4

APPENDIX 5.4 Means of concentrations of NH_4^+ , NO_3^- and pH_{water} and pH_{KCl} , following incubation of organic residues with an acid soil at a rate of 20 mg g^{-1} for 24 weeks.

	Incubation period (Weeks)			
	6	12	18	24
	NH_4^+ (mg kg^{-1})			
Control	7.2	8.9	8.8	1.1
soybean	25.6	20.2	16.3	15.8
cattle kraal manure	28.7	13.3	10.0	8.0
Layer poultry manure	152.0	131.3	32.0	31.0
pig manure	37.4	17.0	14.3	9.6
Sewage sludge	186.0	117.3	103.0	95.0
LSD (P < 0.05)	6.2	6.2	7.2	7.2
	NO_3^- (mg kg^{-1})			
Control	26.5	36.9	34.5	18.6
soybean	39.5	104.2	99.3	88.8
cattle kraal manure	57.6	59	54.1	46.5
Layer poultry manure	232	232.3	72	64
pig manure	54.6	106.2	93.6	65.6
Sewage sludge	209.4	230.3	204	184
LSD (P < 0.05)	10.3	10.3	13	13
	pH_{water}			
Control	4.08	3.93	3.9	3.98
cattle kraal manure	4.49	4.18	4.16	4.2
Layer poultry manure	6.83	5.37	5.5	5.25
pig manure	4.92	4.655	4.555	4.5
Sewage sludge	5.86	4.83	4.31	4.14
LSD (P < 0.05)	0.6	0.6	0.7	0.7
	pH_{KCl}			
Control	3.77	3.75	3.9	3.77
cattle kraal manure	4.3	3.84	3.81	3.83
Layer poultry manure	6.45	5.135	5.155	5.1
pig manure	4.85	4.4	4.1	4.1
Sewage sludge	4.53	4.08	3.885	3.9
LSD (P < 0.05)	0.5	0.5	0.4	0.4

APPENDIX 5.5 Means of concentrations of exchangeable Al, Al_T and Al_{Mono} following incubation of organic residues with an acid soil at two rates: 10 mg g⁻¹ and 20 mg g⁻¹ for 24 weeks.

	10 mg g ⁻¹		20 mg g ⁻¹	
	Incubation Period (Weeks)			
	6	24	6	24
Exchangeable Al concentrations (mmol _c kg ⁻¹)				
Control	11.48	13.04	11.48	13.04
cattle kraal manure	8.00	10.36	6.67	9.5
Layer poultry manure	1.85	4.00	1.19	3.4
pig manure	2.67	4.90	1.89	5.2
Sewage sludge	5.96	10.27	5.96	9
LSD (P ≤ 0.05)	2.5	2.5	2.5	2.5
Al _T concentrations (uM)				
Control	76.7	66	74.8	66
cattle kraal manure	71	53	62.65	49
Layer poultry manure	11.7	19	10.6	13.4
pig manure	13.2	40	13.2	31
Sewage sludge	14.3	45	12.3	41.5
LSD (P ≤ 0.05)	3.5	3.5	3.5	3.5
Al _{Mono} Concentrations (uM)				
Control	50.1	48	51.1	48.4
cattle kraal manure	23.8	26	25.45	21
Layer poultry manure	7.2	14	3.35	4.2
pig manure	6.8	21	7.9	17
Sewage sludge	7	25	7.1	21
LSD (P ≤ 0.05)	3	3	3	3

APPENDIX 6.1

Means of soil pH_{water}, pH_{KCl}, exchangeable Al, Al_T and Al_{Mono}, measured 6 weeks after planting and at tasselling following addition of kraal manure (kraal 1 = 10 t ha⁻¹, kraal 2 = 20 t ha⁻¹), grass residues (grass 1 = 10 t ha⁻¹, grass 2 = 20 t ha⁻¹), lime (lime 1 = 2.5 t ha⁻¹, lime 2 = 20 t ha⁻¹) and fertilizer on an acid soil.

	6 Weeks					Tasselling				
	pH _{water}	pH _{KCl}	Exchangeable Al mmol _c kg ⁻¹	Al _T uM	Al _{Mono} uM	pH _{water}	pH _{KCl}	Exchangeable Al mmol _c kg ⁻¹	Al _T uM	Al _{Mono} uM
Control	5	4.09	28	29	12	4.95	4.08	27	30.4	12
Kraal 1	5.4	4.28	7	23	5	5.3	4.28	9	23	6.6
Kraal 2	5.7	4.4	5	22	2	5.35	4.3	8	19	4
Grass 1	5.01	4.07	26	30	11	5.1	4.1	21	30	12.1
Grass 2	5.03	4.1	23	31	10	5.16	4.13	20.2	30.8	10.5
Lime 1	5.1	4.11	21	27	10	5.2	4.18	18	26	8
Lime 2	5.2	4.13	19	27	9	5.25	4.19	15	24	8.1
Control + F	4.7	4.07	29	33	11	4.8	4.07	29	32	12
Kraal 1 + F	4.8	4.21	14	23	7	4.95	4.2	15	23	7.6
Kraal 2 + F	4.9	4.27	12	24	5	5.1	4.28	12	22	6.4
Grass 1 + F	4.7	4.06	24	33	12	4.95	4.1	23	32	12.2
Grass 2 + F	4.9	4.09	21	32.5	13	5	4.13	18	31	11
Lime 1 + F	4.9	4.15	18.3	29	10	5.1	4.16	18	29	9
Lime 2 + F	5	4.17	18	28	9	5.2	4.2	15	27.2	8.4
inter rows	5.02	4.06	27.2	31	11.2	4.96	4.04	27.4	30	11.5
Undisturbed	5.5	4.5	4	21	2	5.52	4.47	5	19	4
LSD (P < 0.05)	0.20	0.12	5.24	4.56	3.51	0.11	0.12	6.27	4.94	3.07

APPENDIX 6.2

Means of soil pH_{water}, pH_{KCl}, exchangeable Al, Al_T Al_{Mono} and maize yields, measured at harvest following addition of kraal manure (kraal 1 = 10 t ha⁻¹, kraal 2 = 20 t ha⁻¹), grass residue (grass 1 = 10 t ha⁻¹, grass 2 = 20 t ha⁻¹), lime (lime 1 = 2.5 t ha⁻¹, lime 2 = 20 t ha⁻¹) and fertilizer to an acid soil.

	Maize yields	pH _{water}	pH _{KCl}	Exchangeable Al	Al _T	Al _{Mono}
	t ha ⁻¹			mmol _c kg ⁻¹	uM	
Control	2.5	5.04	4.07	26.3	30	13
Kraal 1	5.6	5.25	4.2	16	26	7.7
Kraal 2	7.9	5.3	4.25	14	23	6
Grass 1	3.3	5.26	4.17	17	27	8.6
Grass 2	3.54	5.28	4.18	16	26	8
Lime 1	3.4	5.3	4.25	11	21	7
Lime 2	4.7	5.5	4.33	9	16	4.4
Control + F	6.9	5.1	4.08	26	31	13.2
Kraal 1 + F	8.9	5.3	4.2	15.4	26	7.2
Kraal 2 + F	10.2	5.37	4.26	14.3	25.3	6.2
Grass 1 + F	6.5	5.3	4.19	21	27	9
Grass 2 + F	7.6	5.4	4.21	17	24	7.6
Lime 1 + F	7.5	5.25	4.22	14	23	7.2
Lime 2 + F	10.6	5.46	4.4	7	17	5
inter rows		5.1	4.1	28	31	12.4
Undisturbed		5.6	4.45	6	18.6	4.6
LSD (P < 0.05)	0.85	0.13	0.13	4.24	3.45	2.49

APPENDIX 6.3 Means of microbiological and biochemical indices measured in an acid soil 5 months after addition of kraal manure (kraal 2 = 20 t ha⁻¹), grass residues (grass 2 = 20 t ha⁻¹), lime (Lime 2 = 20 t ha⁻¹) and fertilizer

	Organic C	microbial	C _{mic}	metabolic	Basal	Arginine	Protease	Aryl	Acid	Alkaline
	g kg ⁻¹	quotient	mg C _{mic}	quotient	respiration	Ammonifi		sulphatase	phosphatase	phosphatase
		%	kg ⁻¹	ug CO ₂ -C	ug CO ₂ -C	cation		uM product g ⁻¹ h ⁻¹		
				mg ⁻¹ biomass day ⁻¹	g ⁻¹ day ⁻¹	g ⁻¹ h ⁻¹				
Control	42.00	1.36	572.37	41.93	24.00	32.00	0.14	0.40	14.50	4.60
Kraal 2	41.00	1.69	693.84	43.24	30.00	37.00	0.31	1.00	18.00	6.30
Grass 2	42.00	1.81	758.66	37.96	28.80	36.00	0.28	0.90	20.50	4.60
Lime 2	40.00	1.76	704.37	45.66	32.16	39.00	0.36	2.00	20.10	8.00
Control + F	40.00	1.47	586.00	43.41	25.44	33.00	0.17	0.73	16.30	4.40
Kraal 2 + F	41.00	1.67	683.35	47.41	32.40	38.00	0.35	1.50	21.30	5.20
Grass 2 + F	40.00	1.84	737.00	42.33	31.20	36.00	0.37	2.00	23.00	4.90
Lime 2 + F	40.00	1.73	692.23	49.58	34.32	39.00	0.39	2.50	24.00	7.10
Inter rows	41.00	1.16	477.21	52.30	24.96	31.00	0.13	0.60	15.00	5.00
Undisturbed	63.00	1.25	789.00	47.45	37.44	50.00	0.60	7.00	37.00	13.20
LSD (P ≤ 0.05)	1.348	0.1	35.82	6.72	3.84	2.473	0.04503	0.6105	2.069	1.248

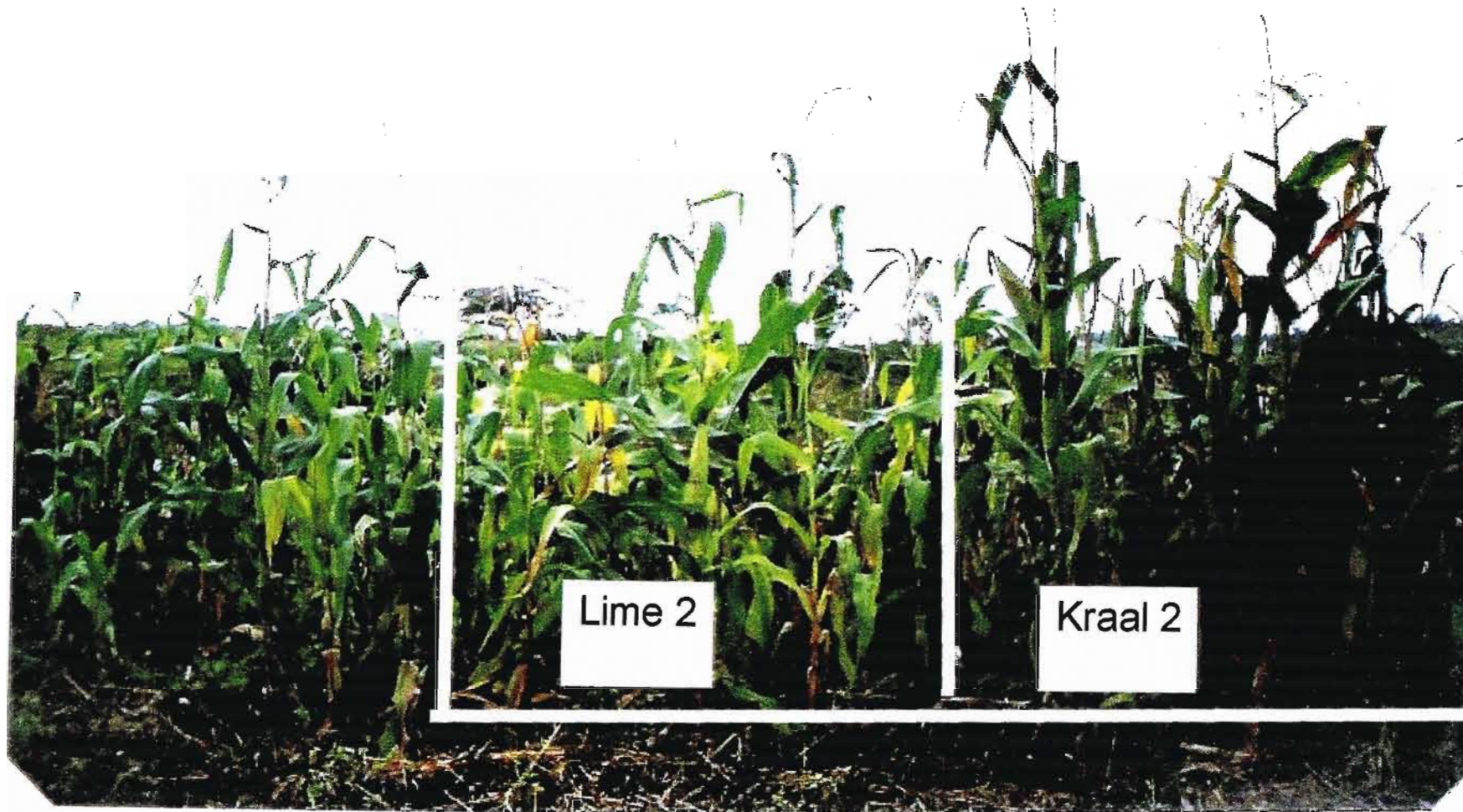
APPENDIX 6.4 Effect of kraal manure (kraal 1 = 10 t ha⁻¹) and grass residues (Grass 2 = 20 t ha⁻¹) on maize growth



APPENDIX 6.5 Effect of kraal manure (20 t ha⁻¹) on maize growth.



APPENDIX 6.6 Effects of lime (recommended rate) and Kraal manure (20 t ha⁻¹) on maize growth

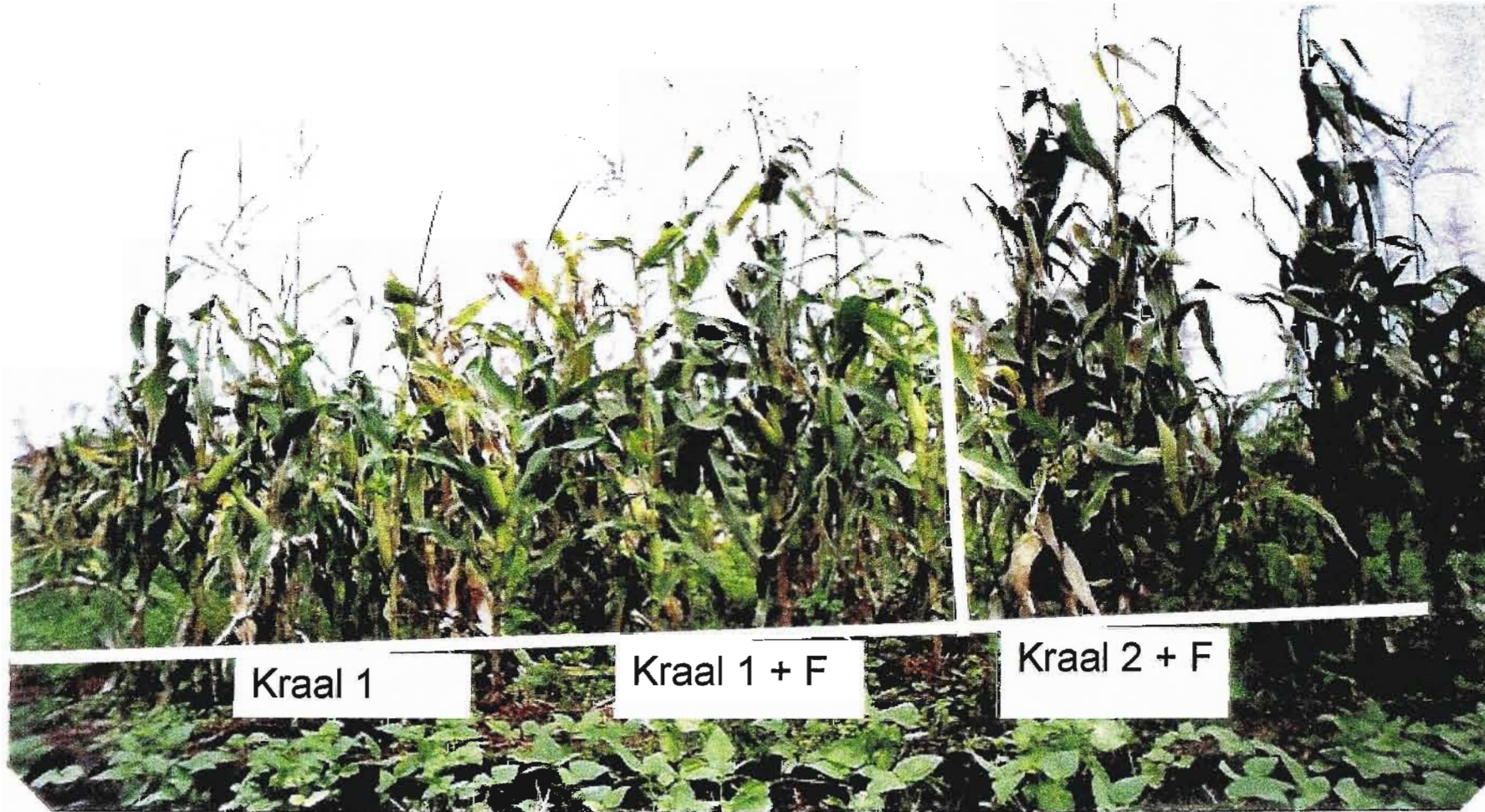


APPENDIX 6.7 Effects of addition of kraal manure (20 t ha^{-1}) and grass residue (20 t ha^{-1}) to an acid soil on maize growth



APPENDIX 6.8

Effects of kraal manure (20 t ha^{-1}) plus fertilizer kraal manure (10 t ha^{-1}) plus fertilizer and Kraal manure (10 t ha^{-1}) on maize growth.



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