

**THE EFFECTS OF SURFACE-APPLIED POULTRY MANURE ON  
TOP- AND SUBSOIL ACIDITY AND SELECTED SOIL FERTILITY  
CHARACTERISTICS**

**By**

**ANGUS JUDGE**

Submitted in partial fulfilment of the requirements for the degree of

**MASTER OF SCIENCE IN AGRICULTURE**

School of Applied Environmental Sciences

University of Natal

Pietermaritzburg

March 2001

## ABSTRACT

The effects of surface applications of poultry manure on pH, exchangeable Al, exchangeable Al saturation and levels of available macronutrients in the surface and subsurface layers were investigated in some acid soils from the KwaZulu-Natal Midlands. Three field sites with a history of long-term applications of poultry manure were compared with adjacent fields where no manure had been applied. Results generally showed an increase in  $\text{pH}_{\text{water}}$ ,  $\text{pH}_{\text{KCl}}$ , exchangeable Ca, Mg, and K and extractable P and a decrease in exchangeable Al and exchangeable Al saturation in the surface soil to the depth to which the manure had been incorporated. Results also provided evidence for substantial downward movement of Ca and Mg into the subsoil layers (i.e. 30-60 cm) and their accumulation in exchangeable forms. There was a concomitant general increase in  $\text{pH}_{\text{KCl}}$  and  $\text{pH}_{\text{water}}$  and decrease in exchangeable Al and exchangeable Al saturation in the subsoil layers. These results demonstrate that, under field conditions, surface applications of poultry manure can cause the amelioration of subsoil acidity. This is an extremely important finding since subsoil acidity is characteristically extremely difficult and costly to ameliorate.

A leaching column study was subsequently conducted to investigate the mechanisms by which surface applications of poultry manure ameliorate both top- and subsoil acidity. The soil used, originating from one of the field sites, had not previously been treated with poultry manure and had a subsoil  $\text{pH}_{\text{KCl}}$  of 4.25 and an exchangeable acidity concentration of 1.79 cmol/kg. Three forms of poultry manure (layer, broiler and free range) were incorporated into the surface 5 cm of soil columns at rates equivalent to 5, 10 and 30 Mg/ha. Columns were maintained in glasshouse conditions for a period of 108 days and over that period they were leached on four separate occasions (receiving a total of 825 mm of simulated rainfall). At the conclusion of the experiment, the soil columns were cut into sections for chemical analysis.

Applications of poultry manure to the surface soil markedly increased  $\text{pH}_{\text{water}}$ ,  $\text{pH}_{\text{KCl}}$ , exchangeable Ca, Mg, K and Na concentrations and decreased exchangeable Al levels in the surface 5 cm layer. They also increased the concentrations of soluble C, soluble salts, total Al and organically-complexed Al in soil solution. These effects were most pronounced with layer manure and greater at the higher rate of application. The manure-induced decrease in exchangeable Al, but increase in total Al, in soil solution was attributed to soluble salts,

originating from the manure, displacing exchangeable Al into solution where it was subsequently complexed by soluble organic matter.

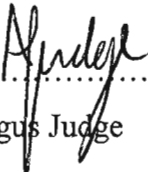
Analysis of subsoil layers (5-15, 15-25, 25-35 and 35-45 cm) at the conclusion of the experiment showed that surface applications of poultry manure decreased concentrations of exchangeable Al in the subsoil but had no effect on  $\text{pH}_{\text{KCl}}$  and depressed values for  $\text{pH}_{\text{water}}$ . It was suggested that manure-derived urea leached into the subsoil and was then hydrolysed causing an increase in pH and precipitation of exchangeable Al as insoluble hydroxy-Al oxides. Towards the conclusion of the experiment nitrification began to proceed, causing subsoil  $\text{pH}_{\text{KCl}}$  values to decrease back to their original values. Analysis of the inorganic-N content of leachates and soil layers provided circumstantial evidence for this mechanism. High concentrations of soluble salts in the subsoil layers (caused by leaching from the manure) resulted in displacement of exchangeable  $\text{Al}^{3+}$  and  $\text{H}^+$  into soil solution so that the electrical conductivity and concentrations of total and monomeric Al were elevated and  $\text{pH}_{\text{water}}$  was depressed in the subsoil (15-45 cm) of poultry manure-treated columns.

It was concluded that the results underline the opposing effects that poultry manure applications have on (i) raising soil pH and lowering exchangeable Al but at the same time (ii) greatly increasing soluble salt concentrations and thus displacing  $\text{Al}^{3+}$  and  $\text{H}^+$  back into soil solution. They also have suggested the importance of the release of N during manure decomposition in influencing soil pH (through the processes of ammonification, urea hydrolysis and nitrification) and therefore other soil chemical properties. It is, however, clear that the long-term effect of surface applications of poultry manure is generally to ameliorate subsoil acidity by raising subsoil pH and lowering exchangeable Al concentrations.

## DECLARATION

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

Signed:

.....  
Angus Judge

## ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to the following:

Professor Dick Haynes for trying to teach me to be a soil scientist and not someone merely studying soil science. His lessons in concise writing will not be forgotten.

The Soil Science Section at Cedara for providing me with an office, a laboratory, chemicals, soil analyses and helpful suggestions. In particular, my thanks go to Guy Thibaud, Alan Manson and Vic Roberts for lots of advice and laughs. Guy's suggestions with regard to the analyses of aluminium were invaluable.

The staff of the Soil Science section at the University of Natal, who were always helpful and willing to share their experience and wisdom.

The staff of the Soil Fertility Advisory Service of the South African Sugar Association Experimental Station, who analysed several soil samples.

Mrs. Margie Whitwell for assisting with biometrical analyses of the data.

The ARC-Institute for Soil, Climate and Water for providing the funding and time necessary to complete this project.

Ms. Iona Hendry, whose help ensured that this thesis was handed in on time.

And lastly, my family for their encouragement and support.

# TABLE OF CONTENTS

	Page
ABSTRACT.....	i
DECLARATION.....	iii
ACKNOWLEDGEMENTS.....	iv
GENERAL INTRODUCTION.....	1
<b>CHAPTER 1: THE EFFECTS OF SURFACE-APPLIED POULTRY MANURE ON SOIL ACIDITY AND SELECTED SOIL FERTILITY CHARACTERISTICS: A LITERATURE REVIEW.....</b>	<b>3</b>
<b>1.1 The chemical composition of poultry manure and the factors     affecting it.....</b>	<b>3</b>
<b>1.2 The effects of poultry manure additions on some soil fertility     characteristics.....</b>	<b>6</b>
1.2.1 Organic carbon.....	6
1.2.2 Nitrogen (N).....	7
1.2.3 Phosphorus (P).....	10
1.2.4 Base cations (Ca, Mg, Na and K).....	12
1.2.5 Cation Exchange Capacity (CEC).....	13
<b>1.3 The effects of poultry manure applications on topsoil and subsoil     acidity.....</b>	<b>13</b>
1.3.1 The development of low pH in soils and the consequences thereof.....	13
1.3.2 Effects on topsoil pH and the possible mechanisms involved.....	15
1.3.3 Effects on subsoil pH and the possible mechanisms involved.....	21
<b>1.4 The effects of poultry manure additions on Al toxicity in soils.....</b>	<b>29</b>

1.4.1	Basic principles of Al in solution and Al-induced toxicity.....	30
1.4.2	Detoxification of soil Al by compounds released from poultry manure.....	34
<b>1.5</b>	<b>Identification of possible areas for future research.....</b>	<b>43</b>
<b>CHAPTER 2: THE EFFECTS OF LONG-TERM APPLICATIONS OF POULTRY MANURE ON SOME SOIL CHEMICAL PROPERTIES, PARTICULARLY TOP- AND SUBSOIL ACIDITY, OF SELECTED KWAZULU-NATAL SOILS.....</b>		
<b>2.1</b>	<b>Materials and methods.....</b>	<b>47</b>
2.1.1	Site selection and sampling procedures.....	47
2.1.2	Chemical analyses.....	48
<b>2.2</b>	<b>The effects on soil chemical properties, particularly soil acidity.....</b>	<b>49</b>
<b>CHAPTER 3: THE EFFECTS OF SURFACE-APPLIED POULTRY MANURE ON SOIL PROFILE ACIDITY: A LEACHING COLUMN STUDY.....</b>		
<b>3.1</b>	<b>Materials and methods.....</b>	<b>57</b>
3.1.1	The soil.....	57
3.1.2	The poultry manures.....	58
3.1.3	The leaching column experiment.....	59
3.1.4	Chemical analyses.....	61
<b>3.2</b>	<b>Effects of poultry manure additions on topsoil acidity, subsoil acidity and aluminium in the soil solution.....</b>	<b>64</b>
3.2.1	Effects on pH, exchangeable Al and soluble Al in the topsoil (zone of application).....	64
3.2.2	Effects on subsoil acidity.....	79
3.2.2	Effects on Al in the soil solution.....	92
<b>GENERAL CONCLUSIONS.....</b>		<b>99</b>
<b>LIST OF REFERENCES.....</b>		<b>102</b>

**APPENDIX 1.....112**



## LIST OF FIGURES

Figure 1.1: Forms and fate of poultry manure derived-N following addition to soils (Sims and Wolf, 1994).....	8
Figure 1.2: Relationship between the base cation content of added organic materials and the pH at day 574 after application of the organic materials (from Pocknee and Sumner,1997)..	18
Figure 1.3: Soil-solution pH of an acid Ultisol profile (packed column) as affected by surface applications of gypsum, lime, chicken manure or sewerage sludge (from Hue and Licudine,1999).....	22
Figure 1.4: Adsorption isotherms of humic acid in 0.1M NaCl on gibbsite and goethite (from Parfitt <i>et al.</i> , 1977a).....	24
Figure 1.5: The adsorption of oxalate onto an Al hydrous oxide surface (from Haynes and Moklobate, 1999).....	27
Figure 1.6: The effect of pH on the solubility of Al in soil solution (from Haynes, 1984a).....	31
Figure 1.7: Exchangeable Al ( <i>a</i> ) and percentage of Al saturation ( <i>b</i> ) of an acid Ultisol profile (packed column) as affected by surface application of gypsum, lime, chicken manure, or sewerage sludge (from Hue and Licudine, 1999).....	35
Figure 1.8: The chelate structure of Al <sup>3+</sup> with citrate (from Stevenson and Vance, 1989).....	39
Figure 1.9: The mechanisms of Al complexation by the active sites on humic molecules (from Stevenson and Vance, 1989).....	41
Figure 2.1: Acid (Al <sup>3+</sup> + H <sup>+</sup> ) saturation (%) values at 10cm depth increments down the profiles of manure-amended and control plots at Sites A, B and C.....	54

Figure 2.2: Exchangeable acidity ( $Al^{3+} + H^+$ ) concentrations at 10cm depth increments down the profiles of manure-amended and control plots at Sites A, B and C.....54

Figure 3.1: Longitudinal section through a leaching column showing the packing structure..60

Figure 3.2: Trial layout of the leaching column experiment.....62

Figure 3.3: The suction system used to bring the leaching columns back to field moisture capacity following each leaching event.....62

Figure 3.4: Soil  $pH_{KCl}$  and exchangeable acidity ( $Al^{3+} + H^+$ ) concentrations in the 0-5cm segment of various treatments at the end of the 108 day experimental period.....65

Figure 3.5: Concentrations (mg N/l) of nitrate and ammonium as measured in the leachates from each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments. Note: LSD (5%) values were calculated on log-transformed data (not shown). A \* represents statistical significance between treatments at the 5% level.....70

Figure 3.6: Concentrations (mmol/l) of Ca, Mg, Na and K as measured in the leachates from each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments. Note: LSD (5%) values were calculated on log-transformed data (not shown). A \* represents statistical significance between treatments at the 5% level.....71

Figure 3.7: (a) Soil  $pH_{KCl}$  values for the control (C), 5 Mg/ha (5L), 10 Mg/ha (10L) and 30Mg/ha (30L) layer manure treatments at the end of the 108 day experimental period; (b) soil  $pH_{water}$  values for the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period.....81

Figure 3.8: Total and monomeric Al concentrations ( $\mu M$ ) as measured in each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments.....84

Figure 3.9: (a) Soluble organic carbon concentrations (mg C/l) down the profiles of the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period; (b) Soluble organic carbon concentrations (mg C/l) as measured in each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments. Note: LSD (5%) values were calculated on log-transformed data (not shown). A \* represents statistical significance between treatments at the 5% level.....85

Figure 3.10: Total and monomeric Al concentrations ( $\mu\text{M}$ ) measured in soil solution at various depths down the profiles of the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period.....94

Figure 3.11: The proportion (%) of total Al in soil solution existing in monomeric form at various depths at the end of the 108 day experimental period.....96

Figure 3.12: Root proliferation into the subsoils of the 10 Mg/ha layer manure (left) and control (right) treatments.....98

## LIST OF TABLES

Table 1.1: Summary of several studies documenting the inorganic composition of different poultry manure types.....	4
Table 1.2: Possible inorganic reactions of Al in the soil solution (from Ritchie, 1989).....	32
Table 1.3: Calculated stability constants for some Al- [organic molecule] complexes (from Hue <i>et al.</i> , 1986).....	37
Table 2.1: Extractable Ca, Mg, Na, K and P concentrations at 10cm depth increments down the profiles of manure-amended and control treatments at Sites A, B and C. Figure in brackets denote standard errors.....	50
Table 2.2: Soil pH values, measured in both water and KCl, at 10cm depth increments down the profiles of manure-amended and control treatments at Sites A, B and C. Figure in brackets denote standard errors.....	52
Table 3.1: Chemical compositions of the three poultry manure types used.....	58
Table 3.2: Carbonate contents (g/kg) measured in the three poultry manure types, ground either to <2mm or <150µm.....	66
Table 3.3: Extractable ammonium-N and nitrate-N concentrations (mg N/l) at various depths down the profiles of the control and layer manure treatments at the end of the 108 day experimental period.....	73
Table 3.4: Ca, Mg, Na and K concentrations (mmol/l) in the soil solution at various depths down the profiles of the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period.....	73

Table 3.5: Soil solution Al concentrations ( $\mu\text{M}$ ) and exchangeable acidity values ( $\text{cmol}_e/\text{kg}$ ) in the 0-5cm segment of the control and 30 Mg/ha layer manure treatments at the end of the 108 day experimental period.....	76
Table 3.6: Concentrations of exchangeable Al ( $\text{cmol}_e/\text{kg}$ ), soluble organic carbon ( $\text{mg C/l}$ ) and Ca, Mg, Na and K ( $\text{mmol/l}$ ) in the soil solution of the 0-5cm segment of the control and 30 Mg/ha layer manure treatments at the end of the 108 day experimental period.....	77
Table 3.7: Exchangeable Al concentrations ( $\text{cmol}_e/\text{kg}$ ) at various depths in the control and layer manure treatments.....	80
Table 3.8: Concentrations of Al ( $\text{cmol}_e/\text{kg}$ ) extracted from the control (C) and 30 Mg/ha layer manure (30L) treatments at various depths with different extractants (KCl, $\text{CuCl}_2$ , ammonium acetate and ammonium oxalate).....	86
Table 3.9: $\Delta\text{NH}_4^+$ and $\Delta\text{K}$ values for the 30 Mg/ha broiler litter (30B) treatment. Note: $\Delta$ represents the difference between the treatment concentration and the control concentration.....	89
Table 3.10: Exchangeable Al ( $\text{cmol}_e/\text{kg}$ ), $\text{NH}_4^+$ and $\text{NO}_3^-$ ( $\text{mg N/kg}$ ) concentrations at various depths for 10 Mg/ha layer manure treatments with plants (10LP) and without plants (10L) at the end of the 108 day experimental period.....	92
Table 3.11: Electrical conductivity (EC) values ( $\text{mS/m}$ ), ionic strength values ( $\text{mol/l}$ ) and concentration and activity of monomeric Al ( $\mu\text{mol/l}$ ) in soil solution at various depths of the control (C) and 30 Mg/ha layer manure (30L) treatments.....	97

## GENERAL INTRODUCTION

Poultry manure contains all of the essential plant nutrients (N, P, K, S, Ca, B, Mg, Na, Cu, Fe, Mn, Mo and Zn) (Sims and Wolf, 1994) and has been reported by many workers to be a valuable source of nutrients when incorporated into a fertilization program for agronomic crops (Wilkinson, 1979; Simpson, 1990). As a result, poultry manure has been widely used to increase crop yields and reduce the inputs of inorganic fertilizers. Poultry manure additions have the additional advantage of increasing the soil organic matter content (Kingery *et al.*, 1994), thereby improving the physical and biological status of the soil. The effects of poultry manure additions on soil fertility, in particular top- and subsoil acidity, will be the focus of this thesis.

Soils become naturally acidified in high rainfall areas as a result of the leaching of basic cations from their profiles, and the replacement of these basic cations with acidic  $\text{Al}^{3+}$  and  $\text{H}^+$  ions (Adams, 1981). These acidic cations are released from weathering minerals in the soil, and the released Al, in the monomeric form, is toxic to plants (Adams, 1981). The long-term use of nitrogenous fertilizers on many commercial farms, coupled with an increase in the volume of acid rain, has exaggerated the acidity problem in many cases (Tisdale, *et al.*, 1985). The Al toxicity associated with soil acidity causes reduced root growth in crop plants (Foy, 1988). This limits the volume of soil that the crop can explore for water and nutrients, thereby reducing crop growth and ultimately yield. Topsoil acidity is usually ameliorated via the incorporation of agricultural lime, whereas subsoil acidity amelioration requires the use of specialised 'deep-liming' equipment or surface applications of gypsum (Farina *et al.*, 2000).

Several workers have reported changes in soil acidity following poultry manure additions, although these reports have been somewhat contradictory (Sims and Wolf, 1994). In many cases, the addition of poultry manure has been reported to increase soil pH and decrease exchangeable Al concentrations in both the top- and subsoils of amended profiles (Kingery *et al.*, 1994; Hue and Licudine, 1999). Given the high costs associated with the amelioration of subsoil acidity by conventional means, this has large implications for farming areas where subsoil acidity is a constraining factor. The aim of this thesis is to study, in more detail, the effects of surface applied poultry manure on both top- and subsoil acidity.

Chapter 1 is a review of the literature pertaining to the effects of poultry manure applications on soil fertility, in particular, soil acidity. This study of the literature highlighted possible areas for future research and, based on these findings, the studies discussed in Chapters 2 and 3 were initiated. The effects of long-term applications of poultry manure on the top- and subsoil acidity of some acid KwaZulu-Natal soils has been discussed in Chapter 2. Based on the findings of this study, a leaching column trial was established to identify the mechanisms by which manure applications caused the changes noted in Chapter 2. The data obtained from the leaching column trial has been reported and discussed in Chapter 3.

It is hoped that this thesis will provide valuable guidance for those wishing to apply poultry manure to their lands, especially with the prediction of the possible changes in soil acidity that may occur. The application of poultry manure to soils should, however, always be preceded by some careful consideration, since it can have some negative effects. These negative effects are beyond the scope of this thesis and shall merely be listed as follows: (a) contamination of groundwater reserves by nitrate leaching; (b) eutrophication of surface waters induced by the surface runoff of phosphorus-rich soil; (c) increased soil concentrations of heavy metals resulting from the continual over-application of the manure; and (d) contamination from pesticides and antibiotics in the manure (Sims and Wolf, 1994).

# **CHAPTER 1**

## **THE EFFECTS OF SURFACE-APPLIED POULTRY MANURE ON SOIL ACIDITY AND SELECTED SOIL FERTILITY CHARACTERISTICS: A LITERATURE REVIEW**

### **INTRODUCTION**

The effects of poultry manure applications on various aspects of soil fertility have been studied extensively, both locally and internationally. The aim of this chapter is to review the available literature and provide a detailed report of the soil chemical changes that occur following poultry manure additions to soils, especially the changes in top- and subsoil acidity. The findings reported in this chapter highlighted possible areas where further research was necessary and, based on these findings, the experiments discussed in Chapters 2 and 3 were established.

Different types of poultry manures can have very different chemical compositions. Since it is the chemical composition that determines the manure's effect on soil fertility, it is important to understand how this can vary between different manures and what the causes are for these variations. Therefore, this chapter will begin with a study of the chemical compositions of different poultry manures, and then move onto the effects of these manures on soil chemical properties.

### **1.1 THE CHEMICAL COMPOSITION OF POULTRY MANURE AND THE FACTORS AFFECTING IT**

The major poultry production operations include layer chickens (egg producers), turkeys and broiler chickens (for meat) (Sims and Wolf, 1994). For the purpose of this review, the focus will be on the manure produced by broiler and layer chickens. Two types of confinement housings are most commonly used for poultry operations, namely cage-pit systems (used mostly for layer chickens) and floor/litter systems (for broiler chickens) (Sims and Wolf, 1994). With the former system, the layer hens are confined in cages that are suspended above a pit into which the waste falls. Manure from a cage-pit system contains no bedding material



and is usually semi-solid or liquid in nature. Floor/litter systems consist of confinement houses with a concrete floor that is covered with 5 to 15cm of litter material such as sawdust or woodchips (Sims and Wolf, 1994). These materials absorb the moisture, and the resulting product (known as broiler litter) is more solid than just the manure on its own. Broiler litter and layer manure consist of both organic and inorganic fractions, and some moisture. Several workers have analyzed the inorganic composition of litters and manures, and their results are summarized in Table 1.1. Poultry manure is normally an alkaline material, with pH values ranging from 7.5 to 8.5 (Sims and Wolf, 1994).

Table 1.1: Summary of several studies documenting the inorganic composition of poultry manures and litters.

Description of poultry waste	Composition of waste (where ranges were published, only averages are given)												
	Content (%)							Content (mg/kg)					
	N	NH <sub>4</sub>	P	K	S	Ca	Mg	B	Cu	Mn	Zn	Fe	
Broiler litter (1)	4.0	-	1.6	2.3	0.5	2.3	0.5	54	473	348	315	-	
Broiler litter (2)	3.9	1.1	1.9	2.4	0.7	2.4	0.7	-	377	355	341	-	
Broiler litter (3)	4.3	1.1	2.1	2.6	0.7	2.3	1.0	-	251	309	338	-	
Broiler litter (4)	4.6	-	1.6	1.9	-	1.9	0.5	41	105	242	253	490	
Hen manure (3)	4.4	1.5	1.9	2.8	0.7	10.1	1.4	-	160	296	226	-	
Hen litter (4)	3.3	-	2.3	2.3	-	6.1	0.54	40	71	251	330	340	
Hen litter (5)	2.0	-	1.9	1.9	0.5	3.42	0.5	28	31	333	120	1347	

(All data reported on a dry weight basis)

- (1) Stephenson *et al.* (1990)
- (2) Malone (1992)
- (3) Bandel, V.A. (personal communication, 1989) (cited in Sims and Wolf, 1994)
- (4) El-Sabben *et al.* (1969)
- (5) Perkins and Parker (1971)

Substantially less research has been done on the organic fraction of poultry manure. However, Smith (1973) showed that the average contents of hemicellulose, cellulose and lignin were 17, 13 and 4% respectively (by weight) for several broiler litters and layer manures studied. Work by Prasad and Sinha (1980) revealed that poultry manure also contains humic and fulvic acids, and Tan *et al.* (1971) reported that infrared analyses of poultry wastes revealed

spectrograms of ligands with a polysaccharide nature.

In birds, excess nitrogen is excreted in the form of uric acid as a means of saving water, and hence uric acid is also an important organic constituent of poultry manure (Schefferle, 1965). Gordillo and Cabrera (1997) found that the uric acid contents of fifteen broiler litter samples ranged from 1.9 to 20.5 g uric acid-N/kg litter. These workers suggested that the moisture content of the manure plays an important role in the uric acid content; if it is too dry, then bacterial activity is reduced and the breakdown of uric acid is retarded (resulting in higher concentrations of uric acid).

Moisture contents of manures can vary greatly depending on the method of storage. In the fifteen samples analysed by Gordillo and Cabrera (1997), moisture contents ranged from 188 to 475 g water /kg litter. Parker *et al.* (1959) took 113 manure samples from commercial poultry farms in Northeast Georgia (USA), and found that the average moisture content of broiler litter and hen manure was 24.9% and 36.9% respectively. Similar results were obtained by Kunkle *et al.* (1981); they showed that the average moisture content of broiler litter after five flocks was 23.8%.

As illustrated in Table 1.1, the chemical composition of poultry manure is highly variable. Factors such as the type of poultry (broiler or hen), the diet and dietary supplements, litter type and handling and storage operations all contribute to the variability (Sims and Wolf, 1994). As an example, Parker *et al.* (1959) found a higher N content in broiler litter when compared with hen litter, which they speculated was caused by the higher protein content of broiler diets relative to hen diets. The longer periods of accumulation of hen manure, which permits greater N losses via volatilization, were also implicated. The moisture content of the manure is dependent on the amount and type of litter that is mixed in (the litter absorbs moisture), the building construction and the time of year of manure collection. Kunkle *et al.* (1981) reported that litter from broiler houses with dirt floors had less moisture than that from houses with concrete floors, and that the moisture content of litter was higher for broilers raised from October to March than for those from April to September.

Therefore, since so many factors affect the composition of poultry litter, it is clear that land applications of the litter should always be preceded by a chemical analysis of the litter to

quantify the amounts of elements/compounds that are being added.

## **1.2 THE EFFECTS OF POULTRY MANURE ADDITIONS ON SOME SOIL FERTILITY CHARACTERISTICS**

The fertilizer value of poultry manure has been well documented (Smith, 1973; Simpson, 1990), and can be highlighted by the following example. If broiler litter (75% solids) is applied at a rate of 9 tons/ha (a rate which is commonly used to provide sufficient N for agronomic crops) it will not only provide approximately the 270 kg N/ha required, but also about 100 kg P/ha, 165 kg Ca/ha, 165 kg K/ha, 45 kg S/ha and 45 kg Mg/ha (Sims and Wolf, 1994). This section will study, in more detail, the changes in soil fertility associated with poultry litter additions.

### **1.2.1. Organic carbon**

When poultry manure is added to a soil, the soil microbes will begin to decompose the organic fraction of the manure. However, not all of this fraction will be decomposed (Gordillo and Cabrera, 1997), and the organic compounds remaining will result in increased organic carbon contents in the soil. Evidence of this has been provided by Kingery *et al.* (1994), who studied paired sites (long-term manure applications versus no manure) and showed that long-term manure applications increased organic carbon to a depth of 15cm. Similar results on paired sites were obtained by Sharpley *et al.* (1993), who reported organic carbon increases to a depth of 25cm following long-term (>12 years) litter applications.

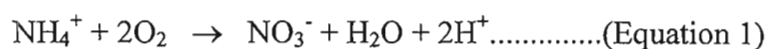
In some cases, however, the above trend does not occur. Jackson *et al.* (1977) reported that, after two litter applications (over a two year period), the organic matter content of the soil decreased, and proposed the following reason: The surface-applied poultry litter was relatively rich in N, of which over 50% was water soluble. It was therefore assumed that water percolating through the surface-applied litter would carry organic molecules with very low C/N ratios into the soil, thereby stimulating the microbial population and causing the increased breakdown of the native organic matter (Jackson *et al.*, 1977).

Gale and Gilmour (1986) measured carbon mineralization kinetics for poultry litter added to

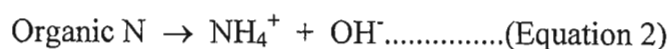
soil in incubation vessels. Based on CO<sub>2</sub> evolution rates, they reported a three-phase decomposition process consisting of an initial rapid phase (during the first 7 days) followed by an intermediate phase (between days 7 and 14) and then a final, slow phase. For the rapid, intermediate and slow phases, 25, 10 and 65% of the total litter C, respectively, were released.

### 1.2.2. Nitrogen (N)

The total N present in poultry waste occurs in 4 major forms (Sims and Wolf, 1994), as shown in Figure 1.1 which outlines the fate of N from poultry manure in the soil. The labile organic N consists largely of uric acid and urea. The uric acid is converted to urea in the fresh manure by the enzyme uricase (Sims and Wolf, 1994). The urea can then be hydrolysed (in the manure and in the soil) to ammonium, a process catalysed by the urease enzyme. It is this hydrolysis reaction that produces alkalinity and the resulting high pH found in the poultry manure (Schefferle, 1965). The presence of ammonium in the manure makes N losses via ammonia volatilization a possibility. In fact, up to 50% of the total N in surface-applied poultry waste can be lost via ammonia volatilization under conditions of high temperatures, moist soil conditions, high pH and windy conditions (Sims and Wolf, 1994). Once in the soil, the ammonium produced from breakdown of the uric acid can then be converted to NO<sub>3</sub><sup>-</sup> during the nitrification process, as outlined in equation 1 below:



The more complex, non-labile forms of organic N cannot simply be hydrolysed by enzyme-catalysed reactions to release inorganic N forms, as in the case of the uric acid described above. These larger organic compounds have to be mineralized, a process which is biologically mediated. Since these nitrogen transformations in soils are biologically controlled, they will be dependent on environmental factors such as temperature, moisture, pH and organic matter content. During this mineralization process the organic N is firstly ammonified, according to equation 2 below.



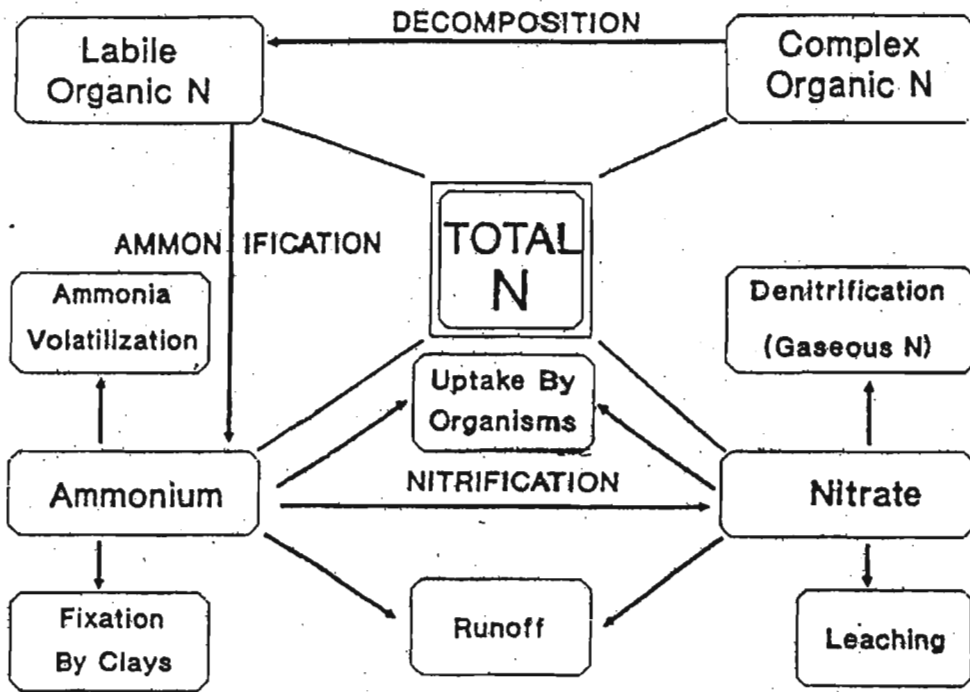


Figure 1.1: Forms and fate of poultry manure derived-N following addition to soils (Sims and Wolf, 1994).

The ammonium produced can then be nitrified to form nitrate, based on equation 1 above. Because equation 1 produces two  $H^+$  ions and equation 2 produces one  $OH^-$  ion, it is clear that these N transformations can have large, relatively short-term impacts on the soil pH. This will be discussed in Section 1.3.2.

Following the addition of poultry manure to soil, one needs to know how much of the total N in the manure is released into the soil, either by hydrolysis of the labile N forms or by mineralization of the non-labile forms. It is estimated that between 60% (Sims, 1987) and 90% (Pratt *et al.*, 1973) of the added N is mineralized to  $NH_4^+$  and  $NO_3^-$  in the first year. This has large implications for farmers wishing to estimate the amount of plant-available N released from the applied manure, and this has prompted workers such as Bitzer and Sims (1988) and Gordillo and Cabrera (1997) to derive equations to estimate the amount of mineralizable N in poultry manure based on the total N content of the manure.

However, not all of this potentially mineralizable-N is released at once. Hadas *et al.* (1983) showed N mineralization from poultry litter to be a two-step process. At 25°C, between 34 and 42% of the total manure N was mineralized during an initial, rapid phase, after which a second, slow-release phase occurred. After about 9-13 weeks, between 42 and 50% of the total N had been mineralized. This 'two-step' mineralization process was substantiated by Bitzer and Sims (1988).

Several workers have shown that the addition of poultry manure to soil results in increased total N contents in the upper 10-20cm of soil (Jackson *et al.*, 1977; Sharpley *et al.*, 1993; Kingery *et al.*, 1994). These same workers have shown that below this depth there is little difference in the total N and ammonium contents between littered and non-littered soils. However, they have shown that littered soils have higher nitrate concentrations down to depths of approximately 100cm when compared with non-littered soils. This occurs because the ammonium released from the decomposing manure is tightly held by 2:1 clay minerals in the soil, and is therefore less mobile than the nitrate that is released. This can have large implications for the leaching of nitrate to groundwaters.

### 1.2.3. Phosphorus (P)

Many workers have reported that the addition of poultry manure to soil results in greatly increased soil test P levels (Robertson and Wolford, 1970; Sims *et al.*, 1991; Sharpley *et al.*, 1993; Kingery *et al.*, 1994). At an application rate of broiler litter recommended for maize, soybeans and wheat for 2 years, the soil test P concentrations (Mehlich 1) increased by between 38 and 121 mg P/kg in littered soils relative to non-littered soils (Sims *et al.*, 1991). O'-Hallorans *et al.* (1997) reported that, 6 months after a 15 tons/ha application of manure, the soil test P concentration had increased from 34.14 to 178.04 mg P/kg. Using a higher application rate of 26 tons/ha/year of hen manure for 5 years, Robertson and Wolford (1970) reported increased soil test P (Bray 1) concentrations from 50 mg P/kg in the control plot to 147 mg P/kg in the manured plot on sandy loam soils.

There are several reasons why poultry manure increases soil test P concentrations. Firstly, as illustrated in Table 1.1, poultry manure contains approximately 1.5% P on a dry weight basis. As shown previously, the addition of 9 tons/ha of broiler litter will provide approximately 100 kg P/ha (Sims and Wolf, 1994) to the soil. Some of this added P will be in an organic form, but will be released as a plant available form as mineralization of the organic matter occurs. It has also been shown, however, that organic matter additions to soils can improve the availability of the P that is added (Hue *et al.*, 1994; Iyamuremye *et al.*, 1996). Several mechanisms have been proposed to explain this phenomenon.

#### A. Release of inorganic P:

As stated above, relatively large amounts of P can be added with poultry manure additions. As the organic matter is mineralized and the phosphate anions ( $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ) are released, so they are specifically adsorbed (via ligand exchange reactions) to the surfaces of amphoteric Fe and Al oxides (Parfitt, 1978) and the broken edges of clay minerals. As more P anions are adsorbed to the specific sites, so the sites become more saturated, and the P adsorption capacity is decreased in relation to subsequently added P (Iyamuremye *et al.*, 1996). This results in an increase in P availability.

### B. Increase in soil pH:

Poultry litter additions to soils have been shown to increase soil pH (Hue, 1992; Kingery *et al.*, 1994). The mechanisms responsible for this rise in pH are discussed in Section 1.3 of this chapter. This increase in soil pH will impart a greater negative charge on the amphoteric Fe and Al oxide surfaces to which the P adsorbed, which in turn could cause a reduction in sorption of the P anions, resulting in increased P availability (Iyamuremye *et al.*, 1996).

### C. Competition with organic molecules:

Low molecular weight organic acids and humic substances are capable of specifically adsorbing to oxide surfaces in soils (Nagarajah *et al.*, 1970; Parfitt *et al.*, 1977a+b). Not only does this reduce the number of sites available to fix P, but it has also been shown to increase the negative charge on the oxide surfaces, thereby reducing P sorption by electrostatic competition (Moshi *et al.*, 1974). The nature of these associations between oxide surfaces and organic molecules will be discussed in more detail in Section 1.3 of this chapter.

### D. Complexation of soluble aluminium (Al):

There is much literature on the ability of soluble organic compounds in the soil solution to form soluble complexes with Al (Hue and Amien, 1989; Stevenson and Vance, 1989; Hue, 1992). This topic will be dealt with in great detail in Section 1.4 of this chapter. Organic complexation of Al in solution lowers that activity of Al in soil solution, which in turn reduces the likelihood of insoluble Al-phosphates forming (Iyamuremye and Dick, 1996). The precipitation of Al-phosphate could be responsible for lowering the amount of available P, particularly in acid soils (Haynes, 1982).

Literature regarding the ability of P to move down the soil profile is somewhat contradictory. Because of the high adsorptive capacity of P in soils, workers such as Sharpley *et al.* (1993) and Lucero *et al.* (1995) have noted little or no downward movement of P beyond the depth of incorporation of the added P. However, other workers have shown significant downward movement of P in soil profiles, especially when the P existed in the organic form (Rolsten *et al.*, 1975; Sommers *et al.*, 1979). Also, Kingery *et al.* (1994) showed that, under long-term



broiler litter applications, profile distributions of extractable P indicated some downward movement of P to a depth of about 60cm in littered soils relative to non-littered soils. It is therefore possible that some of the organically-bound P added in poultry manure to soils could leach down the profile, thereby greatly reducing the problem of P deficiencies often associated with acid subsoils.

#### **1.2.4. Base cations (Ca, Mg, K and Na)**

Kingery *et al.* (1994) reported that long-term (15-28years) applications of broiler litter resulted in greater soil concentrations of extractable K, Ca and Mg at all depths in littered soils when compared with non-littered soils. Similar results were reported by Jackson *et al.* (1975). When one considers the K, Ca and Mg contents of poultry manure (Table 1.1) and the high rates (> 5 tons/ha/annum) of manure applications often used, these results are not surprising.

Jackson *et al.* (1975) used experimental plots with varying broiler litter application rates (for 2 years) to show that increasing application rates of poultry manure can lead to increased concentrations of water-soluble K, Ca and Mg at all soil depths. Both Ca and Mg concentrations were significantly higher at depths greater than 140cm for littered soils relative to non-littered soils, highlighting the downward mobility of these elements in manure amended soils. These workers explained this 'enhanced' downward mobility as follows:

Generally, broiler litter has relatively high contents of K and Ca, and lower contents of Mg. When applied to the soil, the K and Mg are more completely leached from the litter than the Ca. In fact, after 2 years of litter application, these workers found that about 80% of the applied Ca had remained in the litter (related possibly to the relative insolubility of Ca compounds formed in the litter). Over the same period, 99% and 88% of the K and Mg respectively had leached from the litter (Jackson *et al.*, 1975). This means that a relatively larger amount of K is entering the soil solution compared with Ca and Mg and, by the mechanism of mass action, this is forcing more Ca (that has been released) and Mg into solution where it is prone to leaching down the profile (Jackson *et al.*, 1975). The high concentrations of  $\text{NH}_4^+$  in manure-amended soils could enhance this mechanism by displacing K from the specific adsorption sites on 2:1 clay minerals, thereby further

increasing the concentration of K in soil solution (Hileman, 1971).

Hue and Licudine (1999) proposed an alternative mechanism to explain why Ca and Mg are highly mobile in manure-amended soils. They performed a leaching column experiment and suggested that increased concentrations of soil-solution carbon throughout the manure-amended soil columns (relative to a control receiving no manure) are reasonably closely correlated with increases in Ca in the columns ( $r^2=0.66$ ). It is therefore assumed that organic molecules released from the poultry manure are chelating Ca cations in a mobile form and facilitating the downward movement of the Ca. Inorganic anions such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  that are released from the litter can form ion pairs with Ca and Mg and also facilitate the downward movement of these cations. Hue and Licudine (1999) also reported that about 63% of the Ca in the manure was released and leached into the soil after 19 days. This value is in contrast to that of Jackson *et al.* (1975), who reported that only 20% of the Ca had been leached from the manure over a two year period.

#### **1.2.5. Cation Exchange Capacity (CEC)**

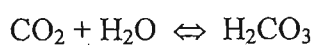
There is relatively little information on the effects of applied poultry litter on soil CEC. Rodella *et al.* (1995) incubated poultry litter with soil for a period of 90 days, and concluded that the efficiency of poultry litter (and other organic fertilizers) for increasing cation retention in acid soils is highly dependent on the resulting soil pH. These workers showed that poultry manure applications increased soil pH from 4.9 to 7.5 over a 90 day period. This increase imparts a greater negative charge to the variable-charge, amphoteric surfaces such as the broken edges of clay minerals, the surfaces of Al, Fe and Mn oxides and the functional groups of soil organic molecules, which in turn causes an increase in soil CEC. Also, as discussed above, it is likely that poultry manure additions will result in higher soil organic matter contents, which in turn will increase the CEC of the soil (Tisdale *et al.*, 1985).

### 1.3. THE EFFECTS OF POULTRY MANURE APPLICATIONS ON TOPSOIL AND SUBSOIL ACIDITY

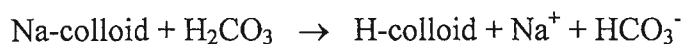
#### 1.3.1. The development of low pH in soils and the consequences thereof

Soil pH is one of the major factors controlling the chemical reactions (and hence the soil fertility) that occur within soils. Acidification of the soil profile occurs naturally in high rainfall areas where there is sufficient water leaching through the profile to cause the removal of basic cations and their replacement by acidic ( $\text{Al}^{3+}$  and  $\text{H}^+$ ) cations (Adams, 1981). Acid soils ( $\text{pH}_{\text{water}} < 5.5$ ) cover a substantial area of the ice-free land surface on earth.

The major chemical reaction associated with soil acidification is the hydrolytic dissociation of exchangeable bases (Fey *et al.*, 1990). The following example is provided: Micro-organisms respiring in the soil produce  $\text{CO}_2$ , which reacts with soil water to form  $\text{H}_2\text{CO}_3$ , according to the following reaction:



The following reaction then occurs, which results in the displacement of base cations ( $\text{Na}^+$ , for this example) from the exchange sites on soil colloids into the soil solution (Fey *et al.*, 1990):



Acidification occurs when the base cations (e.g. Na) are removed by plant uptake or leaching, which leaves the  $\text{H}^+$  ions behind on the soil colloids. An equilibrium exists between these  $\text{H}^+$  ions on the exchange sites and those in solution, and as more  $\text{H}^+$  ions enter the soil solution, so the soil pH decreases. Other biological  $\text{H}^+$ -producing mechanisms (such as the nitrification of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ , or the oxidation of organic-S to  $\text{SO}_4^{2-}$ ) can accelerate the acidification process (Adams, 1981). The microbial decomposition of soil organic matter can produce acidic functional groups on organic molecules that can dissociate and release  $\text{H}^+$  ions (Wong *et al.*, 1998), as can oxidation reactions in soils (Wild, 1994).

The predominant problem associated with low pH (acidic) soils is not directly the presence of the  $H^+$  ions, but rather the 'applied' effects of these ions. The  $H^+$  ions are small, highly charged entities that can react with the soil clay minerals and feldspars, facilitating the release of Al into the soil solution (Sanchez, 1976). At low pH, the Al is soluble and therefore plant available. Aluminium ions are toxic to plants, and it is this Al toxicity that is the predominant problem associated with low pH soils. Aluminium toxicity, and the alleviation thereof, will be dealt with more thoroughly in Section 1.4 of this chapter. The  $H^+$  ions present in low pH soils also impart a more positive charge on the amphoteric, variable-charged surfaces in soils. This can then cause increased sorption and decreased plant availability of nutrients such as P and S, resulting in nutrient deficiencies (Haynes, 1984a).

Except for soils that develop from highly weathered, acidic geologic materials, soil profile acidity generally develops first in the topsoil, where biological activity is greatest (Adams, 1981). As the surface soil pH decreases,  $Al^{3+}$  becomes more soluble and (along with  $H^+$  ions) it moves downward in the profile in conjunction with the leaching of  $NO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$  and organic anions (as ion pairs) (Adams, 1981). In high rainfall areas, as these acidic ions move down the profile, they displace the basic cations into solution, which are then leached out of the profile, generating subsoil acidity. As the subsoil pH gets lower, the Al will become more soluble and will be released from the subsoil clay minerals, generating Al toxicity in the subsoil.

Man's activities can accelerate the processes of soil acidification (Wild, 1994). The excessive use of nitrogenous fertilizers (especially ammonia-based fertilizers) in agriculture and the production of acid rain in the atmosphere (caused by increased concentrations of N and S being pumped out from industries into the atmosphere) produce excess  $H^+$  ions that contribute to acidification of the soil. Anthropogenically derived soil acidity can be very extensive in certain areas (Wild, 1994).

Since the solubility, and related toxicity of Al, depends very largely on the soil pH, the remainder of this chapter will focus on the ability of applied poultry manure to increase both the topsoil and subsoil pH.

### 1.3.2. Effects on topsoil pH and the possible mechanisms involved

Poultry manure is normally an alkaline material, with pH values ranging from approximately 7.5 to 8.5 (Sims and Wolf, 1994). These high pH values occur because birds excrete most of their nitrogenous waste as uric acid, which ultimately is hydrolysed to  $\text{NH}_4^+$ . This hydrolysis reaction generates alkalinity and consequently increases the pH of the manure (Schefferle, 1965). When added to soils, poultry manure can affect soil pH significantly, but the results reported have been somewhat contradictory. Indeed, factors such as experimental time period (related to short- and long-term N transformations) and soil buffer capacity should be considered when studying the effects of manure applications on soil pH.

In a pot trial lasting three months, Hue (1992) reported that poultry manure additions of 5 and 10 g manure/kg soil raised the soil pH the equivalent amount of 3.39 and 6.74 cmol/kg of  $\text{Ca}(\text{OH})_2$ , respectively. Kingery *et al.* (1994) showed that the long-term (15-28 years) application of broiler litter resulted in an increase in pH of approximately 0.5 units over a 0-60cm depth interval. Rodella *et al.* (1995) reported an increase in soil pH from 4.90 to 7.50 after incubating poultry manure with soil for a 90 day period. It was also shown by Sharpley *et al.* (1993) that poultry manure additions increase topsoil pH; they found average pH increases from 5.6 (in non-littered soils) to 6.2 (in a soil that received long-term litter applications). Recent work by Hue and Lucidine (1999) showed increases of nearly two pH units in the topsoil of soil columns that received 20 g/kg of poultry manure, relative to control columns with no manure.

In contradiction, however, Jackson *et al.* (1975) reported decreases in the soil pH after 2 years of broiler litter applications to field soils. Sims (1986) found that the addition of broiler litter to a loamy sand raised the pH from 6.5 to 7.5 immediately after application, but then the pH decreased to about 5.5. A similar trend in pH dynamics was reported by Hileman (1971), also on relatively sandy soils.

Since many workers have shown significant pH increases following poultry manure applications to soils, yet other results can be contradictory, it is important to consider the mechanisms behind the changes in the topsoil pH observed after manure has been added. Several mechanisms have been proposed to explain these changes, and these are outlined

below:

#### A. Nature and composition of the poultry manure:

As stated previously, poultry manure is normally an alkaline material, with pH values ranging from 7.5 to 8.5 (Sims and Wolf, 1994). It stands to reason, therefore, that the addition of an alkaline material to an acid soil could have the effect of raising the soil pH. In addition, Eghball (1999) noted that poultry diets usually contain CaCO<sub>3</sub>, and reported CaCO<sub>3</sub> contents of 11 g/kg and 77 g/kg in the diets of broiler and layer chickens respectively. The greater concentration in the feed of layer chickens is thought to increase the hardness of the eggshells produced. Since not all of this CaCO<sub>3</sub> is used by the bird and some of it is excreted, the manure can be a good lime source for acid soils (Eghball, 1999).

Pocknee and Sumner (1997) reported that the cation contents of organic material could also play a large role in determining its soil liming potential. Although their work was done on plant material, it is likely that similar results could be obtained using animal manures. Following the addition of organic matter to soils, these workers found that the final soil pH was well correlated with the concentrations of basic cations present in the organic matter. This relationship is illustrated graphically in Figure 1.2 (Pocknee and Sumner, 1997). These workers then postulated that the decomposition of base-cation containing organic molecules, such as Ca-oxalate and Ca-gluconate, could result in a pH increase in soils. Following the microbial decomposition of Ca-[organic acid] complexes, CaCO<sub>3</sub> forms, which is well known to increase soil pH upon dissolution. The reactions that lead to the formation of CaCO<sub>3</sub> are given below (shown for Ca-oxalate and Ca-gluconate):



Pocknee and Sumner (1997) showed that Ca-oxalate, Ca-gluconate and CaCO<sub>3</sub> all had identical effects on final pH when added to the soil at equimolar Ca rates. Their results were similar to those of Noble *et al.* (1996), who showed that the pH increase following organic matter additions was proportional to the quantity of ash alkalinity, i.e. the amount of [cation]-

[organic anion] complexes, of the material being added.

Since decomposing poultry manure contains basic cations and organic acids, it is likely that these [base cation]-[organic acid] complexes are forming in the soil following poultry manure additions. Therefore, the above-mentioned mechanism could be playing a large role in the increases in topsoil pH. It should be noted, however, that the organic acid must be complexed with a base cation to have a liming effect during decomposition. If complexed to a  $H^+$  ion, there will be no pH increase according to this proposed mechanism.

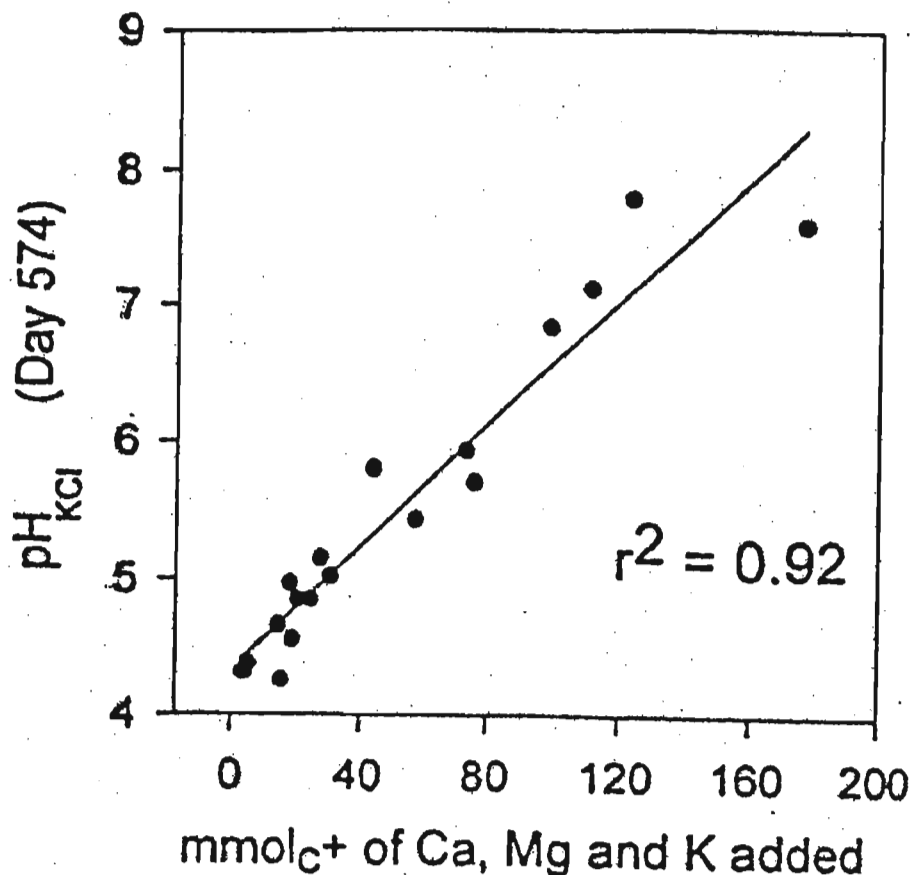


Figure 1.2: Relationship between the base cation content of added organic materials and the pH at day 574 after application of the organic materials (from Pocknee and Sumner, 1997).

The short-chain organic acids discussed above, coupled with the larger humic substances released by the decomposing manure, have been reported to have a proton consumption capacity in acid soils. Wong *et al.* (1998), for example, noted that the functional groups of phenolic humic and fulvic materials derived from organic residues are able to consume protons at their natural pH values, causing increased pH values when added to soils. Other workers have attributed the immediate rise in pH noted when undecomposed plant material is added to soils to the ability of organic acid anions (e.g. oxalate) in the plant material to consume protons (Tang *et al.*, 1999; Wong *et al.*, 2000). That is, if the soil pH is less than the dissociation constants (pKa) for the weak organic acids of the added residues, there will be an increase in soil pH due to the association of  $H^+$  ions in the soil with some of the organic acid anions.

#### B. Nitrogen transformations:

It is likely that N transformations are playing a major role in the changes in the soil pH following poultry manure additions. An initial rise in the soil pH after the manure application would occur via two major processes: Firstly, the ammonification of the organic-N compounds in the manure would cause the release of  $OH^-$  ions into the soil solution, as depicted in equation 2 of Section 1.2.2. Secondly, the uric acid in the manure would be broken down to urea, which in turn would be hydrolysed to  $NH_4^+$  (Sims and Wolf, 1994). This hydrolysis of the urea results in the production of  $HCO_3^-$  and  $OH^-$  anions, both of which are capable of neutralizing soil acidity (Tisdale *et al.*, 1985).

After a longer period, nitrification of the  $NH_4^+$  would occur, which would have an acidifying action, as depicted by equation 1 in Section 1.2.2. The nitrification reaction would produce two  $H^+$  ions per  $NH_4^+$  ion that is nitrified. However, the ammonification of the organic-N would produce only one  $OH^-$  ion per  $NH_4^+$  ion produced, as would the hydrolysis of the urea. Therefore, the nitrogen transformations following poultry manure additions are potentially acidifying in nature, provided that all of the  $NH_4^+$  produced is nitrified. Transient changes in pH will occur as these processes occur at different times. Nitrification, followed by leaching of the  $NO_3^-$  to leave the  $H^+$  behind, is the most likely reason why an initial pH increase is followed by a pH decrease after a longer time period following manure additions (Hoyt and Turner, 1975).

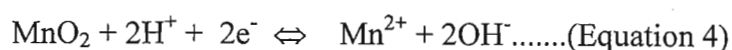
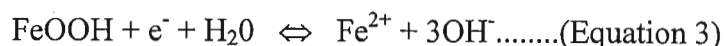


### C. Specific adsorption of organic molecules:

Organic molecules such as humic substances (humic and fulvic acids) and low molecular weight organic acids (e.g. citrate, oxalate and malate) are capable of undergoing specific adsorption reactions with sesquioxide surfaces in soils (Hue and Amien, 1989; Stevenson, 1994; Jones and Brassington, 1998). During these ligand exchange reactions, OH<sup>-</sup> ions are released into the soil solution, causing the pH to rise (Hue, 1992). This process is similar to the 'self-liming' effect of gypsum that was proposed by Sumner (1993). Although the adsorption reactions involving the low molecular weight organic acids and humic substances do occur in topsoils and therefore will play a role in increasing the topsoil pH, the exact nature of these reactions will only be discussed in more detail in Section 1.3.3.

### D. Reduction of oxidised soil compounds:

By adding poultry manure to soils, one is adding relatively large quantities of organic compounds to the soil that will stimulate intense, localized microbial activity around the organic compounds (Hue and Amien, 1989). The soil micro-organisms will begin to oxidise the organic matter, thereby releasing electrons from the organic matter and creating an 'electron-rich', reducing environment in the soil. This in turn causes the redox potential (Eh) of the soil to drop. The drop in soil Eh will be accompanied by the reduction of oxidised elements, such as Fe and Mn. The reduction reactions of these two elements are outlined below in equations 3 (Hue, 1992) and 4 (Hue and Amien, 1989):



It is clear from these two equations, that the reduction of oxidised soil compounds is accompanied by the release of OH<sup>-</sup> ions into the soil solution, thereby causing a localised increase in soil pH.

### **1.3.3. Effects on subsoil pH and the possible mechanisms involved**

As with the effects of poultry manure applications on topsoil pH, the results regarding changes in subsoil pH are contradictory. Sharpley *et al.* (1993) reported no difference in the soil pH below 10cm between sites receiving long term (12-35 years) poultry litter additions and sites that had received no litter. Jackson *et al.* (1975) showed decreases in subsoil pH (to approximately a 100 cm depth) after 2 years of broiler litter application to a field soil. In contrast, Kingery *et al.* (1994) reported that long-term (15-28 years) applications of broiler litter had caused an increase in the soil pH of approximately 0.5 units down to a depth of 60 cm, relative to non-littered soils. The results from some recent work by Hue and Licudine (1999) are illustrated in Figure 1.3. These results show that, in leaching columns, poultry manure significantly increased the soil-solution pH over that of the control at all depths.

Preliminary observations by Dr M.P.W. Farina (pers. comm.) in South Africa have shown that long-term (>10 years) applications of poultry manure at rates greater than 5 tons/ha/year to acid soils have generally resulted in a rise of 0.3 to 0.5 pH units to a depth of 60cm. Using long-term cattle manure applications to land, Lund and Doss (1980) reported pH increases in the depth range of 40-75cm, relative to non-manured soils.

Therefore, although it is somewhat contradictory, there is evidence to suggest that poultry (and cattle) manure additions to soils can lead to increases in subsoil pH. Since the conventional methods for ameliorating subsoil acidity are both costly and time-consuming, poultry manure may play an important role in future subsoil management schemes. It is important to try and elucidate the mechanisms by which the possible increases in subsoil pH occur. Some of the mechanisms that have been proposed are outlined below:

#### **A. Adsorption of humic substances:**

Humic substances are divided into two main types: humic acid and fulvic acid. These compounds are defined as complex systems of high molecular weight organic molecules made up of a core of phenolic polymers that are produced from the biological degradation of plant and animal residues (e.g. poultry litter) and the synthetic activity of micro-organisms (Stevenson, 1994).

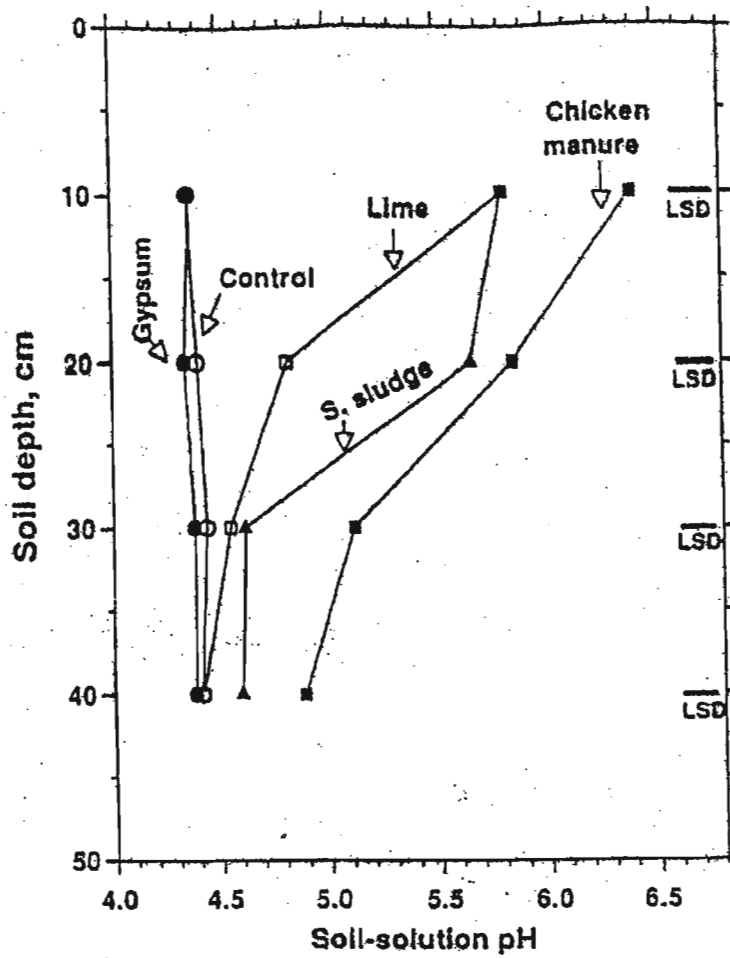


Figure 1.3: Soil-solution pH of an acid Ultisol profile (packed column) as affected by surface applications of gypsum, lime, chicken manure or sewerage sludge (from Hue and Licudine, 1999).

The humic fraction is defined as the organic material extracted from soil with an alkaline solution and then precipitated upon acidification, whereas the fulvic fraction is the fraction that remains in solution (Stevenson, 1994). Several workers have extracted humic and fulvic acids from poultry manure (Prasad and Sinha, 1980; Liu and Hue, 1996), proving that they exist naturally in the manure. Also, as soil micro-organisms degrade the manure, these humic substances will be synthesized by the organisms. There is therefore little doubt that the concentrations of humic substances will be increased in the soil following the addition of poultry manure.

Fulvic and humic acids, occurring as Ca-fulvates and Ca-humates, have been shown to be mobile in the soils and capable of leaching down the profile into the subsoil (van der Watt *et al.*, 1991; Noble *et al.*, 1995; Smith *et al.*, 1995; Liu and Hue, 1996). Noble *et al.* (1995) and van der Watt *et al.* (1991) both reported increases in subsoil pH following the addition of Ca-fulvates and Ca-humates to leaching columns. In contrast to these findings, Liu and Hue (1996) reported that the addition of Ca-fulvates either did not affect or lowered the soil pH below the 10cm depth, but they could give no definitive explanation for the results. The mechanisms behind the reported changes in pH will be discussed below:

Humic substances have a high content of oxygen-containing functional groups, which include COOH, phenolic-OH, enolic-OH, alcoholic-OH, and C=O groups (Stevenson and Vance, 1989). As the pH increases, deprotonation of these functional groups will occur, imparting a negative charge onto the humic molecule. These negatively charged, high molecular weight humic polymers can then form strong bonds with metal hydrous oxide surfaces through both specific adsorption (ligand exchange) and electrostatic bonding (anion exchange) (Stevenson, 1994). The adsorption isotherms of humic acid on gibbsite and goethite are shown in Figure 1.4 (Parfitt *et al.*, 1977a). These isotherms are L-type curves (Langmuir adsorption isotherms), which reflect a relatively high affinity of the humic molecules for the hydrous oxide surfaces. These L-type curves are usually indicative of chemisorption (e.g. ligand exchange reactions) (McBride, 1994).

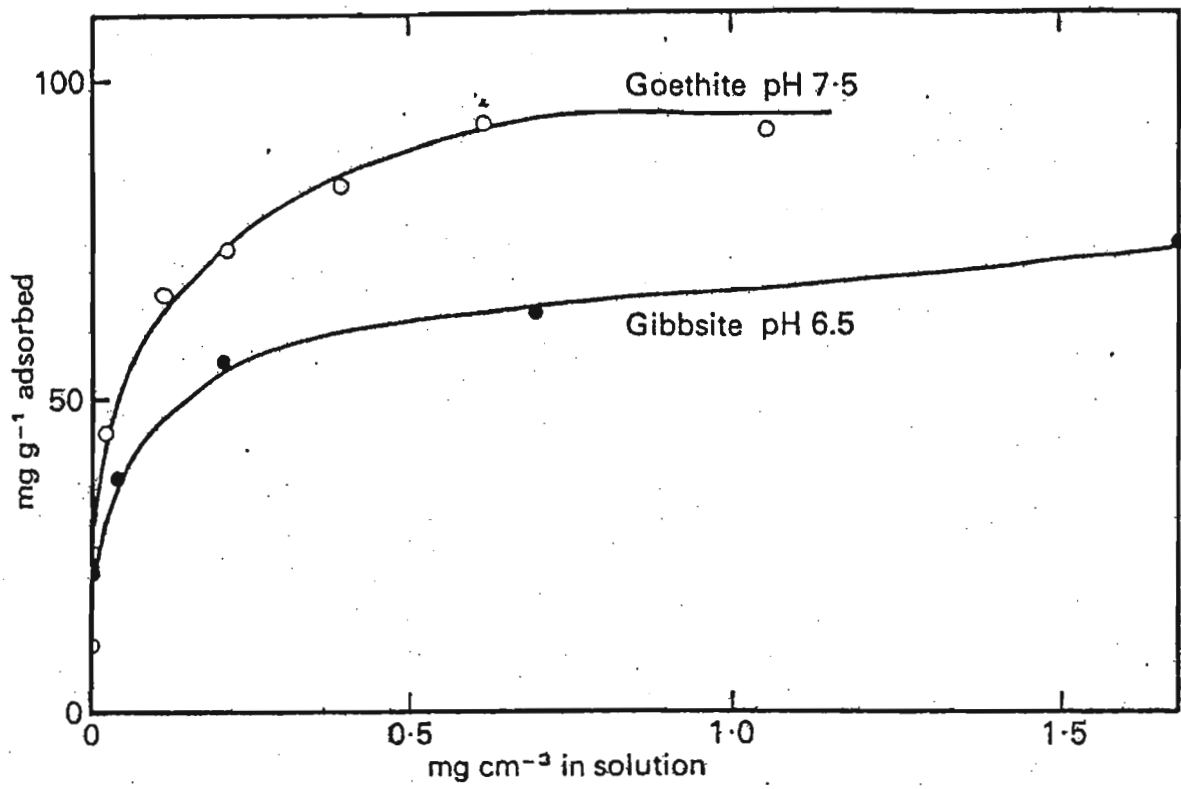


Figure 1.4: Adsorption isotherms of humic acid in 0.1M NaCl on gibbsite and goethite (from Parfitt *et al.*, 1977a)

The above-mentioned ligand exchange reaction occurs through the displacement of  $\text{OH}_2^{0.5+}$  and  $\text{OH}^{0.5-}$  groups at the oxide surfaces by OH and COOH groups on the humic molecule (Parfitt *et al.*, 1977a; Stevenson, 1994). Parfitt *et al.* (1977a) showed that when just the free humic or fulvic acid is added, the proton from the carboxylic acid group reacts with the displaced hydroxyl ion from the oxide surface to form water. However, when a cation-humic complex is added (e.g. Na-fulvate), the displaced hydroxyl groups are released into solution. In fact, poly-carboxylic fulvic acid is strongly adsorbed through multiple contacts and consequently, with each fulvate molecule adsorbed, many hydroxyl groups are released by ligand exchange (Parfitt *et al.*, 1977a).

The hydroxyl ions that are released during the ligand exchange reaction described above could be partially responsible for the increases in subsoil pH that are associated with the addition of poultry manure and Ca-fulvates/humates to soils. The ligand exchange reaction is a 'self-liming' reaction, similar to that reported by Sumner (1993) for gypsum.

#### B. Adsorption of low molecular weight organic acids:

A relatively large number of organic acids are found in the rhizosphere (Stevenson, 1967), and of these, citric, malic and oxalic acids seem to be the most important in soil processes (Jones and Brassington, 1998). The concentrations of these organic acids are usually quite low, but can be significantly higher in soils amended with organic manures (Iyamuremye *et al.*, 1996). It can be assumed, therefore, that higher concentrations of organic acids occur under poultry manure amended soils. During the breakdown of organic matter (like poultry manure), a wide range of organic acids can be synthesized by the soil micro-organisms (Rovira and McDougall, 1967).

Organic acids have been implicated in podzolisation processes and it is evident that, like the humic substances described above, some leaching down the profile (into the subsoil) of these compounds must occur (Lundstrom, 1994). Smith *et al.* (1995) reported that, in a leaching column experiment, Ca-citrate increased the soil solution pH from 5 to a maximum value of 7. The fact that organic acids can move down the profile and have the ability to increase soil pH makes them viable candidates for increasing subsoil pH following poultry litter additions to soils. The mechanism by which organic acids increase soil pH is outlined below:

The organic acids (like the humic substances described above) are specifically adsorbed to Al and Fe hydrous oxide surfaces by ligand exchange reactions (Parfitt *et al.*, 1977b; Jones and Brassington, 1998). These compounds adsorb to the same sites as P (Lopez-Hernandez *et al.*, 1986) and are reported to reduce P sorption in the order: citrate = oxalate > malonate = tartrate > acetate = succinate (Jones and Brassington, 1998). Using the adsorption of oxalate on gibbsite, Parfitt *et al.* (1977b) reported that two modes of sorption are possible: The oxalate can either be directly chelated to an  $Al^{3+}$  cation, or a bridge can form between two cations in adjacent layers. Since, in both cases, the O-O separation between the OH-H<sub>2</sub>O pair that is replaced (by the oxalate) is similar to that of the O-O separation of the oxalate group itself (about 0.28nm), the latter mechanism is quite possible (Parfitt *et al.*, 1977b). Figure 1.5 (Haynes and Moklobate, 2000) illustrates the latter of these two modes of sorption. During the ligand exchange reaction, hydroxyl ions from the oxide surfaces are displaced into the soil solution (Parfitt *et al.*, 1977b). This could lead to an increase in subsoil pH.

At the relatively high pH found in poultry manure (pH 7.5 - 8.5), one can assume that the organic acids occurring naturally in the manure will be in a deprotonated state. This is confirmed by considering the pKa values for the various organic acids (e.g. for citrate, pKa<sub>1</sub> = 3.09; pKa<sub>2</sub> = 4.75; and pKa<sub>3</sub> = 5.41) (Mahler and Cordes, 1966). It is therefore likely that these organic acids will exist in a complexed form with cations (e.g. Ca) to balance their negative charge. As described in Section 1.3.2 above, the decomposition of these Ca-[organic acid] complexes could also cause an increase in soil pH, although this mechanism should play a larger role in topsoils (where microbial decomposition is greater) than in subsoils.

### C. Excess NO<sub>3</sub><sup>-</sup> uptake by roots in the subsoil:

Table 1.1 shows that poultry litter contains about 4% N on a dry weight basis. This means that application rates of broiler litter over 9 tons/ha/year could easily supply over 270 kg N/ha (i.e. more than the requirement of most agronomic crops) (Sims and Wolf, 1994). The N transformations following poultry manure additions to soils have been discussed in Section 1.3.2 of this review. Much of the N released from poultry manure is in forms that are rapidly hydrolysed to, or more slowly ammonified to, NH<sub>4</sub><sup>+</sup>. Nitrification processes then convert this NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>, which can then be taken up by the plant.

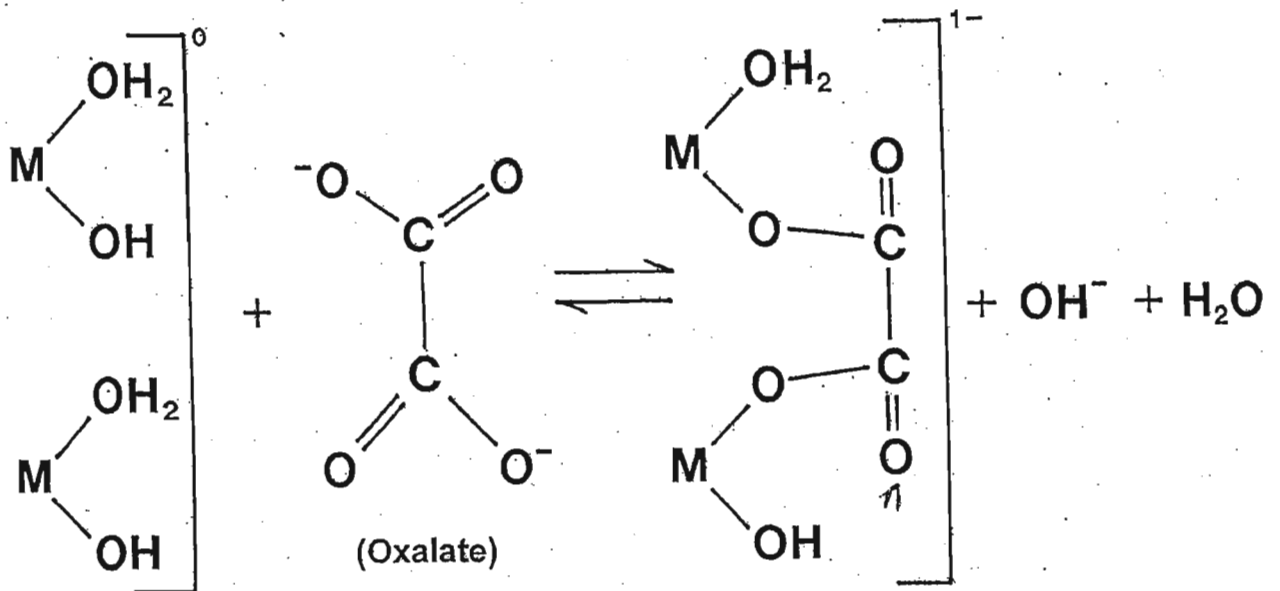


Figure 1.5: The adsorption of oxalate onto an Al hydrous oxide surface (from Haynes and Moklobate, 1999)



If excessive amounts of N have been applied in the poultry manure (and nitrification of this N has run through to completion), there will be more  $\text{NO}_3^-$  present in the topsoil than is needed by the crop. Nitrate is relatively mobile in the soil profile, and it will form ion pairs with basic cations (of which the concentrations will be high following manure applications) that are capable of leaching down the profile into the subsoil, resulting in accumulations of  $\text{NO}_3^-$  in the subsoil. This  $\text{NO}_3^-$  accumulation will affect the balance of anions and cations taken up by the deeper plant roots; the consequences of which are discussed below:

Plants have the ability to adjust the rhizosphere pH during their growth (Haynes, 1983). They typically take up unequal quantities of nutritive cations and anions and, in order to maintain electroneutrality at the soil-root interface, either  $\text{H}^+$  or  $\text{OH}^-$  ions are excreted by the roots in quantities that are stoichiometrically equal to the respective excess cation or anion uptake (Breteler, 1973; Van Beusichem *et al.*, 1985). If the equivalent sum of anions absorbed by the plant ( $\text{NO}_3^- + \text{SO}_4^{2-} + \text{H}_2\text{PO}_4^- + \text{Cl}^-$ ) exceeds that of cations ( $\text{NH}_4^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+$ ), then the growth of the plant will result in a net efflux of  $\text{OH}^-$  into the rhizosphere (Haynes, 1990).

The above scenario is normally the case, since  $\text{NO}_3^-$  is commonly the dominant form of inorganic N present in the soil solution and most plants absorb more N than any of the other nutrients. Therefore, where significant  $\text{NO}_3^-$  has accumulated in the subsoil and is then absorbed by the plant roots, the excess anion uptake will result in the excretion of  $\text{OH}^-$  ions into the subsoil and this could raise the subsoil pH. This mechanism is favoured by some South African workers (M. P. W. Farina, pers. comm.), although currently there is no definitive evidence to show that it has a significant effect.

#### D. Specific adsorption of inorganic phosphate / Precipitation of Al-phosphate minerals:

In Section 1.2.3, evidence was put forward to show that organically bound P is capable of moving down the profile into the subsoil. Kingery *et al.* (1994) showed that long-term broiler litter applications increased the extractable P content down to a depth of 60cm relative to non-littered soils. If it can be assumed that organically bound P is moving down the profile and then being released into the soil solution when the organic molecule breaks down, it is possible that the released inorganic P in the subsoil is reducing exchangeable Al via two

possible mechanisms: Firstly, specific adsorption of the released inorganic P could be causing a small, but significant, increase in subsoil pH (causing Al to precipitate out of solution) according to the following ligand-exchange reaction (Brady, 1974):



Secondly, the release of this phosphate into an acid subsoil could cause the precipitation of insoluble aluminophosphate minerals (Haynes, 1984a), thereby removing Al from the soil solution. Although this mechanism has no direct influence on the subsoil pH, by removing Al from the soil solution it is effectively removing some of the acidic buffering capacity of the subsoil, which might have an indirect influence on the subsoil pH in the long term.

Since the soil pH and the chemistry of Al are so closely linked, one cannot merely discuss the effects of poultry manure additions on soil pH alone, without considering its effects on the chemistry of Al. Indeed, the final sentence of the previous paragraph highlights this point. Therefore, in order to obtain a holistic view of the effects of poultry manure additions on soil acidity, the following section will focus on the changes in the chemistry of Al following manure additions. In many cases, these changes will impact on the soil pH.

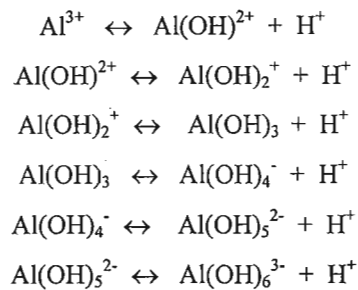
#### **1.4 THE EFFECTS OF POULTRY MANURE ADDITIONS ON AL TOXICITY IN SOILS**

The predominant characteristic of acid soils is the presence of soluble and exchangeable forms of Al (Adams, 1981). Certain species of Al in solution are toxic to plants, and this Al phytotoxicity seriously limits the productivity of many soils around the world (Hue and Amien, 1989). There is evidence from many workers that the addition of organic amendments to soils can significantly reduce Al toxicity in both topsoils and subsoils; this phenomenon will be the focus of this section. Before considering this, however, the basic principles of Al solubility and phytotoxicity will be reviewed briefly.

### 1.4.1. Basic principles of Al in solution and Al-induced toxicity

The concentration of soluble Al in acid soils may be controlled by the dissolution of inorganic compounds, adsorption onto inorganic minerals or by reactions with organic molecules in soils (Ritchie, 1989). One can calculate the concentration of Al in solution, in its simplest form, by considering: (i) The solubility of gibbsite; (ii) The hydrolysis products of Al in solution (shown below); and (iii) The interaction of Al with soluble organic ligands (Rowell, 1988).

Only in very acid soils ( $\text{pH}_{\text{water}} < 4.0$ ) does the  $\text{Al}^{3+}$  species occur solely in the soil solution, where it exists as the aluminohexahydronium ion  $[\text{Al}(\text{6H}_2\text{O})]^{3+}$ . As the pH increases, these ions dissociate  $\text{H}^+$  ions and form a number of monomeric Al species in solution (Haynes, 1984a). The dissociation reactions occur as follows:



The solubilities of these monomeric Al species are shown in Figure 1.6 (Haynes, 1984a). The solid phase in Figure 1.6 is gibbsite,  $\text{Al}(\text{OH})_3$ . In acidic soils ( $\text{pH}_{\text{water}} < 5.5$ ), it is clear that the solution phases of Al will be a mixture of the monomeric ions  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ , and  $\text{Al}(\text{OH})_2^+$ . The average charge of each Al is between 2 and 3, decreasing as pH increases (Rowell, 1988). The positively charged monomeric species,  $\text{Al}(\text{OH})^{2+}$  and  $\text{Al}(\text{OH})_2^+$ , can polymerize in soil solution to form both large and small positively charged polynuclear complexes. As the pH and the OH:Al ratio in soil solution increase, so polymers of increasing complexity are formed (Rengasamy and Oades, 1978).

The monomeric and polymeric forms of Al are not the only forms of Al in soil solution. Indeed, the Al in soil solution can react with many different ligands, thereby forming different Al complexes with varying toxicities to plants. Table 1.2 (Ritchie, 1989) shows the possible

inorganic reactions of Al in the soil solution.

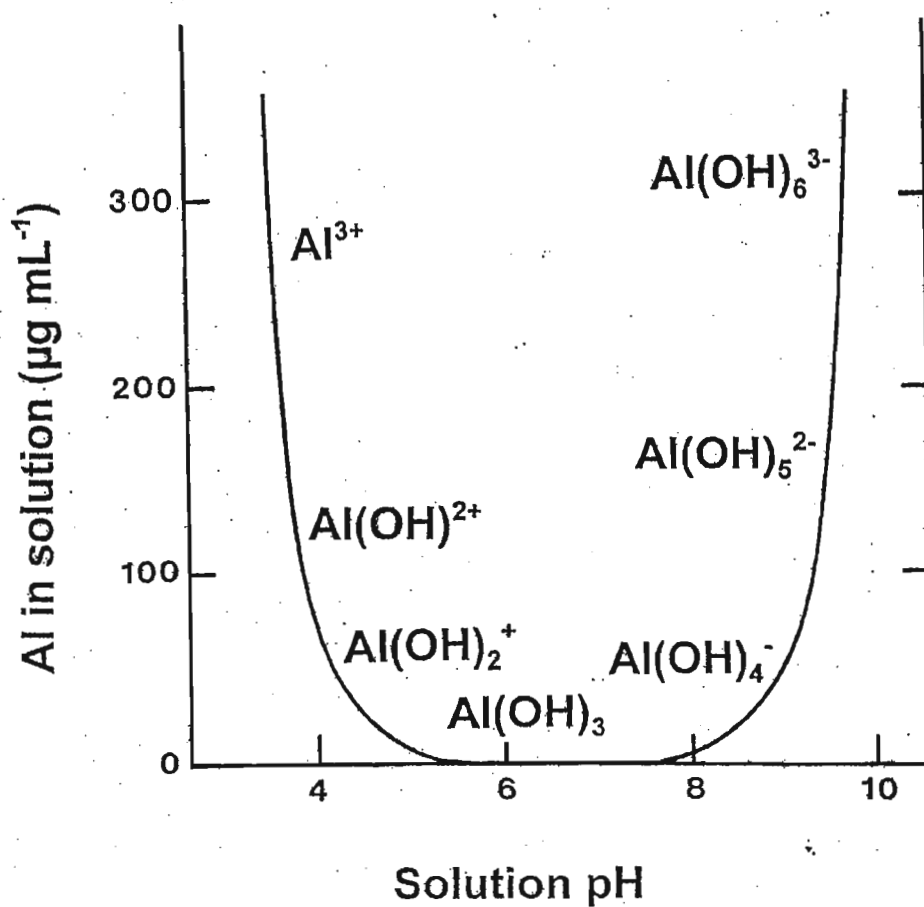


Figure 1.6: The effect of pH on the solubility of Al in soil solution (from Haynes, 1984a)

Table 1.2: Possible inorganic reactions of Al in the soil solution (from Ritchie, 1989).

1.  $\text{Al}^{3+} + \text{OH}^- \rightleftharpoons \text{AlOH}^{2+}$
2.  $\text{Al}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_2^+$
3.  $\text{Al}^{3+} + 4\text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^-$
4.  $\text{Al}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{Al}(\text{SO}_4)^+$
5.  $\text{Al}^{3+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Al}(\text{SO}_4)_2^-$
6.  $\text{Al}^{3+} + \text{F}^- \rightleftharpoons \text{AlF}^{2+}$
7.  $\text{Al}^{3+} + 2\text{F}^- \rightleftharpoons \text{AlF}_2^+$
8.  $\text{Al}^{3+} + 3\text{F}^- \rightleftharpoons \text{AlF}_3^0$
9.  $\text{Al}^{3+} + 4\text{F}^- \rightleftharpoons \text{AlF}_4^-$
10.  $2\text{Al}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Al}_2(\text{OH})_2^{4+}$
11.  $3\text{Al}^{3+} + 4\text{OH}^- \rightleftharpoons \text{Al}_3(\text{OH})_4^{5+}$
12.  $13\text{Al}^{3+} + 28\text{OH}^- \rightleftharpoons \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+} + 4\text{H}^+$
13.  $\begin{array}{c} \text{Al} \\ \diagdown \\ \text{OH} \end{array} + \text{Si}(\text{OH})_4 \rightleftharpoons \begin{array}{c} \text{Al} \\ \diagdown \\ \text{O} - \text{Si}(\text{OH})_3 \end{array} + \text{H}_2\text{O}$
14.  $\begin{array}{c} \text{Al} \\ \diagdown \\ \text{Al} \\ \diagdown \\ \text{OH} \end{array} + \text{H}_2\text{PO}_4^- \rightleftharpoons \begin{array}{c} \text{Al} \\ \diagdown \\ \text{Al} \\ \diagdown \\ \text{O} - \text{P} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OH} \\ \diagdown \text{OH} \end{array} \end{array} + \text{OH}^-$

Aluminium can also form soluble monomeric complexes with organic anions; these complexes will be discussed in more detail in Section 1.4.2 below. As stated previously, the different soluble forms of Al have varying toxicities to plants (Bartlett and Riego, 1972). The most obvious symptom of Al toxicity is the inhibition of root growth. Affected roots are characteristically stubby with reduced growth of the main axis and inhibited lateral root formation (Foy, 1988). Reduced root growth severely limits the volume of soil that the plant can explore for both water and nutrients, with the result that plants affected by Al toxicity often show signs of water and nutrient stress too. Workers have also reported Al-induced reductions in Ca and P uptake (Huang *et al.*, 1992).

Ritchie (1989) reported that  $\text{Al}^{3+}$  and the monomeric Al-hydroxy species in solution are more toxic to plants than the other forms of Al. Kinraide and Parker (1990) found that plant growth was more sensitive to  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_2^+$  than to  $\text{Al}^{3+}$ . This is because, at the low pH at which  $\text{Al}^{3+}$  predominates (Figure 1.6), there are also higher concentrations of  $\text{H}^+$  ions in solution. These  $\text{H}^+$  ions compete with the  $\text{Al}^{3+}$  at the root plasma membrane, thereby reducing the phytotoxic effects of the  $\text{Al}^{3+}$  (Kochian, 1995).

Phosphate, sulphate and fluoride are inorganic anions that can complex Al and reduce its phytotoxicity. Cameron *et al.* (1986) reported that Al complexed by sulphate and fluoride did not inhibit root elongation in barley seedlings, and concluded that these complexes are not toxic to plants. The possible formation of non-toxic, Al-[inorganic anion] complexes following the application of poultry manure to soils will be discussed in more detail in Section 1.4.2 below.

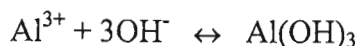
Aluminium toxicity can also be reduced in the presence of organic anions such as citrate and tartrate, as well as EDTA and various soil organic matter extracts (Bartlett and Riego, 1972; Hue *et al.*, 1986). Stevenson and Vance (1989) reported that acid soils rich in native organic matter, or soils amended with large quantities of organic residues, give low  $\text{Al}^{3+}$  concentrations in the soil solution. It has been noted in previous discussions that poultry manure additions can increase the organic matter content of the soils to which they are added, and that the decomposing manure can release humic substances and short-chain organic acids into the soil solution. The ability of these compounds to reduce the toxicity of monomeric Al in the soil solution will be discussed in more detail in Section 1.4.2:

#### 1.4.2. Detoxification of soil Al by compounds released from poultry manure

Hue (1992) stated that poultry manure additions to soil “inactivated” Al in the soil. A similar result was also obtained by O’-Hallorans *et al.* (1997) who reported that, 6 months after a poultry manure application of 15 tons/ha, the extractable Al had decreased from 0.38 to 0.20 cmol/kg, and the Al saturation had decreased by 7.71%. Figure 1.7 illustrates the results obtained by Hue and Licudine (1999) from a leaching column experiment. It is clear that applications of poultry manure decreased both exchangeable Al and Al saturation relative to the control treatment (with no manure). At the rates applied, the poultry manure was the most effective treatment relative to the lime, gypsum and sewage sludge treatments. There are several possible mechanisms causing the observed detoxification of Al following poultry manure additions to acid soils; these mechanisms will be discussed below:

##### A. Increased soil pH:

In Section 1.3, the mechanisms behind the increases in topsoil and subsoil pH following poultry manure additions to acid soils were discussed. It is clear from Figure 1.6 that the solubility of Al is directly controlled by the soil solution pH. As the pH increases towards about pH 5, the solubility of Al decreases and it begins to precipitate out of solution as Al hydrous oxides, as illustrated by the reaction below (Adams, 1981):



As more of the solution Al precipitates out as hydrous oxides, so the activity of the toxic monomeric Al species in solution decreases, and thus the effects of Al toxicity are greatly reduced. This is the same mechanism by which lime applications to an acid soil will operate.

##### B. Complexation of Al by organic molecules released from the poultry manure:

As noted in Section 1.4.1, many workers have studied the ability of organic molecules to form non-toxic complexes with soil solution Al (Hue *et al.*, 1986; Hue and Amien, 1989; Wong and Swift, 1995).

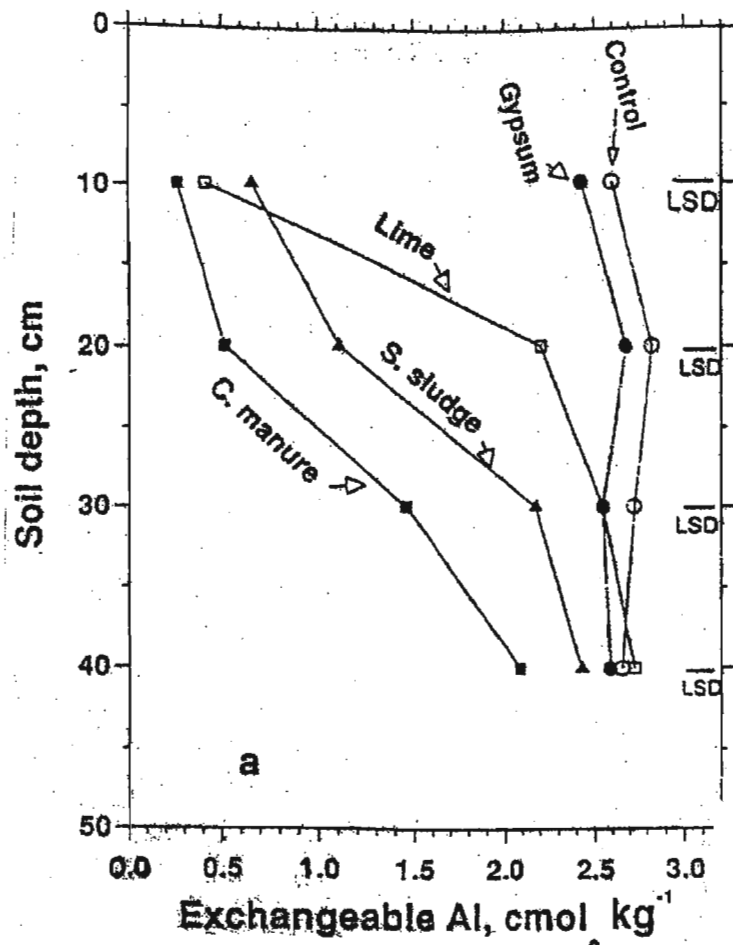
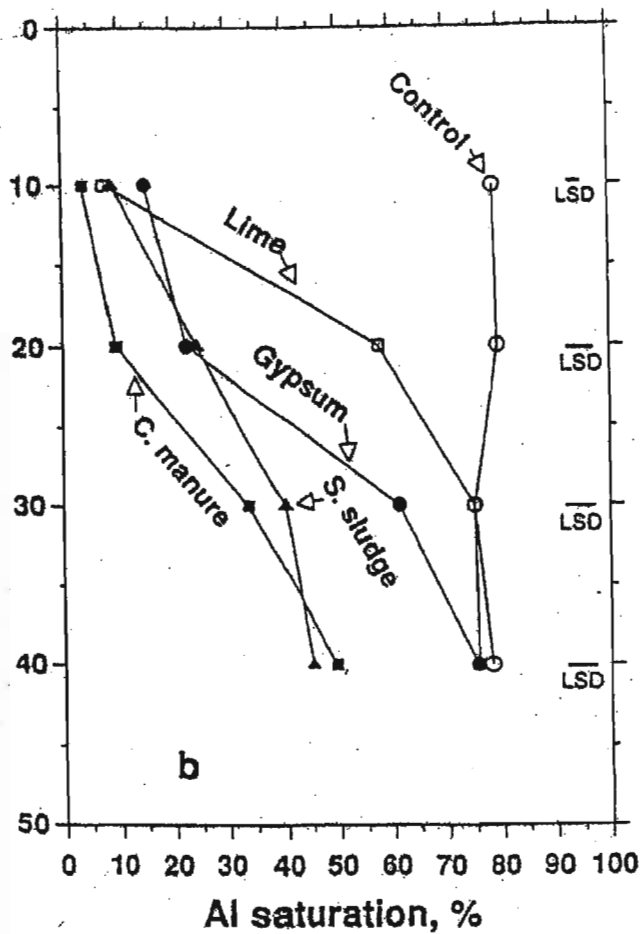


Figure 1.7: Exchangeable Al (a) and percentage of Al saturation (b) of an acid Ultisol profile (packed column) as affected by surface application of gypsum, lime, chicken manure, or sewerage sludge (from Hue and Licudine, 1999).



The organic molecules that complex Al can be divided into two main groups: (i) Well-defined biochemical compounds such as organic acids, phenols, phenolic acids, sugar acids and polymeric phenols, and (ii) Humic and fulvic acids (Stevenson and Vance, 1989). As discussed previously, poultry manure contains (initially and following partial decomposition) simple organic acids and humic substances. It was made clear in Section 1.3 that these organic compounds are capable of leaching down the profile, and therefore the following discussion on the detoxification of Al by these compounds applies to both topsoils and subsoils.

#### *Complexation by organic acids:*

Organic acids can form stable chelate complexes with  $Al^{3+}$  in soil solutions. Although concentrations of these compounds in soils are normally low ( $1 \times 10^{-3} M$  to  $4 \times 10^{-3} M$ ), substantially higher amounts can be found in soils amended with organic matter (e.g. poultry litter) (Stevenson and Vance, 1989). It is important to consider, however, that these organic acids are highly susceptible to microbial degradation, and are thus only present for relatively short periods in the soil solution (Ritchie, 1994). The complexation of Al by organic acids is therefore considered to be a short-term phenomenon. Long-term alleviation of Al toxicity with just organic acids alone would require regular applications of the organic acids (e.g. every two to three months; Haynes and Moklobate, 2000). Due to the lower microbial activity in subsoils, organic acids would presumably exist for longer periods lower down the profile, and therefore one could expect the Al-[organic acid] complexes to exist for longer periods.

Stability constants for Al-[organic acid] complexes have been calculated by several workers. The constants calculated by Hue *et al.* (1986) are in good agreement with those from other workers, and are presented in Table 1.3. These results show that the stability of Al-[organic acid] complexes decreases in the order: citrate > tartrate = malate > salicylate (at pH 5). From the structural configurations of these organic acids it appears that their Al-detoxifying abilities are strongly correlated with the relative positions of OH and COOH groups on the main carbon chain of the organic molecule. The most effective Al-detoxifying organic acids have either two pairs of OH/COOH groups attached to two adjacent carbons (e.g. citric and tartaric acids) or two COOH groups directly connected (e.g. oxalic acid). Acids that are weak at detoxifying Al do not possess these configurations (Hue *et al.*, 1986).

Table 1.3: Calculated stability constants for some Al- [organic molecule] complexes (from Hue *et al.*, 1986).

Log Ks for Al	
Reaction	Calculated†
<u>L = Citric</u>	
$2 \text{ Al} + \text{ L} \rightleftharpoons \text{ Al}_2\text{L}$	$12.26 \pm 0.28$
<u>L = Oxalic</u>	
$\text{ Al} + \text{ L} \rightleftharpoons \text{ AlL}$	$6.53 \pm 0.13$
<u>L = Tartaric</u>	
$\text{ Al} + \text{ L} \rightleftharpoons \text{ AlL}$	$6.21 \pm 0.07$
<u>L = Malic</u>	
$\text{ Al} + \text{ L} \rightleftharpoons \text{ AlL}$	$6.00 \pm 0.24$
<u>L = Malonic</u>	
$\text{ Al} + \text{ L} \rightleftharpoons \text{ AlL}$	$5.70 \pm 0.20$
<u>L = Salicylic</u>	
$\text{ Al} + \text{ L} \rightleftharpoons \text{ AlL}$	$4.74 \pm 0.14$
<u>L = Succinic</u>	
$\text{ Al} + \text{ L} \rightleftharpoons \text{ AlL}$	$4.62 \pm 0.08$

The chelate structure formed between  $\text{Al}^{3+}$  (in solution) and a known strongly Al-detoxifying organic acid (citrate) is shown in Figure 1.8 (Stevenson and Vance, 1989). Note that the  $\text{OH}_2$  groups coordinated to the  $\text{Al}^{3+}$  react with the  $\text{COOH}$  and  $\text{OH}$  groups from the citric acid. Because the two pairs of  $\text{OH}/\text{COOH}$  groups are attached to two adjacent carbons (Figure 1.8), this allows three adjacent  $\text{OH}_2$  groups on the  $\text{Al}^{3+}$  to react with the citric acid, thereby forming a strong complex.

The formation of the Al-organic acid complexes in solution can significantly reduce the toxicity of Al to plants. In fact, it is believed that plants can actually release organic acids into the rhizosphere to detoxify Al. Malic acid release from root tips is speculated to be a mechanism of Al resistance for wheat genotypes, whilst the release of citric acid has been related to Al resistance associated with resistant maize and snapbean genotypes (Miyasaka *et al.*, 1991; Pellet *et al.*, 1994; Delhaize and Ryan, 1995). Whether plants can transport metal-organic acid complexes into the root is unknown. Jones and Darrah (1994), however, showed that under solution culture conditions maize roots could not directly reabsorb metal-citrate complexes from outside the root, even under deficiency situations. This may be one of the reasons why organic acids can detoxify Al in solution (i.e. by decreasing the plant uptake of Al).

#### *Complexation by humic substances:*

The nature of humic substances and their release from decomposing poultry manure in soil has been discussed in Section 1.3 above. Humic and fulvic acids have consistently been reported to ameliorate Al toxicity in both top- and subsoils (Harper *et al.*, 1995; Smith *et al.*, 1995; Wong and Swift, 1995). The complexation of Al by humic and fulvic acid and its consequent detoxification has been reviewed in great detail by Stevenson and Vance (1989); the current review provides only a brief outline of these associations.

The ability of humic substances to form stable complexes with Al can be attributed to the large number of oxygen-containing functional groups on the humic molecule (as discussed in Section 1.3).

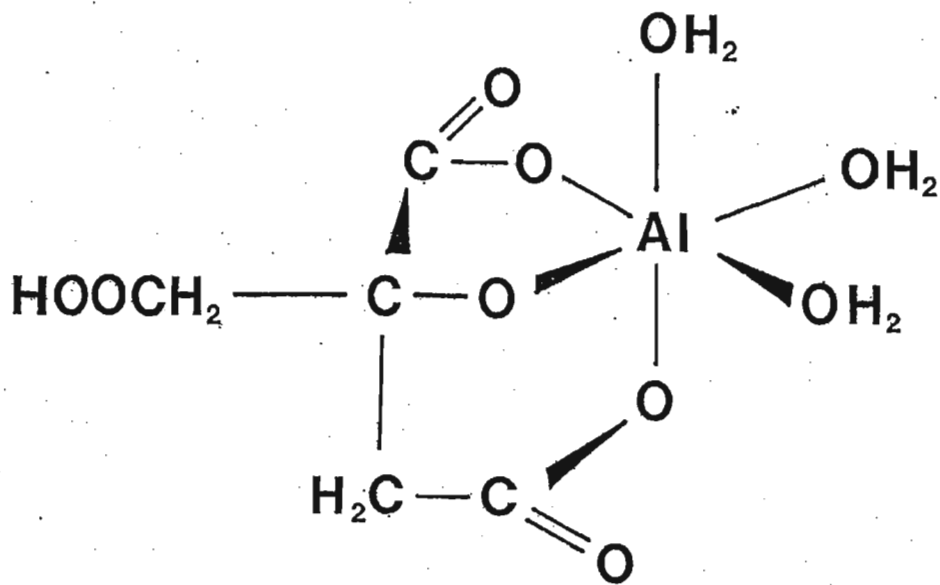


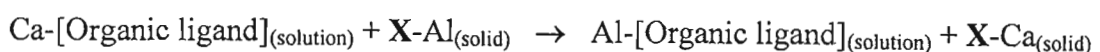
Figure 1.8: The chelate structure of  $\text{Al}^{3+}$  with citrate (from Stevenson and Vance, 1989).

These binding sites can complex Al via the following reactions, which are illustrated by structures 1-4 in Figure 1.9: a) water bridges (structure 1), b) electrostatic attraction (structure 2), c) the formation of a coordinate linkage with a single donor group (structure 3), and d) the formation of a chelate complex (structure 4) (Stevenson and Vance, 1989).

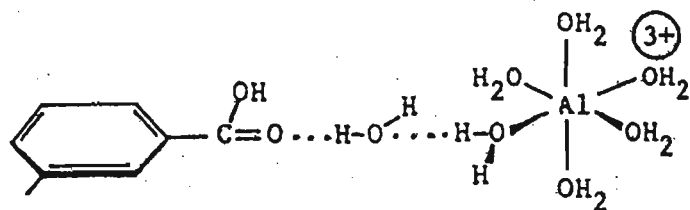
Humic substances can form both soluble and insoluble complexes with Al, depending on environmental factors such as pH, ionic strength and the degree of saturation (Stevenson and Vance, 1989). Nevertheless, both of these forms of complexation have been shown to be non-toxic to plants. Suthipradit *et al.* (1990) found that the addition of fulvic acid to solutions greatly reduced the amount of monomeric Al present in solution and reduced the toxic effect of Al on the growth of soybean and cowpea. Similar results have been reported by other workers (Harper *et al.*, 1995; Stevenson and Vance, 1989). Given the above information and the ability of these humic substances to leach down the soil profile (as discussed previously in Section 1.3), there is little doubt remaining as to the ability of humic substances to form long-term, non-toxic complexes with soil solution Al in both top- and subsoils.

The discussion above has centered around the ability of short-chain organic acids and larger humic molecules to form non-toxic complexes with monomeric Al in soil solution. This, however, is not the only method by which these Al-[organic ligand] complexes can reduce the problem of Al toxicity in acid soils. If these complexes remain soluble, it is possible that they will leach deeper into the soil profile, thereby removing Al from the plant-rooting depth. The mechanisms behind this process will be discussed below:

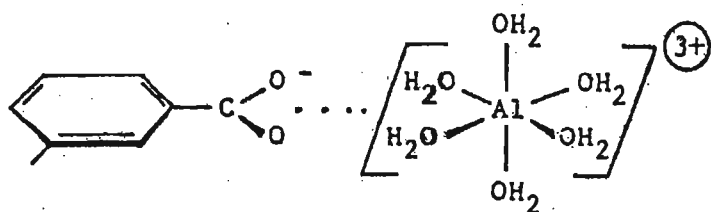
As discussed in Section 1.3, it is likely that the organic molecules in the poultry manure would exist in a deprotonated state (resulting from the high pH of the poultry manure and the relatively low pKa values of the organic functional groups) and would therefore be associated with basic cations such as Ca. Hue and Licudine (1999) reported that organically complexed Ca molecules (that are generated by the poultry manure in the incorporation zone) are mobile and can move down the soil profile. During their downward path, they react with exchangeable Al according to the following reaction:



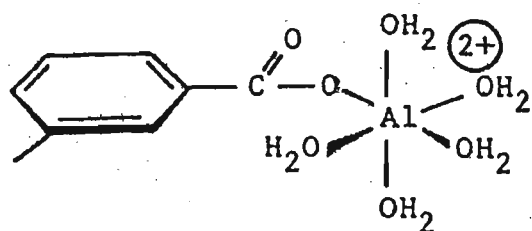
Structure 1:



Structure 2:



Structure 3:



Structure 4:

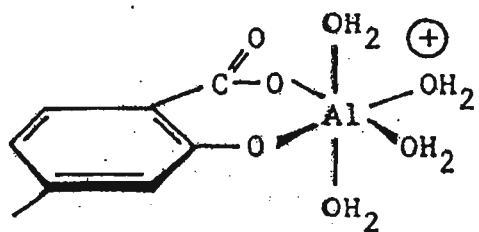


Figure 1.9: The mechanisms of Al complexation by the active sites on humic molecules (from Stevenson and Vance, 1989).

Smith *et al.* (1995) added Ca-citrate and Ca-fulvate to leaching columns and reported a very similar reaction to the one above. Smith *et al.* (1995), however, also noted that it was possible for the complexed Al to be removed by leaching. This has two beneficial effects on soil acidity: (a) it is possible that the Al-[organic ligand] complex could leach out of the rooting depth of the plant, thereby removing toxic Al from the system. In the long-term, the removal of Al from the system will decrease the acidic buffering capacity of the soil, and (b) the Ca ions that were exchanged for the Al will remain on the exchange sites, thereby increasing the Ca content of the soil (deficiencies of which are a common problem in acid soils; Hue and Licudine, 1999).

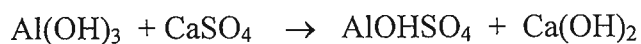
Evidence was provided in Section 1.3 to show that the Ca-[organic ligand] complexes can leach into subsoils; hence the above mechanism has implications for both top- and subsoils.

#### C. Complexation by inorganic molecules:

Reactions 4 and 5 in Table 1.2 show that  $\text{Al}^{3+}$  in the soil solution is capable of forming complexes with  $\text{SO}_4^{2-}$  anions. Poultry manure contains approximately 0.5 - 0.7% S on a dry weight basis (Table 1.1). Mineralization of this organically-bound S will result in the release of  $\text{SO}_4^{2-}$ , which can either remain in the topsoil or form mobile ion pairs with basic cations (also released from the litter) and leach into the subsoil. This  $\text{SO}_4^{2-}$  can therefore complex toxic Al in the top- and subsoil and, as stated previously in Section 1.4, these Al- $\text{SO}_4$  complexes are considered to be less toxic than the monomeric forms of Al. In this way, the S released from poultry manure could be playing a role in the detoxification of soluble Al.

The release of P from poultry manure and its possible movement in soils (as organically-bound P) has been discussed previously. The large increases in P in the topsoil following manure additions can play a role in the detoxification of Al in this horizon, due to the precipitation of aluminophosphates such as variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ) (Haynes, 1984a). These compounds are insoluble and their formation results in a decrease in the activity of Al in solution, which in turn decreases the Al toxicity. Although it is possible that organically-bound P can move into the subsoil, the above mechanism will play a much greater role in the topsoil, where there are large accumulations of P following manure additions.

The release of  $\text{H}_2\text{PO}_4^-$  and  $\text{SO}_4^{2-}$  into an acid soil (from decomposing poultry manure) and the subsequent reactions of these molecules with the Al and Fe hydroxide surfaces could cause a small, but significant, increase in the soil pH with the resulting precipitation of Al out of soil solution. The ligand exchange reaction, and the associated release of  $\text{OH}^-$  ions into the solution following the specific adsorption of  $\text{H}_2\text{PO}_4^-$ , was discussed previously in Section 1.3.3. A similar ligand exchange reaction for the adsorption of  $\text{SO}_4^{2-}$  onto Al and Fe hydroxide surfaces and the release of  $\text{OH}^-$  ions was proposed by Sumner (1993) and is given below:



In conclusion of this section, it is clear that the chemistry of Al and the changes in soil pH are very closely linked and need to be considered together in order to obtain a holistic view of the effects of poultry manure additions on soil acidity. Several mechanisms have been proposed to explain the changes that occur, and the aim of the following section is to isolate which of these mechanisms could be focus areas for future research.

## 1.5 IDENTIFICATION OF POSSIBLE AREAS FOR FUTURE RESEARCH

As discussed previously, several mechanisms have been proposed to explain the ameliorative effects of poultry manure additions on soil acidity, especially in the subsoil. From these proposed mechanisms, two major schools of thought have developed.

The first school of thought was proposed by workers in South Africa (Dr. M.P.W. Farina pers. comm.) and has been discussed in Section 1.3. It is based on the high N content of the poultry manure and the subsequent release of relatively large amounts of inorganic N into the soil upon decomposition of the manure. This could result in high concentrations of  $\text{NO}_3^-$  in the top- and subsoils of amended soil profiles following nitrification of the added N. Since  $\text{NO}_3^-$  is one of the major nutrient anions taken up by plants, its accumulation in amended subsoils could result in the excess uptake of anions relative to cations. Under these conditions, the plant will excrete  $\text{OH}^-$  ions into the soil solution in order to maintain the charge balance, thereby increasing the rhizosphere pH.



The second school of thought is based on the work of Parfitt *et al.* (1977b), who described the adsorption reactions of organic molecules onto sesquioxide surfaces. Hue (1992) applied the results of this work to poultry manure additions and reported that the adsorption reactions of humic substances and short-chain organic acids (associated with the poultry manure and its decomposition) onto sesquioxide surfaces are predominantly ligand-exchange reactions. During these reactions, OH<sup>-</sup> ions are displaced from the clay surface into the soil solution, thereby causing an increase in the soil solution pH. It has been shown that the organic compounds mentioned above are mobile in soils and capable of leaching into the subsoil, making this mechanism applicable to both top- and subsoils.

Although other suggestions have been put forward to explain the increases in soil pH following general organic residue additions to acid soils, the above two theories seem to be the most prominent when describing the changes associated with poultry manure. The need for more information pertaining to these possible mechanisms has provided numerous areas for future research. These research areas have been used to plan the experiments that are discussed in Chapters 2 and 3 that follow.

With the aim of studying the effects of long-term (>10 years) applications of poultry manure on top- and subsoil acidity in some acid soils in the KwaZulu-Natal Midlands, samples were taken from farmlands having received long-term manure applications and compared with those taken from suitable control fields. The results from this study are presented and discussed in Chapter 2 and, based on these findings, a leaching column trial was established to identify the possible mechanisms responsible for the ameliorative action of poultry manure on soil acidity, as noted in the field samples.

This leaching column experiment is discussed in Chapter 3. It was established to monitor the short-term changes in the chemistry of an acid soil profile following poultry manure additions to the topsoil. In order to study the first major school of thought (discussed above), plants were grown in some of the manure-amended columns, but not in others. In this way the effects of the plant roots on the top- and subsoil chemistry of manure-amended soil columns could be studied. With the aim of studying the second major school of thought (as discussed above), the dynamics of soluble organic carbon concentrations throughout the amended soil profiles were measured. In this way, the movement and adsorption of these compounds

(derived from the manure) in acid soil profiles could be monitored. Numerous other measurements were taken throughout the experiment (as discussed in Chapter 3) with the hope of providing more information on the two currently proposed mechanisms, and possibly identifying any new mechanisms.

By combining the information from both the short- and long-term studies, the aim of the following chapters is to discuss, in more detail, the changes in soil profile acidity that occur following poultry manure additions to acid soils, and the mechanisms behind these changes.

## CHAPTER 2

### THE EFFECTS OF LONG-TERM APPLICATIONS OF POULTRY MANURE ON SOME SOIL CHEMICAL PROPERTIES, PARTICULARLY TOP- AND SUBSOIL ACIDITY, OF SELECTED KWAZULU-NATAL SOILS

#### INTRODUCTION

Subsoil acidity is an important yield limiting factor in KwaZulu-Natal, and naturally occurring subsoil acidity (below 15cm depth) is present in many areas of the province. In addition, there is evidence that there are extensive areas under commercial farming where subsurface horizons have been acidified due to long-term use of nitrogenous fertilisers and neglect of topsoil acidity generated (Fey *et al.*, 1990). As discussed previously, subsoil acidity essentially prevents crop roots from penetrating into the subsoil (due to toxic levels of Al in the subsoil; Farina and Channon, 1988). As a result, the crop is unable to explore the full soil volume for nutrients and water. In dry periods, crops often show symptoms of water stress.

Preliminary observations in the KwaZulu-Natal Midlands have shown that long-term (>10 years) applications of poultry manure at rates of about 5 Mg/ha/year to acid soils has generally resulted in a rise in soil pH of 0.3 to 0.5 units to a depth of 60cm and a reduction in acid saturation from 40-60% down to about 5-30% over the same soil depth (Dr. M.P.W. Farina, pers.comm.). On the strength of such observations (and its known high nutrient content), commercial farmers in the Midlands have contracted chicken producers to buy large quantities of poultry manure to spread on their land. The reason why poultry manure apparently has such beneficial effects on subsoil acidity is speculative. Indeed, in a recent detailed review on the use of poultry manure, Sims and Wolf (1994) state that reports on the effects of its application are somewhat contradictory.

The work reported in this chapter involved the selection of, and sampling from, three acid farmlands around the KwaZulu-Natal Midlands where poultry manure has been applied annually for more than 10 years, and where Dr. M.P.W. Farina (pers.comm.) suspected that these applications had an ameliorative effect on soil acidity. The aims of this study were to

verify the ameliorative action of poultry manure on acid soils and to provide direction for the establishment of a leaching column trial (discussed in Chapter 3) which, in turn, aimed to study the mechanisms by which poultry manure additions effect top- and subsoil pH.

## 2.1 MATERIALS AND METHODS

### 2.1.1. Site selection and sampling procedures

Three sites (farmlands) with naturally high top- and subsoil acidity levels, and on which some of the fields have received long-term applications of poultry manure, were selected and given the following names for experimental use: Site A (in the Nottingham Road district), Site B (in the same district) and Site C (in the Eston district). On each site, sampling was carried out on a field that had received poultry manure and on an adjacent field where no manure had been applied (which served as a control). In cases where a suitable adjacent field did not exist, either virgin land or pasture soils were sampled. The details of each site and the farming practices are given below:

- Site A: The soil was of the Kranskop form, with a humic A horizon overlying a yellow-brown apedal B1 horizon and red apedal B2 horizon (Soil Classification Working Group, 1991). An unknown but relatively high amount of layer manure (estimated at over 10 Mg/ha) had been applied to the soil annually for approximately 12 years. After application, the manure was incorporated to an estimated depth of 20-30cm with a plough. Forty kilograms of nitrogen was also applied with the planting of the maize crop. The control field was natural veld about 5m from the field.
- Site B: The soil was of the Inanda form and has been under maize production for 16 years. Five Mg/ha of lime was applied in the first growing season (i.e. 16 years ago) and incorporated to 20-30cm, and inorganic fertilizers were used during the first five seasons of production. Thereafter, only approximately 5-10 Mg/ha of poultry manure has been used (amount and type depending on availability and source). Once again, manure was incorporated with a plough to an estimated depth of 30-40cm. The control field was natural veld about 10m from the field.
- Site C: The soil was of the Nomanci form, with a humic A horizon overlying a lithocutanic B horizon. It was initially under wattle production, but subsequently has

been used for sugar cane production for approximately 20 years. The site receives 8 Mg/ha of poultry manure every second year (with each ratoon). At planting, the manure has been incorporated with a plough to an estimated depth of 20-30cm. The control field was an adjacent field with the same history as the manured soil, except that, after coming out of wattle production, it was left to veld.

For both fields (at each site) three samples were taken from a representative portion of the land at 10cm increments down to a depth of 60cm. These samples were then air-dried and stored for one week until the following analyses could be performed.

### **2.1.2. Chemical analyses**

Each of the soil samples described above had the following chemical analyses performed on them:

- *Organic carbon*: Analysed according to the method of Allison (1965).
- *pH*: 25 ml of either 1.0M KCl or de-ionized water was added to 10g of soil and the suspension stirred at 400 r.p.m. for 5 minutes. The suspension was then allowed to stand for 30 minutes, after which pH was measured using a gel-filled combination glass electrode while stirring
- *Exchangeable acidity*: 25ml of 1.0M KCl was added to 2.5g of soil and stirred for 10 minutes at 400 r.p.m. Extracts were filtered through a Whatman No. 1 filter paper and titrated with 0.005M NaOH to the phenolphthalein endpoint. This is assumed to be the concentration of exchangeable  $Al^{3+}$  and  $H^+$  ions.
- *Extractable Ca, Na and Mg*: 25 ml of 1.0M KCl was added to 2.5g of soil and stirred for 10 minutes at 400 r.p.m. Extracts were filtered through a Whatman No. 1 filter paper and then diluted four times with 0.0356M  $SrCl_2$ . Samples were then analysed for Ca, Na and Mg by AA spectrophotometry.
- *Extractable P and K*: The Ambic-2 extracting solution consists of 0.25M  $NH_4CO_3$  + 0.01M  $Na_2EDTA$  + 0.01M  $NH_4F$  + 0.05 g/l Superfloc (N100), adjusted to pH 8 with conc. ammonia solution. Twenty five ml of extractant was added to 2.5g soil and stirred at 400 r.p.m. for 10 minutes. The extracts were filtered through a Whatman No. 1 filter paper. Phosphorus (P) was determined using a modification of the Murphy and

Riley (1962) molybdenum blue procedure (Hunter, 1974). Potassium (K) was determined by AA spectrophotometry.

## 2.2 THE EFFECTS ON SOIL CHEMICAL PROPERTIES, PARTICULARLY SOIL ACIDITY

As mentioned above, soil samples were taken at 10cm increments down to a depth of 60cm. It must, however, be noted that a straightforward comparison of the 0-30cm and 0-40cm depths of the manured and control fields on sites A and B, respectively, should be interpreted with caution. This is because the control plots on these sites were virgin soils that had never been ploughed, whereas their manured counterparts had been ploughed annually to a depth of 20-40cm. That is, above the 30cm depth of site A and the 40cm depth of site B, there has been extensive mixing of the manured soil, but not of the control. One can, however, safely assume that the control and the manured soils have been equally undisturbed below the plough-depth, and that the only differences below these depths would have been caused by the downward movement of mobile inputs from the overlying zone of application.

On all three sites, poultry manure applications increased the concentrations of extractable cations,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , at all depths down to 60cm (Table 2.1), except for Mg at depths 0-10cm (Site B), 40-50cm (Site C) and 50-60cm (Site C). Similar results have been reported by other workers (Jackson *et al.*, 1975; Kingery *et al.*, 1994). This is attributed to the relatively high contents of these cations in poultry manure (Table 1.1), which would be released into the soil upon decomposition of the manure. Topsoil accumulation of these cations, and their subsequent leaching as counterions with anions (e.g.  $\text{NO}_3^-$  and  $\text{Cl}^-$ , that are released from the manure), is a likely mechanism to explain their movement into the subsoils of amended fields. Indeed, continual applications of poultry manure can cause accumulation of inorganic N in the soil and increased leaching of  $\text{NO}_3^-$  into the groundwater (Cooper *et al.*, 1984; Sharpley *et al.*, 1993). Liebhardt *et al.* (1979) applied poultry manure at rates of 0 to 179 Mg/ha to sandy soils in Delaware, USA, and found a direct relationship between application rate and  $\text{NO}_3^-$ -N in groundwater.

Table 2.1. Extractable Ca, Mg, Na, K and P concentrations (mg/kg) at 10cm depth increments down the profiles of manured and control treatments at Sites A, B and C. Figures in brackets denote standard errors

Depth (cm)	Extractable Elements (mg/kg)									
	SITE A									
	Ca		Mg		Na		K		P	
	Manure	Control	Manure	Control	Manure	Control	Manure	Control	Manure	Control
0-10	1412 (293)	588 (176)	205 (33)	121 (24)	25 (1)	18 (3)	177 (67)	98 (66)	40 (22)	5 (0)
10-20	1486 (384)	230 (37)	198 (36)	66 (5)	20 (6)	25 (10)	126 (43)	67 (43)	22 (13)	5 (1)
20-30	1231 (209)	124 (12)	185 (31)	45 (1)	21 (7)	23 (6)	120 (45)	48 (21)	20 (7)	2 (2)
30-40	784 (264)	99 (14)	120 (16)	38 (5)	23 (8)	21 (3)	74 (26)	39 (14)	9 (4)	1 (0)
40-50	510 (89)	86 (19)	91 (10)	29 (4)	22 (6)	20 (8)	44 (7)	40 (14)	3 (1)	1 (0)
50-60	480 (80)	64 (20)	89 (9)	26 (5)	23 (6)	19 (3)	42 (8)	27 (9)	2 (1)	0 (0)
SITE B										
	Ca		Mg		Na		K		P	
	Manure	Control	Manure	Control	Manure	Control	Manure	Control	Manure	Control
0-10	1209 (179)	510 (45)	155 (37)	196 (28)	32 (6)	32 (5)	240 (86)	219 (101)	45 (9)	6 (1)
10-20	1509 (151)	224 (46)	197 (32)	124 (28)	42 (8)	30 (8)	349(122)	156 (90)	57 (40)	4 (1)
20-30	1529 (136)	141 (39)	209 (29)	85 (32)	28 (1)	25 (6)	460 (174)	118 (71)	60 (17)	3 (1)
30-40	1234 (76)	103 (28)	176 (22)	63 (17)	29 (3)	29 (6)	352 (168)	80 (54)	47 (16)	1 (1)
40-50	664 (72)	103 (51)	119 (18)	60 (15)	38 (6)	30 (5)	195 (97)	71 (51)	8 (4)	1 (1)
50-60	626 (83)	66 (15)	133 (11)	49 (12)	34 (3)	19 (7)	220 (132)	57 (30)	4 (1)	1 (0)
SITE C										
	Ca		Mg		Na		K		P	
	Manure	Control	Manure	Control	Manure	Control	Manure	Control	Manure	Control
0-10	716(320)	104 (59)	113 (49)	63 (24)	-	-	250 (47)	47 (4)	53 (9)	6 (3)
10-20	609 (212)	67 (19)	99 (51)	50 (15)	-	-	231 (40)	34 (4)	35 (6)	6 (3)
20-30	468 (87)	59 (9)	81 (24)	72 (31)	-	-	153 (57)	23 (3)	13 (1)	4 (2)
30-40	304 (8)	49 (22)	54 (10)	47 (16)	-	-	76 (20)	18 (4)	5 (1)	3 (1)
40-50	195 (70)	45 (25)	33 (16)	39 (14)	-	-	60 (28)	17 (6)	4 (1)	2 (1)
50-60	197 (40)	48 (5)	34 (4)	57 (15)	-	-	44 (19)	14 (3)	3 (1)	2 (1)

Application rates >13 Mg/ha consistently resulted in  $\text{NO}_3^-$  concentrations in groundwater in excess of the recommended 10mg N/l limit set by the U.S. Environmental protection agency. Nitrate pollution of groundwater below lands in the KwaZulu-Natal Midlands where poultry manure is being applied regularly has not been monitored and would be an appropriate area of future study.

It is interesting to note that the nitrification of manure-derived N in the topsoil and its subsequent leaching would, in fact, tend to acidify the surface soil (Adams, 1981). This serves to emphasize the central importance of the initially high pH,  $\text{CaCO}_3$  content and proton consumption capacity of the poultry manure, since topsoil pH was increased appreciably by its application (Table 2.2).

In addition to leaching of  $\text{Ca}^{2+}$  as a counterion with  $\text{NO}_3^-$ , Hue and Licudine (1999) proposed an alternative mechanism to explain the downward mobility of basic cations (especially  $\text{Ca}^{2+}$ ) in manure-amended soils. In a leaching column experiment, these workers found that increased concentrations of soluble organic carbon in poultry manure-amended subsoils were reasonably well correlated with increases in  $\text{Ca}^{2+}$  ( $r^2=0.66$ ). They suggested that organic molecules, originating from the poultry manure, were complexing  $\text{Ca}^{2+}$  ions in a mobile form and facilitating the downward movement of  $\text{Ca}^{2+}$ . A similar mechanism could be operative for  $\text{Mg}^{2+}$ .

Exchangeable  $\text{Na}^+$  concentrations were not greatly increased by manure applications at sites A and B (Table 2.1). Of the major exchangeable bases,  $\text{Na}^+$  is least strongly held by cation exchange surfaces (Talibudeen, 1981)). Therefore, the lack of  $\text{Na}^+$  accumulation in the profile is presumably attributable to leaching of  $\text{Na}^+$  to below the study depth of 60cm. Certainly, poultry manure usually has a significant  $\text{Na}^+$  content since poultry are often fed dietary feed supplements of NaCl (Sims and Wolf, 1994).



Table 2.2: Soil pH values, measured in water and KCl, at 10cm depth increments down the profiles of manure-amended and control treatments at Sites A, B and C. Figures in brackets denote standard errors.

Depth (cm)	pH (KCl)		pH (Water)	
	Manure	No Manure	Manure	No manure
<b>SITE A</b>				
0-10	5.08 (0.39)	4.19 (0.07)	5.64 (0.26)	4.71 (0.13)
10-20	5.03 (0.41)	4.11 (0.02)	5.74 (0.26)	4.59 (0.10)
20-30	4.95 (0.31)	4.16 (0.08)	5.67 (0.26)	4.54 (0.08)
30-40	4.68 (0.27)	4.23 (0.06)	5.29 (0.38)	4.66 (0.14)
40-50	4.56 (0.17)	4.32 (0.06)	5.13 (0.21)	4.75 (0.30)
50-60	4.58 (0.11)	4.39 (0.03)	5.10 (0.31)	4.81 (0.31)
<b>SITE B</b>				
0-10	4.74 (0.18)	4.10 (0.09)	5.37 (0.21)	4.94 (0.02)
10-20	5.00 (0.15)	4.11 (0.05)	5.67 (0.21)	4.94 (0.03)
20-30	5.03 (0.15)	4.14 (0.08)	5.62 (0.21)	4.98 (0.02)
30-40	4.88 (0.08)	4.18 (0.08)	5.44 (0.09)	5.12 (0.01)
40-50	4.70 (0.06)	4.22 (0.10)	5.20 (0.12)	5.08 (0.00)
50-60	4.88 (0.09)	4.23 (0.12)	5.31 (0.01)	5.24 (0.04)
<b>SITE C</b>				
0-10	4.34 (0.21)	3.97 (0.05)	5.00 (0.34)	4.68 (0.08)
10-20	4.26 (0.17)	3.95 (0.03)	4.92 (0.20)	4.62 (0.03)
20-30	4.19 (0.05)	3.98 (0.04)	4.60 (0.09)	4.63 (0.15)
30-40	4.16 (0.03)	4.00 (0.06)	4.69 (0.16)	4.43 (0.16)
40-50	4.20 (0.01)	4.02 (0.04)	4.71 (0.15)	4.38 (0.20)
50-60	4.24 (0.03)	4.00 (0.03)	4.73 (0.14)	4.43 (0.16)

The increased concentrations of exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^{+}$  in the subsoil of manure-amended soils was accompanied by an increase in soil pH (Table 2.2), and a decrease in acid saturation (Figure 2.1) and exchangeable acidity (Figure 2.2). Basic cations leached into the subsoil would tend to compete with exchangeable  $\text{Al}^{3+}$  and  $\text{H}^{+}$  ions and displace some of them into soil solution (where they could be leached). Nevertheless, the strong affinity that  $\text{Al}^{3+}$  and  $\text{H}^{+}$  ions have for cation exchange sites (Talibudeen, 1981) means that such leaching is likely to be very limited. The downward movement of alkalinity (evident from the increased subsoil pH values; Table 2.2) in the soil profile under manure applications would, however, result in the precipitation of exchangeable and soluble Al as gibbsite and/or amorphous hydroxy-Al oxides (Adams, 1981). The leached basic cations could then replace the precipitated  $\text{Al}^{3+}$  on the cation exchange sites. As a result, there was a decrease in exchangeable acidity and a concomitant increase in exchangeable bases. This is reflected in the greatly reduced acid saturation values in manure-amended subsoils (Figure 2.1).

In addition, it is possible that, because of the dominance of variable charge clay colloids in the subsoils at the study sites, the increased soil pH (induced by leaching of alkalinity from the surface-applied manure) could have conferred greater negative charge on the soil surfaces and therefore increased the capacity of the soil to retain cations (Talibudeen, 1981)). Evidently, this effect was not great since calculation of the effective CEC values in the subsoils did not reveal any such discernible trend.

Some other workers have also reported that surface applications of poultry manure have ameliorated subsoil acidity. Kingery *et al.* (1995), for example, showed that long-term (15-28 years) applications of poultry manure resulted in an increase in soil pH of approximately 0.5 units over a 0-60cm depth interval. Also, Hue and Licudine (1999) reported increased soil pH values and decreased exchangeable Al contents throughout the profiles of 50cm-long leaching columns that received surface-applications of poultry manure.

Several mechanisms have been proposed to explain the reported increases in top- and subsoil pH in manure-amended soils; these have been reviewed in Section 3 of Chapter 1. Briefly, the major mechanisms associated with increases in topsoil pH appear to be related to the lime content and proton consumption capacity of the manure (Wong *et al.*, 1998; Eghball, 1999).

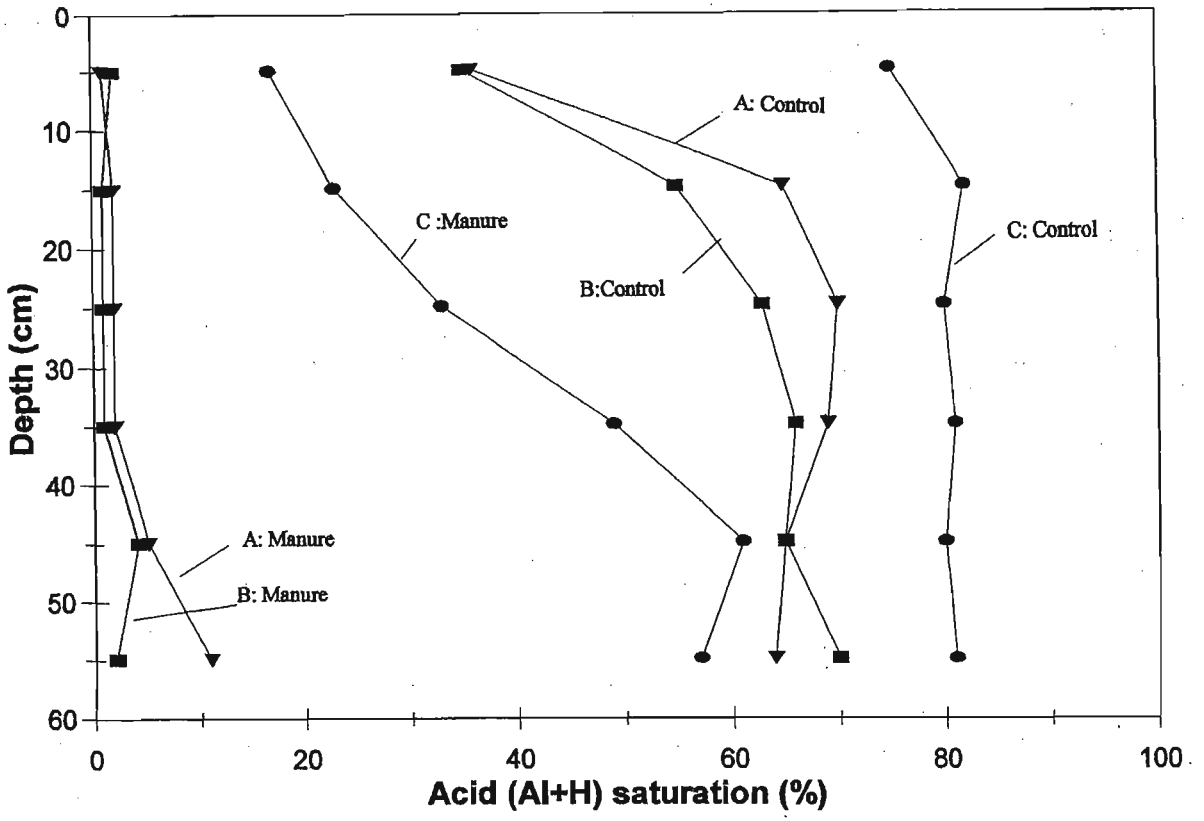


Figure 2.1: Acid ( $Al^{3+} + H^+$ ) saturation (%) values at 10cm depth increments down the profiles of manure-amended and control plots at Sites A, B and C.

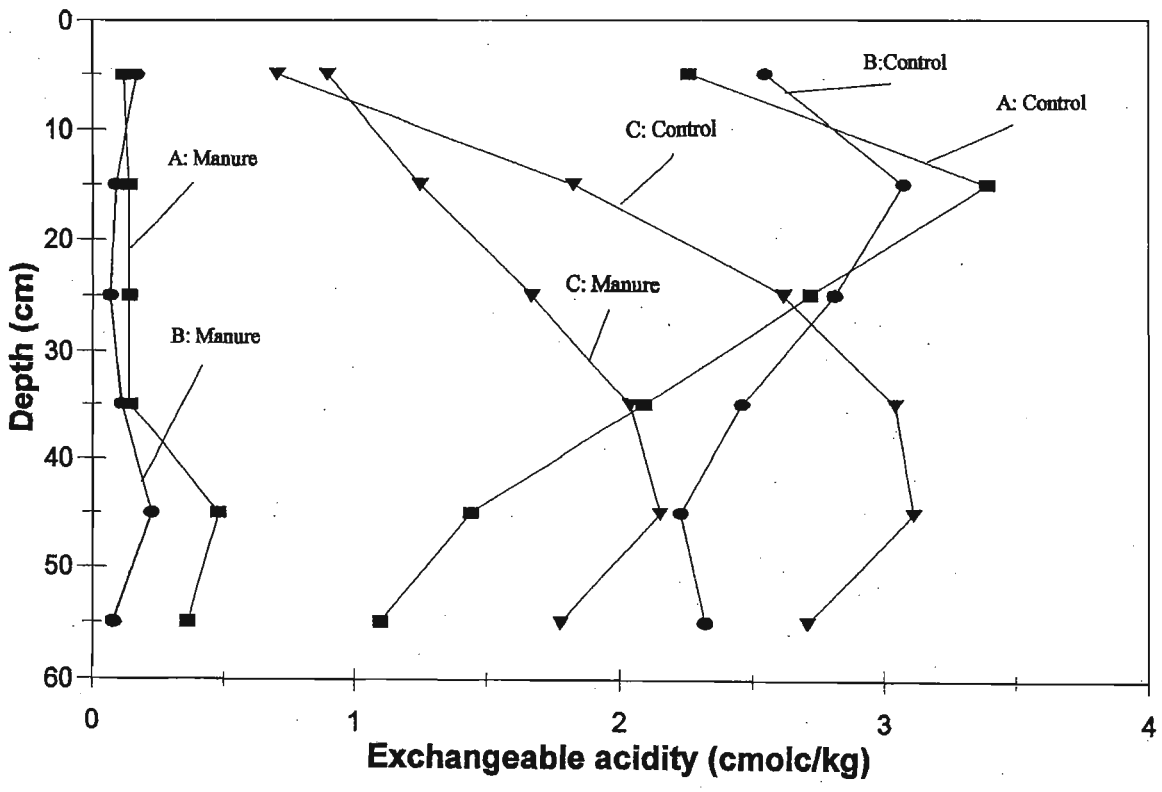


Figure 2.2: Exchangeable acidity ( $Al^{3+} + H^+$ ) concentrations at 10cm depth increments down the profiles of manure-amended and control plots at Sites A, B and C.

Increases in subsoil pH are thought to occur mainly through ligand-exchange reactions whereby surface hydroxyl groups are displaced into soil solution (with a concomitant increase in soil pH) by soluble organic compounds that have been released by the decomposing manure and have leached into the subsoil (Parfitt *et al.*, 1977a,b; Hue, 1992; Smith *et al.*, 1995). Evidence for other mechanisms is discussed in detail in Chapter 3.

In relation to soil fertility and the growth of crop roots into the soil, the greatly increased exchangeable  $\text{Ca}^{2+}$  concentrations, and concomitant decreases in exchangeable Al, in manure-amended top- and subsoils are of particular interest. McCray and Sumner (1990) reported that  $\text{Ca}^{2+}$  and Al in soil solution have antagonistic effects on root growth. That is, increased solution  $\text{Ca}^{2+}$  values will result in decreased susceptibility to Al toxicity. Such is the importance of this relationship that these workers state that, in studies of soil acidity, the relative levels of Ca and Al in acid soils should always be considered, in addition to the actual levels of each.

At all three sites, long-term applications of poultry manure increased extractable P contents in the 0-30cm depth of incorporation (Table 2.1). This is attributed to the relatively high P content of poultry manure (Table 1.1); this P would be released into the soil upon decomposition of the manure. It is possible that some of the exchangeable Al in the topsoils of amended soils could have precipitated as insoluble Al-phosphate minerals (Haynes, 1984a), thereby contributing to the decreased exchangeable Al content in the surface soil. The precipitation of Al-phosphates has been demonstrated in aqueous solutions approximating acid soils (Kodama and Webster, 1975).

The increases in extractable P in manure-amended soils are not only accounted for by a straightforward release of manure-P into the soil. It has been shown that organic matter additions to soils can improve the availability of P in acid soils by reducing the P-sorption capacity of the soil (Hue *et al.*, 1994; Iyamuremye *et al.*, 1996). Organic molecules (e.g. humic substances and organic acid anions) can become specifically adsorbed to soil colloids, therefore blocking P-sorption sites (Nagarajah *et al.*, 1970; Parfitt *et al.*, 1977a,b). In addition, the large amount of P released from poultry manure (that has been incorporated into the soil for long periods) will also tend to saturate P adsorption sites, so decreasing the capacity of the soil to adsorb subsequently added P (Iyamuremye *et al.*, 1996). This will favour some

downward movement of P in the soil profile. Some evidence for this is provided in Table 2.1. At sites A and B, the manure was incorporated to a maximum depth of 30cm and 40cm respectively. However, in the segments directly below these incorporation depths, there have been increases in extractable P of 8 and 7 mg P/kg, indicating the movement of P into deeper soil layers.

The results of this study demonstrate that, under field conditions, long-term surface applications of poultry manure can cause the amelioration of top- and subsoil acidity. Significant increases in  $\text{pH}_{\text{KCl}}$  were observed in the subsoil (30-60cm layer), which were accompanied by decreases in exchangeable acidity and increases in exchangeable Ca, Mg and K. It seems likely that the decrease in acid saturation would encourage greater rooting of crops into the subsoil. The increased Ca:Al ratio in the subsoil would also encourage root growth through further amelioration of Al toxicity. Several mechanisms have been proposed to explain the increases in soil pH following manure applications to soils (reviewed in Chapter 1). With the aim of studying previously proposed mechanisms, and possibly proposing new mechanisms, a leaching column trial was established; the results of which will be presented in the following chapter.

## **CHAPTER 3**

### **THE EFFECTS OF SURFACE APPLIED POULTRY MANURE ON SOIL PROFILE ACIDITY: A LEACHING COLUMN STUDY**

#### **INTRODUCTION**

Poultry manure and other farmyard wastes have been used as fertilizers for centuries, but it is only since analytical techniques have improved sufficiently that their effects on soil characteristics have been described adequately. The effects of poultry manure additions on both top- and subsoil acidity have been fairly well documented internationally by workers such as Jackson *et al.* (1975), Hue (1992), Kingery *et al.* (1994) and Hue and Licudine (1999). Although the literature has been somewhat contradictory in this respect (see Chapter 1), there are many workers that have reported increased soil pH values and decreased exchangeable Al values in both top- and subsoils following poultry manure additions to the topsoil. Indeed, the data reported in Chapter 2 shows that these trends occur in acidic KwaZulu-Natal soils that have been amended with long-term poultry manure applications.

Several mechanisms have been put forward to explain the above-mentioned changes in soil profile acidity following poultry manure additions (Chapter 1). The aim of this chapter is to describe and discuss the findings of a leaching column trial that was established to: (a) test the effects of surface applied poultry manure on the top and subsoil acidity of a KwaZulu-Natal soil under controlled conditions; (b) verify which of the previously proposed mechanisms of acidity amelioration are the most valid and propose possible new mechanisms; and (c) evaluate which type of poultry manure (layer manure, broiler litter or free-range poultry manure) is the most effective at ameliorating soil acidity.

#### **3.1 MATERIALS AND METHODS**

##### **3.1.1. The soil**

The soil used in the leaching column experiment was collected from the Nottingham Road

district in KwaZulu-Natal, South Africa. It was from a Kranskop soil form (family 1100), comprising of a humic A horizon overlying a non-luvic yellow-brown apedal B1 horizon and a red apedal B2 horizon (Soil Classification Working Group, 1991). The soil was chosen for its acidity in both the top and subsoil. The topsoil had a pH of 4.16 (1:2.5 in 1.0M KCl) and a titratable acidity ( $Al + H^+$ ) concentration of 2.72 cmol<sub>e</sub>/kg (see Section 3.1.4 for method of analysis) which gave rise to an acid saturation of 41%. The subsoil had a pH of 4.25 (1:2.5 in 1.0M KCl) and a titratable acidity ( $Al + H^+$ ) concentration of 1.79 cmol<sub>e</sub>/kg which gave rise to an acid saturation of 66%. After collection of both top and subsoil samples, the soil was partially air-dried (to a mass water content of 0.172g/g) and ground to pass through a 2mm sieve.

### 3.1.2. The poultry manures

Three different poultry manures were selected from very different poultry operations. The manure hereafter referred to as layer manure was collected from a laying operation and contained no form of bedding material at all. The manure hereafter termed broiler litter was collected from a broiler house and contained sawdust as the bedding material. The manure termed free-range was collected from the yard of a small-scale, subsistence farmer and contained some bedding material consisting largely of soil and dried grass. The chemical analyses of these manures are presented in Table 3.1. The water contents of the three manure types at sampling were 13.24%, 31.80% and 17.60% for the layer, broiler and range manures respectively. These values were taken into account when different rates were applied to each column.

Table 3.1: Chemical compositions of the three poultry manure types used

Manure	pH	g/kg							mg/kg			
		C	N	S	Ca	Mg	Na	K	P	Zn	Cu	Mn
Layer	6.48	310.2	42.5	4.9	89.8	12.7	2.1	11.6	27.4	374	37	423
Broiler	6.82	360.4	33.9	6.1	25.2	6.1	5.4	24.4	16.0	586	131	413
Free-range	7.75	268.4	21.9	4.6	23.3	5.9	3.8	15.9	14.7	515	67	576

(All data presented on a 100% dry matter basis)

### **3.1.3. The leaching column experiment**

Leaching columns were made from polyvinyl chloride (PVC) tubing with an internal diameter of 10.4cm. The tubing was cut into 55cm long segments, which were in turn cut in half longitudinally so that they could be opened on completion of the experiment. The two halves were then sealed together again, and wire mesh was placed at the bottom of the column. Acid-washed gravel was then placed over the mesh, and covered with a layer of glass wool. Into the column, 45cm of the unamended subsoil was packed, followed by 5cm of the amended topsoil (Figure 3.1). The columns were packed to a bulk density of 1.114 g/cm<sup>3</sup>.

The trial was laid out in a greenhouse as a randomised block design with three replications. Each replication comprised of the following twelve treatments:

- Control (no manure) (C)
- Layer manure at an equivalent rate of 5 Mg/ha (5L)
- Layer manure at an equivalent rate of 10 Mg/ha (10L)
- Layer manure at an equivalent rate of 30 Mg/ha (30L)
- Broiler litter at an equivalent rate of 5 Mg/ha (5B)
- Broiler litter at an equivalent rate of 10 Mg/ha (10B)
- Broiler litter at an equivalent rate of 30 Mg/ha (30B)
- Free-range manure at an equivalent rate of 5 Mg/ha (5R)
- Free-range manure at an equivalent rate of 10 Mg/ha (10R)
- Layer manure at an equivalent rate of 10 Mg/ha with crop (10LP)
- Broiler litter at an equivalent rate of 10 Mg/ha with crop (10BP)
- Control with crop (CP)

These treatments were mixed into the top 5cm (topsoil) segment of the relevant columns. The crop in the last three treatments listed was *Eragrostis curvula*.



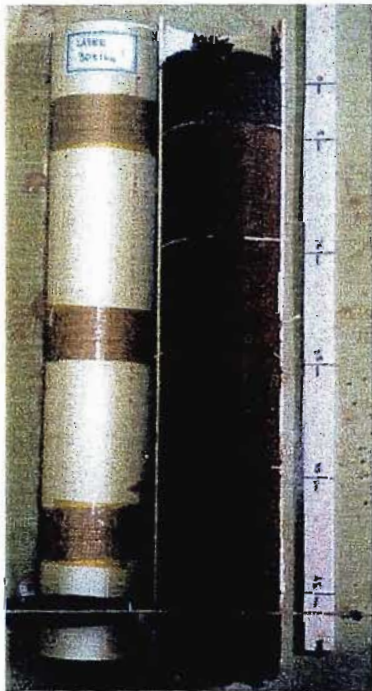


Figure 3.1: Longitudinal section through a leaching column showing the packing structure.

The trial layout is shown in Figure 3.2. The trial ran for a period of 108 days during which each column received 825mm of simulated rainfall. This rainfall was divided into the following six events of which the second, third, fourth and fifth events were main leaching events:

- 28 September 1999: 120mm
- 04 October 1999: 165mm
- 01 November 1999: 165mm
- 22 November 1999: 165mm
- 20 December 1999: 165mm
- 07 January 2000: 45mm

Leachate was collected from each column after each of the four main leaching events and pH and electrical conductivity measured immediately. Thereafter, samples were stored in a freezer until further analyses could be performed. After each leaching event, a suction of 30kPa was applied to each column for 30 minutes. In a preliminary experiment it was shown that this was sufficient to bring each column back to field moisture capacity (on a mass basis). This suction system is illustrated in Figure 3.3.

On completion of the trial, the columns were opened up (Figure 3.1) and the soil column was divided up into the following segments from the top down: 0-5cm; 5-15cm; 15-25cm; 25-35cm; 35-45cm. These samples were then frozen until further analyses could be done.

#### **3.1.4. Chemical Analyses**

The soil segments described above had the following chemical analyses performed on them:

- *Exchangeable Al*: The extraction procedure is the same as described in Section 2.1.2 for the exchangeable acidity, except that the filtrates are analysed for Al by atomic absorption (AA) spectrophotometry and not titrated with NaOH.
- *CuCl<sub>2</sub> extractable Al*: Analysed according to the method of Juo and Kamprath (1979).



Figure 3.2: Trial layout of the leaching column experiment.



Figure 3.3: The suction system used to bring the leaching columns back to field moisture capacity following each leaching event.

- *NH<sub>4</sub>OAc extractable Al*: Analysed according to a variation of the method of McLean (1965). 25ml of 1.0M NH<sub>4</sub>OAc (pH 4.8) was added to 2.5g soil and placed on a horizontal shaker at 180 r.p.m for 2hrs. Extractants were then centrifuged and filtered through a 0.48um membrane filter and Al determined by AA spectrophotometry.
- *NH<sub>4</sub>Oxalate extractable Al*: Analysed according to the method described by Soon (1993).
- *Extractable Ammonium-N (NH<sub>4</sub><sup>+</sup>) and Nitrate-N (NO<sub>3</sub><sup>-</sup>)*: Ammonium-N and nitrate-N were extracted from 2.5g of soil with 25ml of 1.0M KCl. Extracts were filtered through a Whatman No. 1 filter paper, and filtrates were analysed using bubble-segmented flow analysis using the sodiumsalicylate-sodium nitropusside-hypochlorite method for ammonium-N (Perstorp Analytical, 1993) and the sulphanilamide-naphthyl-ethylenediamine method for nitrate-N and nitrite-N after having reduced nitrate to nitrite with copperized cadmium wire (Willis and Gentry, 1987).
- *Exchangeable acidity*: Same procedure as described in Section 2.1.2.
- *Extractable Ca and Mg*: Same procedure as described in Section 2.1.2.
- *Extractable P and K*: Same procedure as described in Section 2.1.2.
- *Organic carbon*: Same procedure as described in Section 2.1.2.
- *pH*: Same procedure as described in Section 2.1.2.

Soil solutions were also extracted from the soil segments. The solutions were extracted by centrifugation using a modification of the method of Elkhatib *et al.* (1987). After extraction, pH and EC were measured immediately and samples were frozen until further analyses could be done. The following analyses were performed on the extracted solutions and on the leachates:

- *Total Al in solution*: Analysed according to the method of Menzies *et al.* (1992).
- *Inorganic, monomeric Al in solution*: Analysed according to the method of Kerven *et al.* (1989).
- *Ca, Mg, Na, and K*: Solutions were diluted with 3125ppm SrCl<sub>2</sub> and analysed by AA spectrophotometry.
- *Soluble Organic Carbon*: Solutions were analysed on a soluble carbon analyser.

- *pH and EC*: pH was measured using a gel-filled combination glass electrode, and EC by using a MeterLab CDM210 conductivity meter.
- *Ammonium-N and Nitrate-N*: These analyses were performed directly on the leachate samples, using the same methods described above for the analyses of ammonium-N and nitrate-N in soil extracts.

### **3.2. EFFECTS OF POULTRY MANURE ADDITIONS ON TOPSOIL ACIDITY, SUBSOIL ACIDITY AND ALUMINIUM IN THE SOIL SOLUTION**

The effects of surface-applied poultry manure on top- and subsoil acidity and Al in the soil solution for each treatment forms the basis of the following discussion. For each of the three sub-sections, the relevant data and observations will be reported and the possible mechanisms behind the changes discussed. Although the effects on Al in the soil solution could essentially be incorporated into the other two sub-sections, it has been included as a separate sub-section, because the unexpected results warranted some individual attention and explanation.

#### **3.2.1. Effects on pH, exchangeable Al and soluble Al in the topsoil (zone of application)**

As discussed in Chapter 1, several workers have reported marked changes in the pH of soils that have been amended with poultry manure. In most cases, the pH has increased, resulting in significantly lower exchangeable Al values in amended soils. Data presented in Figure 3.4 shows the final soil  $\text{pH}_{\text{KCl}}$  and exchangeable acidity values induced by the experimental treatments in the surface 5cm.

The following two trends are evident: (a) the more poultry manure that is applied to the soil, the greater the increase in pH and the greater the resultant decrease in exchangeable acidity, and (b) different types of poultry manures have different effects. Since the layer manure (especially the 30Mg/ha treatment) proved to be the most effective at ameliorating soil acidity in the topsoil, more detailed soil analyses were performed on treatments containing this material to determine the mechanisms by which the poultry manure influenced topsoil acidity. These possible mechanisms are discussed below.

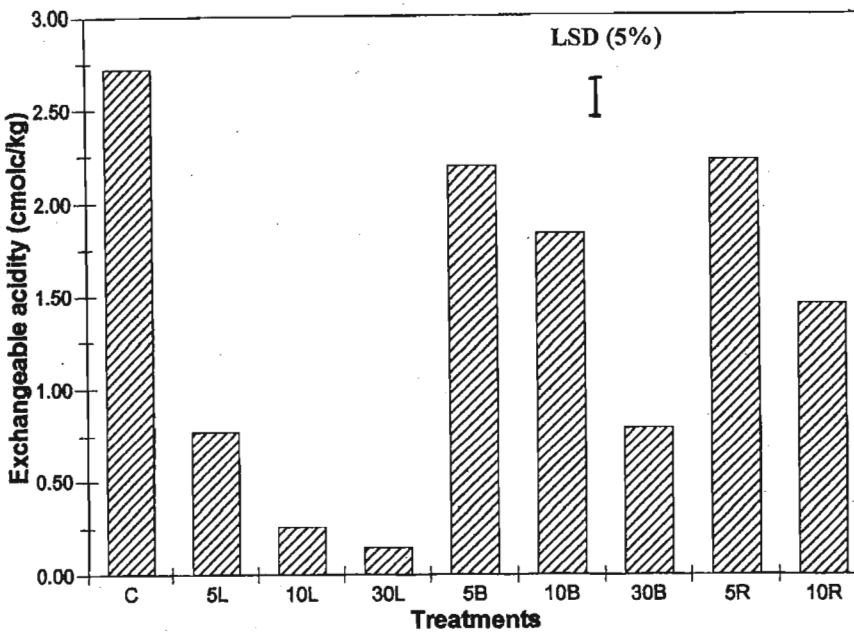
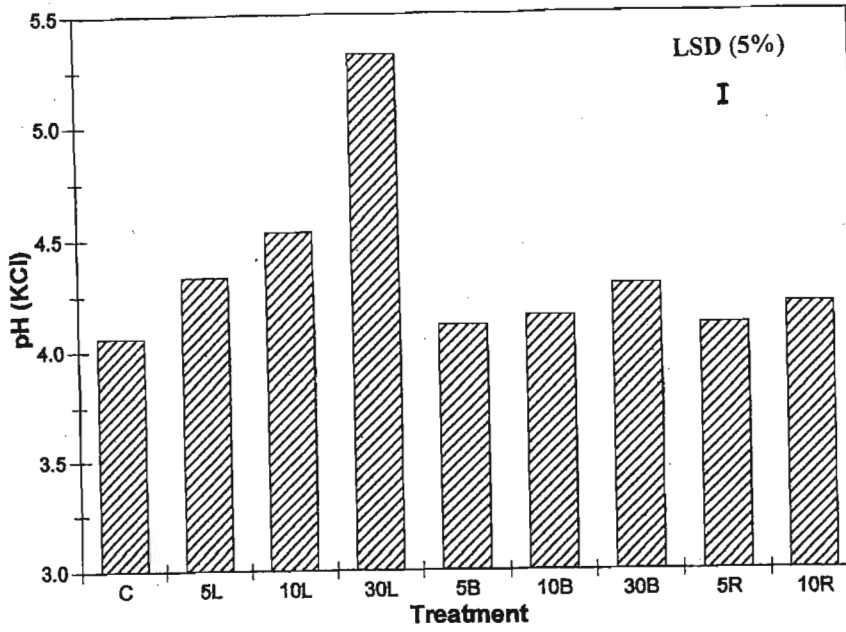


Figure 3.4: Soil  $pH_{KCl}$  and exchangeable acidity ( $Al^{3+} + H^+$ ) concentrations in the 0-5cm segment of various treatments at the end of the 108 day experimental period.



A) Initial pH and lime content of the poultry manure:

All of the manures studied had a pH considerably greater than that of the soil used and would therefore be expected to tend to raise the soil pH. The increased pH induced by their addition was not, however, directly related to their initial pH. For example, free-range manure had the highest initial pH, yet layer manure (with the lowest initial pH) raised the soil pH the most.

Upon the addition of 1.0M HCl to all three types of poultry manure, it was noted that the manure bubbled, indicating the possible presence of carbonates in the manure. Subsequently, carbonates in the manures were measured using the method of Bundy and Bremner (1972); the results of which are shown in Table 3.2. For each manure type, the determination was done on two samples; one ground to pass through a 2mm sieve and one ground to pass through a 150µm sieve (the reasons for which are discussed below).

Table 3.2: Carbonate contents (g/kg) measured in the three poultry manure types, ground either to <2mm or <150µm

Sample	Carbonate (g/kg)
Layer manure (2mm)	80.8
Layer manure (150µm)	85.6
Broiler litter (2mm)	14.4
Broiler litter (150µm)	14.8
Range manure (2mm)	14.8
Range manure (150µm)	15.2

(Data on a dry matter basis)

The above data shows two important facts: Firstly, Bundy and Bremner (1972) recommend the use of finely ground material, but results presented here demonstrate that similar results can be obtained using <2mm sieved samples. The use of <2mm sieved samples would be more appropriate for routine analyses of large numbers of samples for prediction of the liming

capacity of manures prior to land application.

Secondly, layer manure has a lot more carbonate in it than the other manure types. This is because laying hens are fed more carbonate compounds than broiler chickens with the aim of improving the hardness of the egg-shells that are produced. Indeed, Eghball (1999) reported that the calcium carbonate content in the diets of broiler chickens averaged only about 11 g/kg, while the diets of laying hens contained about 77 g/kg of calcium carbonate. Since some of this calcium carbonate is excreted by the birds, poultry manure can be a good lime source for acid soils requiring lime application (Eghball, 1999).

The liming capacity of this carbonate in the manure should not be underestimated. Assume that a farmer applies 10 Mg/ha of this layer manure (not an unreasonable amount) to his land every year. Assuming a moisture content of 200 g/kg at the time of spreading, the farmer is actually applying 8 Mg/ha of dry matter, which contains approximately 80 g/kg of carbonate. The farmer has therefore applied about 640 kg/ha of carbonate to his field, which (assuming this carbonate exists mostly as calcium carbonate) equates to approximately 1.07 Mg of lime/ha. If the farmer uses 10 Mg/ha of layer manure every year at planting, after 5 years approximately 5.5 Mg of lime will have been added. The other benefit is that this lime is being added with the nitrogenous compounds in the manure, and is therefore 'nearby' to neutralize the acidity generated by the nitrification of the nitrogen compounds in the manure. These benefits would obviously not be as great for broiler or free-range manures.

The pH increases induced by manure applications (Figure 3.4) were closely related to the amount of carbonate added with each manure type and amount. Indeed, simple linear regression of these two variables yielded an  $r^2 = 0.99$ .

#### B) Proton consumption capacity of the poultry manure:

As discussed in Chapter 1, composts and manures contain humic and fulvic materials with functional groups such as carboxyl groups that are able to consume protons at their natural pH values (Wong *et al.*, 1998). Their capacity to consume protons is a major factor controlling their buffer characteristics and therefore their ability to neutralize soil acidity. Wong *et al.* (1998) developed a method of measuring this property by titration of the materials down to a



pH 4.0 with 0.05M H<sub>2</sub>SO<sub>4</sub>. This was not attempted with the present manures because of their significant CaCO<sub>3</sub> contents which would also be reflected in such titration values (Mokolabate, 2000).

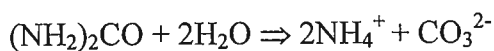
The presence of other organic compounds containing functional groups in the manures could also be important. For example, there is an immediate rise in soil pH when undecomposed plant material is added to soils. This is attributable to the ability of organic acid anions (e.g. oxalate) present in the plant material to consume protons (Tang *et al.*, 1999; Wong *et al.*, 2000). That is, if the soil pH is less than the dissociation constants (pK<sub>a</sub>) for the weak organic acids in the added residues, there will be an increase in soil pH due to the association of H<sup>+</sup> ions in the soil with some of the organic acid anions. This phenomenon is not limited to additions of plant material. As discussed in Chapter 1, decomposing poultry manure will also release various organic acid anions into the soil solution.

It is possible that uric acid present in poultry manure could have a similar proton consuming ability as discussed above. Although the uric acid contents of the poultry manures used in this experiment were not measured, the following values have been reported by other workers. In ten samples of layer manure, Gale *et al.* (1991) found an average concentration of 5.2 g uric acid-N/kg of manure. Similarly, Gordillo and Cabrera (1997) analysed fifteen broiler litter samples, and found that the uric acid contents ranged from 1.9 to 20.5 g uric acid-N/kg litter.

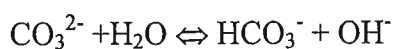
The pK<sub>a</sub> of the most acidic group in uric acid is 5.4 (Stryer, 1975). The pH values of the three manures used in this experiment range from 6.48 to 7.75, and fifteen broiler samples studied by Gordillo and Cabrera (1997) ranged from 7.7 to 8.6. Results published by other workers are in a similar range. At these high pH values found in poultry manure, one could expect that the most acidic group of the uric acid would have deprotonated and formed a uric acid salt, for example calcium-urate. When this calcium-urate salt is added to an acid soil with a pH<sub>water</sub> of less than 5.0, the urate molecule will dissociate from the calcium ion and re-associate with a hydrogen ion. In this way, it is possible that the uric acid in poultry manure can consume protons.

### C. Delayed or inhibited nitrification

The uric acid discussed above is broken down in the manure during storage and/or once it is applied to the soil (by bacteria producing the enzyme uricase) to form urea and glyoxylate (Stryer, 1975). The urea then hydrolyses according to the following reaction:



The carbonate produced in this reaction then reacts with water as follows:



The bicarbonate and hydroxide ions produced are then free to neutralize acidity in the soil. Under normal circumstances however, the two ammonium ions produced in the first reaction would undergo nitrification, a reaction that produces two hydrogen ions for each ammonium ion (with a resulting acidifying action in the soil). However, if these ammonium ions are leached from their zone of formation before nitrification can occur, then that zone has been left with net alkalinity derived from the hydrolysis of urea. Similarly, if nitrification is temporarily delayed then there will be a temporary rise in pH (Haynes and Swift, 1989). Transformations of N originating from organic residues have previously been shown to influence soil pH following additions of organic residues to soils (Hoyt and Turner, 1975; Yan *et al.*, 1996; Pocknee and Sumner, 1997).

In the current leaching column study, it is clear that delayed nitrification could have been a source of alkalinity in the topsoil. Evidence of this is presented in Figures 3.5 and 3.6. Figure 3.5 shows that increases in nitrate-N in the leachate of the 10 Mg/ha layer manure treatment, relative to the control, occurred only during the fourth leaching event. That is, only during the fourth pore volume (i.e. after about 600mm of simulated rainfall and around the 84<sup>th</sup> experimental day) did the nitrate produced from the decomposing manure appear in the leachate. However, the concentrations of cations such as Ca, Mg, Na and K (Figure 3.6) increased in the leachates of manured columns (relative to control) from as early as the second leaching event (i.e. during the second pore volume).

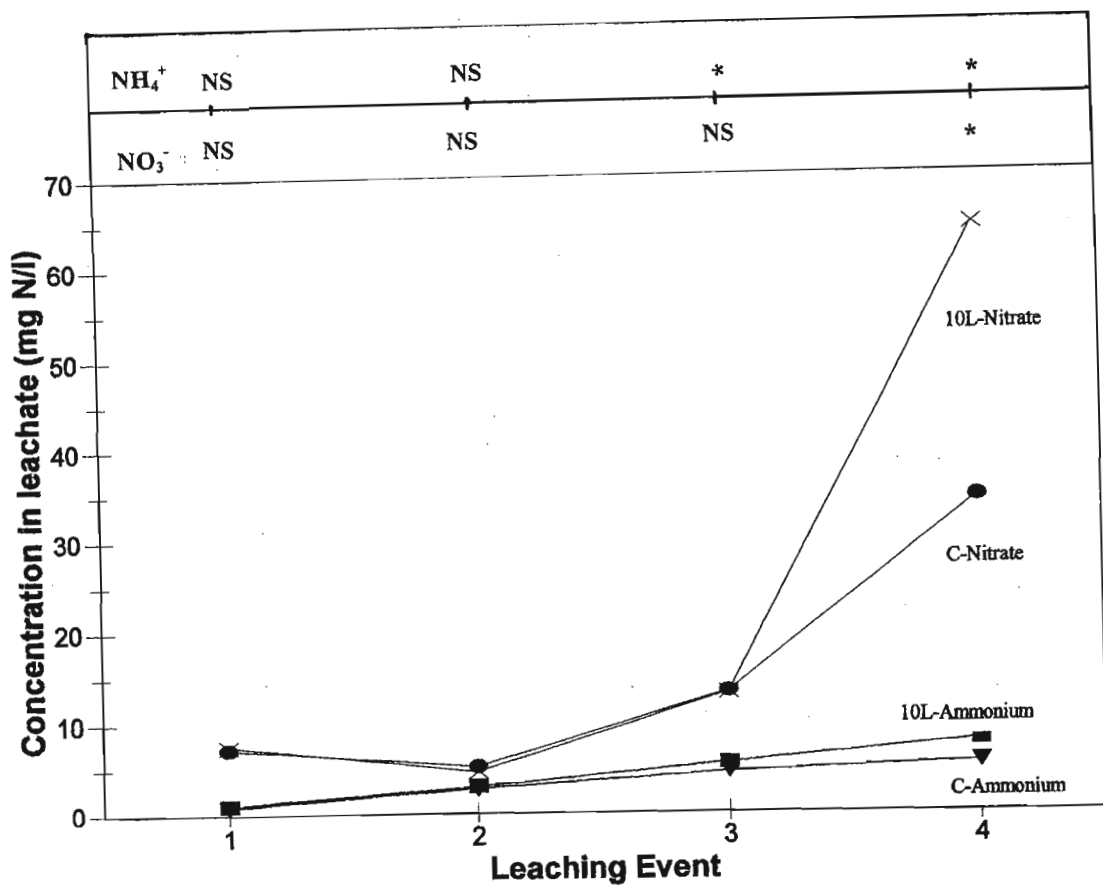
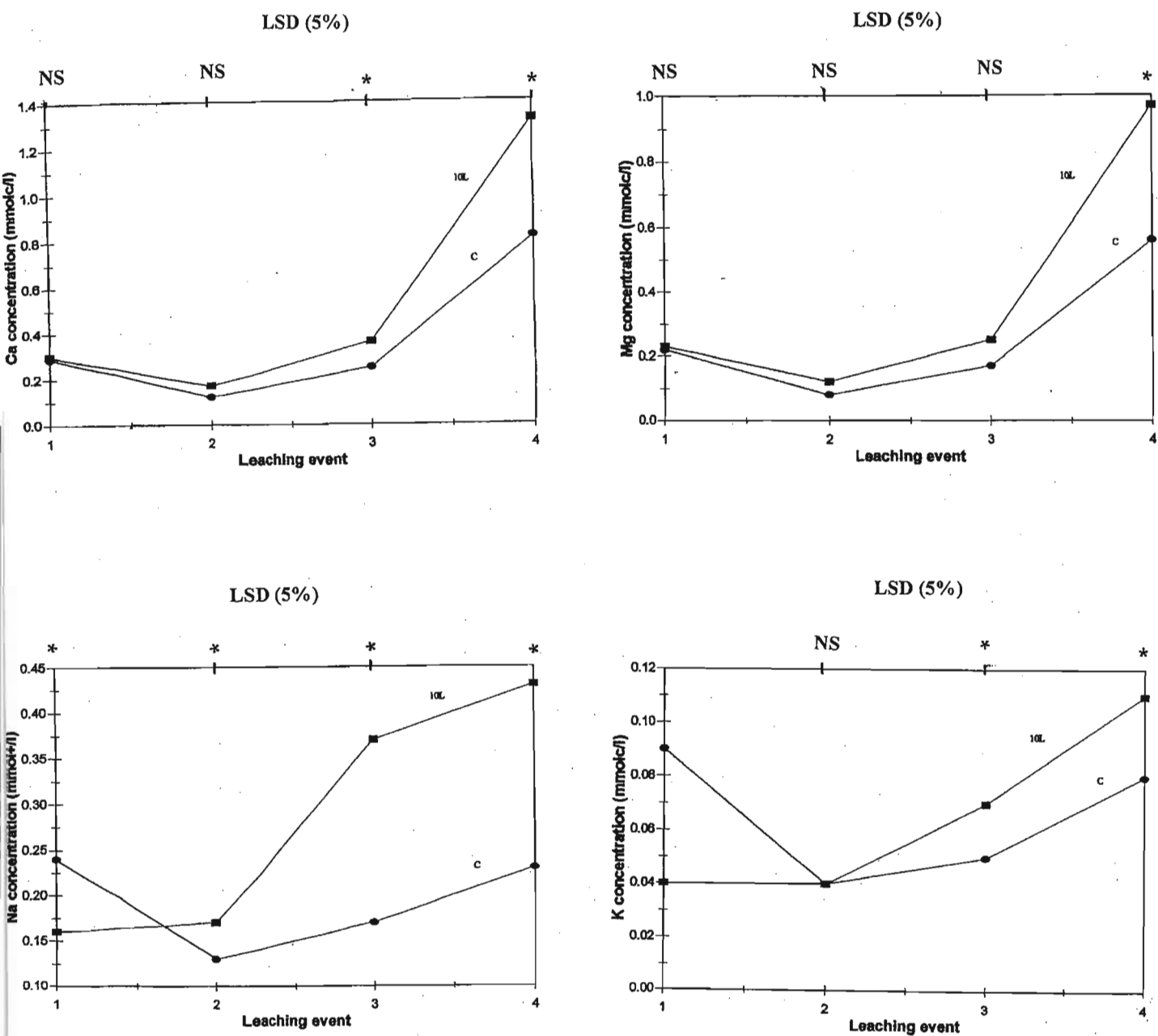


Figure 3.5: Concentrations (mg N/l) of nitrate and ammonium as measured in the leachates from each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments. Note: LSD (5%) values were calculated on log-transformed data (not shown). A \* represents statistical significance between treatments at the 5% level.



**Figure 3.6: Concentrations (mmol/l) of Ca, Mg, Na and K as measured in the leachates from each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments. Note: LSD (5%) values were calculated on log-transformed data (not shown). A \* represents statistical significance between treatments at the 5% level.**

Based on the high N content of poultry manure (Table 3.1), nitrate is usually the dominant anion in manure-amended soils and therefore the cations would be expected to leach down the profile as counterions with nitrate. In this case, however, since the cations (from the manure) appeared in the leachates before nitrate (from the manure), the cations were evidently leaching as counterions with other anions (e.g. Cl<sup>-</sup>) during the first three leaching events. This suggests that large quantities of nitrate were only formed in the manured columns just prior to the fourth major leaching event (i.e. nitrification of the manure-N had been delayed).

It was only at the fourth leaching event that substantial nitrate concentrations were measured in the leachates from either the control or the manure-amended treatments (Figure 3.5), indicating an initial slow nitrification rate in the soil. Therefore, only after a prolonged presence of increased ammonium in the topsoil did the nitrifying bacteria become sufficiently active to produce large amounts of nitrate. This then leached and appeared in the final leaching event. During the intervening period, the poultry manure was releasing ammonium (via urea hydrolysis and the associated release of alkalinity), but without subsequent nitrification. Some of these ammonium ions may then have been leached out of the topsoil, leaving alkalinity in the topsoil. Downward movement of ammonium in manure-amended soils is evident from Table 3.3. That is, elevated concentrations of both ammonium and nitrate were evident in the 5-45cm layer of manure-amended soils at the end of the experiment. The high divalent cation (Ca<sup>2+</sup> and Mg<sup>2+</sup>) content in soil solution of the poultry manure-amended soils (Table 3.4) will tend, by cation exchange, to maintain high concentrations of monovalent cations, such as NH<sub>4</sub><sup>+</sup>, in soil solution and thus favour its movement by leaching.

Also notable are the high nitrate-N concentrations in the 0-5cm segments of the 10 and 30 Mg/ha layer manure treatments. This is another possible indication that this nitrate was formed only towards the end of the experiment; otherwise it would have leached down the profile prior to sampling.

Table 3.3: Extractable ammonium-N and nitrate-N concentrations (mg N/l) at various depths down the profiles of the control and layer manure treatments at the end of the 108-day experimental period

	Control		5Mg/ha Layer		10Mg/ha Layer		30Mg/ha Layer	
Depth	All units in mg N /kg							
	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>
0-5cm	9	6	9	15	11	62	11	306
5-15cm	12	7	16	8	25	14	25	46
15-25cm	23	10	38	11	50	25	91	61
25-35cm	23	22	44	33	56	60	141	99
35-45cm	23	34	36	58	39	76	81	110

LSD (5%) at same depth level for NH<sub>4</sub><sup>+</sup> = 10

LSD (5%) at same depth level for NO<sub>3</sub><sup>-</sup> = 30

Table 3.4: Ca, Mg, Na and K concentrations (mmol/l) in the soil solution at various depths down the profiles of the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108-day experimental period

	All units in mmol/l							
Depth	Ca		Mg		Na		K	
	C	30L	C	30L	C	30L	C	30L
0-5cm	0.25	18.60	0.12	6.90	0.11	0.55	0.08	1.30
5-15cm	0.18	1.67	0.09	0.77	0.04	0.08	0.04	0.47
15-25cm	0.23	0.66	0.15	0.62	0.04	0.08	0.05	0.37
25-35cm	0.45	0.68	0.28	0.46	0.06	0.11	0.07	0.30
35-45cm	0.62	1.54	0.42	1.16	0.11	0.19	0.08	0.25
LSD (5%) at same depth level	2.47		0.87		0.05		0.13	

The above discussion leads one to the following two important questions:

i) Why was there a delay in nitrification in this soil?

Many workers have documented the inhibitory effect of soil acidity on nitrification in soils

(Cornfield, 1959; Dancer *et al.*, 1973 and Ishaque and Cornfield, 1976). Arora *et al.* (1986) measured nitrate accumulation following urea additions to soils amended with different rates of lime. They found a three-fold and a five-fold increase in nitrate accumulation in soils which received two and four Mg/ha of lime, respectively, in comparison with an unlimed soil. Pleyseir *et al.* (1987) added urea (amongst other N sources) to leaching columns and found that, after 2420mm of simulated rainfall, relatively little nitrate had leached from the columns treated with urea. They also found that, as occurred in the current leaching experiment, ammonium was the dominant form of nitrogen remaining in the column. They concluded that the highly acidic soil ( $\text{pH}_{\text{water}} = 4.5$ ) used in their experiment caused slow nitrification rates, resulting in the increased concentrations of ammonium in the soil profile.

Haynes and Swift (1989) also concluded that soil acidity is an important factor in determining the nitrification potential of soils. They found that in acid soils with a  $\text{pH}_{\text{water}}$  of less than 5.0, ammonification proceeded but there was no significant nitrification following re-wetting of air-dried soils. In soils with a  $\text{pH}_{\text{water}}$  of between 5.0 and 5.5, although ammonification also proceeded unretarded, there was a delay in nitrification of 2 to 6 weeks. It is suggested that the  $\text{pH}_{\text{water}}$  of 5.10 in the topsoil used for the current experiment may have been a major contributing factor to the low initial rate of nitrification. This delayed nitrification allowed ammonium to move out of the zone of application, leaving alkalinity behind.

ii) Do poultry manure applications induce delayed nitrification?

Accumulations of  $\text{NH}_4^+$  following poultry manure additions to soils have been reported to inhibit nitrification (Weil *et al.*, 1979; Nielson and Revsbech, 1998). Weil *et al.* (1979), for example, found higher concentrations of nitrite in soils amended with poultry manure (relative to unamended soils) and concluded that one of the possible reasons for this was the high concentrations of ammonium in the amended soils (from the breakdown of uric acid and urea present in the manure) which suppressed the activity of *Nitrobacter*; the bacteria species involved in the oxidation of nitrite to nitrate (Aleem and Alexander, 1960). The accumulation of nitrite, in turn, inhibits the oxidation of ammonium to nitrite. Similarly, Nielson and Revsbech (1998) found that the incubation of duck litter with soil led to high rates of ammonium liberation which inhibited nitrification for a period of about ten days, after which the nitrifying activity increased slowly.

Other workers, such as Warman (1980), studied the possibility of antibiotics, coccidiostats and pesticides in the manure being the cause of the temporarily inhibited nitrification. Although the work of Warman (1980) showed that amprolium (a coccidiostat) and aureomycin (an antibiotic) had no effect on the nitrification rate when added with poultry manure, it is still possible that other chemicals used in the treatment of poultry manure might have an inhibitory effect on nitrification.

Detailed work on the effects of poultry manure on nitrification is beyond the scope of this project and, indeed, in this particular study, nitrification was inhibited/delayed in the control treatments as well as those amended with manure (indicating a naturally low initial nitrification capacity of the soil). Nevertheless, it is evident that following poultry manure applications, the urea from the manure will hydrolyse to form ammonium ions that can move out of the zone of application, effectively leaving alkalinity behind. This process could contribute to the pH increases in the zone of application. It should, however, be noted here that the downward movement of  $\text{NH}_4^+$  may also be attributable to leaching of urea followed by its hydrolysis at depth (see Section 3.2.2).

#### D) Organically-complexed Al:

Organically-complexed Al species are non-phytotoxic and a great deal of work has been done on the ability of organic amendments to complex toxic, monomeric Al species in soil solution (Hue *et al.*, 1986; Hue and Amien, 1989; Wong and Swift, 1995). Aluminium concentrations in soil solution in the 0-5cm segment for the control and 30 Mg/ha layer manure treatments are presented in Table 3.5. Inorganic monomeric Al in soil solution was analysed using the pyrocatechol violet (PCV) 60 second method (Kerven *et al.*, 1989). This method is designated as monomeric Al, but it is accepted that the PCV will react some Al existing as soluble Al-organic matter complexes (Close and Powell, 1989; Parfitt *et al.*, 1995).



Table 3.5: Soil solution Al concentrations ( $\mu\text{M}$ ) and exchangeable Al values ( $\text{cmol}_e/\text{kg}$ ) in the 0-5cm segment of the control and 30 Mg/ha layer manure treatments at the end of the 108-day experimental period

Treatment	Total Al ( $\mu\text{M}$ )	Monomeric Al ( $\mu\text{M}$ )	% Al in the monomeric form	Exchangeable Al ( $\text{cmol}_e/\text{kg}$ )
Control	4.43	1.75	40	2.27
30Mg/ha Layer	7.11	1.43	20	0.04
LSD (5%)	12.11	13.17	-	0.10

It is interesting to note that, even with a vastly lower exchangeable Al concentration in the manure treatment, the monomeric Al concentration in the soil solution is similar to that of the control. Furthermore, the total Al in soil solution is, in fact, higher in the manured soil. Therefore, soil solution Al concentrations in manure-amended soils are not closely related to those for exchangeable Al. Similar findings were recently reported by Mokolobate (2000). This means there are questions regarding the use of exchangeable Al and/or exchangeable Al saturation as indicators of potential Al toxicity and the need for lime in manure-amended soils

From a soil fertility viewpoint it is the percentage of soil solution Al present in the phytotoxic, monomeric form that is of considerable importance (Ritchie, 1989; Kinraide and Parker, 1990). In the control, 40% of the soil solution Al is present in the toxic form, whereas in the manured soil, even though the total Al in solution is higher, only 20% of this is in the monomeric form. If one assumes that the difference between the total and monomeric Al concentrations represents the organically-complexed Al in solution, then these amount to 2.68 and 5.68 $\mu\text{M}$  for the control and manured soils respectively. Therefore, poultry manure applications increase the concentration of organically-complexed, non-toxic Al species in soil solution and reduce the proportion of toxic, monomeric Al species.

The increased concentration of total Al in the soil solution of the manured soil, despite the increased soil pH, can be explained by considering the increased salt and soluble organic

carbon concentrations of the manured soil relative to the control (Table 3.6).

Table 3.6: Concentrations of exchangeable Al (cmol<sub>e</sub>/kg), soluble organic carbon (mg C/l) and Ca, Mg, Na and K (mmol/l) in the solution of the 0-5cm soil segment of the control and 30 Mg/ha layer manure treatments at the end of the 108-day period

Treatment	Exchangeable Al (cmol <sub>e</sub> /kg)	Soluble organic carbon (mg C/l)	Ca (mM)	Mg (mM)	Na (mM)	K (mM)
Control	2.27	46.93	0.25	0.12	0.11	0.08
30Mg/ha layer	0.04	106.67	18.60	6.90	0.55	1.30
LSD (5%)	0.10	16.59	2.47	0.87	0.05	0.13

It seems likely that, even though the manured soil has a higher pH and lower exchangeable Al concentration than the control, the higher salt concentration in the solution of the amended column is displacing Al from the exchange sites into the solution (even though there is much less exchangeable Al when compared to that of the control). Other workers have observed a similar phenomenon. Brenes and Pearson (1973), for example, showed that a small addition of KCl to soil samples increased the concentration and activity of Al in the soil solution. Similarly, Manson and Fey (1989) demonstrated that additions of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> at increasing ionic strengths resulted in lower pH and higher Al concentrations and activities in soil solution.

Once in solution, the displaced Al in amended columns is being complexed by the soluble organic carbon that is released from the decomposing manure, which results in a larger amount of organically complexed Al in solution. It is interesting to note that the complexation of monomeric Al by soluble organic matter will, in fact, tend to result in an increased supply of monomeric Al from the solid phase. That is, a decrease in monomeric Al activity in soil solution due to complexation will result in the movement of exchangeable Al into the soil solution through exchange reactions and, in the longer term, to more dissolution of Al-containing minerals (e.g. gibbsite and amorphous hydroxy-Al oxides) and thus a replenishment of monomeric Al in the soil solution. Indeed, the supply of soluble organic

matter is generally thought to be an important factor that maintains high concentrations of total Al in the soil solution of organic residue-amended soils (Berek *et al.*, 1995). Slattery and Morrison (1995) also observed that applications of crop residues to an acid soil increased total Al concentrations in soil solution.

The nature of the soluble organic matter present in soil solution was not investigated in the present study. However, a number of other workers have observed that additions of decomposing organic residues, including poultry manure, to acid soils can reduce the concentration of monomeric Al in soil solution through complexation reactions (Hue *et al.*, 1986; Hue and Amien, 1989; Wong and Swift, 1995, Hue and Licudine, 1999). Soluble organic molecules produced during residue decomposition such as organic acids (e.g. citric, tartaric and oxalic acids) and phenolic humic substances can effectively complex and detoxify soluble monomeric Al (Hue and Amien, 1989; Stevenson and Vance, 1989; Wong and Swift, 1995). It is interesting to note that Tan *et al.* (1971) showed that water extracts of poultry litter had a chelating effect on Al and they concluded that soluble polysaccharide compounds were important agents of complexation.

#### E) Formation and precipitation of Al phosphates

The phosphorous (P) content of the layer manure is 27.4 g/kg manure (on a dry matter basis). This means that a 10Mg/ha application of this manure would supply approximately 274 kg P/ha, whereas the 30 Mg/ha application would supply 822 kg P/ha. Assuming that about 70% of this P is available in the first growing season (Sims and Wolf, 1994), then effectively 192 and 575 kg P/ha has been applied for the 10 and 30 Mg/ha treatments respectively. As a result, large increases in extractable P occurred; the soil P test increased by 16 and 52 mg P/kg (Appendix 1) for the 10 and 30 Mg/ha treatments respectively (relative to the control).

It is possible that, with such high P loading rates (especially for the 30Mg/ha treatment), some of the exchangeable Al was precipitated as insoluble Al-phosphate minerals. Haynes (1984a) noted that the addition of phosphate to soils initially high in exchangeable Al results in precipitation of aluminophosphates; this has been demonstrated in aqueous solutions approximating acid soils (Kodama and Webster, 1975).

## F) Perspective

A number of different mechanisms have been discussed above. Certainly, the application of poultry manure to acid soils results in an increase in topsoil pH, and this will cause the precipitation of exchangeable Al as insoluble hydroxy-Al species and therefore a reduction in exchangeable Al concentrations. The cause of the increase in soil pH appears to be primarily related to the lime content and, to a lesser extent, the proton consumption capacity of the manure. Ammonification of manure-N, the hydrolysis of urea (following the breakdown of uric acid in the manure) and the leaching of  $\text{NH}_4^+$ , coupled with an initial delay in nitrification, may be another contributing factor. In addition, there is a possibility that the high P content of the manures may have resulted in a reduction in exchangeable Al concentrations through precipitation of insoluble Al-phosphates (particularly at the manure application rates used).

Despite the above processes working to cause a marked reduction in exchangeable Al concentrations in manure-amended topsoils, concentrations of total Al in soil solution were, in fact, increased by manure applications. This seems to be primarily attributable to the high soluble salt concentrations present in soil solution induced by manure applications, which result in the displacement of exchangeable Al back into soil solution. In turn, the increased quantities of soluble carbon in soil solution, originating from the manure, are able to complex this Al so that a large proportion of the soil solution Al is present as organic matter-Al complexes. As a result, the proportion of total Al in soil solution present in the toxic, monomeric form is greatly reduced by manure applications in the topsoil.

### 3.2.2. Effects on subsoil acidity

Several researchers have studied the effects of surface-applied poultry manure on subsoil acidity and their findings have been reviewed comprehensively in Chapter 1. Hue and Licudine (1999) performed a leaching column experiment in which the effects of different surface-applied amendments on subsoil acidity were compared against each other and a control. These workers found that surface applications of poultry manure decreased exchangeable Al concentrations at all soil depths down to 50cm. In the current study, similar findings were observed, although the magnitude of the decreases were not as large. This data

is reported in Table 3.7.

Table 3.7: Exchangeable Al concentrations (cmol<sub>c</sub>/kg) at various depths in the control and layer manure treatments

Depth	Exchangeable Al (cmol <sub>c</sub> /kg)			
	Control	5Mg/ha Layer	10Mg/ha Layer	30Mg/ha Layer
0-5cm	2.27	0.71	0.27	0.04
5-15cm	1.53	1.39	1.19	0.87
15-25cm	1.51	1.36	1.37	1.29
25-35cm	1.56	1.36	1.44	1.39
35-45cm	1.55	1.38	1.44	1.40

Note: LSD (5%) = 0.10

Coupled with Table 3.7, the data presented in Figure 3.7 conveys some interesting points: (a) although manure applications decrease exchangeable Al in all of the subsoil segments (i.e. below 5cm depth), the largest effect occurs in the 5-15cm segment, (b) the decreases in exchangeable Al in the deepest three segments of the manure-amended columns (15-25cm, 25-35cm and 35-45cm) appear to be unrelated to manure amount; rather just the presence of manure, (c) the manure has no effect on the pH<sub>KCl</sub> below 15cm, yet the exchangeable Al decreases, and (d) the manure decreases the pH<sub>water</sub> below the 15cm depth, but has little effect on soil solution pH. The significance of these points will be discussed below.

Effects on soil acidity in the 5-15cm segment:

It is clear that the manure applications had the largest ameliorative effect on the first subsoil segment. Relative to the control, manure applications decreased exchangeable Al by 0.14, 0.34 and 0.66 cmol<sub>c</sub>/kg for the 5L, 10L and 30L treatments respectively (Table 3.7). Coupled with these decreases were small increases in pH<sub>KCl</sub> of 0.0, 0.05 and 0.10 for the 5L, 10L and 30L treatments respectively. The pH<sub>water</sub> in this segment was the same for the control and the 30L treatment. It is believed that this was caused by a balance between the liming effect of the manure treatment (which is evident in the increased pH<sub>KCl</sub>) and the salt-effect caused by the high salt content in the manure (which results in the displacement of exchangeable Al back into soil solution).

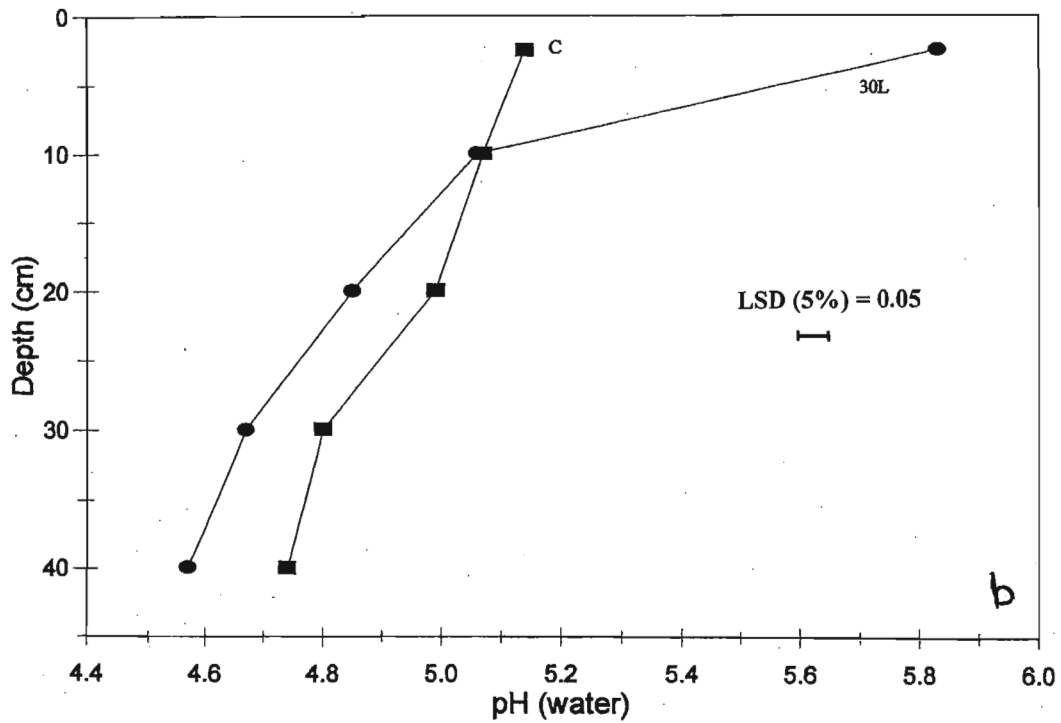
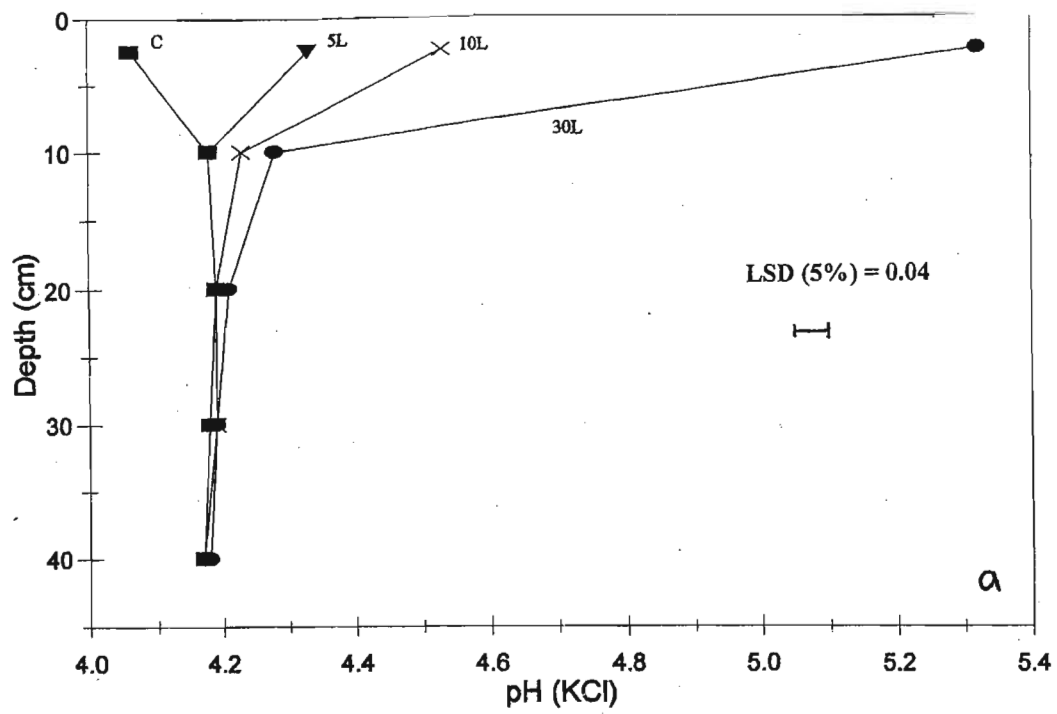


Figure 3.7: (a) Soil pH<sub>KCl</sub> values for the control (C), 5 Mg/ha (5L), 10 Mg/ha (10L) and 30Mg/ha (30L) layer manure treatments at the end of the 108 day experimental period; (b) soil pH<sub>water</sub> values for the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period.

A probable explanation for the increase in  $\text{pH}_{\text{KCl}}$  is that alkalinity has moved from the zone of application (0-5cm) into the 5-15cm segment. Helyar (1991) stated that, provided topsoil pH levels are sufficiently increased (above a  $\text{pH}_{\text{water}}$  of 6.0), the potential exists for the downward movement of alkalinity ( $\text{OH}^-$  and  $\text{HCO}_3^-$ ) by mass flow, and the consequent amelioration of deeper soil layers. Sumner (1995) also cited instances where the downward movement of lime has been noted and, on examination of this literature, Farina (1997) found that in each of the instances the topsoil  $\text{pH}_{\text{water}}$  had been elevated to above 6.0.

The final  $\text{pH}_{\text{water}}$  of the 0-5cm segment from the 30L treatment was 5.83. When this pH was measured, the soil contained 306mg nitrate-N/kg (Table 3.3) which, as discussed previously, was only produced near the eighth week of the experiment due to delayed nitrification. The production of this nitrate by nitrification would have been accompanied by acidification of the soil. It is therefore likely that before this nitrification, and the associated acidification, occurred the topsoil pH was above 6.0, therefore allowing movement of alkalinity from the topsoil into the 5-15cm segment. It is also possible that this mechanism occurred to a lesser extent in the 10L treatment, due to the lower pH in the topsoil of this treatment. It is suggested that the 5 Mg/ha layer manure treatment would not have raised the pH in the topsoil sufficiently to allow downward movement of alkalinity, hence the  $\text{pH}_{\text{KCl}}$  was no different from that of the control in the 5-15cm segment. However, the exchangeable Al in this segment still decreased under the 5 Mg/ha layer manure treatment relative to the control; the processes responsible for this are not clear. The mechanism responsible (for this decrease in exchangeable Al, coupled with an unchanged  $\text{pH}_{\text{KCl}}$ ) is likely to be the same as that for the lower depths. This will be the topic of discussion below.

#### Effects in the 15-25cm, 25-35cm and 35-45cm depths:

The data in Table 3.7 shows significantly lower exchangeable Al values in the 15-25cm, 25-35cm and 35-45cm segments of all three manured columns relative to the control. Figure 3.7, however, shows that these decreases have been accompanied by no change in  $\text{pH}_{\text{KCl}}$  and a by decrease in  $\text{pH}_{\text{water}}$  (caused by a salt-effect). Such results are surprising and indicate that processes occurring in the subsoil are not straightforward.

One possibility is that Al has leached out of the subsoil of manure-amended treatments. Hue and Licudine (1999), for example, found significantly more Al and soluble carbon in the leachates of manured columns relative to the control. They postulated that organic-Ca complexes, generated by the chicken litter in the incorporation zone, reacted with exchangeable Al in the subsoil while leaching. They postulated further that Al displaced the Ca from the organic complex, thereby forming a mobile Al-organic complex. In the current experiment, the concentration of Al in the leachate is also higher under manured columns relative to the control (Figure 3.8), particularly in the 3<sup>rd</sup> and 4<sup>th</sup> leaching events (as noted by Hue and Licudine, 1999). In addition, the leachates of the manured columns had a slightly higher soluble C content than those from the control (Figure 3.9b), particularly in the first and second leaching events.

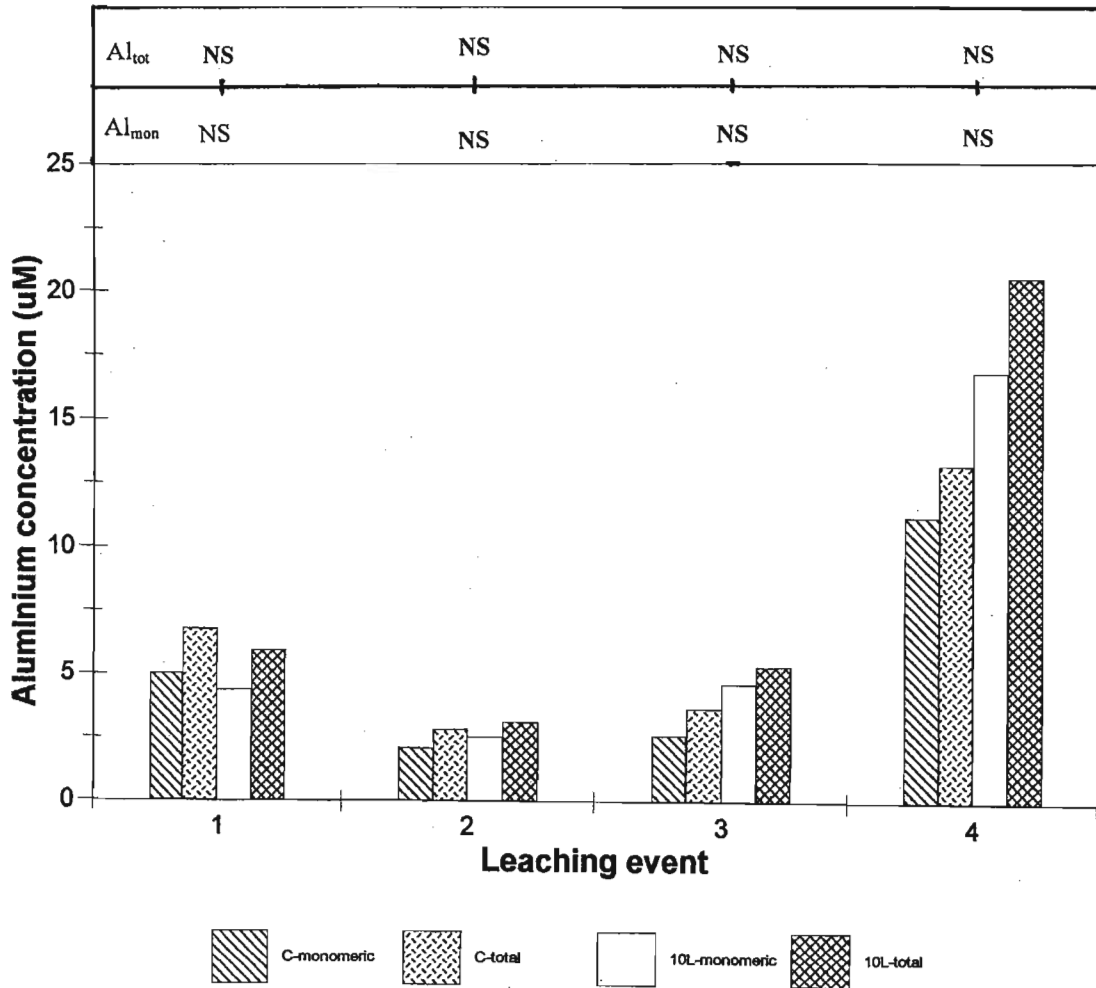
Nevertheless, even though more Al was leached from the manured columns than from the control, the differences were micro-molar in quantity. The total amount of Al leached from the 10 Mg/ha layer manure treatment, relative to the control, was about 7.0  $\mu$ moles. However, the difference between the total amount of exchangeable Al in the 15-45cm layer of the amended and control columns was about 1100  $\mu$ moles. Therefore, although occurring in small amounts, the leaching of Al from the amended profile has not significantly affected exchangeable Al concentrations in the 15-45cm layer.

Furthermore, the percentage of Al in the monomeric form in the leachates of manured columns was either the same or higher than that of the control (Figure 3.8). As previously discussed, this was caused by the salt-effect from the manure, which resulted in displaced inorganic Al species entering the soil solution where they can be leached. Since the manured columns have a greater proportion of Al in the monomeric form in the leachate than the control, it seems unlikely that the manured soils in this experiment are losing substantial quantities of Al by the mechanism proposed by Hue and Licudine (1999); i.e. the formation of mobile organic-Al complexes.

If the 'missing' exchangeable Al in the manured columns (relative to the control) has not been leached, then it must still exist in the soil in a form that is not extractable with 1.0M KCl. Based on this assumption, Al in the soil segments from the control and 30Mg/ha layer manure treatment was extracted with a number of different extractants in order to identify the



nature of the missing exchangeable Al (Table 3.8).



**Figure 3.8: Total and monomeric Al concentrations ( $\mu\text{M}$ ) as measured in each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments.**

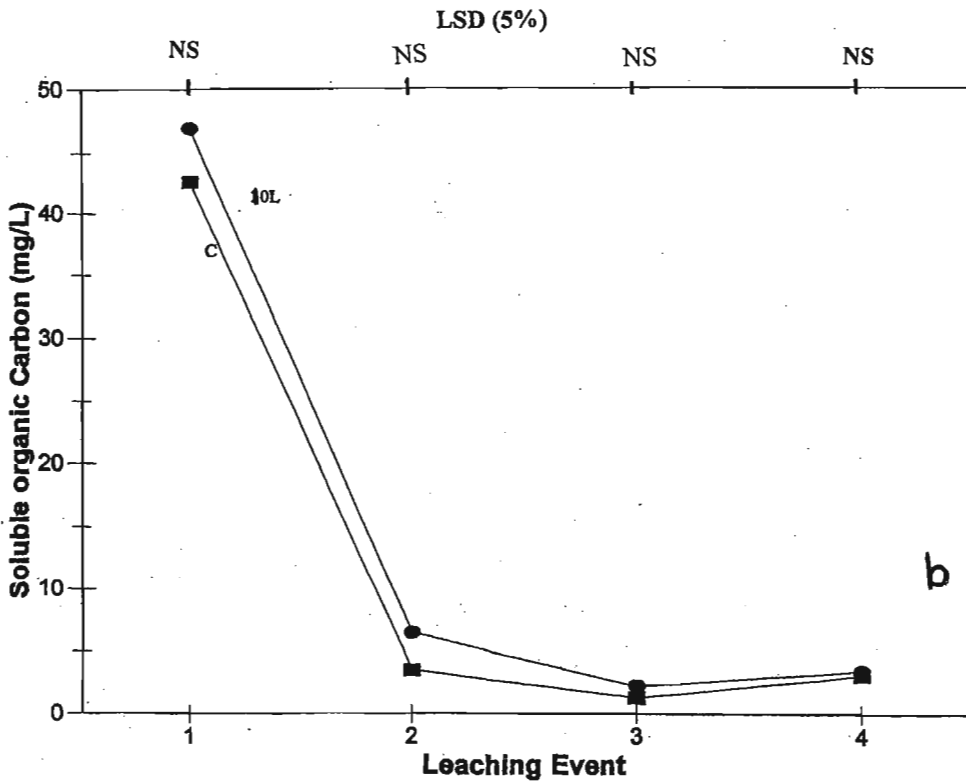
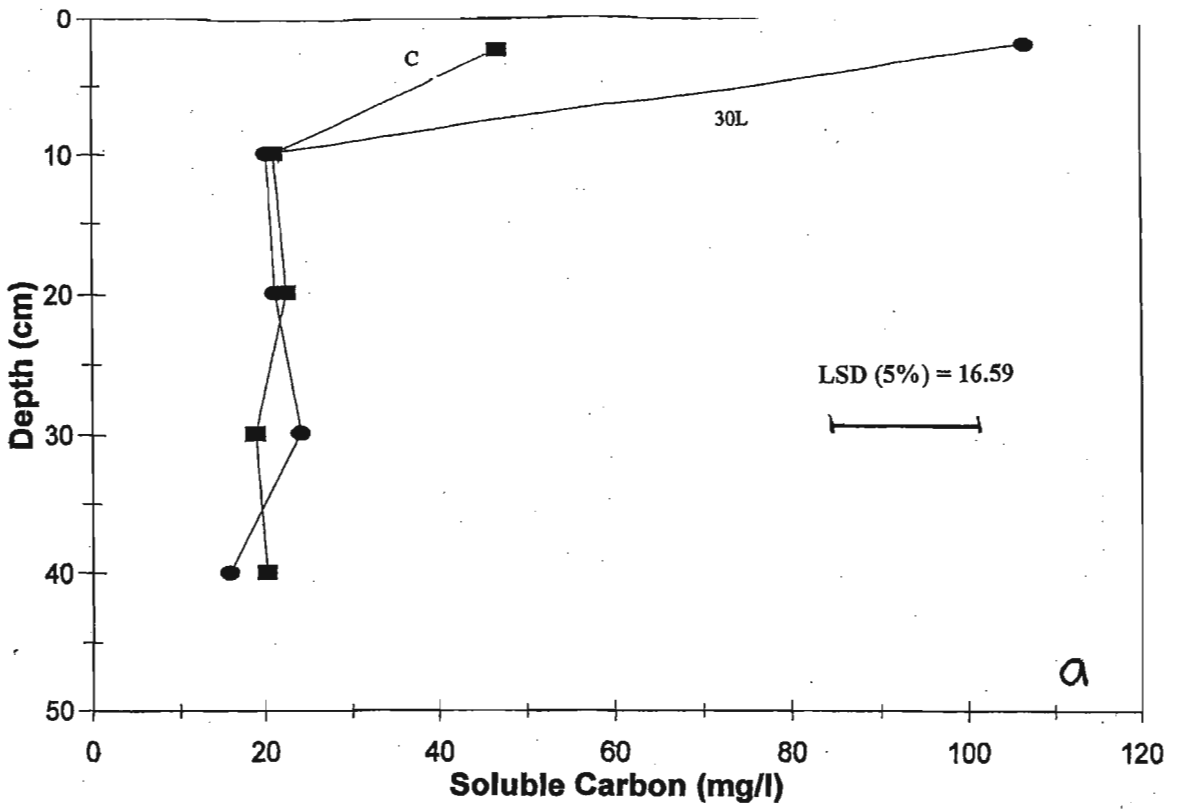


Figure 3.9: (a) Soluble organic carbon concentrations (mg C/l) down the profiles of the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period; (b) Soluble organic carbon concentrations (mg C/l) as measured in each of the four leaching events for the control (C) and 10 Mg/ha layer manure (10L) treatments. Note: LSD (5%) values were calculated on log-transformed data (not shown). A \* represents statistical significance between treatments at the 5% level.

Table 3.8: Concentrations of Al (cmol<sub>e</sub>/kg) extracted from the control (C) and 30 Mg/ha layer manure (30L) treatments at various depths with different extractants (KCl, CuCl<sub>2</sub>, ammonium acetate and ammonium oxalate)

Depth	Treatment	1.0M KCl 10 min	0.5M CuCl <sub>2</sub> 2 hrs	1.0M Amm-Acetate pH 4.8 2hrs	1.0M Amm-Oxalate pH3.0 4hrs
0-5cm	C	2.27	12.74	8.91	91.77
	30L	0.04	5.13	2.06	82.10
5-15cm	C	1.53	8.54	9.79	91.54
	30L	0.87	7.06	8.21	88.39
15-25cm	C	1.51	8.41	9.89	92.51
	30L	1.29	8.10	9.40	92.02
25-35cm	C	1.56	8.53	9.76	95.25
	30L	1.39	8.37	9.57	93.14
35-45cm	C	1.55	8.29	9.72	94.26
	30L	1.40	8.11	9.47	86.43
LSD at same depth	5%	0.10	0.25	0.24	5.01

However, at all depths, there existed a trend (although not always significant) for the manured soil to have lower concentrations of both CuCl<sub>2</sub>- and ammonium acetate-extractable Al than the control. It is thought that CuCl<sub>2</sub> extracts exchangeable Al, organically-bound Al and some interlayer Al whilst ammonium acetate extracts exchangeable Al as well as the more reactive portions of hydroxy-Al species that are strongly sorbed to clay surfaces (Schuman, 1990). Therefore, exchangeable Al did not appear to accumulate into the buffering reserve of labile, non-exchangeable Al in either the organic or inorganic phases. When ammonium oxalate was used as an extractant there was still a trend for manure treatments to have lower values, although this was not always significant. Ammonium oxalate extracts exchangeable Al plus a large quantity of Al present in amorphous Al hydroxides and oxyhydroxides (Soon, 1993).

When surface soils are limed there is often a decrease in both exchangeable and oxalate-extractable Al (as is clearly evident in the 0-5cm layer; Table 3.8), since Al precipitates as hydroxy-Al species which then crystallize in forms that are not oxalate-extractable (Haynes, 1984b). It seems that at depths below 5cm in manure-treated soils, Al has also precipitated in

a predominantly non-extractable form. This has occurred even though, at the end of the experiment,  $\text{pH}_{\text{KCl}}$  was unchanged and  $\text{pH}_{\text{water}}$  was decreased due to a manure-amended salt effect (as described in Section 3.2.3). A similar phenomenon was observed by Farina and Channon (1988) in field sites that had received gypsum applications. At depths of 60-75cm and 75-90cm, these workers found that the sites receiving gypsum showed lower  $\text{pH}_{\text{water}}$  values (due to a salt-effect from the gypsum) and unchanged  $\text{pH}_{\text{KCl}}$  values when compared with plots without gypsum. At these depths, however, the exchangeable Al concentrations had decreased by about 0.5 cmol/kg. This decrease was explained in terms of the precipitation of Al-SO<sub>4</sub> minerals such as alunite (Sumner, 1993). However, such a mechanism is unlikely to have occurred in the current experiment due to the relatively small amounts of S in poultry manure (Table 3.1).

The most likely explanation for the phenomenon in this experiment is that the soil pH at the conclusion of the experiment does not reflect that which was prevalent throughout most of the experimental period. That is, a rise in subsoil pH induced by manure applications occurred and this resulted in the precipitation of Al in predominantly non-extractable, crystalline form. However, by the conclusion of the experiment,  $\text{pH}_{\text{KCl}}$  in the subsoil had been restored back to that in the control. Such a fluctuation in subsoil pH is explicable in relation to the previous discussion (Section 3.2.1) on the inhibition of nitrification during most of the experimental period. Urea, originating from the breakdown of uric acid in the manure, may have leached downward into the subsoil and then ammonified, resulting in a rise in subsoil  $\text{pH}_{\text{KCl}}$  and the precipitation of exchangeable Al in an insoluble form. Later, nitrification began to occur and the  $\text{pH}_{\text{KCl}}$  decreased back to the original value. It seems, however, that this decrease in pH was insufficient to bring all of the precipitated Al back into an extractable phase.

Indeed, these fluctuations in soil pH during the experimental period are evident from the changes in the pH values of the leachates from the 4 leaching events. For example, consider the leachates of the control and 30 Mg/ha broiler litter treatments. Leachate pH values for the control treatment were 4.20, 4.24, 4.28 and 4.20 for the first, second, third and fourth leaching events respectively. For the 30 Mg/ha broiler litter treatment, the corresponding pH values were 4.54, 4.47, 4.22 and 4.01. It is clear that, during the period of the first two leaching events, the subsoil pH of manured columns increased sharply relative to control columns (caused by the hydrolysis of urea). These conditions of increased subsoil pH then

persisted for a large proportion of the experimental period, before the pH began to decrease again in the third leaching event, probably caused by the salt-effect. Subsequently, delayed nitrification (which started only around the 84<sup>th</sup> experimental day) then decreased the soil pH of manured columns sharply in the fourth leaching event, as indicated by the decreased leachate pH values of manured columns relative to the control. This decrease reduced the soil pH<sub>KCl</sub> back to its original value (hence the unchanged pH<sub>KCl</sub> values at the end of the experiment), but insufficient experimental time was allowed for all of the precipitated Al to dissolve back into solution.

As already noted, uric acid is a major form of N present in poultry manure. Uric acid and its salts are relatively insoluble in water (Stryer, 1975) and therefore unlikely to leach in substantial quantities. By contrast, its degradation product, urea is highly mobile in soils (Singh *et al.*, 1984; Haynes, 1988) and has been shown to leach readily with percolating water (Haynes, 1988). The conversion of uric acid to urea is believed to occur both during manure storage and following its application to the soils (Sims and Wolf, 1994). In this experiment, 24 hours after application of the manure, the soil columns received 120mm of simulated rainfall, and this was followed by another 165mm seven days later. Any urea accumulated in the applied manure would therefore tend to be leached down the soil profile. Due to the ubiquitous nature of the urease enzyme (Sims and Wolf, 1994), this urea would be rapidly hydrolysed to ammonium in the subsoil, thus generating a rise in pH. As a result, exchangeable Al would precipitate as insoluble hydroxy-Al species, which are possibly too crystalline to be extracted with any of the extractants used, hence the lower exchangeable Al concentrations in manured columns.

The above explanation is somewhat speculative, but there is some evidence to support the downward movement of urea in the soil columns. The broiler litter used in this experiment contains approximately 33.9 and 24.4 g/kg of total N and K respectively. Gordillo and Cabrera (1997) analysed 15 broiler litter samples and derived the following equation to estimate the proportion of total N that is potentially mineralizable:

$$\text{Mineralizable N} = -7.71 + 0.57(\text{Total N}) \quad (r^2=0.83)$$

Application of this equation to the broiler litter used in the current experiment would estimate

that approximately 52% of the total N would be released into the soil. This is in close agreement with the results obtained by other workers (Hadas *et al.*, 1983; Bitzer and Sims, 1988). Assuming that during the 108 day experiment, 52% of the total N was released into the soil as  $\text{NH}_4^+$ , this would mean that the 30 Mg/ha application would have supplied about 732 and 531 kg/ha of  $\text{NH}_4^+$  and K respectively. Ammonium and K are both monovalent cations with similar atomic radii, and are commonly considered to be adsorbed onto the clay fraction by similar mechanisms, and hence they have similar mobilities in the soil (Talibudeen, 1981). Nevertheless, as shown in Table 3.9, exchangeable K had accumulated mainly in the surface 15cm as a consequence of manure application, yet  $\text{NH}_4^+$  had accumulated mainly in the 15-45cm layer. This, of course, also reflects nitrification which generally occurs most actively in the surface layers (Haynes, 1986) so that  $\text{NH}_4^+$  near the surface had already been converted to  $\text{NO}_3^-$ . Even so, accumulation of  $\text{NH}_4^+$  in the 25-45cm layer was substantially greater than that for K. Such a phenomenon may well reflect leaching of urea followed by hydrolysis and accumulation of  $\text{NH}_4^+$  at depth. By contrast, K leaching has been retarded by cation exchange reactions.

Table 3.9:  $\Delta\text{NH}_4^+$  and  $\Delta\text{K}$  values for the 30 Mg/ha broiler litter (30B) treatment. Note:  $\Delta$  represents the difference between the treatment concentration and the control concentration.

Depth	30Mg/ha Broiler litter	
	Units in mg/kg	
	$\Delta\text{NH}_4^+$	$\Delta\text{K}$
0-5cm	5	322
5-15cm	9	138
15-25cm	48	43
25-35cm	57	2
35-45cm	19	0
LSD (5%)	19	

Several workers have investigated the effects of surface applications of Ca humates and fulvates (van der Watt *et al.*, 1991; Noble *et al.*, 1995; Smith *et al.*, 1995; Liu and Hue, 1996) and organic manures (Hue and Licudine, 1999) on subsoil acidity in leaching column studies. These studies have generally shown increased downward movement of Ca into the subsoil, an

increase in soil pH and decrease in exchangeable and soluble Al and an increase in leaching of Al in the form of Al-organic matter complexes. Most workers have not forwarded an explanation for the induced increase in subsoil pH, although Smith *et al.* (1995) suggested that it was attributable to a “self-liming effect”, similar to that induced by leaching of  $\text{SO}_4^{2-}$  into the subsoil (Sumner, 1993). That is, soluble organic material (e.g. organic acid anions and humic substances) is leached downward and then specifically adsorbed to variable charge soil colloids in the subsoil. Specific adsorption involves ligand exchange with the release of hydroxyl ions into soil solution, and this causes a small increase in pH (as discussed in Chapter 1). Hue (1992) suggested the same mechanism is at least partially responsible for a rise in pH in surface soils amended with poultry manure.

There is no evidence in this experiment to suggest whether leached soluble organic matter was specifically adsorbed in the subsoil or not. Certainly, the subsoil of the oxisol used had a high content of Al and Fe hydrous oxides and therefore a high adsorption capacity. The fact that a large increase in leaching of soluble organic matter was not detected in response to poultry manure applications suggests that soluble organic matter was adsorbed and/or microbially degraded within the soil columns. Specific adsorption of organic molecules did not, however, appear to be a factor influencing soil pH at the conclusion of the experiment since no change in subsoil  $\text{pH}_{\text{KCl}}$  was detected. If this mechanism initially occurred, it is possible that many of the adsorbed organic molecules were subsequently degraded.

The reason that Hue and Licudine (1999), in a similar study, measured a significant increase in soil solution pH in the subsoil following surface applications of poultry manure, whilst in this study no such increase was found, may be related to the dissimilar experimental conditions employed in the two experiments. For example, Hue and Licudine (1999) incubated soils for 14 days and then leached columns for another 5 consecutive days (a total of 19 days reaction time) with a total of 378mm of simulated rainfall. The current experiment continued for 108 days and columns received 825mm of water in four leaching events. The greater reaction time and much larger quantity of water applied in the present study allowed for much greater leaching of soluble salts (particularly Ca and Mg; Table 3.4) into the subsoil. Indeed, in a comparison with this study, Hue and Licudine (1999) recorded very small increases in soil solution and exchangeable Ca in the 30-40cm layer of manure-amended columns. As a result, the salt effect induced by manure application was evident in the subsoil

in the present study (causing depressed  $\text{pH}_{\text{water}}$  values) but was not operative in the other study. Indeed, large increases in electrical conductivity in the subsoil of manured treatments were clearly evident in the present study (Table 3.11).

Perhaps more importantly, the longer experimental period of this study allowed time for nitrification to proceed, therefore causing a decrease in soil pH (even though this process was initially delayed). Therefore, any increase in subsoil pH, as noted by Hue and Licudine (1999), was effectively counteracted by the end of the 108 day study period. In this regard, it is interesting to note that the soil used by Hue and Licudine (1999) was highly acidic ( $\text{pH}_{\text{water}} = 4.4$ ) and autotrophic nitrification is often inhibited at such pH values (Cornfield, 1959; Dancer *et al.*, 1973; Ishaque and Cornfield, 1976; Arora *et al.*, 1986; Haynes and Swift, 1989).

In Chapter 1 it was suggested that excess  $\text{NO}_3^-$  generated by manure decomposition could leach into the subsoil as Ca- or Mg- nitrate. When the plants take up this nitrate in excess to cations from the soil solution, the plant releases  $\text{OH}^-$  ions into the soil solution to maintain electroneutrality. It was proposed that this could have caused the subsoil pH to increase, with a consequent decrease in exchangeable Al. Table 3.10 shows the exchangeable Al contents of the 10 Mg/ha layer manure treatment with and without a crop. It is clear that in this experiment the inclusion of a crop had no effect on the exchangeable Al at the deeper soil depths. This is likely to be caused by the initial slow nitrification rate in this soil and the resulting high ammonium concentrations and relatively low nitrate concentrations in the subsoils of manured columns (Table 3.3). The plants therefore absorbed their required nitrogen as  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , resulting in no anion over cation excess. Consequently there was no increase in pH or decrease in exchangeable Al in cropped columns relative to uncropped ones. The depressions in the concentrations of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in cropped relative to uncropped columns measured at the conclusion of the experiment (Table 3.10) certainly suggests that uptake of both forms of N had occurred.



Table 3.10: Exchangeable Al (cmol<sub>e</sub>/kg), NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (mg N/l) concentrations at various depths for the 10 Mg/ha layer manure treatments with plants (10LP) and without plants (10L) at the end of the 108 day experimental period.

Depth	Treatment	Exchangeable Al cmol <sub>e</sub> /kg	Exchangeable NH <sub>4</sub> <sup>+</sup> mg N/kg	Exchangeable NO <sub>3</sub> <sup>-</sup> mg N/kg
0-5cm	10L	0.46	11	62
	10LP	0.38	13	5
5-15cm	10L	0.97	25	14
	10LP	1.06	11	1
15-25cm	10L	1.15	50	25
	10LP	1.14	12	1
25-35cm	10L	1.17	56	60
	10LP	1.16	9	1
35-45cm	10L	1.18	39	76
	10LP	1.17	10	2
LSD at same depth	5%	0.11	6	24

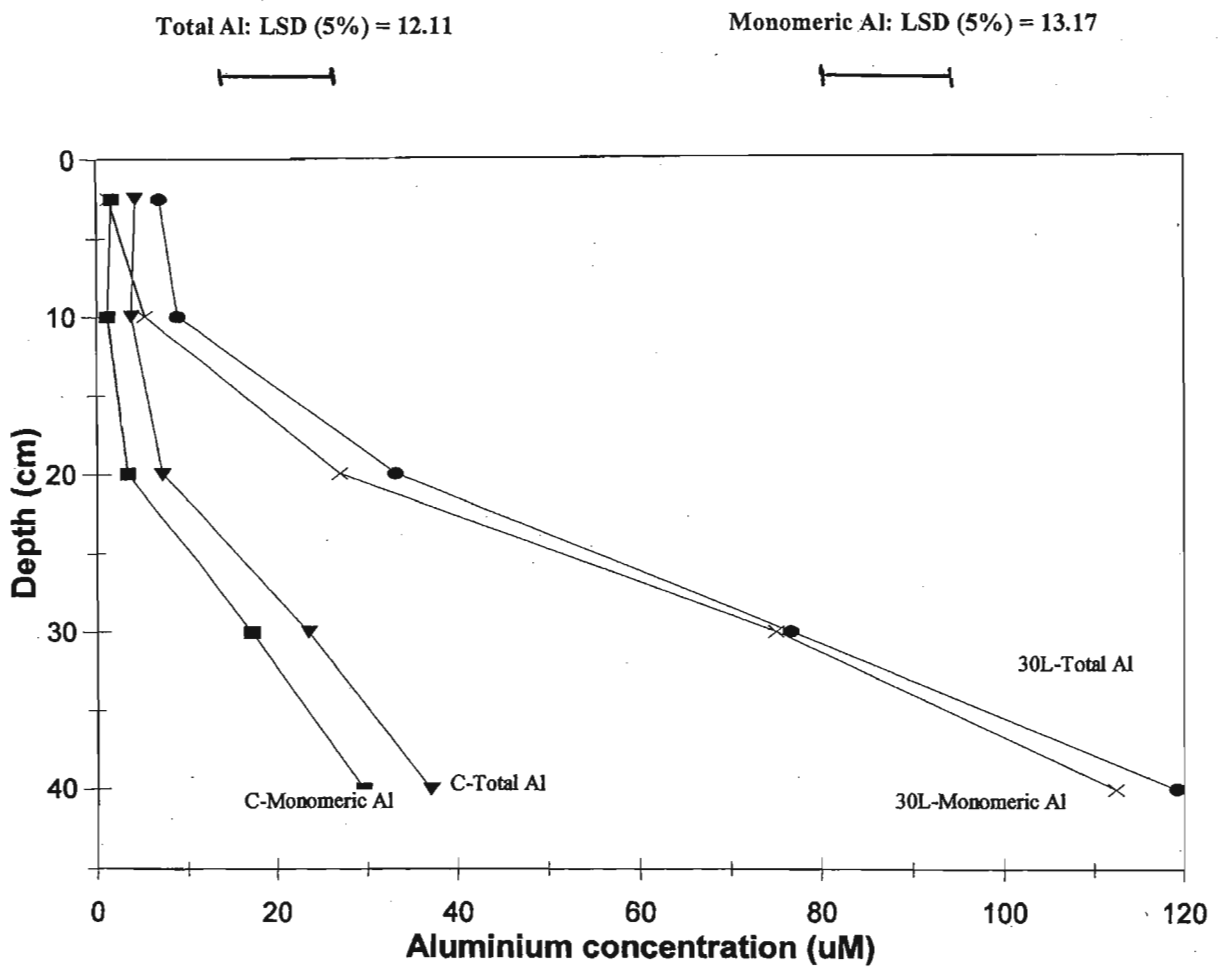
It must be noted, however, that even though this mechanism has not had a major effect on the soil used in this experiment, it could be operational in a field soil that does not have a naturally low nitrifying capacity, i.e. a soil where most of the nitrogen from the chicken manure can be rapidly converted into nitrate in the surface soil and then leached with the cations from the salts in the manure. Nonetheless, as noted in Section 3.2.1, components in the manure can also potentially inhibit nitrification.

### **3.2.3. Effects on Al in the soil solution**

This section has been included separately from the above two sections because the unexpected results that were observed warranted some individual attention. The effects of manure applications on soil solution Al in the 0-5cm zone of incorporation was discussed previously in Section 3.2.1. This section focuses on the changes in soil solution Al that occurred below 5cm depth following manure applications.

Figure 3.10 shows the soil solution Al concentrations in the 30 Mg/ha layer manure and the control treatments. The total Al concentrations ranged from about 4 to 120 $\mu$ M, which falls approximately into the range of 10 to 350 $\mu$ M typically found in soil solutions extracted from acid soils (Bruce *et al.*, 1988; Ritchie, 1989; Parfitt *et al.*, 1995). It is clear that at deeper soil depths the manured columns have more monomeric and total Al in the soil solution than the control columns, despite the decreased exchangeable Al concentrations in the manured columns (Table 3.7). Therefore, as previously noted for the topsoil (Section 3.2.1) the amount of Al in the soil solution is unrelated to the exchangeable Al concentration. Another point of interest is that the amount of Al in solution increases with soil depth in both the manured and control treatments. These observations may be explained in terms of a salt-effect.

The increased salt content of manure-amended soils has been discussed previously, and is evident from the tabulated EC and ionic strength values presented in Table 3.11. Soil solutions from manured soils have far greater EC values at all soil depths than in the control. The increase in EC down the profile of the control is presumably caused by the decomposition of the high organic matter, humic A topsoil (which would naturally have formed in a cool, humid environment) under the warm glasshouse conditions. As the organic matter in this horizon decomposed, it would have released ionic species which leached down the profile, generating increased EC values in deeper soil horizons. In the manured columns, the salts from the manure have leached down the profile causing a) increased EC values relative to the control; and b) increased EC values at deeper profile depths.



**Figure 3.10: Total and monomeric Al concentrations ( $\mu\text{M}$ ) measured in soil solution at various depths down the profiles of the control (C) and 30 Mg/ha layer manure (30L) treatments at the end of the 108 day experimental period.**

The elevated ionic strength values in manure-amended profiles are very likely to be the cause of the increased total and monomeric Al concentrations in the solutions of these columns. The salts from the manure are displacing Al from the exchange complex into the soil solution, resulting in increased concentrations of monomeric Al in the soil solution.

The proportion of solution Al in the phytotoxic, monomeric form at each depth for the control and 30 Mg/ha layer manure treatment is presented in Figure 3.11. These values are relatively high (especially in the subsoil layers) when compared with results obtained from other workers. Berek *et al.* (1995), for example, recorded values of 38% for an acid podzol, whereas Slattery and Morrison (1995) reported values ranging from 16 to 41% for Australian podzols. The high proportion of monomeric Al in the subsoils of manure-amended columns results from the high salt content of the amended profiles (Table 3.11), which tends to displace exchangeable Al into the soil solution, hence the Al exists predominantly in the monomeric form. These results demonstrate that, in this study, the effects of organic complexation of Al in the subsoils of manured columns is not likely to be of any significance in detoxification of phytotoxic monomeric Al. Indeed, it is interesting to compare the data in Figure 3.11 with that in Figure 3.9. In the surface 5cm of soil there was a large increase in soluble C induced by manure applications but no effect was evident below that layer. In agreement with this, the only layer where the percentage of Al present in soil solution in monomeric form was decreased by manure applications was, in fact, the 0-5cm layer (Figure 3.11).

In the subsoil layers (>5cm depth) the proportional increase in the activity of monomeric Al, induced by manure applications, is less than that for the concentration (Table 3.11). This is to be expected because of the higher ionic strength in soil solution in the manured soils (Table 3.11). Lindsay (1979), for example, states that as the ionic strength of the solution increases, ions of opposite charge interact in such a way that their "effective" concentration or activity decreases.

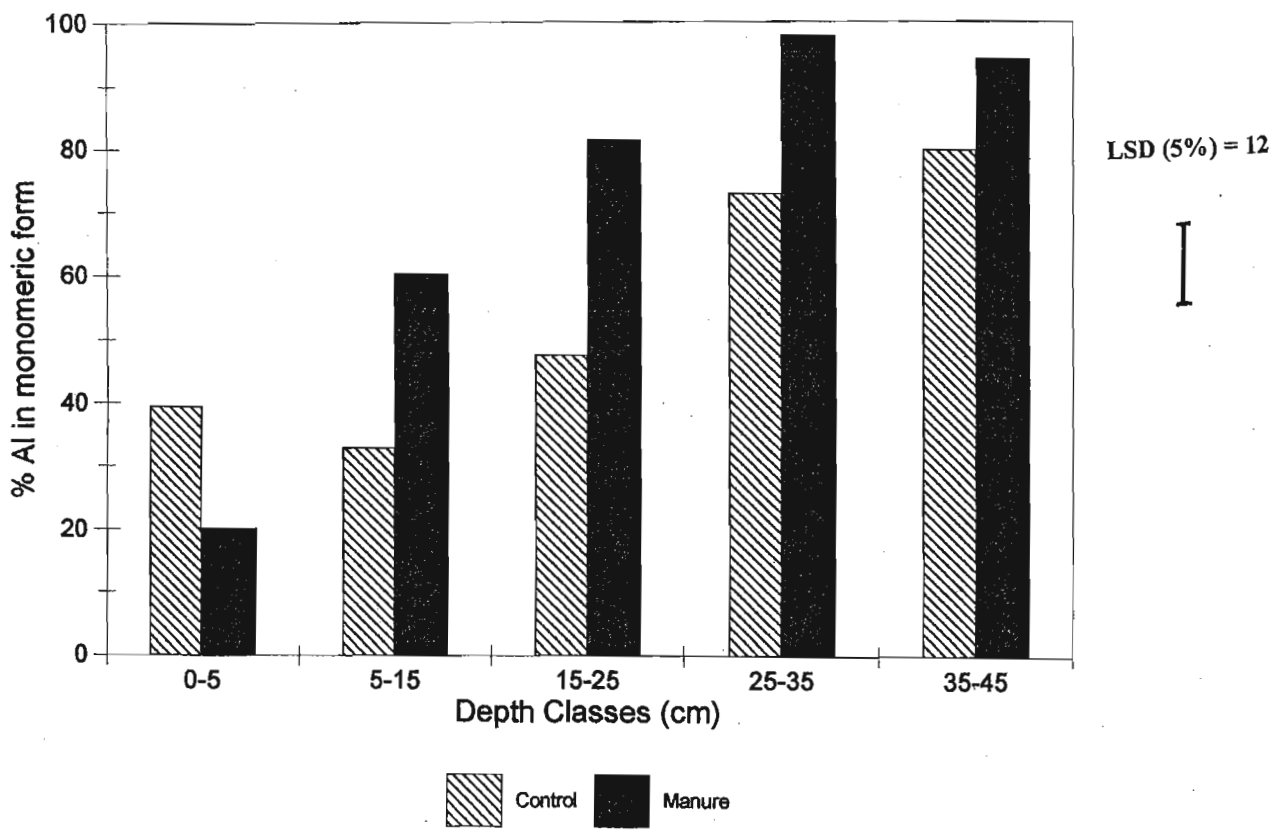


Figure 3.11: The proportion (%) of total Al in soil solution existing in monomeric form at various depths at the end of the 108 day experimental period.

Table 3.11: Electrical conductivity (EC) values (mS/m), ionic strength values (mol/l) and concentration and activity of monomeric Al ( $\mu\text{mol/l}$ ) in soil solution at various depths of the control (C) and 30 mg/ha layer manure (30L) treatments

Depth	Treatment	EC mS/m	Ionic Strength Molar	Conc. of monomeric Al ( $\mu\text{M}$ )	Activity of monomeric Al ( $\mu\text{M}$ )
0-5cm	C	9.62	0.001	1.75	1.23
	30L	459.00	0.060	1.43	0.22
5-15cm	C	7.70	0.001	1.3	0.94
	30L	60.33	0.008	5.44	2.36
15-25cm	C	12.44	0.002	3.48	2.33
	30L	64.57	0.008	27.05	11.40
25-35cm	C	22.28	0.003	17.21	10.13
	30L	97.93	0.013	74.94	26.78
35-45cm	C	30.83	0.004	29.64	16.02
	30L	103.60	0.013	112.33	39.14
LSD at same depth	5%	58.28	0.008	13.17	3.24

- (1) Ionic strength calculated as follows: Ionic strength =  $0.013\text{EC}$ , with EC in mS/cm (Griffin and Jurinak, 1973)  
(2) Al activities calculated from the extension of the Debye-Huckel equation by Davies (1962).

The data presented in this chapter provides evidence of the ability of surface-applied poultry manure to reduce exchangeable Al concentrations in acid subsoils. Despite these decreased concentrations, the high salt content of manure-amended profiles tends to maintain higher concentrations of toxic monomeric Al species in soil solution, due to the displacement of exchangeable Al into soil solution. It seems, however, that even though the subsoils of manured columns had higher concentrations of monomeric Al in solution, the phytotoxicity of this Al has been somewhat reduced. Indeed, Figure 3.12 shows markedly increased root proliferation into the subsoil of the amended column (left), relative to the control column (right). It is suspected that the increased concentrations of soluble salts (especially Ca and Mg) in manured columns is responsible for the decreased susceptibility to Al toxicity. Firstly, as discussed previously, the high salt content tends to reduce the activity of monomeric Al in solution, thereby reducing its phytotoxicity (Table 3.11). Secondly, it has been reported that Ca and Al have an antagonistic relationship in soils (McCray and Sumner, 1990). These workers postulated that increased solution Ca levels decreases susceptibility to Al toxicity,

thereby allowing greater root proliferation into acid soils, as occurred in this experiment (Figure 3.12). The leaching of macronutrients (e.g. Ca, Mg, Na, N and, to a lesser extent K) into the subsoils of manured-amended profiles also contributes to the increased root growth in this region. It must be noted, however, that the grass species used in this trial (*Eragrostis curvula*) was selected for its resistance to Al toxicity. Therefore, the enhanced root growth in manure-amended profiles (Figure 3.12) may well relate more to the increased nutrient content than to Al toxicity factors.

Coupled with the data from Chapter 2, which shows increased subsoil pH values and markedly reduced exchangeable Al concentrations induced by long-term surface applications of poultry manure, this chapter provides an understanding of some of the mechanisms affecting top- and subsoil pH following manure additions.



Figure 3.12: Root proliferation into the subsoils of the 10 Mg/ha layer manure (left) and control (right) treatments.

## GENERAL CONCLUSIONS

It is evident from the laboratory column experiment that the incorporation of poultry manure into the surface 0-5 cm soil layer causes a substantial increase in soil pH to the depth of incorporation. This increase in pH, which has been noted by a number of other workers (Chapter 1), occurs because the manure has a high initial pH, a significant  $\text{CaCO}_3$  content, the capacity to consume protons and the ability to produce alkalinity from the ammonification of manure-N and the hydrolysis of urea in the manure. As expected, the liming effect of poultry manure causes precipitation of exchangeable Al as hydroxy-Al species and a substantial reduction in Al saturation. Nonetheless, as shown by other workers, additions of poultry manure cause a substantial accumulation of soluble salts in soil solution (Weil *et al.*, 1979). The high concentrations of cations in soil solution displace exchangeable Al back into soil solution. In addition, the high concentrations of soluble organic matter, originating from the decomposing manure, tend to complex this Al and maintain it in soil solution. As a result, even though manure-treated surface soils had a lower exchangeable Al content, the concentrations of total Al and organically-complexed Al in soil solution were considerably higher in the manure-treated soil than the control soil. This salt effect induced by poultry manure applications has been observed previously in pot experiments (Mokolobate, 2000) where soluble salts cannot leach away.

Immediately below the layer of poultry manure incorporation (in the 5-15 cm layer) small increases in  $\text{pH}_{\text{KCl}}$  were found which were attributed to downward movement of alkalinity from the soil in the 0-5 cm layer. However, in layers below 15 cm (15-45 cm) no changes in  $\text{pH}_{\text{KCl}}$  were recorded. The  $\text{pH}_{\text{water}}$  was similar in the control and manure-treated columns in the 5-15 cm layer but was, in fact, depressed in manure treatments in the 15-45 cm layers. It is suggested that following manure application to soils, the uric acid-N in the manure was rapidly converted to urea, which was then leached down the profile during the first leaching events. In the subsoil layers this urea was hydrolysed to  $\text{NH}_4^+$  with the liberation of  $\text{OH}^-$  ions. The resulting rise in pH caused precipitation of exchangeable Al as insoluble hydroxy-Al species. However, subsequently (near the end of the incubation period) nitrification began to occur and this caused a decrease in pH with the result that, at the conclusion of the experiment,  $\text{pH}_{\text{KCl}}$  was similar in the 15-45 cm layer in manure and control treatments but the former contained depressed exchangeable Al concentrations. Values of  $\text{pH}_{\text{water}}$  reflected a balance between the change in the dynamics of  $\text{H}^+/\text{OH}^-$  in the soil system and the effect of



soluble salts accumulating in the soil due to manure additions. The depressions in  $\text{pH}_{\text{water}}$  in the subsoil layers of amended columns were accompanied by substantial increases in the electrical conductivity and total and monomeric Al concentrations in soil solution. That is, the high concentrations of soluble salts in soil solution in the subsoil displaced  $\text{Al}^{3+}$  and  $\text{H}^+$  on exchange sites back into soil solution.

There is no reason to believe that the effects observed in the column study would not also occur under field conditions. Indeed, accumulation of soluble salts in the surface soil after poultry manure applications has been observed previously in the field (Weil *et al.*, 1979). Leaching over the high-rainfall season will, however, leach these salts down the profile and eventually out of the subsoil layers. Under such conditions the salt effect would no longer be operative and both exchangeable and soil solution Al would then tend to be depressed by poultry manure applications.

The fact that in the leaching column experiment manure applications markedly decreased exchangeable Al concentrations in both the top- and subsoil, yet phytotoxic monomeric Al concentrations in soil solution were virtually unaffected in the topsoil and greatly increased in the subsoil is of particular interest. If such effects are common in the field then the use of exchangeable Al and/or exchangeable Al saturation as indicators of the potential for Al toxicity and the need for lime will be inappropriate and misleading for manure-amended fields, particularly where Al-sensitive crops are grown. More detailed time-course studies of changes in exchangeable and soil solution Al concentrations after field applications of poultry manure seem warranted. It must be noted, however, that the increased concentration of  $\text{Ca}^{2+}$  in manure-amended soils may decrease susceptibility to Al toxicity by increasing the Ca:Al ratio (McCray and Sumner, 1990).

The movement and transformations of manure-derived N in the soil can have large effects on the influence that poultry manure applications have on top- and subsoil pH, which does not appear to have been considered previously. The large N content of the manure means that the relative rate and period over which the alkali-forming ammonification process and the acidifying nitrification process occur will be of great significance. Indeed, in some short-term leaching experiments that have been recently reported (Hue and Licudine, 1999), transformations of manure-N may not have proceeded to completion (i.e., nitrification may

not yet have occurred) so that results may not reflect what would actually occur in the field in the longer-term.

The apparent movement of urea-N down the profile in this study followed by ammonification and nitrification seemed to increase subsoil pH but then decrease it back to initial values. However, subsequent uptake of this nitrate by crop roots would result in concomitant excretion of OH<sup>-</sup> ions into the subsoil and a net increase in subsoil pH. Unfortunately, the current study was terminated before this could occur. Nevertheless, if the bulk of the nitrate was lost by leaching, then the overall effect of the N transformations would be net acidification of the subsoil. The nature of the manure will also be important. For example, where manure has a low CaCO<sub>3</sub> content and a high N content and a large amount of this N is lost via nitrate leaching, then its application to the soil could well have an overall acidifying effect. This may explain why Jackson *et al.* (1977) found a decrease in soil pH in fields with a history of long-term applications of manure.

By contrast, where layer manure, with a high CaCO<sub>3</sub> content, is applied and most of the manure-N is cycled in the soil-crop system, then manure applications are likely to substantially raise soil pH in the topsoil and subsoil. Adequate rainfall and/or irrigation will, however, be needed at some time in order to leach soluble salts from the plant rooting zone so that exchangeable Al is not displaced back into soil solution. Under field conditions in the KwaZulu-Natal Midlands it seems that the sources of poultry manure and the conditions favour its use as an ameliorant of subsoil acidity. Certainly, the data from the very limited number of field sites showed a substantial increase in subsoil pH and decrease in exchangeable Al.

It will be important to extend this research into the field situation under controlled experimental conditions. It is of significance to note that many soils in the KwaZulu-Natal midlands have an acid subsoil that limits crop growth. Resource-poor, small scale farmers generally do not have access to gypsum as an ameliorant for subsoil acidity. They often do, however, have access to poultry and other manures and the use of these materials as a source of nutrients, organic matter and an ameliorant for subsoil acidity may be a viable low-input strategy to improve their crop yields.

## LIST OF REFERENCES:

(Format: Plant and Soil, Kluwer Academic Publishers, Netherlands)

- Adams F 1981 Alleviating chemical toxicities: liming acid soils. *In* Modifying the root environment to reduce crop stress. Eds G F Arkin and H M Taylor. pp 269-301. American Society of Agricultural Engineers, Michigan, USA.
- Aleem M I H and Alexander M 1960 Nutrition and physiology of *Nitrobacter agillus*. *Appl. Microbiol.* 8, 80-84.
- Allison L E 1965 Organic carbon. *In* Methods of soil analysis. Eds C A Black *et al.* *Agronomy* 9, 1367-1378
- Arora Y, Mulongoy K and Juo A S R 1986 Nitrification and mineralization potentials in a limed Ultisol in the humid tropics. *Plant Soil* 92, 153-157.
- Bartlett R J and Riego D C 1972 Effect of chelation on the toxicity of aluminum. *Plant Soil* 37, 419-423.
- Berek A K, Radjagukguk B and Maas A 1995 The effect of different organic materials on the alleviation of Al toxicity in soybean on red-yellow podzolic soils. *In* Plant Soil Interactions at Low pH. Eds R A Date *et al.* pp 579-584. Kluwer Academic Publishers, Dordrecht.
- Bitzer C C and Sims J T 1988 Estimating the availability of nitrogen in poultry manure through laboratory and field studies. *J. Environ. Qual.* 17, 47-54.
- Brady N C 1974 The nature and properties of soils. 8th edition. Macmillan Publishing Co., New York.
- Brenes E and Pearson R W 1973 Root responses of three Gramineae species to soil acidity in an Oxisol and Ultisol. *Soil Sci.* 116, 295-302.
- Breteler H 1973 A comparison between ammonium and nitrate nutrition of young sugar-beet plants grown in nutrient solutions at constant acidity. 1. Production of dry matter, ionic balance and chemical composition. *Neth. J. Agric. Sci.* 21, 227-244.
- Bruce R C, Warrell L A, Edwards D G and Bell L C 1988 Effects of aluminum and calcium in the soil solution of acid soils on root elongation of *Glycine max* cv. Forest. *Aust. J. Agric. Res.* 38, 319-338.
- Bundy L G and Bremner J M 1972 A simple titrimetric method for determination of inorganic carbon in soils. *Soil Sci. Soc. Amer. Proc.* 36, 273-275
- Cameron R S, Ritchie G S P and Robson A D 1986 Relative toxicities of inorganic complexes to barley. *Soil Sci. Soc. Am. J.* 1231-1236.

- Close E A and Powell H K J 1989 Rapidly extracted (0.02M CaCl<sub>2</sub>-soluble) "reactive" aluminium as a measure of Al toxicity in soils. *Aust. J. Soil Res.* 27, 663-672.
- Cooper J R, Reneau R B, Kroontje W and Jones D G 1984 Distribution of nitrogenous compounds in a Rhodic Paluedult following heavy manure application. *J. Environ. Qual.* 13, 189-193.
- Cornfield A H 1959 Mineralization, during incubation, of the organic-N compounds in soils as related to soil pH. *J. Sci. Food. Agric.* 10, 27-28.
- Dancer W S L, Peterson L A and Chesters G 1973 Ammonification and nitrification of N as influenced by soil pH and previous N treatments. *Soil Sci. Soc. Am. Proc.* 37, 67-69.
- Delhaize E and Ryan R R 1995 Update: aluminium toxicity and tolerance in plants. *Plant Physiol.* 107, 315-321.
- Davies C W 1962 *Ion Association*. Butterworths, London.
- Eghball E 1999 Liming effects of beef cattle feedlot manure or compost. *Commun. Soil Sci. Plant Anal.* 30, 2563-2570.
- Elkhatib E A, Hern J L and Staley T E 1987 A rapid centrifugation method for obtaining soil solution. *Soil Sci. Soc. Am. J.* 51, 578-573.
- El-Sabben F F, Long T A, Gentry R F and Frear D E 1969 The influence of various factors on poultry litter composition. *Anim. Waste Manage., Cornell Univ. Conf.* pp 340-346.
- Farina M P W 1997 Management of soil acidity in environments outside the humid tropics. *In Plant-Soil Interactions at Low pH*. Eds. A C Moniz *et al.* pp 179-190. Brazilian Soil Science Society, Brazil.
- Farina M P W and Channon P 1988 Acid-Subsoil amelioration: I. A comparison of several mechanical procedures. *Soil Sci. Soc. Am. J.* 52, 169-175.
- Farina M P W, Channon P and Thibaud G R 2000 A comparison of strategies for ameliorating subsoil acidity: I. Long-term growth effects. *Soil Sci. Soc. Am. J.* 64, 646-651.
- Fey M V, Manson A D and Schutte R 1990 Acidification of the pedosphere. *South African Journal of Science* 86, 403-406.
- Foy C D 1988 Plant adaptation to acid, aluminium-toxic soils. *Comm. Soil Sci. Plant Anal.* 19, 959-987.
- Gale P M and Gilmour J T 1986 Carbon and nitrogen mineralization kinetics for poultry litter. *J. Environ. Qual.* 15, 423-426.
- Gale P M, Phillips J M, May M L and Wolf D C 1991 Effect of drying on the plant nutrient

- content of hen manure. *J. Prod. Agric.* 4, 246-250.
- Griffin R A and Jurinak J J 1973 Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. *Soil. Sci.* 116, 26-30.
- Gordillo R M and Cabrera M L 1997 Mineralizable nitrogen in broiler litter: I. Effect of selected litter chemical characteristics. *J. Environ. Qual.* 26, 1672-1679.
- Hadas A, Bar-Yosef B, Davidov S and Sofer M 1983 Effect of pelleting, temperature, and soil type on mineral nitrogen release from poultry and dairy manures. *Soil Sci. Soc. Am. J.* 47, 1129-1133.
- Harper S M, Edwards D G, Kerven G L and Asher C J 1995 Effects of organic acid fractions extracted from *Eucalyptus camaldulensis* leaves on root elongation of maize (*Zea mays*) in the presence and absence of aluminium. *Plant Soil* 171, 189-192.
- Haynes R J 1982 Effects of liming on phosphate availability. *Plant Soil* 68, 289-308
- Haynes R J 1983 Soil acidification induced by leguminous crops. *Grass Forage Sci.* 38, 1-11.
- Haynes R J 1984a Lime and phosphate in the soil-plant system. *Adv. Agron.* 37, 249-315.
- Haynes R J 1984b Effect of lime, silicate, and phosphate applications on the concentrations of extractable Al and phosphate in a Spodosoil. *Soil Sci.* 138, 8-14.
- Haynes R J 1986 Nitrification. *In* Mineral nitrogen in the plant-soil system. Eds. R J Haynes. Pp 127-165, Academic Press, Orlando.
- Haynes R J 1988 Comparison of fertigation with broadcast urea-N applications on levels of available soil nutrients and on growth and yield of trickle-irrigated peppers. *Scientia Hort.* 35, 189-198.
- Haynes R J and Swift R S 1989 Effect of rewetting air-dried soils on pH and accumulation of mineral nitrogen. *J. Soil Sci.* 40, 341-347.
- Haynes R J 1990 Active ion uptake and maintenance of cation-anion balance: a critical examination of their role in regulating rhizosphere pH. *Plant Soil* 126, 247-264.
- Haynes R J and Moklobate M S 1999 Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. Unpublished.
- Haynes R J and Mokolobate M S 2000 Amelioration of Al toxicity and P deficiency in acid soils by addition of organic residues: a critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling Agrecos* (In press).
- Helyar K R 1991 The management of acid soils. *In* Plant-Soil Interactions at Low pH. Eds. R J Wright, V C Baliger and R P Murrmann. Pp 365-382. Kluwer Academic Publishers,

Dordrecht, The Netherlands.

- Hileman L H 1971 Effect of rate of poultry manure application on selected soil chemical properties. *In* Livestock waste management and pollution abatement. Proc. Int. Symp. On Livestock Wastes. pp 247-248. Am. Soc. Agric. Eng., St. Joseph, Michigan.
- Hoyt P B and Turner R C 1975 Effects of organic materials added to very acid soils on pH, aluminum, exchangeable  $\text{NH}_4$ , and crop yields. *Soil Sci.* 199, 227-237.
- Huang J W, Grunes D L and Kochian L V 1992 Aluminium effects on the kinetics of calcium uptake into cells of the wheat root apex. *Planta* 188, 414-421.
- Hunter A 1974 Tentative ISFEI soil extraction procedure. International soil fertility and improvement project. N.C. State University, Raleigh, NC.
- Hue N V 1992 Correcting soil acidity of a highly weathered ultisol with chicken manure and sewage sludge. *Comm. Soil Sci. Plant Anal.* 23, 241-264.
- Hue N V and Amien I 1989 Aluminium detoxification with green manures. *Comm. in Soil Sci. Plant Anal.* 20, 1499-1511.
- Hue N V, Craddock G R and Adams F 1986 Effect of organic acids on aluminium toxicity in subsoils. *Soil Sci. Soc. Am. J.* 50, 28-34.
- Hue N V, Ikawa H and Silva J A 1994 Increasing plant available phosphorous in an Ultisol with a yard-waste compost. *Comm. Soil Sci. Plant Anal.* 25, 3291-3303.
- Hue N V and Licudine D L 1999 Amelioration of subsoil acidity through surface application of organic manures. *J. Environ. Qual.* 28, 623-632.
- Ishaque M and Cornfield A H 1976 Evidence for heterotrophic nitrification in an acid Bangladesh soil lacking autotrophic nitrifying organisms. *Trop. Agric.* 53, 157-160.
- Iyamuremye F and Dick R P 1996 Organic amendments and phosphorous sorption by soils. *Adv. Agron.* 56, 139-185.
- Iyamuremye F, Dick R P and Baham J 1996 Organic amendments and phosphorous dynamics: 1. Phosphorous chemistry and sorption. *Soil Sci.* 161: 426-435.
- Jackson W A, Leonard R A and Wilkinson S R 1975 Land disposal of broiler litter - changes in soil potassium, calcium and magnesium. *J. Environ. Qual.* 4, 202-206.
- Jackson W A, Wilkinson S R and Leonard R A 1977 Land disposal of broiler litter: changes in concentration of chloride, nitrate nitrogen, total nitrogen, and organic matter in a Cecil sandy loam. *J. Environ. Qual.* 6, 58-62.
- Jones D L and Brassington D S 1998 Sorption of organic acids in acid soils and its implications in the rhizosphere. *Eur. J. Soil Sci.* 49, 447-455.

- Jones D L and Darrah P R 1994 Role of root derived organic acids in the mobilization of nutrients from the rhizosphere. *Plant Soil* 166, 247-257.
- Juo A S R and Kamprath E J 1979 Copper chloride as an extractant for estimating the potentially reactive aluminium pool in acid soils. *Soil Sci. Soc. Am. J.* 43, 35-38.
- Kerven G L, Edwards D G, Asher C J, Hallman P S and Kokot S 1989 Aluminium determination in soil solution. II. Short-term colorimetric procedures for the measurement of inorganic monomeric aluminium in the presence of organic acid ligands. *Aust. J. Soil Res.* 27, 91-102.
- Kingery W L, Wood C W, Delaney D P, Williams J C and Mullins G L 1994 Impact of long-term land application of broiler litter on environmentally related soil properties. *J. Environ. Qual.* 23, 139-147.
- Kinraide T B and Parker D R 1990 Apparent phytotoxicity of mononuclear hydroxy-aluminium to four dicotyledonous species. *Physiol Plant* 79, 283-288.
- Kochian L V 1995 Cellular mechanisms of aluminium toxicity and resistance in plants. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 46, 237-260.
- Kodama H and Webber M D 1975 *Can. J. Soil Sci.* 55, 195-205.
- Kunkle W E, Carr L E, Carter T A and Bossard E H 1981 Effect of flock and floor type on the levels of nutrients and heavy metals in broiler litter. *Poult. Sci.* 60, 1160-1164.
- Liebhardt W C, Golt C and Tupin J 1979 Nitrate and ammonium concentrations of groundwater resulting from poultry manure applications. *J. Environ. Qual.* 5, 459-462.
- Lindsay W L 1979 *Chemical equilibria in soils.* John Wiley and Sons, Inc. USA.
- Liu J and Hue N V 1996 Ameliorating subsoil acidity by surface application of calcium fulvates derived from common organic materials. *Biol. Fertil. Soils* 21, 264-270.
- Lopez-Hernandez D, Siegert G and Rodriguez J V 1986 Competitive adsorption of phosphate with malate and oxalate by tropical soils. *Soil Sci. Soc. Am. J.* 50, 1460-1462.
- Lucero D W, Martens D C, McKenna J R and Starner D E 1995 Accumulation and movement of phosphorous from poultry litter application on a Starr clay loam. *Comm. Soil Sci. Plant Anal.* 26, 1709-1718.
- Lund Z F and Doss B D 1980 Coastal bermudagrass yield and soil properties as affected by surface applied dairy manure and its residue. *J. Environ. Qual.* 9, 157-162.
- Lundstrom U S 1994 Significance of organic acids for weathering and podzolization process. *Environ. Int.* 20, 21-30.
- Mahler H R and Cordes E H 1966 *Biological chemistry.* Harper & Row, New York. 192p.



- Malone G W 1992 Nutrient enrichment in integrated broiler production systems. *Poult. Sci.* 71, 1117-1122.
- Manson A D and Fey M V 1989 Cation type and ionic strength effects on the soil solution composition of an acidic subsoil. *J. Soil Sci.* 40, 577-583.
- McBride M B 1994 *Environmental chemistry of soils*. O.U.P., New York.
- McCray J M and Sumner M E 1990 Assessing and modelling Ca and Al levels in acid subsoils. *Adv. Soil Sci.* 14, 45-75.
- McLean E O 1965 Aluminium. *In Methods of Soil Analysis (Part 2)*. Ed. C A Black, pp 994-997. Soc. Agron., Madison, Wis.
- Menzies N W, Kerven G L, Bell L C and Edwards D G 1992 Determination of total soluble aluminium in soil solution using pyrocatechol violet, lanthanum and iron to discriminate against micro-particulates and organic ligands. *Comm. Soil Sci. Plant Anal.* 23, 2525-2545.
- Miyasaka S C, Buta J G, Howell, R K and Foy C D 1991 Mechanism of aluminium tolerance in snapbeans. Root exudation of citric acid. *Plant Physiol.* 96, 737-743.
- Mokolobate M S 2000 Amelioration of Al toxicity and P deficiency in acid soils by addition of organic residues. MSc. Agric Thesis. University of Natal. Unpublished.
- Moshi A O, Wild A and Greenland D J 1974 Effect of organic matter on the charge and phosphate adsorption characteristics of Kikuyu red clay from Kenya. *Geoderma* 11, 275-285.
- Murphy J and Riley J R 1962 A modified single solution method for the determination of phosphate in natural waters. *Anal. Chem. Acta* 27, 31-36.
- Nagarajah S, Posner A M and Quirk J P 1970 Competitive adsorption of phosphate with polygalacturonate and other organic anions on kaolinite and oxide surfaces. *Nature* 228, 83-85.
- Nielson T H and Revsbech N P 1998 Nitrification, denitrification, and N-liberation associated with two types of organic hot-spots in soil. *Soil Biol. Biochem.* 30, 611-619.
- Noble A D, Randall P J and James T R 1995 Evaluation of two coal-derived organic products in ameliorating surface and subsurface soil acidity. *Eur. J. Soil Sci.* 46, 65-75.
- Noble A D, Zenneck I and Randall P J 1996 Leaf litter ash alkalinity and neutralisation of soil acidity. *Plant Soil* 179, 293-302.
- O'-Hallorans J M, Munoz M A and Marquiz P E 1997 Chicken manure as an amendment to correct soil acidity and fertility. *J. Agric. Univ. Puerto Rico* 81, 1-8.



- Parfitt R L 1978 Anion adsorption by soils and soil minerals. *Adv. Agron.* 20, 323-359.
- Parfitt R L, Fraser A R and Farmer V C 1977a Adsorption of hydrous oxides. III. Fulvic acid and humic acid on goethite, gibbsite and imogolite. *J. Soil Sci.* 28, 289-296.
- Parfitt R L, Fraser A R, Russell J D and Farmer V C 1977b Adsorption on hydrous oxides II. Oxalate, benzoate and phosphate on gibbsite. *J. Soil Sci.* 28, 40-47.
- Parfitt R L, Percival H J and van der Lee G 1995 Aluminium species and pH in soil solution under different crops. *In Plant Soil Interactions at Low pH*. Eds R A Date *et al.* pp 817-822. Kluwer Academic Publishers, Dordrecht.
- Parker M B, Perkins H F and Fuller H L 1959 Nitrogen, phosphorous, and potassium content of poultry manure and some factors influencing its composition. *Poult. Sci.* 38, 1154-1158.
- Pellet D M, Grunes D L and Kochian L V 1994 Organic acid exudation as an aluminium tolerance mechanism in maize (*Zea mays* L.). *Planta* 196, 788-795.
- Perkins H F and Parker M B 1971 Chemical composition of broiler and hen manures. University of Georgia Agric. Exp. Sta. Res. Bull. 90. 1-6.
- Perstorp Analytical 1993 Total Kjeldahl nitrogen. Environmental methodology Doc. 000579, Rev. C. Perstorp Analytical.
- Pleysier J L, Arora Y and Juo A S R 1987 Nitrogen leaching and uptake from calcium cyanamide in comparison to urea and calcium ammonium nitrate in an ultisol from the humid tropics. *Fert. Res.* 12, 193-199.
- Pocknee S and Sumner M E 1997 Cation and nitrogen contents of organic matter determine its soil liming potential. *Soil Sci. Soc. Am. J.* 61, 86-92.
- Prasad B and Sinha M K 1980 Physical and chemical characterization of soil and poultry litter humic and fulvic metal complexes. *Plant Soil* 54, 223-232.
- Pratt P F, Broadbent F E and Martin J P 1973 Using organic wastes as nitrogen fertilizers. *Calif. Agric.* 27, 10-13.
- Rengasamy P and Oades J M 1978 Interaction of monomeric and polymeric species of metal ions with clay surfaces. III. Aluminum (III) and chromium (III). *Aust. J. Soil Res.* 16, 53-66.
- Ritchie G S P 1989 The chemical behaviour of aluminium, hydrogen and manganese in acid soils. *In Soil Acidity and plant growth* Ed. A D Robson. pp 1-60. Academic Press, San Diego.
- Ritchie G S P 1994 Role of dissolution and precipitation of minerals in controlling soluble aluminium in acid soils. *Adv. Agron.* 53, 47-83.

- Robertson L S and Wolford J H 1970 Corn grain yields and changes in soil fertility levels as affected by five rates of poultry manure. *Mich. State Univ. Res. Rep.* 269, 14-20.
- Rodella A A, Fischer K R and Alcarde J C 1995 Cation exchange capacity of an acid soil as influenced by different sources of organic litter. *Comm. Soil Sci. Plant Anal.* 26, 2961-2967.
- Rolsten D E, Rauschkolb R S and Hoffman D L 1975 Infiltration of organic phosphorous compounds in soil. *Soil Sci. Soc. Am. Proc.* 39, 1089-1094.
- Rovira A D and McDougall B M 1967 Microbiological and biochemical aspects of the rhizosphere. *In Soil Biochemistry*. Eds. A D McLaren and G H Peterson. pp 417-463. Marcel Dekker, New York.
- Rowell D L 1988 Soil acidity and alkalinity. *In Russell's soil conditions and plant growth*. 11th edition. Ed. A Wild. pp 844-898. Longman, Harlow.
- Sanchez P A 1976 Properties and management of soils in the tropics. John Wiley & Sons, New York.
- Schefferle H E 1965 The decomposition of uric acid in built up poultry litter. *J. Appl. Bact.* 28, 412-420.
- Schuman L M 1990 Comparison of exchangeable Al, extractable Al, and Al in soil fractions. *Can. J. Soil Sci.* 70, 263-275.
- Sharpley A N, Smith S J and Bain W R 1993 Nitrogen and phosphorous fate from long-term poultry litter applications to Oklahoma soils. *Soil Sci. Soc. Am. J.* 57, 1131-1137.
- Simpson T W 1990 Agronomic use of poultry industry waste. *Poult. Sci.* 70, 1126-1131.
- Sims J T 1986 Nitrogen transformations in a poultry manure amended soil: temperature and moisture effects. *J. Environ. Qual.* 15, 59-63.
- Sims J T 1987 Agronomic evaluation of poultry manure as a nitrogen source for conventional and no-tillage corn. *Agron J.* 79, 563-570.
- Sims J T and Wolf D C 1994 Poultry waste management: agricultural and environmental issues. *Adv. Agron.* 52, 1-83.
- Sims J T, Schilke-Gartley K L and McGowan W 1991 Evaluation of best management practices for the agricultural use of poultry manure in Delaware. 75pp. Final Tech. Rep. Delaware Dep. Nat. Res. Environ. Control, Dover.
- Singh M, Yadav D S and Kumar V 1984 Leaching and transformation of urea in dry and wet soils as affected by irrigation water. *Plant Soil.* 411-420
- Slattery W J and Morrison G R 1995 Relationship between soil solution and low molecular

- weight organic acids in a conservation cropping system. *In* Plant Soil Interactions at Low pH. Eds R A Date *et al.* pp 589-593. Kluwer Academic Publishers, Dordrecht.
- Smith L W 1973 Nutritive evaluations of animal manures. *In* Symposium: processing agricultural and municipal wastes. Ed. G E Inglett. pp 55-74. Avi. Pub. Co., Westport, CT.
- Smith C J, Goh K M, Bond W J and Freney J R 1995 Effects of organic and inorganic calcium compounds on soil-solution pH and aluminium concentration. *Eur. J. Soil Sci.* 46, 53-63.
- Soil Classification Working Group 1991 Soil classification: A taxonomic system for South Africa. Department of Agricultural Development, South Africa.
- Sommers L E, Nelson D W and Owens L B 1979 Status of inorganic phosphorous in soils irrigated with municipal wastewater. *Soil Sci.* 127, 340-350.
- Soon Y K 1993 Fractionation of extractable aluminium in acid soils: a review and a proposed procedure. *Commun. Soil Sci. Plant Anal.* 24, 1683-1708.
- Stephenson A H, McCaskey T A and Ruffin B G 1990 A survey of broiler litter composition and potential value as a nutrient source. *Biol. Wastes* 34, 1-9.
- Stevenson F J 1967 Organic acids in soil. *In* Soil Biochemistry. Eds A D McLaren and G H Peterson. pp 119-146. Marcel Dekker, New York.
- Stevenson F J 1994 Humus chemistry: genesis, composition, reactions. Wiley, New York.
- Stevenson F J and Vance G F 1989 Naturally occurring aluminum-organic complexes. *In* The environmental chemistry of aluminum. Ed G Sposito. pp 117-146. Boca Raton, CRC Press.
- Stryer L 1975 Biochemistry. W. H. Freeman and Co. San Fransisco, USA.
- Sumner M E 1993 Gypsum and acid soils: the world scene. *Adv. Agron.* 51, 1-32.
- Sumner M E 1995 Amelioration of subsoil acidity with minimum disturbance. *In* Subsoil Management Techniques. Eds. N J Jayawardane and B A Steward. pp 147-185. Lewis Publishers, Inc., Bota Raton, FL.
- Suthipradit S, Edwards D G and Asher C J 1990 Effects of aluminium on tap-root elongation of soybean (*Glycine max*), cowpea (*Vigna unguiculata*) and green gram (*Vigna radiata*) grown in the presence of organic acids. *Plant Soil* 124, 233-237.
- Talibudeen O 1981 Cation exchange in soils. *In* The chemistry of soil processes. Eds D J Greenland and M H B Hayes. pp 115-179, John Wiley and Sons, UK.
- Tan K H, Leonard R A, Bertrand A R and Wilkinson S R 1971 The metal complexing capacity and the nature of the chelating ligands of water extract of poultry litter. *Soil Sci.*

- Soc. Amer. Proc. 35, 265-269.
- Tang C, Sparling C P, McLay C D A and Raphael C 1999 Effect of short-term residue decomposition on soil acidity. *Aus. J. Soil Res.* 37, 561-573.
- Tisdale S L, Nelson W L and Beaton, J D 1985 *Soil fertility and fertilizers*. Macmillan Publishing Company, New York.
- van der Watt H H, Barnard R O, Cronje I J, Dekker J, Croft G J and van der Walt M M 1991 Amelioration of subsoil acidity by application of a coal-derived calcium fulvate to the soil surface. *Nature* 350, 146-148.
- Van Beusichem M L, Baas R, Kirkby E A and Nelemans J A 1985 Intracellular pH regulation during NO<sub>3</sub>- assimilation in shoots and roots of *Ricinus communis*. *Plant Physiol.* 78, 768-773.
- Warman P R 1980 The effect of amprolium and aureomycin on the nitrification of poultry manure-amended soil. *Soil Sci. Soc. Am. J.* 44, 1333-1334.
- Weil R R, Kroontje W and Jones G D 1979 Inorganic nitrogen and soluble salts in a Davidson clay loam used for poultry manure disposal. *J. Environ. Qual.* 8, 86-91.
- Wild A 1994 *Soil and environment: an introduction*. Cambridge University Press, Cambridge.
- Wilkinson S R 1979 Plant nutrient and economic value of animal manures. *J. Anim. Sci.* 48, 121-131.
- Willis R B and Gentry C E 1987 Automated method for determining nitrate and nitrite in water and soil extracts. *Comm. Soil Sci. Plant Anal.* 18, 625-636.
- Wong M T F and Swift R S 1995 Amelioration of aluminium phytotoxicity with organic matter. *In Plant soil interactions at low pH*. Eds. R A Date, N J Grundon, G E Rayment and M E Probert. pp 41-45. Kluwer Academic Publishers, Netherlands.
- Wong M T F, Nortcliff S and Swift R S 1998 Method for determining the acid ameliorating capacity of plant residue compost, urban waste compost, farmyard manure and peat applied to tropical soils. *Comm. Soil Sci. Plant Anal.* 29, 2927-2937.
- Wong M T F, Gibbs P, Nortcliff S and Swift R S 2000 Measurement of the acid neutralizing capacity of agroforestry tree-prunings added to tropical soils. *J. Ag. Sci. (Camb.)* 134, 269-276.
- Yan F, Schubert S and Mengel K 1996 Soil pH increase due to biological decarboxylation of organic acids. *Soil Biol. Biochem.* 28, 617-623.

## APPENDIX 1

### NOTES:

- 1) Data presented is the mean of 3 replications.
- 2) Where indicated, units are in mg / l soil. To convert to mg / kg soil, use the following soil densities: 0-5cm segment = 0.86 mg/l; 5-45cm segment = 0.97 mg/l.

TREATMENT	DEPTH	ACID SAT %	EXCH ACIDITY cmol+/l	pH (KCl)	Ca mg/l	Mg mg/l	K mg/l	P mg/l	NITRATE mg N/l	AMMONIUM mg N/l
CONTROL: NO LITTER	0-5cm	49	2.34	4.06	357	58	71	9	5	8
	5-15cm	66	1.69	4.18	113	26	35	1	7	12
	15-25cm	69	1.70	4.19	91	26	33	1	10	22
	25-35cm	71	1.80	4.18	87	25	35	2	21	22
	35-45cm	68	1.77	4.17	100	29	36	2	33	22
LAYER MANURE 30 tons/ha	0-5cm	1	0.13	5.32	2,118	261	248	54	264	9
	5-15cm	31	1.05	4.28	301	67	132	2	45	24
	15-25cm	60	1.56	4.21	105	43	68	1	59	88
	25-35cm	67	1.61	4.19	96	28	43	1	96	137
	35-45cm	62	1.79	4.18	125	42	42	1	107	79
LAYER MANURE 10 tons/ha	0-5cm	3	0.22	4.53	1,146	142	153	23	53	9
	5-15cm	46	1.37	4.23	225	43	60	1	14	24
	15-25cm	66	1.64	4.19	107	27	34	1	24	48
	25-35cm	66	1.69	4.19	105	33	35	1	58	54
	35-45cm	63	1.74	4.17	117	42	34	1	74	38
LAYER MANURE 5 tons/ha	0-5cm	11	0.66	4.33	798	106	111	15	13	8
	5-15cm	62	1.70	4.18	139	27	47	1	8	15
	15-25cm	68	1.64	4.19	97	26	32	1	11	37
	25-35cm	67	1.63	4.19	93	29	37	2	32	43
	35-45cm	66	1.78	4.17	104	35	37	1	56	35
BROILER LITTER 30 tons/ha	0-5cm	9	0.68	4.29	825	174	348	46	189	11
	5-15cm	42	1.32	4.23	187	57	169	1	31	18
	15-25cm	70	1.78	4.19	75	26	75	1	40	58
	25-35cm	70	1.69	4.18	87	27	37	1	60	65
	35-45cm	64	1.68	4.18	111	38	35	1	61	37
BROILER LITTER 10 tons/ha	0-5cm	31	1.57	4.15	481	88	163	16	19	11
	5-15cm	59	1.62	4.18	127	31	88	1	10	11
	15-25cm	69	1.69	4.19	89	27	38	1	15	37
	25-35cm	70	1.73	4.17	83	27	34	1	35	35
	35-45cm	66	1.76	4.17	101	36	34	1	58	27
BROILER LITTER 5 tons/ha	0-5cm	39	1.88	4.11	406	72	122	11	12	9
	5-15cm	67	1.70	4.17	102	23	56	2	8	12
	15-25cm	69	1.74	4.19	92	26	37	2	12	25
	25-35cm	70	1.77	4.17	87	28	36	1	33	26
	35-45cm	68	1.83	4.17	98	32	35	1	52	23
LAYER 100/ha WITH PLANTS	0-5cm	3	0.20	4.61	1,121	126	33	13	4	11
	5-15cm	54	1.36	4.21	163	35	18	1	1	11
	15-25cm	65	1.48	4.20	100	30	20	2	1	12
	25-35cm	70	1.69	4.18	92	27	19	1	1	9
	35-45cm	67	1.49	4.18	89	27	20	1	2	10

	0-5cm	27	1.28	4.19	518	94	45	10	5	9
JILER 100/ha	5-15cm	68	1.76	4.16	107	27	26	1	1	10
WITH	15-25cm	66	1.61	4.19	104	31	20	1	1	10
PLANTS	25-35cm	69	1.70	4.19	98	27	20	1	1	10
	35-45cm	69	1.70	4.19	97	26	23	1	1	9
	0-5cm	45	2.06	4.10	387	63	39	6	6	7
CONTROL	5-15cm	65	1.58	4.18	112	29	24	1	1	10
WITH	15-25cm	69	1.70	4.17	92	25	30	2	1	8
PLANTS	25-35cm	70	1.68	4.18	89	25	25	1	1	9
	35-45cm	71	1.77	4.18	84	24	30	1	2	8
	0-5cm	23	1.25	4.20	577	104	154	15	8	9
RANGE	5-15cm	60	1.73	4.19	145	30	83	2	7	11
MANURE	15-25cm	68	1.65	4.19	93	25	35	1	14	30
10 tons/ha	25-35cm	69	1.85	4.18	95	29	37	1	30	31
	35-45cm	67	1.77	4.18	102	33	41	1	53	24
	0-5cm	35	1.91	4.11	518	89	112	7	9	9
RANGE	5-15cm	61	1.69	4.18	144	30	53	1	7	18
MANURE	15-25cm	65	1.71	4.19	120	32	34	1	12	32
5 tons/ha	25-35cm	63	1.57	4.18	112	31	38	1	25	33
	35-45cm	65	1.77	4.19	118	31	45	2	36	29