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**AN INVESTIGATION OF COMPOSTING POULTRY MANURE IN  
RELATION TO NITROGEN CONSERVATION AND  
PHOSPHATE ROCK DISSOLUTION**

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the requirements for the degree of  
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## ABSTRACT

Gaseous losses of nitrogen (N) through ammonia ( $\text{NH}_3$ ) volatilization and denitrification diminish the fertilizer value of animal and poultry manures and form atmospheric pollutants. Appropriate methods of composting can improve the fertilizer value by conserving manure N and minimise the risk of environmental pollution. Additionally, acids produced during composting and nitrification of conserved N in manure, provide a source of protons ( $\text{H}^+$ ) which have the potential to dissolve phosphate rock (PR) when composted with manure. The objective of this research was to examine the methods of composting poultry manure with different amendments in relation to N conservation and PR dissolution.

Firstly, the methods for preserving and measuring N in manure samples were evaluated. The results suggested that freeze drying and inclusion of a strong oxidizing agent ( $\text{KMnO}_4$ ) prior to routine Kjeldahl digestion were required to achieve complete recovery and accurate measurement of N in manure samples.

Methods for reducing the loss of N through  $\text{NH}_3$  volatilization and denitrification during aerobic and anaerobic composting of poultry manure with different amendments were investigated in controlled 'flow through' incubation experiments. The amendments included carbonaceous bedding materials (woodchip, paper waste, wheat straw and peat), acidifier (elemental sulphur- $\text{S}^0$ ) and adsorbents (zeolite and soil).

The loss of N through  $\text{NH}_3$  volatilization from aerobic composting was about 17% of the manure N which was reduced by 90-95% under anaerobic composting. Under aerobic composting the addition of various amendments reduced the volatilization loss by 33 to 60%. Although the rate of denitrification was negligible ( $<1\mu\text{g kg}^{-1} \text{ day}^{-1}$ ) in fresh manure, it increased enormously ( $3.7\text{mg kg}^{-1} \text{ day}^{-1}$ ) during composting. The presence of nitrate ( $\text{NO}_3^-$ ) was found to be a rate determinant for denitrification in manure. Amongst the treatments, the addition of  $\text{S}^0$  was very effective in reducing  $\text{NH}_3$  volatilization and denitrification.

The dissolution of PR during composting with poultry manure was examined using radioactively ( $^{32}\text{P}$ ) labelled synthetic francolite and North Carolina phosphate rock (NCPR). The use of  $^{32}\text{P}$  labelled francolite indicated that PR dissolution in poultry manure/PR composts could be measured more accurately from the increases in NaOH extractable phosphorus ( $\Delta\text{NaOH-P}$ ) than from the decreases in HCl extractable P ( $\Delta\text{HCl-P}$ ). Low levels of francolite and NCPR dissolution (<16%) occurred when PR is mixed with poultry manure. This was attributed to the high concentrations ( $4.8 \times 10^{-2} \text{ mol L}^{-1}$ ) of calcium ( $\text{Ca}^{2+}$ ) in manure solution which inhibited the dissolution of PR through the Ca common-ion effect. Addition of  $\text{S}^0$  to poultry manure/PR compost reduced the pH and thereby enhanced PR dissolution.

A system for the dissolution of PR, using the acid ( $\text{H}^+$ ) produced during the nitrification of  $\text{NH}_3$  released from poultry manure, was developed. The inhibitory effect of manure Ca on PR dissolution is avoided if the  $\text{NH}_3$  released from decomposing manure is absorbed in bark and soil materials containing PR, which are kept either as manure covers or in separate columns. Although both methods were found effective in the absorption of  $\text{NH}_3$ , the result demonstrated that bark absorbs more  $\text{NH}_3$  than does soil.

Extensive PR dissolution occurred in the bark (82.3%) and the soil (33.2%) even in the absence of  $\text{NH}_3$  absorption from poultry manure. Higher levels of PR dissolution in bark is attributed to its high exchangeable acidity ( $80.5 \text{ cmol (+) kg}^{-1}$ ) and large Ca sink size ( $82.7 \text{ cmol (+) kg}^{-1}$ ). However, when the bark and soil materials were kept as manure covers, accumulation of Ca in the covers due to the diffusion of manure Ca, reduced the PR dissolution. When the bark and soil materials were kept separately in columns, nitrification of absorbed  $\text{NH}_3$  resulted in small increases in PR dissolution in bark (15%) and soil (5%). However, most of the protons (50-95%) released during nitrification are involved in the buffering of the bark and soil materials.

The laboratory studies showed that the addition of  $\text{S}^0$  to poultry manure during aerobic composting not only reduced the loss of N, but also enhanced PR dissolution. Based on this observation, sulphocompost (a blend of poultry manure, woodchip with  $\text{S}^0$  and PR) and phosphocompost (a blend of poultry manure, woodchip with PR) were prepared

and their agronomic effectiveness were compared with fresh manure mixtures and urea using field grown winter cabbage and summer maize crops. The crop yield, N use efficiency and N recovery were greater for sulphocompost than for phosphocompost. The sulphocompost and phosphocompost were approximately 60% and 12%, respectively, as effective as urea treatments for winter cabbage. Both composts were equally effective as urea for the second season's maize crop. The study has shown that poultry manure enriched with PR and S<sup>o</sup> can be used as a source of N, P and S.

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## CHAPTER 1

### INTRODUCTION

Animal and poultry manures are valuable, renewable nutrient sources which have been used successfully to improve soil fertility for many centuries. With the introduction of low cost chemically synthesized fertilizers, suitable for high yielding crop varieties, the use of manures became less cost effective, and in some countries organic manures have been largely replaced. As a result, they have become wastes and have created disposal problems. However, the increasing trend towards organic farming has renewed interest in the use of animal and poultry manures.

As an outcome of intensive farming, large amounts of animal and poultry manures are produced around the world. For example, it is estimated that approximately 4.6, 160.5, 396.8 and 1335 million tons of fresh manures are produced in New Zealand (Bolan, 1989), U.K (Anon, 1983), United States (USDA, 1978) and India (Gaur, 1983), respectively. Unless appropriate methods of management of these manures are evolved, large scale accumulation of manure from housed animals will continue to pose disposal and pollution problems (Hauck, 1981).

One of the problems associated with the animal and poultry manures is the loss of plant nutrients, especially nitrogen (N) during the storage, handling, and subsequent land application. The loss of N occurs mainly through ammonia ( $\text{NH}_3$ ) volatilization and denitrification (Goulding and Webster, 1989; Kirchmann and Witter, 1989). Gaseous losses of N are of concern because they not only reduce the fertilizer value of the manure, but also deteriorate the quality of the environment (Breemen *et al.*, 1982; Buijsman *et al.*, 1987). Gaseous  $\text{NH}_3$  is also found to be responsible for some respiratory diseases in poultry birds (Carlile, 1984).

Manure may once again become a valuable resource for agriculture if N is conserved efficiently through the development of environmentally sensible management practices. This may be accomplished through effective composting (Gotaas, 1956; Parr *et al.*, 1986). As a natural process, composting has many advantages. It reduces the bulk

volume of the waste and yields stabilised products suitable for handling and land application (Crawford, 1983). Composting eliminates animal and human pathogens (Savage *et al.*, 1973) and can also reduce the risks of polluting ground water (Crawford, 1983).

Appropriate techniques of composting manure with suitable materials can greatly conserve N and therefore can improve fertilizer value of manure, while at the same time the protection of the environment can also be accomplished. The addition of carbonaceous materials to N-rich manure is found to be the most effective way to reduce N losses during composting (Witter and Lopez-Real, 1987). However, information is scarce on the effectiveness of such materials in reducing the loss.

Composting animal manure and organic wastes with phosphate rock (PR) has been long practised in developing countries for increasing the agronomic value of compost and PR (Mishra and Bangar, 1986). Composting manure with PR has been reported to enhance the dissolution of PR, whereby enrichment of phosphorus (P) can be achieved (Bangar *et al.*, 1985; Singh and Amberger, 1991). The organic acids produced through microbial metabolism and nitrification of conserved N during composting may provide a source of protons ( $H^+$ ) for PR dissolution. Therefore, it would appear to be appropriate to develop composting systems which are capable of turning both the large amounts of animal manure and local PR materials into valuable fertilizers.

Much research has been carried out on the N loss after the land application of manure. In this study, investigation is limited to the N loss and its conservation during composting of poultry manure, a subject on which only limited information exists. Such a study may provide fundamental information for effective utilization of poultry manure.

The overall objective of the study presented in this thesis is to examine the methods of composting poultry manure in relation to N conservation and PR dissolution. The thesis comprises of 9 Chapters. Following this introduction the review of literature (Chapter 2) examines the biological and chemical transformations of N and P, and the mechanisms involved in the dissolution of PR during composting of biological wastes.

A suitable method developed for the preservation and measurement of N in manure is presented in Chapter 3. The loss of N from poultry manure through  $\text{NH}_3$  volatilization (Chapter 4) and biological denitrification (Chapter 5) are measured, and the effectiveness of different amendments in reducing the N loss is examined.

The dissolution of PR during composting of poultry manure measured in order to enrich the compost with P is discussed in Chapter 6. Novel methods for absorbing the  $\text{NH}_3$  released from poultry manure using waste materials are developed. In Chapter 7 the use of the absorbed  $\text{NH}_3$  in the dissolution of PR is examined.

Results on the agronomic efficiency of nutrient rich poultry manure composts, prepared using appropriate amendments and evaluated under field conditions, are discussed in Chapter 8. Finally, the summary of the research and the suggestions for future work are presented in Chapter 9.

## CHAPTER 2

### REVIEW OF LITERATURE

#### 2.1 INTRODUCTION

Animal and poultry manures played an important role in sustaining soil productivity until the mid-twentieth century when the development of chemical fertilizers reduced the dependence upon animal manure. However, the continuous use of large quantities of chemical fertilizers on high yielding crop varieties has contributed to the deterioration of water quality (Parr *et al.*, 1986).

The increasing cost of chemical fertilizers together with diminishing non-renewable resources of plant nutrients is likely to affect the farming situation especially in developing countries (Flaig *et al.*, 1977). Further, in developed countries large-scale accumulation of poultry manure, and pig and cow slurries causes severe disposal problems, especially in the United Kingdom, Europe and North America.

There is, therefore, a renewed interest in the efficient use of organic manures, particularly animal and poultry manures. If appropriate technology is developed, manure, once again, will become a potentially valuable resource in agriculture.

#### 2.2 ANIMAL AND POULTRY MANURES

Continued growth in livestock and poultry industries results in large quantities of animal and poultry manures around the world (FAO, 1977). These renewable natural resources can be effectively utilized in agriculture as sources of plant nutrients.

Manure is faecal waste and urinary excretion of animals and poultry and may be combined with litter or bedding materials such as cereal straw or woodchip. The quantities of manure produced by farm animals can vary considerably. The daily values most often quoted for intensive livestock production are 45kg (fresh weight) for mature cattle, 4.5kg for fattening pig, and 0.1kg for chicken (Tunney, 1981).

Fresh manure generally contains about 20 to 30% dry matter, which is rich in cellulose, lignin, nitrogenous compounds and minerals. As manure directly or indirectly originates from plant materials, it contains all the nutrients essential for plant growth. Only small proportions of the nutrients in livestock feeds are retained by the animal; the rest is excreted (Azevedo and Stout, 1974).

The nutrient contents of manures vary considerably with the species and the age of animal, the composition of feed and the manure storage and handling system (Faassen and Dijk, 1987). Nutrient content of various animal and poultry manures, as reported in the literature, is given in Table 2.1.

**Table 2.1 Nutrient content of animal and poultry manures**  
**(g kg<sup>-1</sup> dry weight basis)**

Nutrients	Cattle	Sheep	Pig	Horse	Poultry
Nitrogen	25-40	20-45	20-45	17-30	28-62
Phosphorus	4-10	4-11	6-12	3-7	9-29
Potassium	7-25	20-29	15-48	15-18	8-21
Calcium	5-18	8-19	3-20	7-29	17-67
Magnesium	5-8	3-6	2-3	3-5	3-8
Sulphur	3-4	2-3	3-5	1-3	4-7

Amongst different manures, poultry manure generally contains the highest nitrogen (N), phosphorus (P), and calcium (Ca) contents (Table 2.1). The importance of manure with regard to soil fertility and crop production, has been ascribed, mainly, to the supply of large amounts of primary plant nutrients, N, P and potassium (K). Manures also contain appreciable amounts of other macro and micro nutrients. The organic matter in the manure can replenish the supply of humus and improve the physical properties of soils. In addition, microbiological processes in soil are likely to be enhanced by the addition of manure.

### 2.2.1 Nitrogen

Nitrogen in manure is of primary concern, because of its role in plant growth and its impact on environmental pollution. It is estimated that about 70 to 95% of N in the feed is excreted by the animal in the solid and liquid portions of manure (Waksman, 1952; Barrow, 1961; Floate, 1970a). Three major fractions of N are identified in manure; (1) inorganic N (ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ )) and rapidly mineralizable N (uric acid and urea), (2) easily decomposable organic N with a low C/N ratio (proteins and amino acids), and (3) 'resistant', slowly mineralizable organic N with a high C/N ratio (lignocellulosic fibre complex). Manure also contains easily decomposable N-free organic compounds, such as fats, fatty acids and simple sugars (Faassen and Dijk, 1987).

### 2.2.2 Phosphorus

Phosphorus in manure is present mainly as solid-phase inorganic P and the amount of P varies considerably due to variation in dry matter content and composition of animal feed (Riemsdijk *et al.*, 1987).

In fresh manure the inorganic P ( $\text{P}_i$ ) content ranges from 0.3 to 2.4% of dry matter, whereas the organic P ( $\text{P}_o$ ) content ranges from less than 0.1 to 1% (Peperzak *et al.*, 1959). About 78.4% of total P in sheep manure was estimated to be in  $\text{P}_i$  (Floate, 1970a). Faeces contribute most to the total as well as to the organic P (Gerritse and Zugec, 1977).

According to Gerritse (1978) the main forms of  $\text{P}_o$  in fresh pig slurry are inositol hexaphosphate (phytin) and adenosine triphosphate. A mineral species, struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) has been identified in the solid fraction of manure, and the presence of octocalcium-phosphate ( $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ ) and dicalcium phosphate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) have also been suggested (Fordham and Schwertmann, 1977a,b). Gerritse and Eksteen (1978) found that only a small fraction of the total P in manure solution is present as dissolved  $\text{P}_o$  (1-2%).

### **2.2.3 Potassium and other nutrients**

Animal and poultry manures invariably contain an appreciable amount of K (Table 2.1). The K in manure is considered to be as available as its fertilizer equivalent (Tunney, 1981). Other nutrients like Ca, sulphur (S) and magnesium (Mg), and micronutrients are also present in manure and make a valuable contribution to soil fertility.

### **2.2.4 Decomposition of manure**

Manure undergoes biological decomposition immediately after excretion and therefore its chemical, biological and physical properties continue to change. Bacteria, protozoa, fungi, actinomycetes, worms, and insects are principally involved in the decomposition process. The rates of decomposition of various constituents in manure vary due to difference in carbon (C) source, and C:nutrient ratios, temperature, water, oxygen, and other environmental conditions. It is generally reported that fresh plant materials decompose more readily than fresh manure, because, manure is the result of 'decomposition' of feed plant materials and therefore becomes relatively resistant to further decomposition (Barrow, 1961; Floate, 1970a).

Generally, depending on the supply of oxygen, two types of decomposition processes viz., aerobic and anaerobic, occur during manure storage or composting or after land application of manure.

#### **2.2.4.1 Aerobic decomposition**

According to Waksman (1952), the decomposition of manure involves three important steps: rapid decomposition, synthesis of microbial protoplasm, and formation of new compounds by condensation and polymerization. These steps are indiscrete and overlapping in natural systems and repeat several times during the decomposition process as synthesized microbial bodies are used by others and, in turn, are decomposed (Azevedo and Stout, 1974).

During aerobic decomposition of manure, living organisms utilize oxygen and organic

matter and synthesize protoplasm from N, P and other required nutrients. Approximately 70-80% of the C serves as a source of energy for the organisms and is respired as carbon-dioxide ( $\text{CO}_2$ ).

The various organic constituents of the manure are decomposed at different rates. Starches, hemicellulose (long chains of linked hexose or pentose sugars), cellulose (long chains of linked glucose sugar), and proteins are decomposed rapidly as numerous organisms use these C materials as energy sources. Only a few aerobic species are capable of decomposing the more resistant lignin and fat (Waksman, 1952) which remain in larger proportions in manure.

The active microorganisms in manure synthesize some mineralized decomposition products into their own protoplasm (Azevedo and Stout, 1974). Subsequent polymerization reactions in compost may lead to the production of complex lignoprotein, namely, humus (Poincelot, 1974).

The oxidative process of mineralization of organic N to  $\text{NO}_3^-$ , and the subsequent fate of ionic inorganic nitrogenous products, is of special significance for soil scientists. Hydrolysis of proteins in manure will yield polypeptides, amino acids, and some ammonia ( $\text{NH}_3$ ). Further oxidation of the remaining organic N compounds will release more  $\text{NH}_3$  (see section 2.3.1). Under favourable aerobic conditions  $\text{NH}_3$  after forming  $\text{NH}_4^+$  is oxidised to  $\text{NO}_3^-$ . Since  $\text{O}_2$  is utilized in oxidative microbial metabolic processes, its supply determines the rate of decomposition of the manure. The oxidative energy transformations of rapidly metabolizing microbial cells are responsible for the heat generated in aerobic composting (Azevedo and Stout, 1974).

#### **2.2.4.2      *Anaerobic decomposition***

In the absence of  $\text{O}_2$ , anaerobic microorganisms metabolize nutrients and decompose organic compounds by reduction processes. Lack of  $\text{O}_2$  excludes the efficient fungi and actinomycetes, therefore the anaerobic decomposition by specialized bacteria is slower and less efficient. As in the aerobic process, the organisms use N, P and other nutrients in synthesizing cell protoplasm, but, reduce the organic N to organic acids and  $\text{NH}_3$ .

This process is commonly termed as fermentation process. During anaerobic decomposition there is an accumulation of compounds, which normally require  $O_2$  for further decomposition. According to Azevedo and Stout (1974), these compounds include alcohols and organic acids from the decomposition of carbohydrates, and pyridines, indoles, skatoles,  $NH_3$ , and amines from the decomposition of proteins.

During the initial stages of anaerobic decomposition, a group of metabolic fermentative bacteria hydrolyse complex carbohydrates, proteins and lipids, and ferment their products to fatty acids (organic acids),  $H_2$ , and  $CO_2$  (Torien and Hattingh, 1969). Lactic acid appears to be the first major product of anaerobic fermentation, but soon it is transformed to other compounds, chiefly acetic and butyric acids (Alexander, 1967).

Another metabolic group, called the  $H_2$ -producing acetogenic bacteria, produce acetate,  $CO_2$  and  $H_2$  from the organic acids. Then methanogenic bacteria utilize the products, mainly, acetate,  $CO_2$ , and  $H_2$  to produce  $CH_4$  and  $CO_2$  (Hashimoto *et al.*, 1981). The C from the organic compounds, which is not utilized in the cell protein, is liberated mainly in the reduced form of methane ( $CH_4$ ). A small portion of C may be respired as  $CO_2$ .

### **2.3 LOSSES OF N FROM ANIMAL AND POULTRY MANURES**

It has been well known for a long time that large amounts of N are lost from animal and poultry manures (Russell, 1961). According to one estimate, approximately 60-63% of manure N is easily lost under present management practices (Stewart, 1981). Physical, biological and chemical changes take place during storage, or composting, or after land spreading of manure, resulting in rapid loss of plant nutrients, especially N.

Most of the studies have examined the loss of N from manures after land application (Terman, 1979; Beauchamp, 1983). A limited number of studies have been carried out on the losses of N during storage and composting of manures. Some of the reported losses of N during the storage or composting of animal and poultry manures is summarised in Table 2.2.

**Table 2.2 N losses during the storage or composting of animal and poultry manures**

Type of manure	Storage/composting	Total N loss (%)	References
Cattle slurry	Storage	56.3	Dewes <i>et al.</i> , (1990)
Cattle manure + straw	Composting	57.1	Martins and Dewes (1992)
Cattle slurry + straw	Composting	40-50	Jakobsen (1988)
Cattle manure (solid)	Stall barn storage	30-50	Muck and Richards (1983)
Dairy manure (solid)	Shallow pit storage	56	Moore and Beehler (1981)
Dairy manure (solid)	Deep pit storage	23	Moore and Beehler (1981)
Pig manure + straw	Composting	53.6	Martins and Dewes (1992)
Pig slurry	Composting	26	Loynachan <i>et al.</i> , (1976)
Pig slurry + straw	Composting	27-40	Faassen and Dijk (1979)
Pig slurry + straw	Composting	15	Bernal and Lopez-Real (1993)
Poultry manure	Deep litter under poultry	50.1	Tinsley and Nowakowski (1959a)
Poultry manure	Storage	20-40	Kirchmann (1985)
Poultry manure + straw	Composting	11-53	Tinsley and Nowakowski (1959a)
Poultry manure + straw	Composting	9-44	Kirchmann and Witter (1989)
Poultry manure + straw	Composting	77.4	Martins and Dewes (1992)
Poultry manure + sawdust/corn cob	Composting	27-32	Hansen <i>et al.</i> , (1989)
Sewage sludge + straw mixture	Composting	50	Witter and Lopez-Real (1988)
Sewage sludge + wood chips	Composting	10	Sikora <i>et al.</i> , (1983)

Approximately 9-77% of initial total N in manure was found to be lost, depending upon methods of storage or composting. The probable pathway of N losses from decomposing manure (particularly poultry manure) is illustrated in Figure 2.1. It has often been suggested that the N in manure during storage or composting is lost mainly through  $\text{NH}_3$  volatilization and biological denitrification (Goulding and Webster, 1989; Kirchmann and Witter, 1989). A relatively large number of studies have examined N loss through  $\text{NH}_3$  volatilization, but few have examined denitrification loss.

Substantial amounts of N from manure can also be lost through leaching after land application. In this review the losses due to  $\text{NH}_3$  volatilization and denitrification are discussed.

The principles and factors affecting the N losses from manure during storage or composting are more or less similar to those of N loss from the manure applied to soil; therefore the loss of N from manure either during storage/composting or after land application is discussed together.

### 2.3.1 Loss of N through $\text{NH}_3$ volatilization

Ammonia volatilization has long been considered as an important pathway for N loss during handling, storage and spreading of manure (Lauer *et al.*, 1976; Beauchamp *et al.*, 1978; ; Kirchmann and Witter, 1989).

A large proportion (80%) of the total N in fresh poultry manure is in the form of uric acid ( $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ ) (O'Dell *et al.*, 1960) which is rapidly hydrolysed to urea ( $\text{CO}(\text{NH}_2)_2$ ) by the enzyme uricase of several aerobic bacteria (Eq 2.1).



Through a chain of oxidative-hydrolysis reactions involving the enzyme urease,  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{NH}_4\text{HCO}_3$  are formed from  $\text{CO}(\text{NH}_2)_2$  (Schefferle, 1965) (Eq 2.2). These two chemical compounds ( $(\text{NH}_4)_2\text{CO}_3$  and  $\text{NH}_4\text{HCO}_3$ ) are unstable and therefore

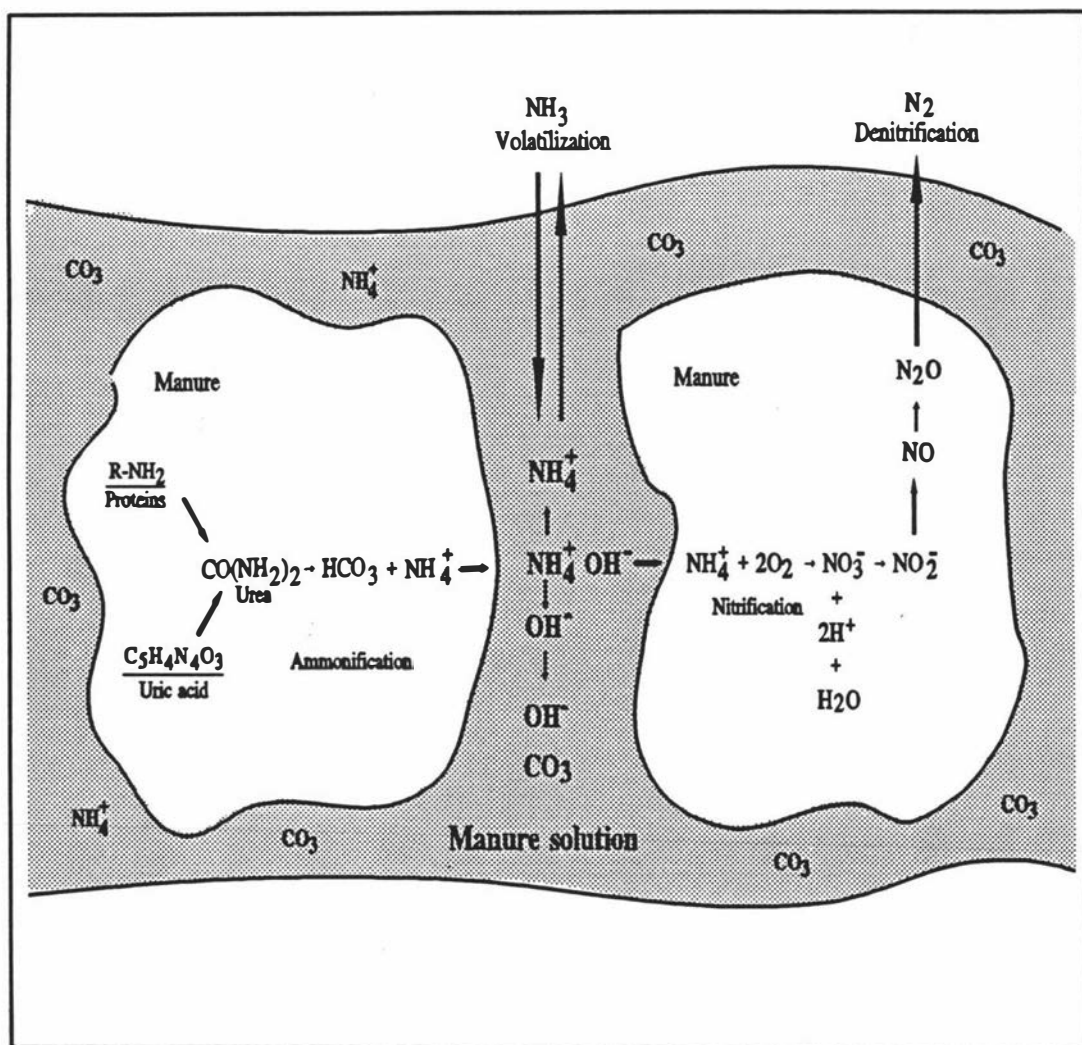
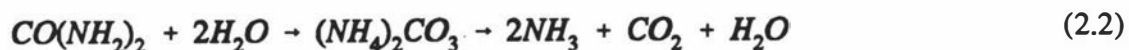


Fig 2.1 Pathway of N losses from decomposing manure during storage or composting

readily dissociate into gaseous  $\text{NH}_3$  and  $\text{CO}_2$  (Schefferle, 1965). Species of *Bacillus*, *Micrococcus*, *Sarcina*, *Pseudomonas*, *Achromobacter*, *Corynebacterium*, *Clostridium*, and a diverse collection of filamentous fungi and actinomycetes are known to synthesize urease (Alexander, 1967). A few organisms are capable of even converting  $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$  directly to  $\text{NH}_3$ .



As a basic gas  $\text{NH}_3$  reacts with protons, metals, and acidic compounds and/or dissolves in the manure solution to form a stable ionic form of ammonium ( $\text{NH}_4^+$ ) (Eq 2.3). The  $\text{NH}_4^+$  formed exists in a chemical equilibrium with gaseous  $\text{NH}_3$ .



The increase in the concentration of  $\text{NH}_4^+$  and  $\text{CO}_3/\text{HCO}_3$  in the manure solution increases pH and results in the volatilization of  $\text{NH}_3$  from manure (Fig 2.1). According to Witter and Lopez-Real (1987), the combination of high  $\text{NH}_4^+$  concentrations, high temperatures and pH levels may lead to high  $\text{NH}_3$  losses during composting.

#### 2.3.1.1 Significance of $\text{NH}_3$ volatilization

The impact of  $\text{NH}_3$  volatilization on the fertilizer value of manure and on the environmental quality is well known. Substantial losses of  $\text{NH}_3$ , sometimes as high as 50 to 80% of the N applied, have been documented from  $\text{NH}_4^+$  forming fertilizers and animal manure applied to the soil (Terman, 1979). In several studies direct measurement of  $\text{NH}_3$  volatilization from surface applied manure/slurry has shown that 24 to 99% of the  $\text{NH}_4^+$  in manure can be lost within the first week (Lauer *et al.*, 1976; Beauchamp *et al.*, 1978; Stevens and Logan, 1987; Thompson *et al.*, 1987; Lockyer *et al.*, 1989).

While  $\text{NH}_3$  volatilization from fertilizers and surface applied manures has been well

documented, corresponding losses from manure during storage or composting have not been adequately quantified. Vanderholm (1975) estimated that 30 to 65% of N in manure is lost during storage. Muck and Richards (1983) reported total N losses between 30 and 50% in free-stall barn. A loss of about 56% of total N within 12 weeks storage of cattle manure was reported by Moore and Beehler (1981). In poultry manure approximately 48% of total N (Giddens and Rao, 1975) and 60-70% of  $\text{NH}_4^+\text{-N}$  (Heck, 1931) are reported to be volatilized within three to seven days after dropping.

The wide variation encountered in N loss from manure between the experiments may be due to several factors including meteorological parameters, nature of manure/slurry and the method of measurements.

In addition to the loss of fertilizer value,  $\text{NH}_3$  volatilization often poses environmental and health problems. Animal manure and slurries have been identified as the main source of  $\text{NH}_3$  emissions to the atmosphere in Europe, contributing to about 81% of total emissions, which results in an increase in atmospheric  $\text{NH}_3$  (Buijsman *et al.*, 1987).

It has been reported that the release of  $\text{NH}_3$  into the atmosphere also enhances the wet deposition of sulphate and increases the N load of surrounding ecosystems (Breemen *et al.*, 1982; Schurkes, 1986). Acidification of the soil due to increased deposition and nitrification of ammonium sulphate has been reported (Ryden *et al.*, 1987; Witter and Lopez-Real, 1988; Van der Molen *et al.*, 1989).

Gaseous  $\text{NH}_3$  affects the health of all types of animals. The high concentration of  $\text{NH}_3$  inside the poultry shed is found to be a health hazard for birds. According to Bullis *et al.* (1950) the  $\text{NH}_3$  from manure is the principal cause of keratoconjunctivitis in chickens and turkeys. Anderson *et al.* (1964) reported on the susceptibility of chickens to Newcastle disease following a 72h exposure to 20ppm of  $\text{NH}_3$ .

Increasing levels of  $\text{NH}_3$  are also found to be closely associated with less feed efficiency, poor productivity, a delay in sexual maturity in chickens, and poor egg production (Charles and Payne, 1966). Carlile (1984) reported that manure gases,  $\text{NH}_3$ , hydrogen sulphide ( $\text{H}_2\text{S}$ ) and  $\text{CO}_2$  are highly poisonous to cattle, and at high levels death

may result. In addition, free  $\text{NH}_3$  becomes an eye and respiratory irritant for the personnel in the shed.

### **2.3.1.2 Factors affecting volatilization**

Several factors have been reported to affect the volatilization loss of  $\text{NH}_3$  from fertilizers and manures. The important factors generally affecting  $\text{NH}_3$  volatilization both during storage and after soil application of manure are discussed here.

#### **2.3.1.2.1 pH**

As  $\text{NH}_3$  is in equilibrium with  $\text{NH}_4^+$  in manure solution, the volatilization of  $\text{NH}_3$  depends primarily on manure pH. In general  $\text{NH}_3$  volatilization increases with increasing soil pH (Du Plessis and Kroontje, 1964; Terry *et al.*, 1978; Ryan *et al.*, 1981). However, it is reported that significant amounts of  $\text{NH}_3$  may be lost when pH is as low as 5.5 if large amounts of urea or  $\text{NH}_4^+$  salts are surface applied, or if high incubation temperatures are used (Ernst and Massey, 1960; Du Plessis and Kroontje, 1964).

According to Floate and Torrance (1970), if the pH of the decomposing substrate rose significantly above 7.0,  $\text{NH}_4^+\text{-N}$  would be lost through  $\text{NH}_3$  volatilization. However, they considered that  $\text{NH}_3$  losses were not simply due to pH dependent volatilization.

#### **2.3.1.2.2 Concentration of N**

The concentration of ammoniacal ( $\text{NH}_3 + \text{NH}_4^+$ )-N present in manure is also an important factor controlling the volatilization of  $\text{NH}_3$  (Beauchamp, 1983). It has been observed that the amount of  $\text{NH}_3$  volatilized increases when increasing amount of  $\text{NH}_4^+$  applied (Chao and Kroontje, 1964; Vlek and Stumpe, 1978).

#### **2.3.1.2.3 Microbial activity**

Since the decomposition of manure is mainly a microbiological process, the nature and

abundance of decomposing microorganisms play a significant role in the process of  $\text{NH}_3$  volatilization. The microbial activity affects the  $\text{CO}_2$  concentration in manure, which in turn affects the equilibrium concentration of  $\text{NH}_3$  in the solution phase and thereby  $\text{NH}_3$  volatilization is affected (Azevedo and Stout, 1974).

#### 2.3.1.2.4 Temperature and moisture content

The temperature and moisture content of manure plays an important role in the process of  $\text{NH}_3$  volatilization. Ernest and Massey (1960) observed a close relation between  $\text{NH}_3$  losses and temperature. Vlek and Stumpe (1978) showed that  $\text{NH}_3$  volatilization from solutions increased with an increase in temperature up to  $46^\circ\text{C}$ . While studying the effect of moisture and temperature, Adriano *et al.* (1974) observed a loss of 26% of initial total N at an incubation temperature of  $10^\circ\text{C}$  and a moisture content of 60%; the loss was increased to 45% with an increase in temperature ( $25^\circ\text{C}$ ) and moisture (90%).

Brunke *et al.* (1988) concluded that for manure with high initial water content, increasing the rate of drying increases the concentration of volatile N and thereby increases the rate of volatilization. Hadas *et al.* (1983) investigated the effects of temperature on N loss from ground and pelleted poultry manure incorporated in soils, and observed that mineral N loss was greatest between  $14^\circ\text{C}$  and  $35^\circ\text{C}$ .

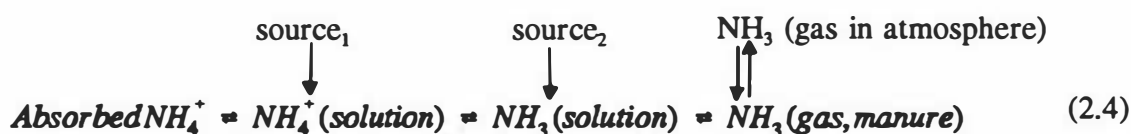
Some researchers have reported that  $\text{NH}_3$  volatilization increases with increasing soil moisture content up to field capacity (Ernst and Massey, 1960; Kresge and Satchell, 1960). Whereas, Martin and Chapman (1951) have found that  $\text{NH}_3$  losses decrease with increasing initial soil moisture content when sufficient water is present to dissolve added N fertilizers. Therefore, Martin and Chapman (1951) concluded that moisture loss was a requirement for  $\text{NH}_3$  volatilization. However, according to Ernst and Massey (1960)  $\text{NH}_3$  volatilization and water loss were not related.

#### 2.3.1.2.5 Atmospheric $\text{NH}_3$ concentration

The rate of volatilization of  $\text{NH}_3$  depends on the difference in  $\text{NH}_3$  partial pressure between the manure solution and the atmosphere. Since  $\text{NH}_3$  is a gas at normal

atmospheric temperature and pressure, it is expected that any  $\text{NH}_3$  present in manure would quickly volatilize to the atmosphere (Freney *et al.*, 1983).

Koelliker and Miner (1973) and Lauer *et al.* (1976) considered the  $\text{NH}_3$  partial pressure gradient between the liquid phase and the ambient atmosphere as a driving force for  $\text{NH}_3$  volatilization. The  $\text{NH}_3$  gas-liquid equilibrium is proportionally related to the concentration of  $\text{NH}_3$  in solution and the partial pressure of  $\text{NH}_3$  in atmosphere (Eq 2.4; Vlek and Stumpe, 1978). Therefore, the rate of  $\text{NH}_3$  volatilization is controlled by the rate of removal and dispersion of  $\text{NH}_3$  into the atmosphere and the concentration of  $\text{NH}_4^+$  or  $\text{NH}_3$  in solution (Freney and Black, 1987).



#### 2.3.1.2.6 Other factors

It has generally been observed that  $\text{NH}_3$  volatilization decreases with an increase in CEC of soil. However, the effect of cation exchange capacity (CEC) of manure on  $\text{NH}_3$  volatilization is unclear. Due to limited CEC of biological wastes, much less  $\text{NH}_4^+$  would be retained; consequently, high  $\text{NH}_3$  volatilization can occur from manure (Nelson, 1982).

Incorporation of decomposable organic materials with urea has been found to accelerate the volatilization of  $\text{NH}_3$  (Moe, 1967). But, Verma *et al.* (1974) found that the addition of farmyard manure did not affect the loss of  $\text{NH}_3$ . The inconsistent effects of organic residue addition on  $\text{NH}_3$  volatilization may result from several factors associated with the nature of wastes. Organic N in waste may be mineralized to form  $\text{NH}_4^+$ , which will increase the  $\text{NH}_3$  concentration in solution, while the high C/N ratio and acidic nature of organic wastes will lower the  $\text{NH}_3$  concentration in solution. Therefore, the net effect on  $\text{NH}_3$  volatilization depends on the nature and rate of the residue added (Nelson, 1982).

### 2.3.1.3 *Measurements of NH<sub>3</sub> volatilization*

Several authors have reviewed various methods used to measure NH<sub>3</sub> volatilization from soil or organic substances (Terman, 1979; Freney and Black, 1987; Brunke *et al.*, 1988).

Under laboratory conditions, Floate and Torrance (1970) described a closed incubation method suitable for studying the mineralization of C, N and P. Using this system they achieved almost complete recovery of NH<sub>3</sub> volatilized from plant materials and sheep faeces. Recently, for measuring the NH<sub>3</sub> volatilization from decomposing manure, Kirchmann and Witter (1989) used a 'flow through system' to trap the NH<sub>3</sub> in acid scrubbers and determine by titration. For laboratory measurements, both the closed system and the 'flow through system' are likely to give accurate estimation of NH<sub>3</sub> release from manure.

For field experiments, most studies employed a closed system, which involves pulling air through an enclosure on the soil surface and then through a dilute acid solution, determining NH<sub>3</sub> by titration or by steam distillation or colorimetric methods. Some open systems, which involve an aerodynamic approach using micrometeorological measurements (Beauchamp *et al.*, 1978; Wilson *et al.*, 1982), are also employed to measure NH<sub>3</sub> volatilization from soil.

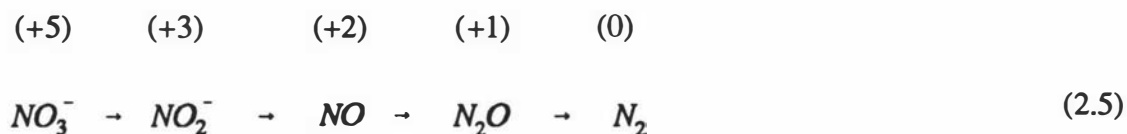
Denmead *et al.* (1974) described a micrometeorological method for field studies based on the energy balance near ground surface and the calculation of transfer coefficients. Beauchamp *et al.* (1978) also employed micrometeorological measurements along with a diffusion model to predict NH<sub>3</sub> flux densities. Van der Molen *et al.* (1989) used a wind tunnel method and the micrometeorological mass balance method to measure volatilization from cattle slurry applied to soil.

### 2.3.2 *Loss of N through denitrification*

Biological denitrification is defined as the microbial reduction of NO<sub>3</sub><sup>-</sup> or nitrite (NO<sub>2</sub><sup>-</sup>) to gaseous nitrogen either as molecular nitrogen (N<sub>2</sub>) or as an oxide of nitrogen (SSSA, 1979).

Most studies on denitrification have shown that nitrous oxide ( $N_2O$ ) and/or  $N_2$  are the primary end products of biological reduction of  $NO_3^-$ . Evolution of nitric oxide (NO) has also been detected (Burford and Bremner, 1975).

The pathway of N oxide reduction during denitrification may be represented as follows (Eq 2.5; Firestone, 1982);



The detail of mechanisms involved in denitrification can be found in several reviews on denitrification (Firestone, 1982; Knowles, 1982; Fillery, 1983).

Early evidence for denitrification loss of manure N was given by Waksman (1952) who indicated that the greatest loss of N from stable manure could be due to biological denitrification. He observed a loss of 20 to 24% of N in manure inoculated with nitrifying bacteria as against only about 3% (largely as  $NH_3$ ) in manure without nitrifying bacteria. He attributed this difference in loss to denitrification.

Though the literature on direct measurement of denitrification loss from manure or composts is scarce, many researchers have recognised that biological denitrification together with  $NH_3$  volatilization could be a significant pathway of N loss from manure (Giddens and Rao, 1975; Hadas *et al.*, 1983; Gale and Gilmour, 1986; Bitzer and Sims, 1988; Goulding and Webster, 1989).

Under anaerobic conditions certain microorganisms use  $O_2$  from  $NO_3^-$  ion as hydrogen acceptor and reduce  $NO_3^-$  to  $N_2$  or  $N_2O$  in manures (Fig 2.1). Several microorganisms are capable of reducing  $NO_3^-$ ,  $NO_2^-$ , or  $N_2O$ , as terminal electron acceptors. Since most denitrifying bacteria are chemoheterotrophs, they use chemical energy sources, and use organic C compounds as electron donors (reductants) and as sources of cellular C (Firestone, 1982). Almost all denitrifiers are aerobic organisms capable of anaerobic growth only in the presence of N oxides. Under conditions of limited  $O_2$  availability,

aerobic respiration can apparently provide the energy needed for synthesis of new enzymes required for  $\text{NO}_3^-$  reduction.

Denitrification results in the loss of valuable N and is therefore considered important in agriculture. In addition, it has been recognised that the denitrification loss of N from fertilizers, animal manures, and biological wastes may contribute significant amounts of  $\text{N}_2\text{O}$  to the atmosphere, and thus cause depletion of stratospheric ozone and add to the greenhouse effect (Knowles, 1982; Breitenbeck and Bremner, 1986). On the other hand denitrification can remove excess  $\text{NO}_3^-$  and minimise the  $\text{NO}_3^-$  contamination of ground water.

### **2.3.2.1      *Factors affecting denitrification***

#### **2.3.2.1.1      Oxygen supply**

The existence of anaerobiosis is considered as a prerequisite for denitrification to occur. All of the N oxide reductases are repressed by  $\text{O}_2$  which also inhibits reductase, probably by competing for electrons. Inhibition of  $\text{NO}_3^-$  reduction by  $\text{O}_2$  does not seem to be due to a direct effect of  $\text{O}_2$  on the enzyme itself;  $\text{O}_2$  must function as a terminal electron acceptor for it to affect  $\text{NO}_3^-$  reduction (Firestone, 1982).

The presence of  $\text{O}_2$ , and its use as an electron acceptor, also affects  $\text{N}_2\text{O}$  reduction. It was observed that the amount of  $\text{N}_2\text{O}$  produced, relative to  $\text{N}_2$ , increased with increasing  $\text{O}_2$  availability, while the overall rate of gas ( $\text{N}_2\text{O}$  and  $\text{N}_2$ ) production declined with  $\text{O}_2$  availability (Knowles, 1982). There are reports that denitrification can occur in soils under apparently aerobic conditions due to the presence of anaerobic microsites and that denitrification does not occur in soils until the oxygen supply is so restricted that the denitrifying bacteria cannot obtain enough  $\text{O}_2$  to meet their requirements (Broadbent and Clark, 1965).

#### **2.3.2.1.2      Availability of carbon**

Since most denitrifiers are heterotrophs, the denitrification process is strongly dependent

on the availability of C in organic matter. Microorganisms, in general, are usually limited by C and energy sources. Therefore, the supply of readily decomposable organic matter in the soil is critical in controlling the rate of denitrification.

Rates of denitrification are highly correlated with amounts of water-extractable soil organic C (Bremner and Shaw, 1958; Burford and Bremner, 1975). The presence of an ample C substrate can result in rapid  $O_2$  consumption and possible depletion, which can also indirectly enhance the potential for denitrification (Firestone, 1982). The addition of plant residues and manure, greatly increases the rate of denitrification from soil mainly by supplying available C to denitrifiers (Burford and Bremner, 1975; Guenzi *et al.*, 1978; Aulikh *et al.*, 1984; Christensen, 1985; Thompson and Pain, 1989).

#### 2.3.2.1.3      Availability of nitrate

A strong dependency of denitrification on  $NO_3^-$  concentration has often been observed (Bowman and Focht, 1974; Stanford *et al.*, 1975). Though the availability of  $NO_3^-$  for denitrifiers is the first step in biological denitrification, studies by Bremner and Shaw (1958), Smid and Beauchamp (1976), Knowles (1982) and Goulding and Webster (1989) failed to show any relationship between  $NO_3^-$  concentration and the rate of denitrification in soil.

It was observed that for many soils which contain endogenous  $NO_3^-$  at concentrations greater than  $10\mu g\ N\ g^{-1}$ , there is no effect of further  $NO_3^-$  supplement on the rate of denitrification (Knowles, 1982). Low concentrations of  $NO_3^-$ , on the other hand, have been shown to promote derepression of the reductases and stimulate  $N_2O$  reduction which has not been previously exposed to  $NO_3^-$  (Blackmer and Bremner, 1978).

#### 2.3.2.1.4      Temperature and moisture

Denitrification generally shows an exponential increase between  $15^\circ C$  and  $30^\circ C$ , but this relationship does not hold below  $12^\circ C$  (Fillery, 1983). The rate of denitrification continues to increase at higher temperatures, reaching a maximum at  $60^\circ C$ - $75^\circ C$ , but falling to zero above this temperature (Bremner and Shaw, 1958; Keeney *et al.*, 1979).

Decreasing temperature was found to increase  $O_2$  solubility in soil solution and decrease  $O_2$  consumption (Firestone, 1982). Therefore increasing  $O_2$  concentration has a greater inhibitory effect on denitrification at lower temperatures (Craswell, 1978).

According to Nommik (1956) and Bremner and Shaw (1958), the optimum temperature for denitrification in soil has been observed to be  $65^\circ\text{C}$ , while Stanford *et al.* (1975) reported the optimum to be at  $35^\circ\text{C}$ . Minimum temperatures at which denitrification occurs in soil ranges from  $2.7^\circ\text{C}$ - $10^\circ\text{C}$  (Bailey, 1976; Craswell, 1978).

#### 2.3.2.1.5      pH

The rate of denitrification is strongly affected by pH, generally being low in acid conditions and rapid at slightly alkaline pHs (Nommik, 1956; Bremner and Shaw, 1958; Blackmer and Bremner, 1978). However, at a pH range of 6 to 8 (optimum for plant growth) there is little effect of pH on denitrification (Burford and Bremner, 1975).

#### **2.3.2.2      *Measurements of denitrification***

Detailed reviews on methods of measurement of denitrification are available (Ryden and Rolston, 1983; Tiedje *et al.*, 1989). One of the principal free products of denitrification is  $N_2$ . Due to its very high ambient concentration, it is very difficult to measure any changes in  $N_2$  due to denitrification. This can be overcome either by the use of  $^{15}\text{N}$  to trace the fate of N or by measuring other intermediary products, mainly  $N_2O$ .

A number of different methods have been used to measure the flux of  $N_2O$  from soil. These include: micrometeorological methods (Mosier and Hutchinson, 1981) based on diffusion theory (Rolston *et al.*, 1976), measuring the increase in  $N_2O$  concentrations under a closed canopy (Findlay and McKenney, 1979; Matthias *et al.*, 1980; Mosier and Hutchinson, 1981), and drawing air from the headspace of a canopy and trapping out  $N_2O$  from the air stream (Ryden *et al.*, 1979).

Acetylene ( $C_2H_2$ ) inhibition technique and  $^{15}\text{N}$  methods are the most reliable and widely used for measuring the rate of denitrification (Smith *et al.*, 1978; Ryden *et al.*, 1979;

Firestone, 1982; Ryden and Rolsten, 1983; Tiedje *et al.*, 1989; Aulakh *et al.*, 1991).  $C_2H_2$  effectively inhibits the reduction of  $N_2O$  to  $N_2$  during denitrification (Yoshinari and Knowles, 1976) and therefore the denitrification measurement based on this method is considered to be valuable and accurate (Smith *et al.*, 1978; Ryden *et al.*, 1987; Tiedje *et al.*, 1989). Several variations of the technique have been proposed, but most involve either *in-situ* treatment of soil with  $C_2H_2$  using an enclosure placed over the soil surface followed by determination of  $N_2O$  emission (Ryden *et al.*, 1979), or incubation of soil cores with  $C_2H_2$  followed by analysis for  $N_2O$  (Ryden *et al.*, 1987).

Ryden *et al.* (1987) showed that the method involving incubation of minimally disturbed soil cores with  $C_2H_2$  can be effectively used for denitrification measurements. The chief advantages of this method include: (i) a simple procedure; (ii) a reduction in problems associated with the inhibition of nitrification by  $C_2H_2$  due to short term exposure of sample to  $C_2H_2$ ; and (iii) possibility of using the soil cores for additional analyses of mineral N and water contents. Therefore, it is considered that the incubation of soil or manure in the presence of  $C_2H_2$  at appropriate concentration and measuring the concentration of  $N_2O$  provides a reliable estimate of the rate of denitrification.

## 2.4 COMPOSTING

Composting is a method of solid waste management whereby the organic component of the solid waste is biologically decomposed and stabilized under controlled conditions to a state where it can be handled, stored and/or applied to the land without adversely affecting the environment (Golueke, 1977). It is a self-heating, thermophilic, and aerobic biological process which occurs naturally in heaps of biodegradable organic matter such as manure, moist hay and straw, and damp sawdust.

During the composting process the readily decomposable substrates are utilized by microorganisms as energy sources and for conversion to microbial tissue and products. The composting is therefore simply a means of converting raw waste organic matter into a usable humus (Gray and Biddlestone, 1971).

Composting is considered as a viable alternative for the stabilization of organic manures

and solid wastes, which are high in volatile solids (Sikora and Sowers, 1985; Parr *et al.*, 1986). The degradation of the volatile solids during composting results in the production of heat and in a subsequent temperature increase. Proper techniques of composting can reduce the loss of N and increase the fertilizer value of manures. Further, in biological or organic farming, it is required that the biological wastes need to be composted prior to land application. Composting can destroy all animal, human and plant pathogens (Savage *et al.*, 1973; Bollen, 1985).

Manure comprising several fractions of organic components normally has an indigenous population of microorganisms derived from the atmosphere, water, or soil. Once the moisture content is brought to an appropriate level during composting, microbial metabolism speeds up. Energy is obtained by biological oxidation of C. Some of this energy is used in metabolism, and the rest is given off as heat. C, N, P and K are considered to be the primary nutrients for the microorganisms involved in composting.

The organic materials, depending on the O<sub>2</sub> status of composting, follows either aerobic or anaerobic decomposition, which were already discussed in section 2.2.4. The end product (composts) provide a more stabilized form of organic matter and can improve the physical properties of soils.

#### **2.4.1 Factors controlling composting**

Some of the important factors controlling the process of composting are briefly discussed here.

##### **2.4.1.1 C/N ratio**

The rate at which organic matter decomposes during composting is principally dependent upon the C/N ratio of the materials. As mentioned earlier, during composting, microorganisms utilize the C as a source of energy and the N for building cell structure. More C than N is needed, but, if the excess of C is too great, decomposition decreases (Gotaas, 1956). When the availability of C is less than that required for converting available N into protein, microorganisms use most of the available C and there may be

loss of N through  $\text{NH}_3$  volatilization as described in section 2.3.1.

A C/N ratio of 20 has been widely accepted as optimum for composting (Gotaas, 1956). Singh (1987) reported that the decomposition of organic waste increased considerably when the C/N ratio was narrowed down to 30 through the addition of urea-N. Witter and Lopez Real (1987) observed excessive loss of N during composting of manure at a lower C/N ratio.

Quoting several literature, Gotaas (1956) reported that at a C/N ratio between 26 to 38, the N loss was greatly reduced. At low C/N ratio, more N is available than is required for the microorganisms to utilize the C; therefore considerable amounts of  $\text{NH}_3$  and volatile forms of N will be lost (Gotaas, 1956; Poincelot, 1974). When N is low in relation to C (i.e. high C/N ratio), the mineral N will become immobilized in the microbial biomass during the decomposition of C materials (Witter and Lopez-Real, 1987), and when some of the microorganisms die, the microbial N will be utilized by other microorganisms.

#### **2.4.1.2      *Temperature***

Proper temperature control is an important factor in aerobic composting process. High temperatures (above  $50^\circ\text{C}$ ) are essential for the destruction of pathogenic organisms and undesirable weed seeds (Gotaas, 1956). The preponderance of information on the effects of temperature on composting indicates that optimum decomposition takes place between  $55$  and  $60^\circ\text{C}$  (Sikora and Sowers, 1985).

Decomposition also proceeds much more rapidly in the thermophilic temperature range ( $60$ - $70^\circ$ ). Bhoyar *et al.* (1979) found that greater  $\text{NH}_3$  formation occurred during composting at temperatures between  $60$  and  $70^\circ\text{C}$  than at  $30$  and  $50^\circ\text{C}$ . But, according to Gotaas (1956), the optimum temperature range is  $50^\circ$ - $70^\circ\text{C}$ , around  $60^\circ\text{C}$  usually being the most satisfactory for successful composting.

### **2.4.1.3      *Moisture***

Optimum moisture content is essential for the microbial proliferation during composting of wastes. Aerobic decomposition can proceed at a moisture content between 30% and 100% if adequate aeration can be provided. However, Floate (1970a,b) concluded that moisture content has less influence than temperature on the decomposition of organic materials of plant and animal origin.

However, a high moisture content must be avoided because water displaces air from the interstices between particles and creates anaerobic conditions. A very low moisture content may deprive the organisms of the water needed for their metabolism, and consequently inhibits their activity.

Gotaas (1956) stated that little decomposition takes place in manure heaps both under dry and waterlogged conditions, and suggests a moisture content of 65-85% depending on the characteristics of the composting materials. Waksman (1952) recommended 75-80% moisture for composting farmyard manure. Singh (1987) reported that the loss of organic matter increased as moisture content increased up to 70%, and further increases in moisture content decreased the rate of decomposition. For anaerobic composting the maximum moisture content is not important, since O<sub>2</sub> maintenance is not a factor under such conditions.

### **2.4.1.4      *Aeration***

Adequate supply of oxygen to the organisms should be maintained if composting is to proceed rapidly (Crawford, 1983). The two types of composting processes viz., aerobic and anaerobic largely depend on the oxygen supply. Aeration is also useful in reducing a high initial moisture content in composting materials (Gotaas, 1956).

The supply of oxygen can be increased by blowing air into the compost, agitation, the provision of air vents into the base of the composting mass, or by 'turning' or regular mixing of compost heaps (Crawford, 1983). If, however, the rate of air flow through the compost is too great heat losses and desiccation will occur, and the rate of

composting will be reduced. 'Turning' the material is the most common method of aeration when composting is done in stacks. The amount of aeration in relation to temperature and moisture can be accurately controlled in mechanically aerated digesters.

#### **2.4.1.5      *Microorganisms***

Composting is a dynamic process in which the physical and chemical changes are caused by a rapid succession of mixed microbial populations. Biological waste materials contain a large number of many different types of bacteria, fungi, mould, and other living organisms. Therefore, the microbial activity has the most significant effect on composting (Waksman, 1952).

It appears that more species of bacteria are involved in aerobic decomposition than in anaerobic fermentation (Gotaas, 1956). Marked changes take place in the nature and abundance of the microbial population during the decomposition. Temperature and availability of nutrients sources probably exert the greatest influence in determining the species of organisms comprising the population at any stage.

The facultative and obligate aerobic representatives of bacteria, actinomycetes, and fungi are the most active during aerobic composting. Mesophilic bacteria are characteristically predominate at the start of the process, followed by thermophilic bacteria, and actinomycetes. No attempt was made in this review to show the detailed role of groups of organisms or specific organisms in decomposing different biological waste material.

#### **2.4.1.6      *pH***

The pH of compostable material influences the type of organisms involved in the composting process. Fungi tolerate a wider pH range than do bacteria. The optimum pH range for most bacteria is between 6.0 and 7.5; whereas for fungi it can be between 5.5 and 8.0. According to Gotaas (1956) most of the waste materials available for composting are within the above pH range and hence present no problem of pH control.

Other factors such as the blending or proportioning of materials, the method of mixing

and placing, and the composting duration also appear to have considerable influence on the success of the composting process. The porosity, texture, and structure also affect the composting process by their influence on aeration and moisture retention. These factors can be adjusted by selection of the composting materials and by grinding or shredding and mixing.

#### **2.4.2 Composts**

The end product of the composting process is commonly known as compost. Composting is often associated with relatively high losses of plant nutrients, especially N (Witter and Lopez-Real, 1987). Therefore, there is a definite need to improve the nutrient content of compost in order to effectively utilize waste products in agricultural and horticultural systems.

Conservation of N in compost, and enrichment of compost with other nutrients, can be achieved through using appropriate materials and techniques in composting. The low C/N ratio of manure is one of the main reasons for  $\text{NH}_3$  loss, composting N rich manure with C rich waste materials like straw or wood wastes appears to be the most effective and the most practical method to reduce N loss. On the other hand, composting manure with phosphate rock (PR) is likely to enrich the compost with P.

### **2.5 CONSERVATION OF N DURING COMPOSTING**

Conservation of N in manure through proper composting methods not only increases the fertilizer value of the manure, but considerably minimises environmental pollution. The conservation of N by reducing  $\text{NH}_3$  volatilization and denitrification can be achieved through various biological, chemical and physical methods.

#### **2.5.1 Biological methods of N conservation**

Biological methods include improved composting techniques, proper storage methods and the use of different biological waste materials.

### 2.5.1.1 *Anaerobic composting*

Several studies have shown that the loss of  $\text{NH}_3$  through volatilization is higher under aerobic conditions than under anaerobic conditions (e.g. Russell and Richards, 1917; Jansson and Clark, 1952; Moore and Beehler, 1981; Hansen *et al.*, 1989). Working with poultry manure Kirchmann and Witter (1989) recorded a 44% N loss through  $\text{NH}_3$  volatilization during aerobic decomposition as against only <1% loss during anaerobic decomposition.

Field *et al.* (1985) have also shown that anaerobic digestion of poultry manure conserved about 70 to 90% of manure N. Anaerobic digestion has been reported to be most efficient in conserving N (Qi-xiao Wen, 1984). The organic acids produced by fermentation of carbohydrates and lipids and the lower rate of decomposition during anaerobic composting (Acharya, 1935a; Waksman, 1952) contributed to a reduction in N loss through volatilization.

Further, as the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-/\text{NO}_3^-$  is restricted under anaerobic conditions, the loss through denitrification is also prevented. Composting manure anaerobically is likely to conserve more N, but it is not always found to be feasible because of its odour problems.

### 2.5.1.2 *Composting with carbonaceous waste materials*

The low C/N ratio of manure (usually <15) favours the loss of  $\text{NH}_3$ . Increasing the C/N ratio by the addition of carbonaceous materials is likely to reduce the N loss (Witter and Lopez-Real, 1987). In the presence of C materials the  $\text{NH}_3$  formed will become rapidly immobilized into new microbial biomass (Hoyle and Mattingly, 1954; Faassen and Dijk, 1979; Kirchmann, 1985b) and thereby reduce N losses during the composting. Readily oxidizable C compounds have a higher impact on immobilization than more slowly oxidizable compounds (Kirchmann and Witter, 1989). Kirchmann (1985a) studied the relationship between the C/N ratio and  $\text{NH}_3$  losses during manure storage by varying the ratio of manure to straw. He reported highest losses of 36-42% at a C/N ratio of 16-18, which were found reduced to 8% at a C/N ratio of 40.

## 2.5.2 Chemical methods of N conservation

There were several reports showing the effectiveness and feasibility of using various chemical substances to reduce the loss of N from manure. Pain *et al.* (1987) suggested three important mechanisms for using chemicals to conserve manure N; inhibition of urea hydrolysis, chemical stabilisation of  $\text{NH}_3$  and adsorption of  $\text{NH}_3$ .

### 2.5.2.1 *Inhibition of urea hydrolysis*

As already mentioned the faeces and urine contain large amounts of uric acid and urea that are rapidly hydrolysed by the enzyme urease to  $\text{NH}_3$ . Inhibition of this first step in manure N transformation may result in the reduction of N loss. Maximum urease activity in animal manure occurs between pH 7.0 and 7.5 and decreases markedly with increasing pH (Muck, 1982). Therefore, it is possible to inhibit the urease activity at high pH.

The use of lime would, at first, seem counterproductive in conserving manurial N, because increasing the pH would accelerate the rate of  $\text{NH}_3$  volatilization by increasing the concentration of  $\text{NH}_3$  in the manure. Muck and Herndon (1985) tested hydrated lime in both laboratory and barn experiments. Their result showed that the low levels of hydrated lime increased the N losses, whereas rates sufficient to increase the pH of manure to pH 9.6 to 9.8 conserved both urea and total N, which was attributed solely to complete inhibition of urea hydrolysis at high pH.

Some chemical substances in plant materials are known to have microbial inhibitory properties. For example, extract of yucca saponin was found to inhibit urea hydrolysis (Carlile, 1984). The use of such products has not been widely practised.

### 2.5.2.2 *Chemical stabilization*

Addition of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), monocalcium phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), or kainite ( $\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$ ) to freshly excreted manure has often been found to reduce the manure N loss (Carlile, 1984). These chemicals react

with  $\text{NH}_4^+$  in manure which is frequently not in a free state but rather is found as ammonium carbonate and form stable ammonium salts.

Phosphates have traditionally been added to composts in parts of India and China, and have been shown to reduce N losses (Flaig *et al.*, 1977). Comparing different additives, such as dicyandiamide, bentonite and ground superphosphate, Jurgens (1987) reported that the greatest reduction in  $\text{NH}_3$  volatilization from cattle and pig slurry was achieved with superphosphate, which lowered the pH of the slurry.

Both superphosphate and phosphoric acid have the advantage of reacting with free  $\text{NH}_3$  and  $\text{NH}_4^+$  to form stable ammonium salts (Pain *et al.*, 1987). Safley *et al.* (1983) reported that superphosphate and phosphoric acid are effective in conserving the N in cattle manure, but are not cost effective.

The addition of soluble Ca or Mg salts was found to reduce the  $\text{NH}_3$  volatilization from urea fertilizer after surface application (Fenn *et al.*, 1979). Similarly, Witter and Kirchmann (1989b) found that the addition of Ca and Mg salts is effective in reducing  $\text{NH}_3$  losses during the aerobic decomposition of poultry manure.

Recently, Witter (1991) showed that the addition of  $\text{CaCl}_2$  at a rate of  $36\text{ g kg}^{-1}$  poultry slurry (dry wt) decreased the total loss of  $\text{NH}_3$  by 37%. According to him the addition of  $\text{CaCl}_2$  decreased  $\text{CO}_2$  output from slurry through precipitation of  $\text{HCO}_3^-$  as  $\text{CaCO}_3$ , thereby removing a source of alkalinity from solution. However, treatment of manure with gypsum is a more common practice (Kirchmann, 1985a) which not only improves the fertilizer value but also reduces N loss.

### 2.5.2.3 *Use of acidifying materials*

As discussed in section 2.3.1.2.1, pH plays an important role in the volatilization loss of  $\text{NH}_3$ . The pH of manure affects enzyme activity, microbial growth and also the dissociation equilibrium concentration of the ammonium compounds. By regulating the pH of manure solution, enzyme activity and microbial growth can be inhibited and thereby reduce the production of volatile compounds. Considerable effort has been

directed towards the use of various acidifying materials to reduce the loss of N (Pain *et al.*, 1987).

Bangar *et al.* (1988) reported that sulphur containing iron pyrite was very effective in conserving N during composting of straw and PR, which was attributed to the production of  $\text{H}_2\text{SO}_4$  as *Thiobacillus spp.* oxidizing pyrite in the compost. Manure or slurry can be acidified with strong acids or acid salts prior to field application. Although phosphoric acid and monocalcium phosphate are effective, they are not economical (Safley *et al.*, 1983; Pain *et al.*, 1987). Sulphuric and nitric acids, however, are cheaper than phosphoric acid.

Lockyer (1984) observed only a little loss of  $\text{NH}_3$  when cattle slurry was acidified to pH 5.5 with sulphuric acid and applied to grassland soil. According to Stevens *et al.* (1989) up to 80% of the  $\text{NH}_3$  loss from pig and cow slurry can be prevented by acidifying the slurry to pH 6.0 and 5.5, respectively. Miyamoto *et al.* (1975) used  $\text{H}_2\text{SO}_4$  for the treatment of ammoniated irrigation water and achieved about 50% reduction in  $\text{NH}_3$  loss.

Although, Ames and Richmond (1917) and Alexander (1967) reported that the treatment of animal wastes with sulphur reduced the loss of N significantly, the use of elemental sulphur ( $\text{S}^0$ ) as a reinforcing material for manure treatment has not yet received much attention. Cheap sources of  $\text{S}^0$  are available from oil refinery and geo-thermal industries, which could be used for this purpose. In the present study the potential of using  $\text{S}^0$  is investigated.

Paraformaldehyde, which is a mixture of polyoxymethylene glycol containing 90 to 99% polymerized formaldehyde ( $\text{HO}[\text{CH}_2\text{O}]_n\text{H}$ ), was found to be effective in reducing the loss of  $\text{NH}_3$ . As  $\text{NH}_3$  reacts with the vapour of formaldehyde it produces hexamethylenetetramine, a non-toxic and odourless substance (Seltzer *et al.*, 1969). Using paraformaldehyde Seltzer *et al.* (1969) have shown a high retention of N in manure apart from controlling odour problems caused by free  $\text{NH}_3$  and hydrogen sulphide ( $\text{H}_2\text{S}$ ).

#### 2.5.2.4 *Adsorbents*

The clinoptilolite type zeolite, an aluminosilicate mineral has a high affinity for  $\text{NH}_4^+$  (Barbarick and Pirella, 1984), and has been used widely to remove  $\text{NH}_4^+$  from waste waters and to reduce  $\text{NH}_3$  odours from animal wastes (Koelliker *et al.*, 1980; Miner, 1984). Zeolite was also found to reduce the N loss during sewage sludge composting (Witter and Lopez Real, 1988). Gaseous  $\text{NH}_3$  reacts with the hydrous zeolite to form  $\text{NH}_4^+$  ions which are selectively held in the zeolite structure and reduces the N loss (Miner, 1984).

In poultry sheds the adsorbents can be used as  $\text{NH}_3$  scrubbers by placing them in the spent airstream, or by mixing them with the manure. Results from the studies of Witter and Kirchmann (1989a) show that placement in the airstream is considerably more effective in reducing  $\text{NH}_3$  emissions. A small, simple air scrubber packed with clinoptilolite was found to remove 15 to 45% of  $\text{NH}_3$  from the air from a poultry shed (Koelliker *et al.*, 1980).

Peat moss has been reported to have high  $\text{NH}_3$  binding capacity due to its high CEC (Kemppainen, 1987), and therefore found to be more effective as a bedding material than sawdust and barley straw, with respect to manure N conservation (Peltola, 1986; Witter and Kirchmann, 1989a).

Nitrogen loss can also be reduced by adding soil to manure or covering the manure heaps with soil (Gotaas, 1956) a practice followed by the Chinese (F.A.O., 1978). Soils with fine texture, high cation exchange capacity, low base saturation and low pH can be effective adsorbents of  $\text{NH}_4^+/\text{NH}_3\text{-N}$  (Nommik and Vahtras, 1982). According to Mortland (1958) and Parr and Papendick (1966),  $\text{NH}_3$  is mainly retained by reaction with clay minerals to form adsorbed ammonium, as described earlier for zeolite.

#### 2.5.2.5 *Use of nitrification inhibitors*

A large number of studies on nitrification inhibitors have been carried out in an attempt to reduce the loss of  $\text{NO}_3^-$  from soil through denitrification or leaching. Many

substances have been shown to inhibit nitrification processes in soil. Nitrapyrin, carbon disulphide and trithiocarbonate are promising for the reduction of N loss in field application (Pain *et al.*, 1987).

Some plant products (e.g. substances present in the Indian plants karanja and neem) are effective nitrification inhibitors (Sahrawat, 1982), and may also have a useful role in conserving N in manure. Nitrapyrin (N-serve) was found to be very effective and economical in conserving N in cattle manure (Safley *et al.*, 1983). However, dicyandiamide (DCD) was found to be a more effective inhibitor than nitrapyrin (Pain *et al.*, 1987).

#### **2.5.2.6 Use of rock powders**

A few researchers have indicated that the addition of phosphate rock (PR) during composting of organic manure could reduce the loss of N, through immobilization of N or formation of ammonium complexes with the inorganic constituents of PR (Kirchmann, 1985a; Singh, 1987). Fragstein and Vogtmann (1983) suggested the use of the dust of silicate rock, with high adsorption capacity, to remove odours like  $\text{NH}_3$ , indole and mercaptan, and also to minimise the loss of N.

It has also been claimed that the presence of phosphates conserves N by causing a decrease in the number of denitrifying bacteria and stimulating the growth of the N-fixing microflora (Matthur *et al.*, 1986). However, dissolution of PR may result in an increase in pH which may favour  $\text{NH}_3$  volatilization. Detailed investigation is lacking in this regard.

#### **2.5.3 Physical methods**

The type of manure storage system affects the supply of oxygen and therefore affects the N losses from the manure. Deep storage or bottom loaded storage restricts the oxygen supply and reduces the volatilization loss. Using different storage systems for dairy manure, Moore and Beehler (1981) observed that the shallow storage pit system lost about 56% of its total manure N, while deep storage pits experienced a loss of about

23%. A loss of <10% under deep storage system has been widely reported (Moore and Beehler, 1981; Muck *et al.*, 1984). Excellent manure N conservation is often achieved in manure storage ponds to which manure has been transported from the bottom of animal/poultry shed, whereas high losses are expected to occur in top-loaded storage facilities (Muck and Richards, 1983).

It has been observed that slow drying of animal manures at low temperature causes greater losses of N (Adriano *et al.*, 1974; Giddens and Rao, 1975). This is presumably because longer times and low temperatures favour microbial growth and enzymes activities to release  $\text{NH}_3$ . High temperatures denature enzymes, kill microorganisms and remove transport media (water) rapidly. Therefore, rapid drying of manure at high temperature reduces the loss of N considerably.

## 2.6 COMPOSTING IN RELATION TO PR DISSOLUTION

The effect of organic matter (manure, plant residue, and biological waste materials) on the availability of the P in PR has been the subject of numerous investigations. These studies show that the addition of organic matter increased the availability of both soil and fertilizer phosphate (Mishra *et al.*, 1984; Bangar *et al.*, 1985).

Most of the early investigators recommended that the PR be used in combination with either farm manure or green manure crops (Dalton *et al.*, 1952; Sperber, 1958a,b; Seatz *et al.*, 1959). This is based on the hypothesis that the release of  $\text{CO}_2$  and the production of organic acids during decomposition of the organic residues would solubilize some of the PR and thereby increase the availability of P (Seatz *et al.*, 1959). This in fact, stimulated the interest in the possibility of increasing the fertilizer value of manure and waste materials by composting with PR.

### 2.6.1 Phosphate rock

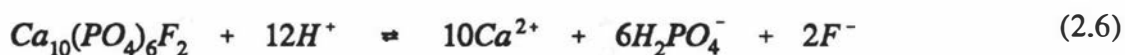
Due to the ever increasing cost of commercial P fertilizers (eg. diammonium phosphate and triple superphosphates), considerable attention has been focused on the use of cheaper alternative sources of P fertilizers. The direct application of PR to soils has

proved effective and economical around the world (Khasawneh and Doll, 1978, Bolan *et al.*, 1990).

Phosphate rock forms the main source of raw material from which P fertilizers are manufactured. PR is insoluble in water and therefore it needs to be dissolved for the P to become available for plant uptake. Commercially, the P fertilizers are manufactured by treating PR with mineral acid such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$ .

#### 2.6.1.1 *Dissolution of PR*

When a PR is directly applied to soil the dissolution of the major mineral component of PR (apatite) occurs according to the following ideal reaction (Eq 2.6) (Khasawneh and Doll, 1978), resulting in the release of  $\text{H}_2\text{PO}_4^-$  and  $\text{Ca}^{2+}$  for plant uptake (Kirk and Nye, 1986b).



For the forward dissolution reaction (Eq 2.6) to continue an adequate supply of moisture and protons ( $\text{H}^+$ ) and the removal of  $\text{Ca}^{2+}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{F}^-$  from the reaction site are required (Kirk and Nye, 1986b). At the  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$  ion concentrations are likely to be found near dissolving PR, the activity of  $\text{F}^-$  in solution is controlled by the precipitation of  $\text{CaF}_2$  (Lindsay, 1985). The dissolution rate will therefore depend on the lowering of the  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$  ion activities, through the diffusion and surface exchange reactions (Nye and Kirk, 1987), and the supply of protons (Kanabo and Gilkes, 1987).

The pH of soil (Ellis *et al.*, 1955; Chien and Hammond, 1978) and the concentration of P and Ca in the soil solution (Wilson and Ellis, 1984; Kirk and Nye, 1986a; Mackay *et al.*, 1986) have been reported to largely affect the dissolution of PR in soil.

## 2.6.2 Dissolution of PR during composting

Several biological processes occurring during composting may be beneficial for the dissolution of PR. Microbial synthesis of organic and inorganic acids, nitrification induced acidity, CO<sub>2</sub> production, chelation of Ca<sup>2+</sup> and microbial immobilization of P are relatively important.

### 2.6.2.1 Organic acid production

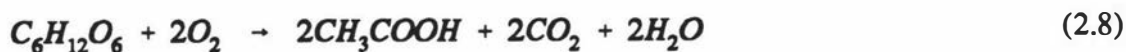
The production of organic acids is the major microbiological means by which insoluble P compounds are transformed into soluble forms during pedogenesis (Alexander, 1967; Ross, 1989). Microbial decomposition of organic matter results in the loss of CO<sub>2</sub> and NH<sub>3</sub>. A part of the original material is transformed into new microbial substances synthesised as a result of C and N assimilation.

As sugars and water soluble nitrogenous compounds offer a very readily available source of C, N and energy for the microorganisms, they are the first to be microbially decomposed. Under optimum conditions of aeration, pH, and nutrient supply, CO<sub>2</sub> is the only excretory product formed. For example, under aerobic conditions glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) is decomposed to form mainly CO<sub>2</sub> (Eq 2.7).



Under restricted supply of nutrients and oxygen, a number of partially oxidised compounds are produced in addition to CO<sub>2</sub>. A variety of aliphatic acids (eg. acetic, formic, propionic, butyric), alcohols (eg. ethyl alcohol) and simple dibasic and hydroxy acids (eg. succinic, citric, lactic) are formed as intermediate products (Acharya, 1935a,b; Schwartz and Martin, 1955; Sperber, 1958a; Cooper and Cornforth, 1978; Lynch, 1978).

Cellulose, under similar conditions, is first hydrolysed to glucose which is then converted into organic acids, CO<sub>2</sub>, CH<sub>4</sub> and H<sup>+</sup> (Eq 2.8).



The type of organic acids produced depend on the nature of organic materials that undergo decomposition and the type of microorganisms present in the system. These organic acids produced during decomposition supply  $H^+$  for the dissolution of PR depending on their pKa values.

Several studies have been conducted to determine the effects of microorganisms on the sparingly soluble inorganic phosphate (Johnston, 1952; Sperber, 1958b), and have shown that organic acids produced through microbial activity can promote the solubilization of P. Johnston (1954) showed that hydroxy-acids with a hydroxyl group in the ortho position (e.g. salicylic and 2,4-dihydroxybenzoic acids) are most powerful in solubilizing P, followed by some aromatic acids derived from acetic acids.

Moghimi *et al.* (1978a) considered that the dissolution of hydroxyapatite by rhizosphere products is due to both the supply of  $H^+$  and the complexing of  $Ca^{2+}$ . Moghimi *et al.* (1978a) identified 2-ketogluconic acid one of the strongest monobasic carboxylic acids in rhizosphere products (about 20%). This acid is produced from the oxidation of glucose by many species of *Pseudomonas*, *Aerobacter* and *Acetobacter* (Moghimi and Tate, 1978). In a later study Moghimi *et al.* (1978b) demonstrated that 2-ketogluconic acid is effective in dissolving apatite rock. They attribute this effect solely to the supply of  $H^+$  and not to its chelation properties.

Struthers and Sieling (1950) have shown that many organic substances produced as a result of microbial metabolic processes are very effective in preventing the precipitation of phosphate by aluminum and iron. These organic substances, particularly hydroxyorganic acids produced by action of microorganisms during decomposition, are effective in dissolving the precipitate of Al and Fe phosphate (Dalton *et al.*, 1952). Large amounts of humic substances are produced during decomposition of lignocellulosic substrates which may also help in the mobilization of insoluble phosphate (Singh and Amberger, 1991).

The amount of organic acids produced during composting may be insufficient to cause PR dissolution. This can partly be overcome by using cultures of phosphate solubilising microorganisms (Subba Rao, 1982). Inoculation of PR-compost with *Aspergillus awamori* was found to increase the citric acid soluble P from PR (Kapoor *et al.*, 1983).

#### 2.6.2.2 *Inorganic acid production*

Inorganic acids are also generated during composting due to several microbial metabolism. As already mentioned, part of  $\text{CO}_2$  produced during microbial decomposition dissolves in the manure solution and forms carbonic acid ( $\text{H}_2\text{CO}_3$ ) (Eq 2.9).



This  $\text{H}_2\text{CO}_3$  partly dissolves PR (Dalton *et al.*, 1952; Sperber, 1958a,b; Seatz *et al.*, 1959). But, later, the study of Johnston and Olsen (1972) showed that  $\text{CO}_2$  production had no significant effect on dissolution of PR.

The microbial oxidation of sulphur compounds in manure produces  $\text{H}_2\text{SO}_4$  during composting (Eq 2.10) which may react with PR and increase the soluble P (Alexander, 1967).



The composting of PR and soil with colloidal S was at one time recommended for the preparation of on-the-farm available phosphate (Alexander, 1967). However, due to cheap availability of readily soluble superphosphate, such practice was not commercialised. As manure contains only small amount of S, the amount of  $\text{H}_2\text{SO}_4$  generated through this process may be very small. However, manure is rich in S oxidizing bacteria (Nodar *et al.*, 1990), therefore, addition of S containing materials may be helpful to generate more  $\text{H}_2\text{SO}_4$  which can be very effective in dissolving PR.

Brown and Warner (1917) examined the effect of pure S added to composting manure with PR and observed that the addition of S resulted in greater solubilization of P from PR in the compost. Except for the work of Brown and Warner (1917), no detailed study has been reported so far on the usage of S<sup>o</sup> during composting of manure to increase PR solubilization. Several studies have, however, examined the effect of S<sup>o</sup> oxidation on PR dissolution in soils. When molten S<sup>o</sup> or dry screened S<sup>o</sup> is incorporated with PR fertilizers, the release of H<sub>2</sub>SO<sub>4</sub> during the oxidation of S<sup>o</sup> has been found to induce the dissolution of PR, which is termed as 'Biosuper effect' (Swaby, 1975; Rajan and Edge, 1980; Rajan, 1987).

The incorporation of S compounds to the compost pile has some additional advantages. The acidity generated can effectively reduce the NH<sub>3</sub> loss thereby conserving more N (see section 2.5.2.3) and also enriches the compost with S nutrient which is essential for better plant growth.

Recently, the study of Bangar *et al.* (1988) indicated the combined effect of iron pyrite and PR added to compost. Though they have not measured the PR dissolution during composting, the results showed a significant increase in the crop uptake of N and P due to improved N and P availability in compost containing PR and pyrite.

#### 2.6.2.3 *Nitrification of NH<sub>4</sub><sup>+</sup>-N*

During the process of ammonification, the microbial hydrolysis of nitrogenous compounds (proteins, amino acids and amides) results in the formation of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. This is subsequently converted into nitrous acid (Eq 2.11), and further oxidizes to nitric acid (Eq 2.12) (Waksman, 1952).



Though there is no experimental evidence to show the effect of this HNO<sub>3</sub> on PR dissolution, such an effect can also be expected.

Under aerobic conditions  $\text{NH}_4^+$  ions are oxidized to  $\text{NO}_3^-$  by different autotrophic organisms, like *Nitrosomonas*, *Nitrobacter* and *Nitrococcus spp.*, and some heterotrophic organisms, like *Achromobacter*, *Corynebacterium* and *Aspergillus spp.*, (Schmidt, 1982). First, the  $\text{NH}_4^+$  is oxidized into nitrite ( $\text{NO}_2^-$ ) (Eq 2.13), which, subsequently, oxidized to  $\text{NO}_3^-$  (Eq 2.14).



The overall reaction gives,



During the process of nitrification two  $\text{H}^+$  ions are produced per  $\text{NH}_4^+$  ion oxidized (Eq 2.15). These  $\text{H}^+$  ions can increase the dissolution of PR during composting of manure.

The results of Chien (1979) and Aphorp *et al.* (1987) demonstrated that nitrification of ammonium fertilizers increases the dissolution of PR in soil. Alexander (1967) suggested similar mechanisms for increasing the dissolution of PR in compost. In most of the studies of composting organic wastes and PR, the effect of nitrification related acidification on PR dissolution is obviously overlooked.

#### 2.6.2.4 Chelation of Ca and P

The removal of  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$  away from the reactive surface of the PR particle will increase the rate of dissolution of PR (Kirk and Nye, 1986b). During composting the removal of  $\text{Ca}^{2+}$  can be partly achieved by the release of organic substances having chelating properties (including some organic acids).

Numerous studies have shown that soil organic matter forms chelates with polyvalent metal ions. The principal chelating groups present in organic matter are amino, imino, keto, hydroxy, carboxyl and phosphate groups (Mortensen, 1963). These organic groups, formed during decomposition of organic matter, are capable of forming chelates with

$\text{Ca}^{2+}$  released during the dissolution of PR.

Humic, fulvic and uronic acid fractions of organic matter usually exhibit considerable chelating properties. After an extensive investigation of chelation of  $\text{Ca}^{2+}$  by organic anions of varying structure, Johnston (1956) found that quite a number of organic anions form chelates with  $\text{Ca}^{2+}$ , amongst them citric acid chelates  $\text{Ca}^{2+}$ , more strongly than other organic acids. He also reported that  $\text{Ca}^{2+}$  chelates, to a minor extent, with  $\alpha$ -hydroxy aliphatic monobasic acids and more strongly with dibasic acids. Chien (1979) reported that organic substances release P from PR mainly through chelating  $\text{Ca}^{2+}$ . Similarly, Mishra *et al.* (1984) showed that the effect of humic acid in increasing the availability of P from PR in a compost was mainly due to chelation of  $\text{Ca}^{2+}$ .

A number of low molecular weight compounds have been isolated from soils which are known to chelate metals. Some investigators (eg. Struthers and Sieling, 1950) have suggested that such compounds, particularly aliphatic acids are responsible for most of the chelating ability of soil. Duff *et al.* (1963) have shown that 2-ketogluconic acid, produced by soil bacteria, chelates  $\text{Ca}^{2+}$  from number of calcium salts and minerals. However, the work of Moghimi and Tate (1978) demonstrated that the effect of 2-ketogluconic acid on phosphate dissolution is not due to chelation, but to the supply of  $\text{H}^+$ .

#### **2.6.2.5      *Microbial immobilization***

The concentration of  $\text{H}_2\text{PO}_4^-$  in the solution can be decreased considerably through microbial immobilization during composting, thereby enhancing the dissolution of PR. During composting, in the presence of excess soluble P, some bacteria or fungi store P in excess of their minimum requirements (Singh and Amberger, 1991). As the P demand for microbes is increased during the decomposition, soluble inorganic P is immobilized into organic forms (Alexander, 1967). A lowered solution P concentration will increase PR dissolution (Kirk and Nye, 1986b). However, there is no experimental evidence to demonstrate this mechanism under a composting condition.

From the literature, the major biological processes which influence the PR dissolution during composting of manure are diagrammatically illustrated in Figure 2.2. The organic acid production and oxidation of  $\text{NH}_4^+$  may provide sources of  $\text{H}^+$  for the dissolution of PR, while chelation by organic substances and microbial immobilization of P may provide sink for the dissolution products  $\text{Ca}^{2+}$  and P and enhance the dissolution of PR.

### 2.6.3 Measurements of PR dissolution during composting

The extent of PR dissolution during composting with organic manure has not been measured directly. Mostly PR dissolution has been inferred indirectly through increases in P extractable in various extracts, such as citric acid, water, and  $\text{NaHCO}_3$  (Mishra *et al.*, 1984; Bangar *et al.*, 1985; Singh and Yadav, 1986b; Singh and Amberger, 1991), or through P uptake (Bangar *et al.*, 1989).

The extent of PR dissolution in soils has been determined directly either from increases in the amounts of soluble and adsorbed (exchangeable) P or Ca, or from decreases in the amounts of residual P or Ca remaining in soils (Hughes and Gilkes, 1984; Apthorp *et al.*, 1987; Bolan and Hedley, 1989). Increases in the amounts of NaOH extractable inorganic P (Pi) in PR treated soil over control soil has been used successfully as a measure of PR dissolution in incubated soil (Mackay *et al.*, 1986). This method provides an estimate of PR dissolution in soils containing minimum amounts of NaOH extractable P where the net rate of microbial immobilization of the dissolved P is negligible.

Organic manure contains high concentrations of NaOH and HCl extractable P, and has high rates of immobilization of the dissolved P. Therefore, both the NaOH and the HCl extractable P is unlikely to provide an accurate estimate of PR dissolution (Bolan and Hedley, 1989). Changes in extractable P during composting may also result from mineralization/immobilization and precipitation reactions in the manure. These changes interfere with the measurement of PR dissolution. Under these circumstances the use of radioactive tracers ( $^{32}\text{P}$ ) technique offers a hope for measuring the PR dissolution during different composting processes.

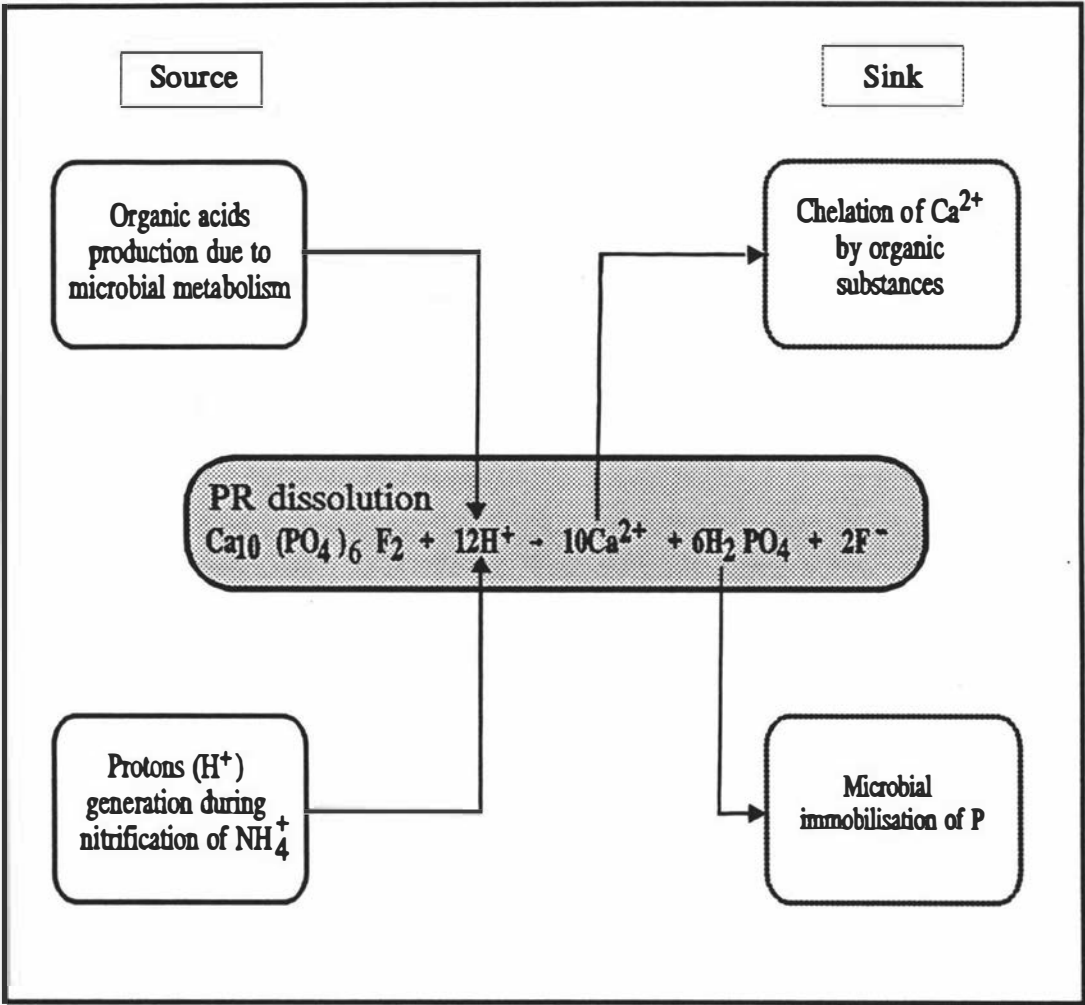


Fig 2.2 Major biological processes which influence phosphate rock (PR) dissolution during composting

#### 2.6.4 Agronomic effectiveness of PR enriched compost

The agronomic effectiveness of composts, prepared from various organic manures plus PR, was examined by several workers through glasshouse and field experiments. Small increases in yield and P uptake occurred when PR was applied in combination with farm manure without composting. Increased yield and P uptake were related mainly to improved physical condition or to the P content of the manure (Seatz *et al.*, 1959). Whereas, a significant increase in crop yield and P uptake was reported due to the application of compost containing manure and PR.

The results of Mishra *et al.* (1984), Singh and Yadav (1986a) and Bangar *et al.* (1989) have shown that the PR enriched compost (phosphocompost) is as effective as single superphosphate with regard to crop yields and P uptake. Significant increase in the yields of green gram (*Vigna radiata*, L.), wheat (Bangar *et al.*, 1989), cluster beans and red gram (Mishra and Bangar, 1986) are reported due to the application of phosphocompost.

Not only yield and uptake of P, but significant increases in the uptake of N and nitrogenase activity are also reported due to the addition of phosphocompost in red gram (Mishra *et al.*, 1984). The addition of iron pyrite during composting of paddy straw and PR is found to give higher yield than superphosphate in wheat, probably because the manure contained both N and P, and pyrite oxidation increased PR dissolution, as discussed earlier in section 2.6.2.2 (Bangar *et al.*, 1989). It was also reported that the phosphocompost increased the quality of grains by increasing the protein and Ca contents (Singh and Yadav, 1986a).

These investigators suggested that the higher agronomic effectiveness of PR enriched compost was due to the solubilization of PR, resulted by the microbial production of organic acids during composting.

With the addition of phosphated compost, Singh and Yadav (1986a) observed a significant increase in residual available P in soil due to the solubilizing effect of certain organic acids released during composting. As the dissolved P forms complexes with

fulvic and humic acids during composting, the fraction of P in the fulvic and humic compounds may be slowly mineralized and available to plants when PR enriched compost is applied to soil (Singh and Amberger, 1991).

## **2.7 SUMMARY**

During storage or composting of animal and poultry manures, large amounts of N are lost through  $\text{NH}_3$  volatilization and denitrification thereby reducing the N fertilizer value. Though the N loss through  $\text{NH}_3$  volatilization is well documented, the denitrification loss has not been quantified directly from manure during storage.

Several biological and chemical methods are found to reduce the loss of N. However, no single method is found to be effective in conserving N without affecting the other biological process during composting. Therefore, further evaluation of combinations of biological and chemical methods is required to develop appropriate and economic composting system.

Composting of manure with C rich biological wastes and S compounds appears to be the most effective and practical way to improve the N content of compost which may be suitable for organic or biological farming systems.

The overall objectives of this thesis are to (a) evaluate different techniques for reducing the potential loss of N from poultry manure through composting, and (b) assess whether phosphocomposting is a suitable technique for improving the agronomic value of PR. The specific objective of various experiments is outlined in the respective Chapter.

## CHAPTER 3

### EVALUATION OF METHODS OF MEASUREMENT OF NITROGEN IN POULTRY AND ANIMAL MANURES

#### 3.1 INTRODUCTION

Total nitrogen (N) in organic materials such as soils, plant materials and animal manure is generally measured by Kjeldahl digestion (Nelson and Sommers, 1980; Bremner and Mulvaney, 1982; Bremner and Yeomans, 1988) and expressed as total Kjeldahl N. Kjeldahl N includes mostly the organic and ammoniacal ( $\text{NH}_4^+$ )-N (Bremner and Mulvaney, 1982). Inorganic forms of N can be measured after extraction with 2M KCl solution (Bremner and Keeney, 1966; Bremner and Mulvaney, 1982) and total N can then be calculated by adding nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ )-N in KCl extract to the Kjeldahl N.

Alternatively, total N is measured by pretreating samples with various oxidizing and reducing agents to include  $\text{NO}_3^-$  and  $\text{NO}_2^-$ -N during Kjeldahl digestion. The effect of some of these oxidizing and reducing agents on the recovery of  $\text{NO}_2^-$  and  $\text{NO}_3^-$ -N in Kjeldahl digestion has been examined for soils and plant materials (Goh, 1972; Haynes, 1980; Bremner and Yeomans, 1988).

The presence of moisture affects the recovery of total N during Kjeldahl digestion, hence soil samples are airdried prior to the measurement of total N (Bremner and Mulvaney, 1982). However, drying of poultry and animal manures causes loss of N mainly through the volatilization of ammonia ( $\text{NH}_3$ ) (Azevedo and Stout, 1974; Carlile, 1984).

No comparative study of these methods for measuring total N in organic manure has been published. Therefore, in this study different methods of measuring the total N in fresh manures, and various drying methods for sample preparation were examined.

### 3.2 OBJECTIVES

The objective of this study was to evaluate the ability of different oxidizing and reducing agents to include  $\text{NO}_2^-$  and  $\text{NO}_3^-$ -N during Kjeldahl digestion of poultry and animal manures and to compare the total N measured by different methods. The effect of different drying methods on the loss of N is also examined in order to develop a suitable method for sample preservation.

### 3.3 MATERIALS AND METHODS

#### 3.3.1 Animal and poultry manures

Fresh samples of manure (sheep, horse and poultry), slurry (dairy and pig) and a compost (poultry manure plus woodchip) were collected and stored in a cool room at  $-4^\circ\text{C}$  until analysis. Some important characteristics are presented in Table 3.1.

**Table 3.1** Some important characteristics of fresh animal and poultry manures (moisture and carbon content are expressed on a freeze dried basis)

Manures	Moisture (%)	pH <sup>1</sup>	Carbon <sup>2</sup> (%)
1. Dairy	92.6	7.4	45.6
2. Sheep	46.7	8.6	41.8
3. Pig	83.2	6.1	36.7
4. Horse	48.5	7.7	42.7
5. Poultry	66.6	5.4	55.2
6. Poultry manure composted with woodchip	8.2	7.0	66.8

<sup>1</sup> pH in water (1:10 manure:water)

<sup>2</sup> Carbon by Leco combustion (Bremner and Tabatabai, 1971)

### 3.3.2 Recovery of forms of N

Recovery of different forms of N by Kjeldahl digestion and its modified methods was examined by adding solutions of known N concentration to freeze dried poultry manure. Solutions containing organic N,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$  or  $\text{NO}_2^-\text{-N}$  were prepared from phenylalanine,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{KNO}_3$  and  $\text{NaNO}_2$ , respectively.

### 3.3.3 Measurement of N

Total Kjeldahl and inorganic forms ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ) of N were measured in poultry and animal manures. To measure Kjeldahl N a standard micro-Kjeldahl digestion technique was followed (Bremner and Mulvaney, 1982). Manure samples containing between 0.25 and 7.5mg of N were taken in a 250cm<sup>3</sup> pyrex tubes. Four cm<sup>3</sup> solution of Kjeldahl digestion mixture (4cm<sup>3</sup> of concentrated  $\text{H}_2\text{SO}_4$  and 1.1g of  $\text{K}_2\text{SO}_4 + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Se}$  (10:0.1:0.1)) was added and the tube heated at 350°C for 4h in an aluminium block heating unit. At the end of the digestion period, the tubes were cooled and the volume made up to 50cm<sup>3</sup> with distilled water and mixed thoroughly using a vortex mixer.

For the measurement of total N, the following pretreatments to recover  $\text{NO}_2^-\text{-N}$  and  $\text{NO}_3^-\text{-N}$  were carried out prior to Kjeldahl digestion.

1. Salicylic acid-thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) (Bremner and Mulvaney, 1982): the sample was treated with 4cm<sup>3</sup> of salicylic acid- $\text{H}_2\text{SO}_4$  mixture (2.5g salicylic acid in 100cm<sup>3</sup> concentrated  $\text{H}_2\text{SO}_4$ ), and the nitroso-compounds formed by reaction of salicylic acid with  $\text{NO}_3^-$  in acid medium were reduced to amino compounds by heating the digest mixture with 0.5g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .
2. Aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (Dalal *et al.*, 1984): the sample was treated with 2 cm<sup>3</sup> of 25% aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  for 30min at room temperature.
3. Devarda's alloy and  $\text{H}_2\text{SO}_4$  (Liao, 1981): the sample was heated with

0.2g of Devarda's alloy (Cu:Al:Zn=10:9:1) and 6cm<sup>3</sup> of 3M H<sub>2</sub>SO<sub>4</sub> at 125°C for 30min.

4. Zinc and acidified (H<sub>2</sub>SO<sub>4</sub>) solution of CrK(SO<sub>4</sub>)<sub>2</sub> (Pruden *et al.*, 1985): the sample was mixed with 0.3g of Zn powder and treated with 5cm<sup>3</sup> of acidified (H<sub>2</sub>SO<sub>4</sub>) solution of CrK(SO<sub>4</sub>)<sub>2</sub> (5g in 100cm<sup>3</sup> of 3M H<sub>2</sub>SO<sub>4</sub>). The mixture was allowed to stand at room temperature for 2h before Kjeldahl digestion.
5. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) + acidified (H<sub>2</sub>SO<sub>4</sub>) reduced Fe: the sample was treated with 5cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> for 30min at 80°C to oxidise NO<sub>2</sub><sup>-</sup> to NO<sub>3</sub><sup>-</sup>, and then 0.3g of reduced Fe and 0.5cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> were added prior to further heating at 80°C for 30min to reduce NO<sub>3</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup>.
6. Alkaline sodium hypochlorite (NaOCl) + acidified (H<sub>2</sub>SO<sub>4</sub>) reduced Fe: the sample was treated with 5cm<sup>3</sup> of 6% NaOCl and 1cm<sup>3</sup> of 4M NaOH and then with reduced Fe and H<sub>2</sub>SO<sub>4</sub>.
7. Potassium permanganate (KMnO<sub>4</sub>) + acidified (H<sub>2</sub>SO<sub>4</sub>) reduced Fe (Bremner and Mulvaney, 1982): the sample was treated with 1cm<sup>3</sup> of 25% KMnO<sub>4</sub> and 0.5cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> and then with reduced Fe.

The first four treatments mostly involve the reduction of NO<sub>3</sub><sup>-</sup> to amino or NH<sub>4</sub><sup>+</sup>-N. The remaining three involve oxidation of NO<sub>2</sub><sup>-</sup> to NO<sub>3</sub><sup>-</sup> followed by reduction of NO<sub>3</sub><sup>-</sup> to amino or NH<sub>4</sub><sup>+</sup>-N. Hydrogen peroxide and NaOCl pretreatments were included because these two reagents cause minimum interference during N measurement by indophenol blue method.

### 3.3.4 Analysis of N

During the Kjeldahl digestion N is recovered in ammoniacal form. This form of N was

measured using an autoanalyzer by following Berthelot's indophenol blue reaction method (Markus *et al.*, 1985).

Inorganic forms of N were measured by extracting samples with 2M KCl for 30min at a solid:solution ratio 1:10 (Bremner and Keeney, 1966). Phenyl mercuric acetate (PMA) was added ( $20\text{mg L}^{-1}$ ) to 2M KCl to preserve  $\text{NH}_4^+\text{-N}$  in the extract (Klingaman and Nelson, 1976). The concentrations of inorganic N in KCl extract were measured by following the nitroprusside method for  $\text{NH}_4^+\text{-N}$  (Weatherburn, 1967) and a diazotization coupling reaction (Griess-Ilosvay reaction) method for  $\text{NO}_2^-\text{-N}$  and  $\text{NO}_3^-\text{-N}$  (Bremner and Mulvaney, 1982). For the measurement of  $\text{NO}_2^-\text{-N}$  alone, hydrazine which reduces  $\text{NO}_3^-$  to  $\text{NO}_2^-$  was not added.

### **3.3.5 Effect of drying on N measurements**

Manure samples were dried by four different methods. These include: airdrying for 10 days at room temperature; oven drying at  $105^\circ\text{C}$  for 48h; microwave oven drying at 700 watts for 30min, and freezing overnight followed by freeze drying for 3 days. Total N was measured by pretreatment with  $\text{KMnO}_4$  plus reduced Fe prior to Kjeldahl digestion. Kjeldahl N and forms of inorganic N were measured as described above.

### **3.3.6 Loss of N during drying**

Preliminary results have shown that significant loss of N occurred during the drying of poultry, pig and dairy manures. Most of these losses have been attributed to the volatilization of  $\text{NH}_3$ . To measure the extent of  $\text{NH}_3$  volatilization these manure samples were dried in a closed system.

Approximately 50g samples of fresh manure were taken in air-tight glass preserving jars and maintained at  $30^\circ\text{C}$  in a water bath for two weeks. Ammonia and carbon dioxide ( $\text{CO}_2$ ) released were absorbed in flasks containing 2.5M  $\text{H}_2\text{SO}_4$  and 5M NaOH, respectively. Oxygen was supplied regularly to the jars.

The amount of  $\text{NH}_3$  and other volatile amino compounds absorbed by  $\text{H}_2\text{SO}_4$  was

measured by the nitroprusside method (Weatherburn, 1967). The amount of  $\text{CO}_2$  absorbed by NaOH was measured by titrating NaOH with standard 0.5M HCl after adding excess  $\text{BaCl}_2$ .

### 3.4 RESULTS AND DISCUSSION

#### 3.4.1 Recovery of forms of N

The recoveries of different forms of N by the standard Kjeldahl and its modified methods are presented in Table 3.2. Complete recovery of organic and  $\text{NH}_4^+$ -N was obtained by Kjeldahl digestion, the recovery was not affected by the presence of poultry manure. However, Kjeldahl digestion alone recovered only a small fraction of the added  $\text{NO}_3^-$  and  $\text{NO}_2^-$ -N.

Pretreatment of samples with different oxidizing and reducing agents has been suggested to include  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N (Nelson and Sommers, 1980; Bremner and Mulvaney, 1982; Bremner and Yeomans, 1988). Salicylic acid- $\text{Na}_2\text{S}_2\text{O}_3$  treatment recovered only 62.9% and 48.4% of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N, respectively, the recovery decreasing slightly in the presence of poultry manure. Similarly Goh (1972) obtained only a partial recovery of  $\text{NO}_3^-$ -N by the salicylic acid method and attributed the lack of complete recovery to the incomplete nitration of salicylic acid in the presence of water (Piper, 1950).

Predrying of soil samples before total N analysis has been suggested to overcome the water interference. However, it has been consistently shown that drying of soil and manure samples causes loss of N (Bremner and Mulvaney, 1982; Kirchmann and Witter, 1989). Cheng and Bremner (1964) and Dalal *et al.* (1984) used only aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  to recover  $\text{NO}_2^-$ -N. Although this treatment recovered more  $\text{NO}_2^-$ -N than by the salicylic acid method it recovered only part of the  $\text{NO}_2^-$ -N.

Pretreatment with Devarda's alloy or  $\text{Zn-CrK}(\text{SO}_4)_2$  recovered most of the  $\text{NO}_3^-$ -N, but only a part of the  $\text{NO}_2^-$ -N. Liao (1981) and Pruden *et al.* (1985) have also observed that these two methods fail to give the complete recovery of  $\text{NO}_2^-$ -N in plant samples. This

**Table 3.2 Percent recovery of different forms of added N in the presence (+PM) and absence (-PM) of freeze d ied poult y manure measured by standard Kjeldahl and its modified methods**

Met ods	Forms of Nitrogen <sup>1</sup>							
	Organic-N		NH <sub>4</sub> <sup>+</sup> -N		NO <sub>3</sub> <sup>-</sup> -N		NO <sub>2</sub> <sup>-</sup> -N	
	+PM	-PM	+PM	-PM	+PM	-PM	+PM	-PM
Kjeldahl alone	100.2±0.9	99.2±0.7	98.2±1.0	99.9±0.5	1.8±0.5	2.6±0.7	1.3 ±0.7	1.8±0.6
Kjeldahl plus <sup>2</sup>								
Salicylic acid-Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	98.2±1.8	98.6±0.9	97.9±1.1	99.7±0.4	52.6±3.2	62.9±2.1	41.7±4.2	48.4±3.1
Aqueous Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	97.8±1.1	99.5±0.8	98.3±1.2	100.5±0.5	79.6±3.1	87.6±1.9	28.7±3.5	39.4±2.9
Devarda's alloy	99.2±1.7	98.9±1.1	99.7±1.4	99.1±0.7	85.2±4.6	96.5±2.8	47.6±3.9	55.2±2.7
Zn-CrK(SO <sub>4</sub> ) <sub>2</sub>	98.7±3.1	99.6±2.9	98.3±2.7	99.3±2.7	97.2±3.7	98.2±3.1	57.6±3.8	62.8±3.1
NaOCl-Fe	102.5±1.8	99.2±1.6	19.2±1.9	31.6±0.8	89.6±1.1	99.2±1.1	77.2±1.7	98.6±1.0
H <sub>2</sub> O <sub>2</sub> -Fe	99.1±1.9	98.7±1.1	98.5±2.1	99.1±1.2	98.5±1.7	98.7±1.7	85.7±1.9	97.0±1.2
KMnO <sub>4</sub> -Fe	99.4±2.6	99.4±2.1	98.1±2.7	99.3±1.9	98.1±2.0	98.9±1.2	98.7±2.1	99.1±1.9

<sup>1</sup> 400µg N was added in 1cm<sup>3</sup> solutions of phenylalanine, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub> or NaNO<sub>2</sub>

<sup>2</sup> Pretreatment was followed by standard Kjeldahl digestion

± Indicates standard deviation

is partly due to the absence of a strong oxidizing agent to oxidize  $\text{NO}_2^-$  to  $\text{NO}_3^-$  which is subsequently reduced to either ammoniacal or amino compounds, and partly due to the loss of N as nitrosocompounds formed by the acid decomposition of  $\text{NO}_2^-$  (Nelson and Sommers, 1980). They have suggested that for samples containing  $\text{NO}_2^-$ -N pretreatment with  $\text{KMnO}_4$  is required for the complete recovery of  $\text{NO}_2^-$ -N.

Although pretreatment with  $\text{H}_2\text{O}_2$  or  $\text{NaOCl}$  improved the recovery of  $\text{NO}_3^-$ -N it failed to give a complete recovery of  $\text{NO}_2^-$ -N especially in the presence of poultry manure. This suggests that in the presence of easily oxidisable carbon sources these two oxidizing agents may not effectively oxidise  $\text{NO}_2^-$  to  $\text{NO}_3^-$ . Pretreatment with  $\text{NaOCl}$  gave a very low recovery of  $\text{NH}_4^+$ -N which may be attributed to the volatilization loss of chloramine ( $\text{NH}_2\text{Cl}$ ) formed by the oxidation of  $\text{NH}_3$  by  $\text{NaOCl}$ .

However, pretreatment with the strong oxidizing agent  $\text{KMnO}_4$ , followed by digestion under reduced condition (reduced  $\text{Fe-H}_2\text{SO}_4$ ), achieved a complete recovery of both  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N without causing low recovery of  $\text{NH}_4^+$ -N. The permanganate method has been found suitable for the analysis of total N in soils, sediments and plant samples (Goh, 1972; Bremner and Mulvaney, 1982).

### 3.4.2 N in animal and poultry manures

Nitrogen content of the various animal and poultry manures measured by the standard Kjeldahl and its modified methods are presented in Table 3.3. Pretreatment with alkaline  $\text{NaOCl}$  gave lower value of N in poultry (fresh and composted), pig and dairy manures than the other pretreatments. These manures contain significant amounts of  $\text{NH}_4^+$ -N which are lost through the oxidation of  $\text{NH}_3$  to  $\text{NH}_2\text{Cl}$ .

Although the other pretreatments gave slightly higher N content in fresh poultry manure than by Kjeldahl method, there was no significant difference between N content in fresh manure measured by the Kjeldahl and these modified methods. This indicated that most of the N in fresh manure is present in organic and ammoniacal form and is recoverable by standard Kjeldahl digestion alone.

**Table 3.3 N contents of fresh animal and poultry manures measured by the standard Kjeldahl and its modified methods (g kg<sup>-1</sup>; expressed on freeze dried weight basis)**

Methods	Dairy	Sheep	Pig	Horse	Poultry	Poultry composted with woodchip
Kjeldahl alone	33.6±3.2	21.3±0.8	46.3±3.2	27.6±0.8	62.6±2.8	35.7±1.56
Pretreatments <sup>1</sup> Kjeldahl plus						
Salicylic acid-Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	34.6±3.7	22.0±1.1	45.8±3.3	28.0±1.1	63.2±2.8	43.6±2.0
Aqueous Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	34.7±3.6	21.8±1.2	46.2±3.7	27.7±1.0	64.2±3.1	41.6±3.1
Devarda's alloy	33.8±3.1	22.0±1.0	46.0±3.0	28.3±1.2	64.6±3.1	42.8±2.1
Zn-CrK(SO <sub>4</sub> ) <sub>2</sub>	33.2±2.9	21.0±1.1	46.1±2.8	27.6±0.9	64.3±2.8	44.8±2.6
NaOCl-Fe	30.0±2.6	22.6±1.0	41.4±2.5	28.2±1.1	58.6±2.7	36.0±2.1
H <sub>2</sub> O <sub>2</sub> -Fe	34.6±2.8	21.0±0.9	46.8±2.5	28.2±1.1	63.9±1.8	43.7±2.0
KMnO <sub>4</sub> -Fe	34.0±3.0	21.5±1.8	46.9±2.8	28.2±1.8	64.3±3.3	44.0±2.6

<sup>1</sup> Pretreatment was followed by standard Kjeldahl digestion

± Indicates standard deviation

However, in the case of the composted poultry manure, the Kjeldahl method gave lower N content than the other modified methods and there was no difference in the amount of N measured by various modified methods. This suggests that part of the N was present in  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N form which was not recovered by the Kjeldahl digestion.

Similarly, when animal manures were dried there was an increase in the amount of  $\text{NO}_3^-$ -N and Kjeldahl digestion underestimated the amount of total N (see later, section 3.4.3). Under these conditions the total N content of animal manures could be measured accurately by the modified Kjeldahl method using  $\text{KMnO}_4$  and reduced Fe.

The total N content of fresh manures followed: poultry > pig > dairy > horse > sheep. While poultry manure, pig slurry and dairy slurry samples were composed of both faeces and urine (or uric acid), horse and sheep manure samples were composed mainly of faeces. This may be one of the reasons for the higher content of total N in the former than in the latter. Nutrient content of animal manure is affected by the type and the age of the animal and the nature of the feed (Faassen and Dijk, 1987).

Composted poultry manure contains much less N than the fresh manure. This may be partly due to the loss of  $\text{NH}_3$  during composting and partly due to the dilution caused by the addition of woodchip for composting (Adriano *et al.*, 1974; Kirchmann and Witter, 1989). The amounts of organic N and the different forms of inorganic N measured in the various manures are presented in Table 3.4.

Approximately 60% to 97% and 3% to 40% of the total N was present in organic and inorganic forms, respectively. Most of the inorganic N was present as  $\text{NH}_4^+$ -N (77-89%) with only a small fraction present as  $\text{NO}_3^-$ -N (6-12%) and  $\text{NO}_2^-$ -N (0.2-2%). Since most of the N is present in organic and ammoniacal forms, only the Kjeldahl digestion method could give close estimates of the total N. However, in the case of composted poultry manure significant amounts of N were present in the  $\text{NO}_3^-$ -N form and this is why Kjeldahl digestion alone slightly underestimated the amounts of total N. Inclusion of a pretreatment with acidified  $\text{KMnO}_4$ -Fe prior to Kjeldahl digestion is therefore preferred to achieve a complete recovery and an accurate measurement of N in manure samples.

**Table 3.4 Forms of N in fresh animal and poultry manures (expressed on a freeze dried weight basis)**

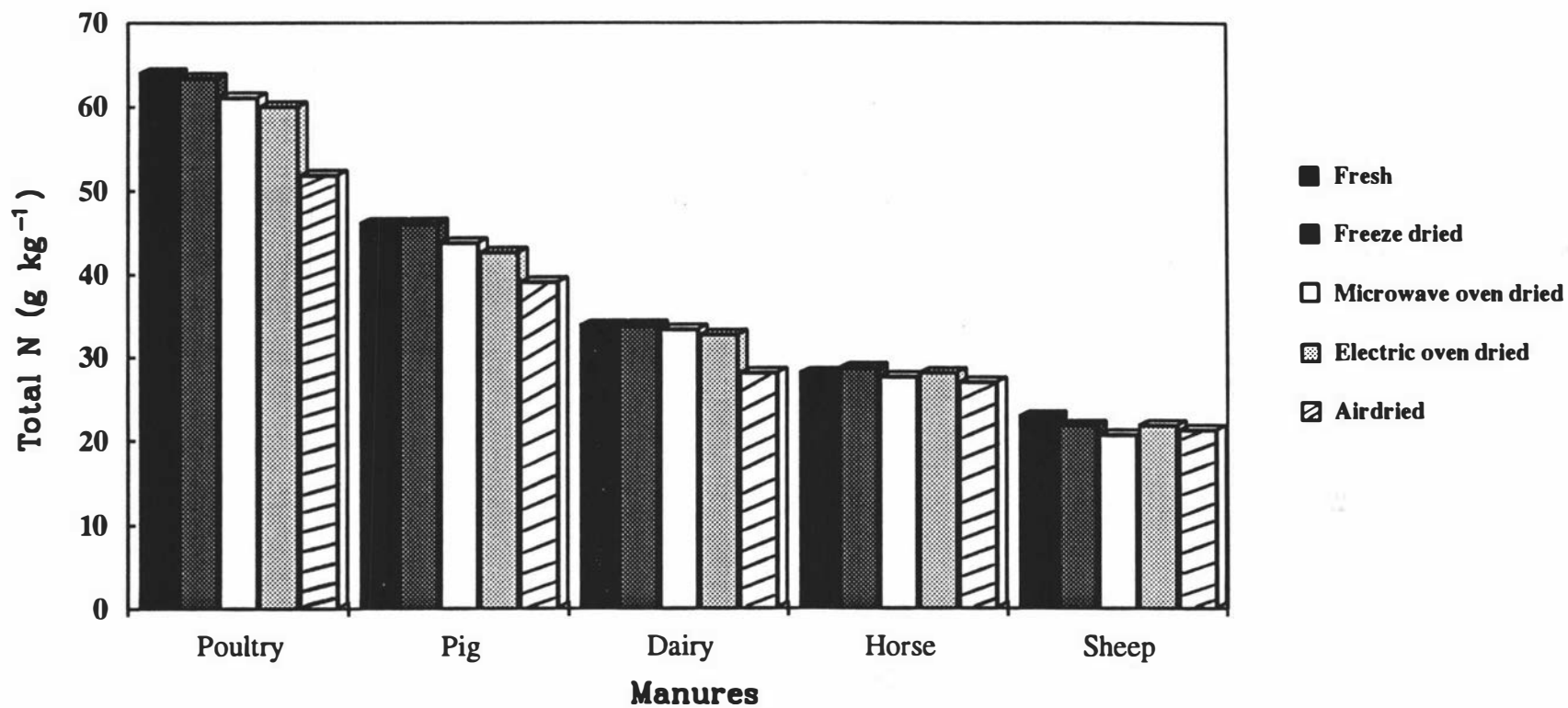
Manures	Inorganic N <sup>1</sup> (mg kg <sup>-1</sup> )			Organic N <sup>2</sup> (g kg <sup>-1</sup> )
	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NO <sub>2</sub> <sup>-</sup> -N	
1. Dairy	5006±69	34±12	19±5	28.6±3.27
2. Sheep	352±41	37±4	11±2	20.9±0.93
3. Pig	6220±82	121±12	12±3	40.1±3.21
4. Horse	489±32	68±14	33±7	27.1±0.82
5. Poultry	7840±51	69±8	27±3	54.7±2.81
6. Poultry <sup>3</sup>	9226±47	7626±76	55±11	26.5±1.59

<sup>1</sup> Inorganic N was measured by 2M KCl extraction  
<sup>2</sup> Organic N was calculated from the difference between the Kjeldahl N and 2M KCl extractable NH<sub>4</sub><sup>+</sup>-N  
<sup>3</sup> Composted with woodchip  
± Indicates standard deviation

### 3.4.3 Effect of drying on N content

The amounts of total N in fresh manure measured by the modified Kjeldahl method (KMnO<sub>4</sub>-Fe) before and after drying by different methods are presented in Figure 3.1. While airdrying, oven drying at 105°C and microwave oven drying caused a significant reduction in the total N contents of poultry manure, pig slurry and dairy slurry, freeze drying had no effect on the total N content. Airdrying caused the maximum reduction in total N followed by drying at 105°C and microwave oven drying.

The extent of reduction in total N due to drying followed: poultry manure > pig slurry > dairy slurry. Drying had no effect on the total N content of horse and sheep manure. While poultry manure, pig slurry and dairy slurry contained both faeces and urine (or uric acid), horse and sheep manure contained mainly faeces. This suggests that most of the N loss occurred from urinary compounds (urea and uric acid). It has often been observed that slow drying of manure at low temperature causes greater losses of N than fast drying at higher temperatures (Adriano *et al.*, 1974; Giddens and Rao, 1975).



**Fig 3.1** Effect of different drying methods on total N content of manures

The difference in N lost between airdried and oven dried samples suggests that uric acid- and urea- hydrolysing microorganisms or extracellular hydrolases are killed or denatured at higher temperatures, or that the rapid loss of moisture at high temperature results in greater conservation of N than in airdrying. Freezing followed by freeze drying inactivates microorganisms and results in less decomposition of uric acid (Schefferle, 1965).

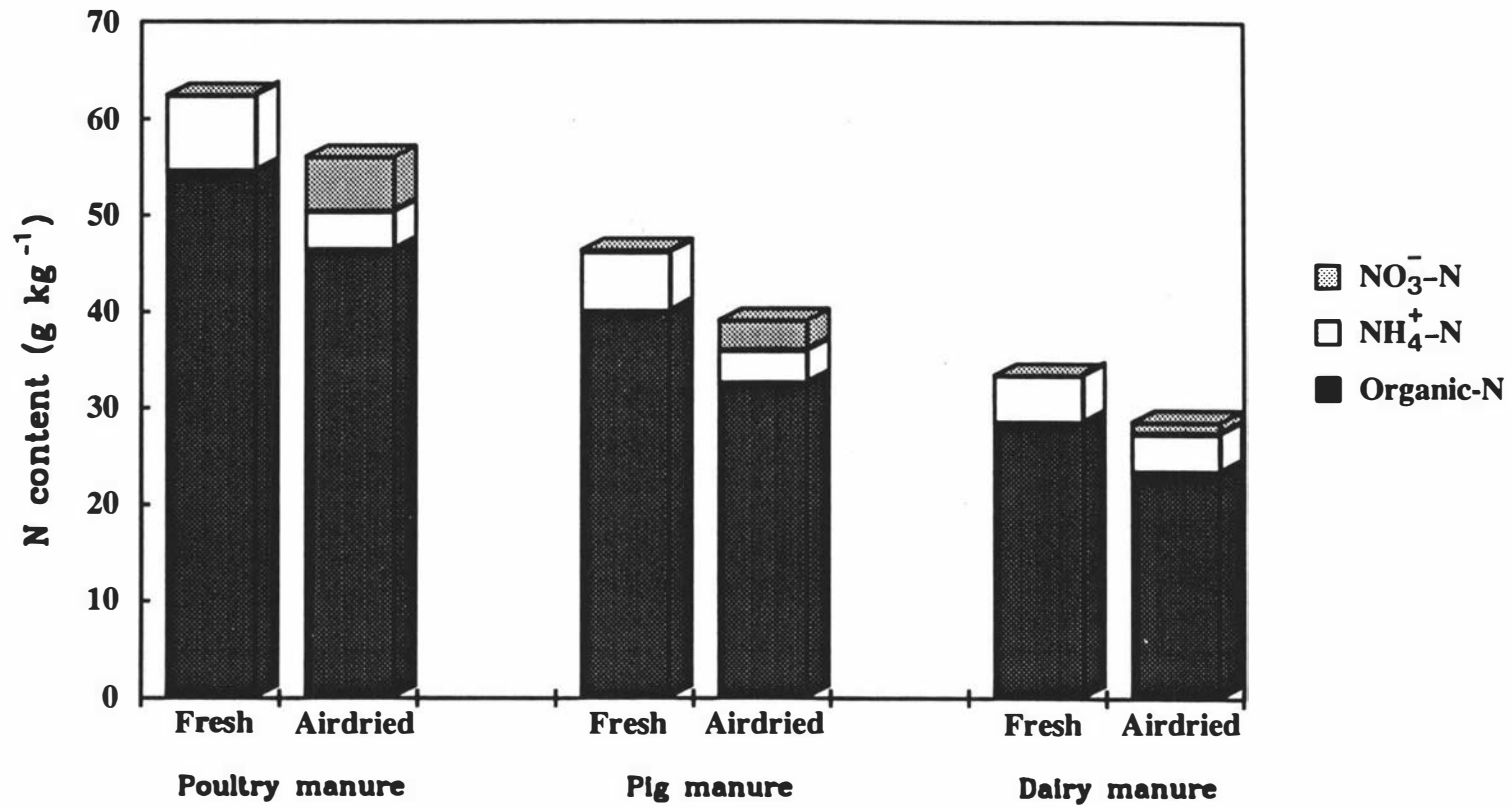
Comparison of the distribution of the different forms of N measured before and after drying (Fig 3.2) indicates that airdrying caused significant reduction in organic- and  $\text{NH}_4^+$ -N. Airdrying also caused a slight increase in the amount of  $\text{NO}_3^-$ -N, especially in the case of poultry manure. Since  $\text{NO}_3^-$ -N was not included in the Kjeldahl digestion, this method alone underestimated the amount of total N in manure samples containing significant amounts of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N. The results suggest that the major reduction in total N during drying may be due to the loss of volatile N compounds such as  $\text{NH}_3$  and amine.

### 3.4.4 Volatilization loss of $\text{NH}_3$

The amount of  $\text{NH}_3$  and  $\text{CO}_2$  released during drying and the amount of total N before and after drying are presented in Table 3.5.

**Table 3.5 Release of  $\text{NH}_3$  and  $\text{CO}_2$  during the drying of different manures (expressed on a freeze dried weight basis)**

Manures	Total N (g kg <sup>-1</sup> )		$\text{NH}_3$ released (g kg <sup>-1</sup> )	$\text{CO}_2$ released (g kg <sup>-1</sup> )	Ratio of $\text{CO}_2:\text{NH}_3$ released
	Fresh	After drying			
1. Dairy	33.8	27.5	5.8	16.7	1:0.35
2. Pig	46.6	40.7	5.5	20.2	1:0.27
3. Poultry	64.8	52.6	11.6	68.1	1:0.17



**Fig 3.2** Distribution of various forms of N in fresh and airdried samples of poultry, pig and dairy manures

As observed earlier, drying results in a decrease in the amount of total N. There was a corresponding release of  $\text{NH}_3$  which accounted for more than 95% of the loss of total N. Approximately 18%, 12% and 10% of total N was lost as  $\text{NH}_3$  from poultry, dairy and pig manure, respectively. Others have also observed loss of  $\text{NH}_3$  from fresh manure during storage and after field application (Adriano *et al.*, 1974; Hoff *et al.*, 1981; Carlile, 1984).

The higher loss of  $\text{NH}_3$  in poultry manure may be related to its higher content of uric acid. It has been shown that most of the N in fresh poultry manure is present mainly as urea or uric acid (Burnett and Dondero, 1969; Azevedo and Stout, 1974) and during drying most of the  $\text{NH}_3$  is released through chemical and/or biological decomposition of these compounds.

The ratio (w/w) of  $\text{CO}_2:\text{NH}_3$  released was less than that of uric acid (1:0.52) which indicates that either  $\text{CO}_2$  is released through the decomposition of organic compounds other than uric acid, or that some of the  $\text{NH}_3$  released from the uric acid decomposition is reimmobilised by the microorganisms and/or readsorbed by the manure.

### 3.5 CONCLUSIONS

Fresh animal and poultry manures contain mostly organic and ammoniacal N which can be measured quantitatively by routine Kjeldahl digestion. However, when the manure is dried or composted part of the N is mineralized to  $\text{NO}_3^-$ -N which is not recovered by a simple Kjeldahl digestion. Under these conditions the total N in the manure can be measured by pretreating the sample with a strong oxidizing agent to reduce the  $\text{NO}_3^-$ -N followed by routine Kjeldahl digestion.

Amongst seven pretreatments tested only oxidation with permanganate prior to Kjeldahl digestion achieved a complete recovery of  $\text{NO}_3^-$ -N. Alternatively, the  $\text{NO}_3^-$ -N may be determined separately after extraction with 2M KCl. Fresh animal and poultry manures can be stored for N analysis by freeze drying which causes minimum loss of N.

Airdrying and composting of manure causes N loss mostly through the volatilization of  $\text{NH}_3$ . Loss of  $\text{NH}_3$  during composting can be reduced by using adsorbing materials or by inhibiting the hydrolysis of urea and uric acid. Biological and chemical methods for reducing  $\text{NH}_3$  loss from poultry manure during composting were investigated and presented in Chapter 4.

## CHAPTER 4

# LOSS OF NITROGEN THROUGH AMMONIA VOLATILIZATION DURING COMPOSTING OF POULTRY MANURE WITH DIFFERENT AMENDMENTS

### 4.1 INTRODUCTION

In poultry manure a large proportion (approximately 80%) of nitrogen (N) is present as uric acid and urea (O'Dell *et al.*, 1960). The uric acid and urea are rapidly hydrolysed to ammonia ( $\text{NH}_3$ ) and carbon-dioxide ( $\text{CO}_2$ ) by urease and uricase and more than 60% of the  $\text{NH}_3$  can be subsequently lost through volatilization (Bacharach, 1957; Schefferle, 1965). It is estimated that >50% of total N in poultry manure is lost through  $\text{NH}_3$  volatilization (Giddens and Rao, 1975; Kirchmann and Witter, 1989) during storage.

Not only does loss of  $\text{NH}_3$  reduce the nutrient value of the manure, but levels of  $\text{NH}_3$  exceeding 25ppm in the atmosphere of poultry sheds may lead to respiratory and other poultry diseases and decrease bird growth (Bullis *et al.*, 1950). Free  $\text{NH}_3$  becomes an eye and respiratory irritant for the personnel working in the shed, and after venting from the shed  $\text{NH}_3$  may contribute to environmental pollution. The release of  $\text{NH}_3$  into the atmosphere enhances the wet deposition of ammonium sulphate and increases the N load of surrounding ecosystems (Breemen *et al.*, 1982; Buijsman *et al.*, 1987).

The N in poultry manure can be conserved by either inhibiting the hydrolysis of uric acid to  $\text{NH}_3$  or by reducing the volatilization of  $\text{NH}_3$ . Various chemicals, such as hydrated lime, formaldehyde and yucca saponin, have been used to reduce uric acid hydrolysis, conserving N in the manure (Carlile, 1984). However, these chemicals are also found to affect nitrification and render the manure unsuitable for composting.

The volatilization of  $\text{NH}_3$  can be reduced by various processes, including: temporary immobilization of ammonium ( $\text{NH}_4^+$ ) ions by composting manure with carbon (C) rich waste materials such as those used for bedding in the broiler chicken industry;

adsorption of  $\text{NH}_3$  and  $\text{NH}_4^+$  using amendments, such as zeolite and peat; and by increasing the acidity of the manure solution (Kirchmann and Witter, 1989). Various inorganic chemicals like calcium sulphate, superphosphate, iron pyrite and sulphuric acid have been used to increase the acidity of manure systems (Safley *et al.*, 1983; Bangar *et al.*, 1988; Stevens *et al.*, 1989; Witter and Kirchmann, 1989a). Elemental sulphur( $\text{S}^0$ ) could also be used for this purpose.

## 4.2 OBJECTIVES

The objectives of these experiments were (i) to measure the loss of N from poultry manure through  $\text{NH}_3$  volatilization during composting under aerobic and anaerobic conditions; and (ii) to examine the potential of different amendments to conserve N in poultry manure during composting.

## 4.3 MATERIALS AND METHODS

### 4.3.1 Poultry manure

Fresh poultry manure (31.5% solids) was collected from under laying hens at the Poultry Research Centre, Massey University. The characteristics of the manure are given in Table 4.1.

### 4.3.2 Amendments used

The amendments used were woodchip, paper waste, wheat straw and peat as C rich bedding materials,  $\text{S}^0$  as an acidifying material and zeolite and soil as adsorbents. The important characteristics of the materials used are given in Table 4.2. The amounts of bedding material (10g dry weight of each material) were calculated to give a C/N ratio of about 10 in the mixture. The amounts of zeolite (49g), soil (18.1g dry) and  $\text{S}^0$  (4.12g) required to absorb the  $\text{NH}_3$  released from the manure (100g fresh weight) were calculated on the basis of the cation exchange capacity of zeolite ( $160\text{cmol}(+) \text{kg}^{-1}$ ), the  $\text{NH}_3$  absorption capacity of soil ( $29\text{mg g}^{-1}$ ) and the amount of acid produced during the oxidation of  $\text{S}^0$  ( $2\text{mol H}^+ \text{mol}^{-1} \text{S}^0$ ). Prior to composting, water was added to mixtures

**Table 4.1 Characteristics of fresh poultry manure**

Characteristics	(freeze dried basis)
1. Moisture content (g kg <sup>-1</sup> )	685.0
2. pH <sub>(water)</sub> at 1:2.5	6.5
3. Nitrogen	
Total N (g kg <sup>-1</sup> )	54.3
Uric acid-N (g kg <sup>-1</sup> )	32.3
NH <sub>4</sub> <sup>+</sup> -N (g kg <sup>-1</sup> )	4.2
NO <sub>3</sub> <sup>-</sup> -N (g kg <sup>-1</sup> )	<0.1
4. Total P (g kg <sup>-1</sup> )	27.1
5. Total K (g kg <sup>-1</sup> )	14.2
6. Total Ca (g kg <sup>-1</sup> )	40.6
7. Total Mg (g kg <sup>-1</sup> )	23.5
8. Total C (g kg <sup>-1</sup> )	461.0
9. C/N ratio	8.47

**Table 4.2 Important characteristics of bedding, acidifying and adsorbent materials**

Materials	pH <sub>w</sub>	N	C	C/N
		(g kg <sup>-1</sup> )		
1. Woodchip ( <i>Pinus radiata</i> ., <2mm)	4.24	1.5	480	320
2. Paper waste (shredded newspaper., <0.5cm square)	5.57	-	340	340
3. Wheat straw ( <i>Triticum sp.</i> , <2mm)	5.32	4.6	420	91.3
4. Peat (Sphagnum moss., <2mm)	3.53	6.8	470	69.1
5. Soil (Ramiha., <2mm)	5.28	3.6	41	11.5
6. Zeolite (Heulandite., <2mm)	9.26	-	-	-

to give 65% moisture content (w/w basis). Three replicates of each treatment were used in the incubation experiments.

### 4.3.3 Incubation experiment

The aerobic incubation apparatus used for laboratory composting was a modification of that reported by Kirchmann (1985a). Glass preserving jars with an internal diameter of 110mm and a capacity of one litre were used for incubation (Fig 4.1a). The lid was fitted with a Terumo Venoject rubber insert to permit the introduction of two syringe needles; one for the inlet of air and the other for exhaust gases. The outlet was connected, in series, to a test tube containing 1M  $\text{H}_3\text{BO}_3$  followed by a conical flask containing 2.5M NaOH to trap  $\text{NH}_3$  and  $\text{CO}_2$ , respectively.

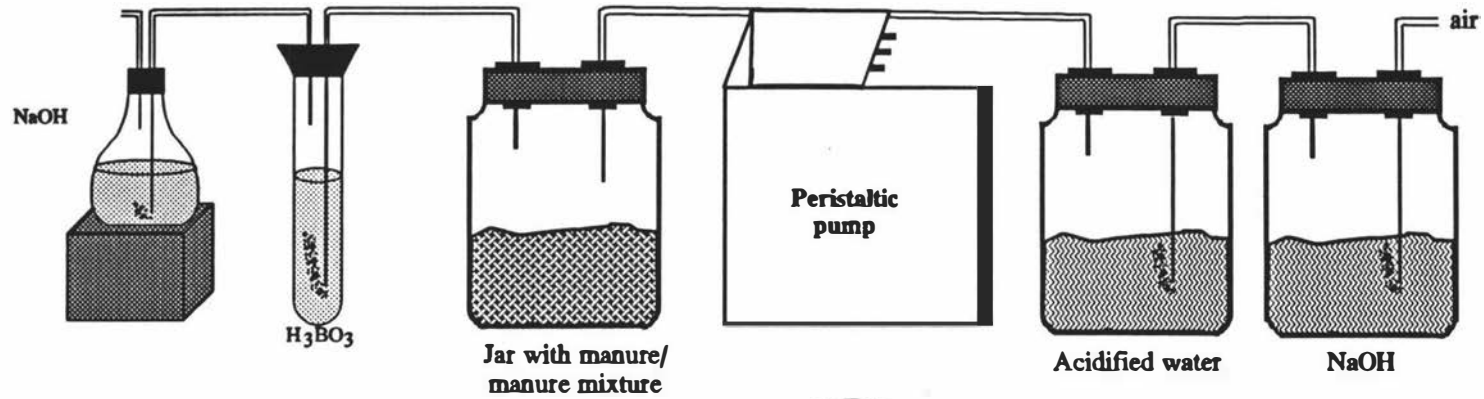
Fresh poultry manure (100g) was mixed thoroughly with the amendments and the mixture was incubated for 12 weeks in jars at room temperature (20-25°C). For aerobic systems a moisturised airstream, free of  $\text{CO}_2$  and  $\text{NH}_3$  was maintained by pumping air into the preserving jars at the rate of  $204\text{cm}^3 \text{ h}^{-1}$  using a peristaltic pump and prebubblers containing 6M NaOH and acidified water (Fig 4.1a). For anaerobic systems, the lid of the jar was modified by connecting a balloon according to a technique developed by Ruz *et al.* (1990) filled with oxygen-free nitrogen gas (Fig 4.1b). Periodically the accumulated gases in the manure jar were flushed out and trapped in  $\text{H}_3\text{BO}_3$  and NaOH. The  $\text{H}_3\text{BO}_3$  and NaOH were removed daily for one week, and on alternate days for a further 11 weeks, for determination of  $\text{NH}_3$  and  $\text{CO}_2$  during the course of incubation. After 4, 8 and 12 weeks, incubating mixtures were thoroughly mixed and samples taken for analysis. Samples were freeze dried and preserved for analysis as described in Chapter 3 (section 3.3.5).

### 4.3.4 Chemical analysis

#### 4.3.4.1 Moisture content

The initial moisture content of poultry manure was determined by drying the samples in an oven at 65-70°C for overnight.

(A) Aerobic



(B) Anaerobic

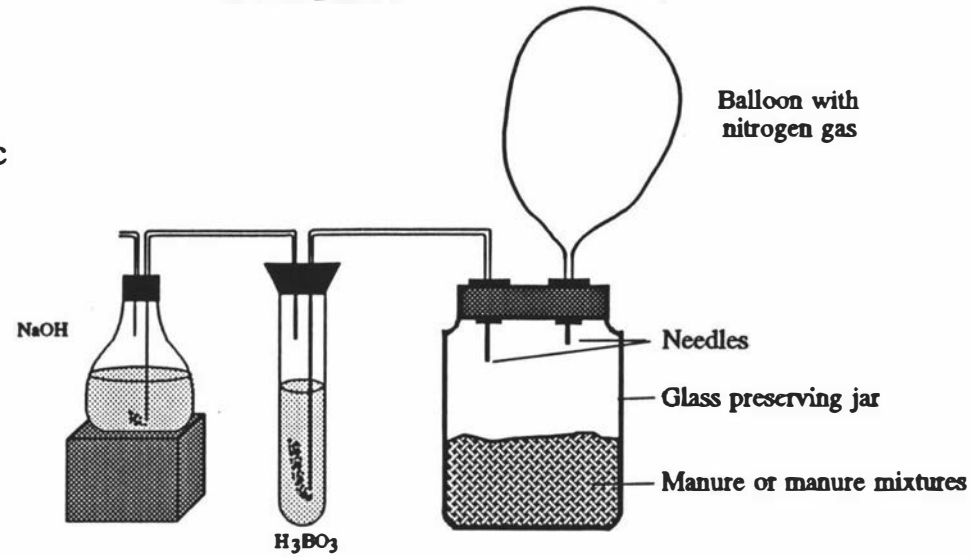


Fig 4.1 Schematic Set-up of the incubation apparatus

#### 4.3.4.2 *pH*

The pH of fresh poultry manure and various amendments was measured in H<sub>2</sub>O (1:2.5) after one hour equilibration using a combined electrode pH meter.

#### 4.3.4.3 *Measurements of NH<sub>3</sub> and CO<sub>2</sub>*

The NH<sub>3</sub> trapped in 1M H<sub>3</sub>BO<sub>3</sub> was determined by titration with 0.01M H<sub>2</sub>SO<sub>4</sub> using bromocresol green plus methyl red indicator (Bremner, 1965). The CO<sub>2</sub> trapped in 2.5M NaOH was determined by titration with 1M HCl after adding excess 3M BaCl<sub>2</sub> (Stotzky, 1965).

#### 4.3.4.4 *Total N*

Samples of fresh poultry manure and manure mixtures collected at different periods of incubation were freeze dried and ground to pass through 2mm sieve. A 250mg sample was digested with 4cm<sup>3</sup> of Kjeldahl digest mixture. The total Kjeldahl N (TKN) was determined by the autoanalyzer methods (Twine and Williams, 1971; Technicon, 1976). The total N content was determined as outlined in Chapter 3 (section 3.3.4).

#### 4.3.4.5 *Uric acid N*

The fresh poultry manure was extracted with 10% perchloric acid and the uric acid was determined by a colorimetric procedure using a spectrophotometer (Marquardt, 1983).

#### 4.3.4.6 *Mineral N*

The mineral N (NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N) content of poultry manure and compost samples was measured by extracting the fresh or freeze dried samples with 2M KCl at a manure:solution ratio of 1:20 and determining the concentrations of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N in the extracts by the autoanalyzer methods (Technicon, 1976; Downes, 1978). Double extractions were carried out to remove some of the strongly adsorbed NH<sub>4</sub><sup>+</sup> ions from the zeolite and soil amended composts (Witter and Kirchmann, 1989a).

#### **4.3.4.7      *Total carbon***

The total carbon content of the poultry manure was determined by the dry combustion method using the Leco furnace (Bremner and Tabatabai, 1971).

#### **4.3.4.8      *Total phosphorus***

For the analysis of total phosphorus (P), samples were digested using Kjeldahl digestion procedure and the concentration was determined using the autoanalyser (Twine and Williams, 1971; Technicon, 1976).

#### **4.3.4.9      *Total potassium, calcium and magnesium***

The total potassium (K), calcium (Ca) and magnesium (Mg) contents were measured by digesting the poultry manure with concentrated  $\text{HNO}_3$  and then evaporating the digest to dryness at  $250^\circ\text{C}$ .  $5\text{cm}^3$  of 2M HCl was added to the dried digest sample and then diluted to  $50\text{cm}^3$  with deionised water. The amounts of K, Ca and Mg in the final solution added with appropriate ionization suppressor ( $2000\text{mg L}^{-1}$ ), such as caesium (for K) and strontium (for Ca and Mg), were measured using atomic absorption spectrophotometer.

#### **4.3.5      Statistical analysis**

Differences between treatment means were tested for significance using analysis of variance test (SAS, 1985).

### **4.4      RESULTS AND DISCUSSION**

#### **4.4.1      Characteristics of poultry manure**

Freshly dropped poultry manure used in this experiment contained no feed or litter materials. The manure had a high moisture content (68.5%) and a near neutral pH (6.5). The manure sample was high in total C ( $461\text{g kg}^{-1}$ ) and N ( $54\text{g kg}^{-1}$ ). Contents of Ca

and Mg were higher than P and K (Table 4.1).

Approximately 60% of total N was in the form of uric acid and <10% was in  $\text{NH}_4^+\text{-N}$ . There were only traces of  $\text{NO}_3^-\text{-N}$  in the fresh manure. The nutrient contents were comparable to values previously reported (Sims, 1986; Bitzer and Sims, 1988; Kirchmann and Witter, 1989). The C/N ratio of the manure was approximately 8.5, suggesting that a rapid mineralization of N could be expected (Sims, 1986).

#### 4.4.2 Volatilization loss of $\text{NH}_3$

##### 4.4.2.1 *Aerobic vs anaerobic*

Cumulative volatilization losses of  $\text{NH}_3$  during aerobic and anaerobic composting of poultry manure with different amendments are presented in Table 4.3. The  $\text{NH}_3$  volatilization from the decomposing manure increased linearly (Fig 4.2). There were 8-17 fold differences in  $\text{NH}_3$  loss between aerobic and anaerobic conditions. The loss of  $\text{NH}_3$  was greater from untreated manure than from treated manure. The highest amount of  $\text{NH}_3$  volatilization ( $3.47\text{mg g}^{-1}$  manure) was recorded in poultry manure alone, and amounted to 17% of the initial manure N (Table 4.3).

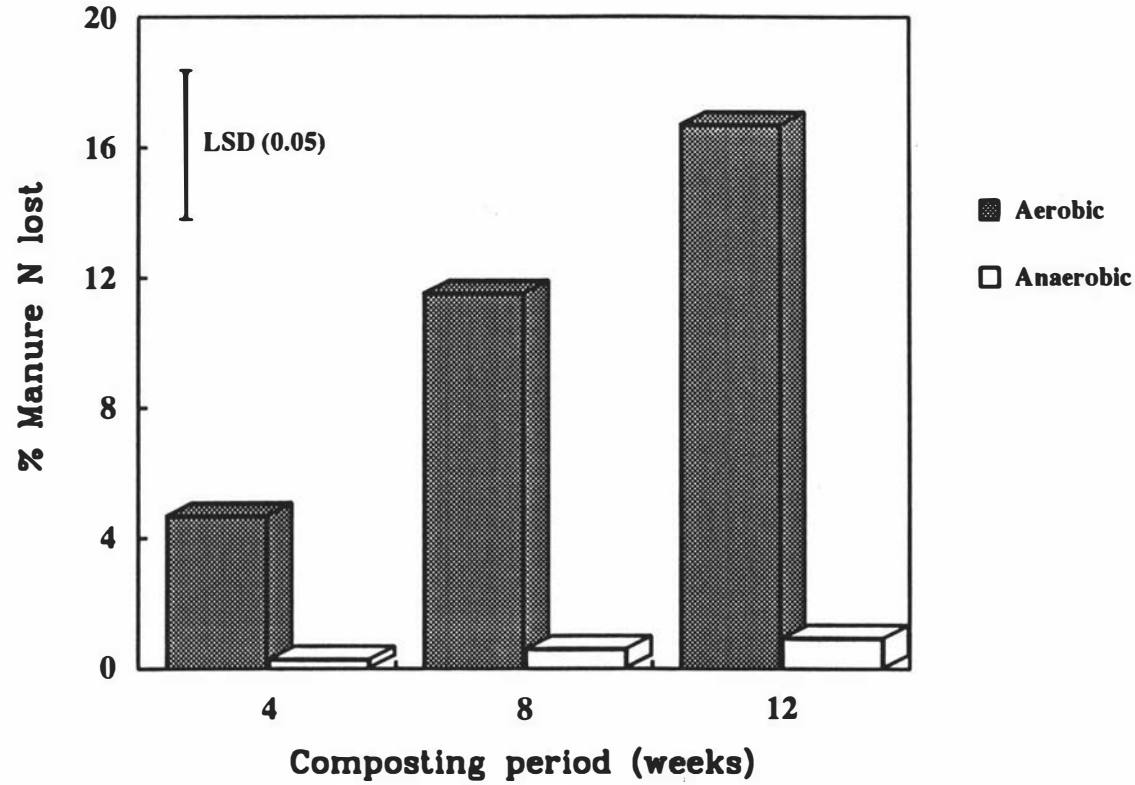
Losses were insignificant under anaerobic conditions amounting to <1% of the manure N (Table 4.3; Fig 4.2). The work of Bacharach (1957) indicated that a variety of aerobic and anaerobic bacteria associated with manure are capable of decomposing the uric acid in freshly excreted poultry manure to  $\text{NH}_3$  and  $\text{CO}_2$ . Reduced losses of N under anaerobic composting were probably due to oxygen deficiency excluding efficient fungi and actinomycetes. Anaerobic decomposition by specialised bacteria was slower and less efficient. In anaerobic conditions some of the  $\text{NH}_3$  formed might have been neutralized by the higher levels of organic acids produced thereby reducing the loss of  $\text{NH}_3$ .

When cumulative  $\text{NH}_3$  volatilization data were plotted against time, a linear model,  $R^2$  ranged from 94.4-98.9 (Eq 4.1), described the data better than did a second order exponential model,  $R^2$  ranged from 90.9-98.5 (Eq 4.2).

**Table 4.3 Cumulative amounts and the rate of loss of NH<sub>3</sub> during 12 weeks aerobic and anaerobic composting of poultry manure with different amendments**

Treatments	Aerobic		Anaerobic	
	Cumulative loss (% total N)	Rate <sup>1</sup> (mg N jar <sup>-1</sup> d <sup>-1</sup> )	Cumulative loss (% total N)	Rate <sup>1</sup> (mg N jar <sup>-1</sup> d <sup>-1</sup> )
1. Manure (m) alone	16.82	4.52	0.99	0.23
<b>(a). Bedding materials</b>				
2. m + woodchip (wc)	13.35	3.51	0.82	0.19
3. m + paper waste (pw)	14.54	3.83	0.76	0.18
4. m + straw	11.19	3.00	0.75	0.17
5. m + peat	12.48	3.27	0.69	0.16
<b>(b). Acidifying material</b>				
6. m + elemental sulphur (S°)	9.63	2.54	0.71	0.16
7. m + wc + S°	7.35	1.95	0.71	0.16
8. m + pw + S°	5.06	1.26	0.66	0.15
<b>(c). Adsorbents</b>				
9. m + zeolite	6.71	1.67	0.73	0.17
10. m + wc + zeolite	6.60	1.63	0.70	0.16
11. m + pw + zeolite	7.57	1.88	0.70	0.16
12. m + wc + soil	10.17	2.62	0.70	0.16
13. m + pw + soil	9.20	2.31	0.69	0.16
LSD (0.05)	1.25		0.08	

<sup>1</sup> Rate of loss was obtained by fitting the data to Eq 4.1



**Fig 4.2** Loss of N through  $\text{NH}_3$  volatilization during aerobic and anaerobic composting of poultry manure

$$Y = a + bt \quad (4.1)$$

$$Y = a * (1 - \exp^{-kt}) \quad (4.2)$$

where,  $Y = \text{NH}_3$  volatilized ( $\text{mg N jar}^{-1}$ );  $t = \text{time (days)}$ ;  $a, b \text{ \& } k = \text{constants}$ . The linear model parameter 'a' was set to zero and the values of parameter 'b' are given in Table 4.3. The rate of  $\text{NH}_3$  released varied considerably from 0.15 to  $4.52 \text{mg N jar}^{-1} \text{ day}^{-1}$ . The highest value was obtained for the poultry manure alone treatment, while the lowest occurred with  $\text{S}^0$  plus paper waste compost.

#### 4.4.2.2 *Effect of bedding materials*

The effect of different C rich and N poor bedding materials on  $\text{NH}_3$  loss was more prominent under aerobic than anaerobic composting. Amongst the bedding materials examined, wheat straw was found to be superior in reducing  $\text{NH}_3$  loss by 33.5% (Fig 4.3) when compared to manure alone, followed by sphagnum peat (25.8%), woodchip (20.6%) and paper waste (13.6%).

The reduction in N loss was mainly due to the immobilization of  $\text{NH}_4^+$  ions by the carbonaceous materials. Notably, bedding materials with the lowest C/N ratios were the most effective in reducing the  $\text{NH}_3$  volatilization loss. The magnitude of gaseous losses from manure during composting is determined by the availability of energy for microbial proliferation. In this respect the reduced loss of  $\text{NH}_3$  in the presence of wheat straw has been attributed to a high content of easily decomposable cellulose, as evident from the data on  $\text{CO}_2$  release (Table 4.4), which forms a readily available energy source for microorganisms to multiply and immobilize manure N.

The partially decomposed nature of the sphagnum peat may be one of the reasons for its efficiency in reducing the loss of  $\text{NH}_3$ . Kemppainen (1987), and Witter and

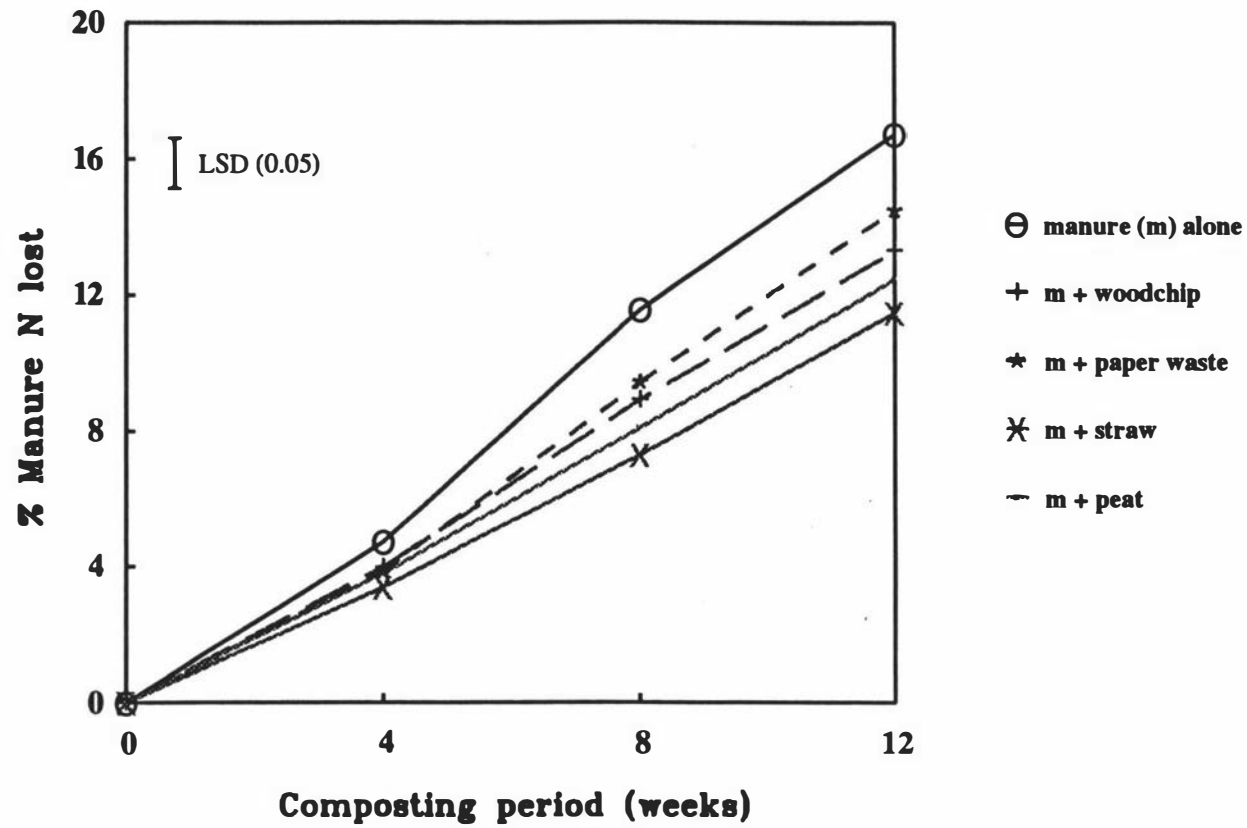


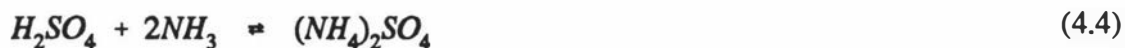
Fig 4.3 Effect of different bedding materials on  $\text{NH}_3$  volatilization loss from poultry manure

Kirchmann (1989a) also have reported a very high affinity of peat for  $\text{NH}_3$ . The high levels of N-free lignin and the low levels of soluble carbohydrate content of woodchip and paper waste resulted in only a small reduction in  $\text{NH}_3$  loss from manure.

#### 4.4.2.3 *Effect of elemental sulphur ( $\text{S}^0$ )*

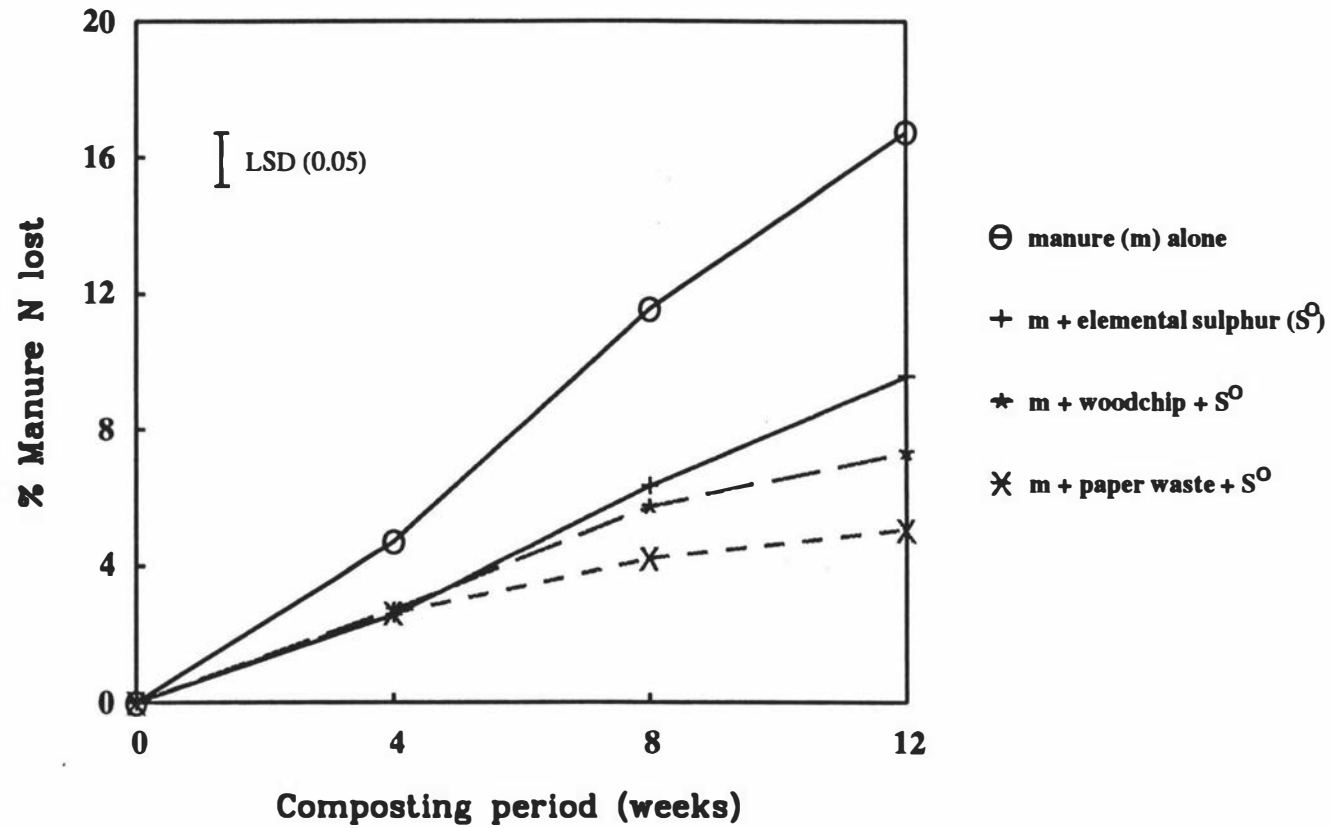
Volatilization of  $\text{NH}_3$  is mainly a pH dependent phenomenon (Freney *et al.*, 1983) and therefore, it is possible to reduce the volatilization of  $\text{NH}_3$  by increasing the acidity of manure compost. The results show that the addition of  $\text{S}^0$  (particle size  $<160\mu\text{m}$ ) alone to the manure reduced the loss by about 43% as against 56 and 70% reduction in the presence of woodchip and paper waste, respectively (Fig 4.4).

The data on  $\text{CO}_2$  release (Table 4.4) suggests that while the  $\text{S}^0$  treatment increased microbial activity under aerobic conditions, it did not reduce  $\text{NH}_3$  volatilization by reducing manure decomposition. The reduction in N loss with  $\text{S}^0$  treated compost is probably due to increased acidity of the compost resulting from  $\text{S}^0$  oxidation. Microbial oxidation of  $\text{S}^0$  produces  $\text{H}_2\text{SO}_4$  which has the potential to neutralize  $\text{NH}_3$  released from the manure (Eq 4.3 and 4.4).



Stevens *et al.* (1989) reported that the acidification of pig and cow slurries to pH 6 with  $\text{H}_2\text{SO}_4$  decreased  $\text{NH}_3$  volatilization by 82 and 95%, respectively. According to Vlek and Stumpe (1978), the bicarbonate formed during the hydrolysis of uric acid and urea induces the loss of  $\text{NH}_3$ . The  $\text{H}_2\text{SO}_4$  produced from  $\text{S}^0$  oxidation may also neutralise bicarbonate into  $\text{H}_2\text{CO}_3$  and  $\text{CO}_2$  and thereby reducing the volatilization of  $\text{NH}_3$ .

The effectiveness of  $\text{S}^0$  in reducing  $\text{NH}_3$  loss was affected by the presence of woodchip, paper waste and soil. The high reduction in  $\text{NH}_3$  loss (70%) observed with  $\text{S}^0$  plus paper waste compost could be due to higher oxidation of  $\text{S}^0$  favoured by the faster



**Fig 4.4** Effect of elemental sulphur ( $S^0$ ) on  $NH_3$  volatilization loss from poultry manure

decomposition of paper waste giving a significantly lower pH than other S° treatments at 8 and 12 weeks.

#### 4.4.2.4 *Effect of adsorbents*

The addition of zeolite significantly reduced the  $\text{NH}_3$  loss. About 60% reduction in  $\text{NH}_3$  loss was recorded in manure treated with zeolite alone as against about 61 and 55% in the presence of woodchip and paper waste, respectively (Fig 4.5). The pH remained high in the manure treated with zeolite, the reduction in  $\text{NH}_3$  volatilization being attributed to zeolite's high exchange capacity and strong selectivity of these exchange sites for  $\text{NH}_4^+$  ions. Gaseous  $\text{NH}_3$  reacts with hydrous zeolite to form  $\text{NH}_4^+$  ions which are selectively adsorbed and held in the zeolite structure (Miner, 1984). Several researchers have reported that the zeolite minerals such as clinoptilolite and heulandite have high cation exchange sites ( $165\text{cmol (+) kg}^{-1}$ ) for  $\text{NH}_4^+$  retention (Miner, 1984; Witter and Kirchmann, 1989a).

Addition of soil to manure reduced the  $\text{NH}_3$  loss by 40 to 45% in the presence of woodchip and paper waste, respectively (Fig 4.6). The soil had a low pH (5.28), high clay contents and CEC which favoured the sorption of  $\text{NH}_4^+$  (Mortland, 1958).

#### 4.4.3 *Release of $\text{CO}_2$*

Table 4.4 shows the cumulative release of C as  $\text{CO}_2$  from poultry manure mixed with different amendments. The loss of C as  $\text{CO}_2$  varied from 17 to 29% of initial total C in the mixture under aerobic condition; only 2.4 to 4.5% loss occurred in anaerobic conditions. All treatments caused greater  $\text{CO}_2$  production than manure alone.

High rates of  $\text{CO}_2$  release occurred in the presence of readily decomposable C compounds derived from paper waste, straw and peat materials. The  $\text{CO}_2$  release rate for woodchip treated manure was low, probably due to the high levels of lignin which is resistant to biological decomposition (Melillo *et al.*, 1982).

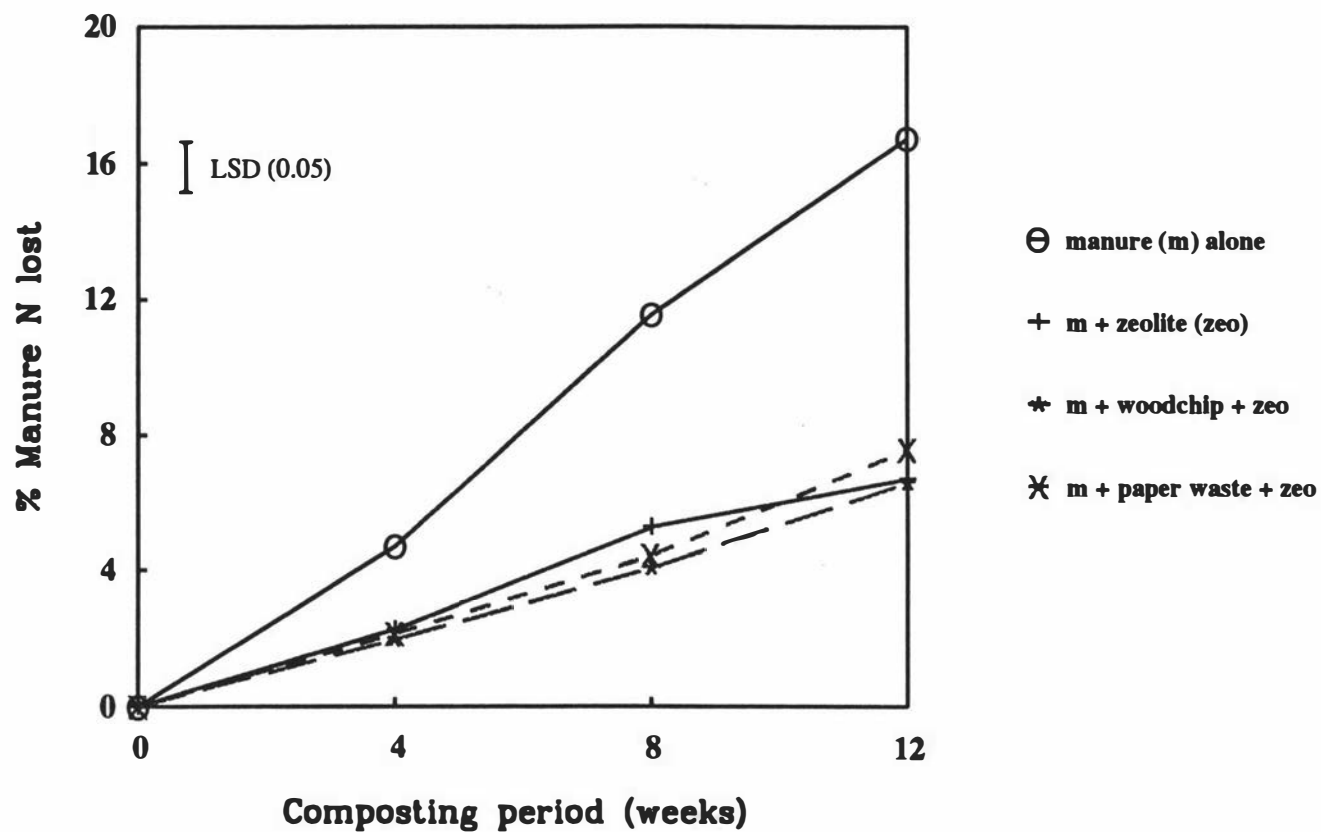
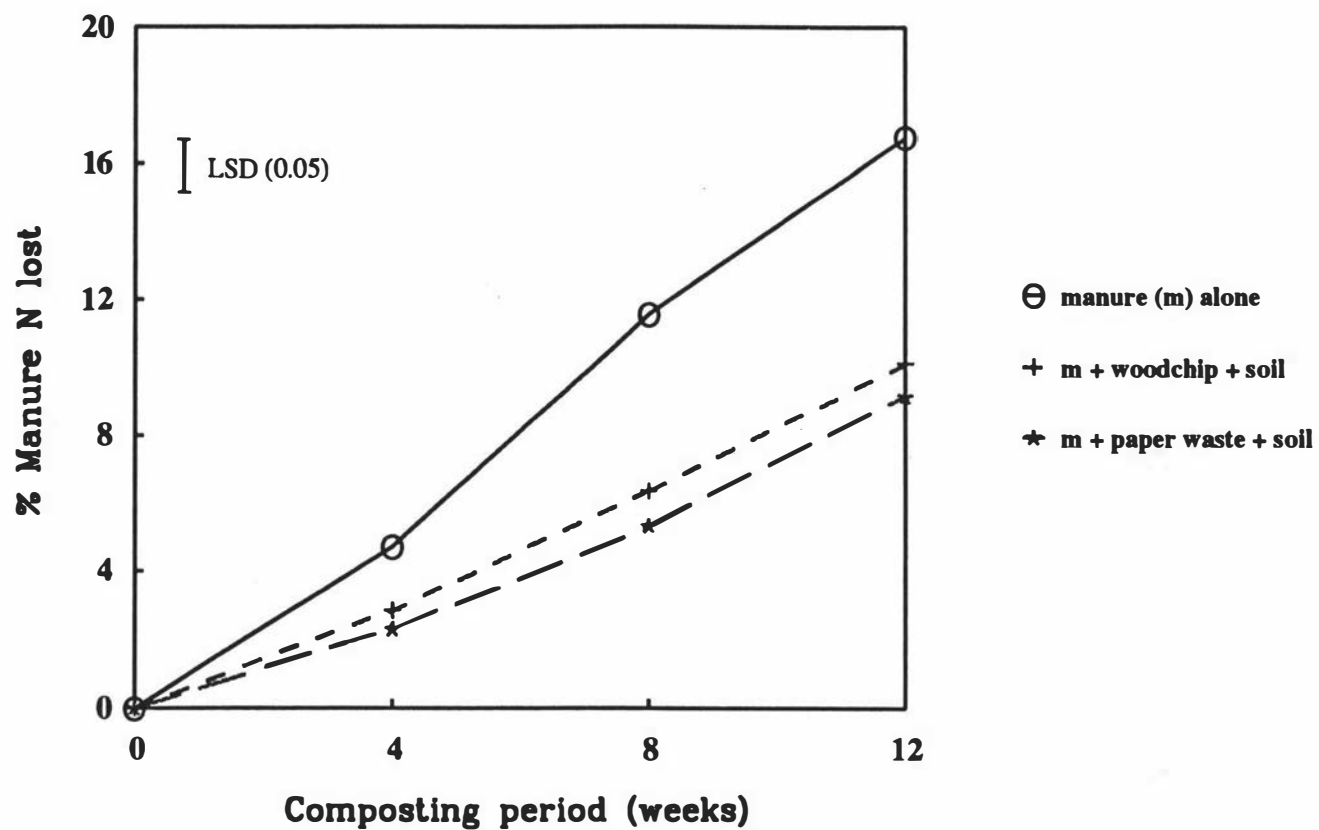


Fig 4.5 Effect of zeolite on  $\text{NH}_3$  volatilization loss from poultry manure



**Fig 4.6** Effect of soil addition on  $\text{NH}_3$  volatilization loss from poultry manure

**Table 4.4. Cumulative amounts of CO<sub>2</sub> released (g jar<sup>-1</sup>) at different periods during 12 weeks aerobic and anaerobic composting of poultry manure with different amendments**

Treatments	Aerobic			Anaerobic		
	4*	8*	12*	4*	8*	12*
1. Manure (m) alone	4.8	8.6	9.6	0.7	1.2	1.5
<b>(a). Bedding materials</b>						
2. m + woodchip (wc)	5.8	10.5	12.3	0.8	1.3	1.7
3. m + paper waste (pw)	6.3	13.9	15.9	1.3	1.7	1.9
4. m + straw	6.5	14.2	16.4	1.5	2.1	2.4
5. m + peat	6.3	14.8	17.1	1.0	1.4	1.7
<b>(b). Acidifying material</b>						
6. m + elemental sulphur (S°)	5.5	12.9	15.1	0.9	1.4	1.7
7. m + wc + S°	6.8	12.7	15.4	1.0	1.6	1.8
8. m + pw + S°	7.1	15.3	19.1	1.7	2.6	3.0
<b>(c). Adsorbents</b>						
9. m + zeolite	6.2	13.5	15.4	1.1	1.5	1.8
10. m + wc + zeolite	7.5	15.7	17.8	0.9	1.4	1.7
11. m + pw + zeolite	7.2	16.5	19.3	1.8	2.4	2.6
12. m + wc + soil	6.1	11.7	14.4	1.2	1.8	2.2
13. m + pw + soil	6.2	12.9	15.5	1.4	1.8	2.1
LSD (0.05)	1.32	1.94	2.01	0.54	0.73	0.77

\* weeks

#### 4.4.4 Changes in pH

The pH of the fresh poultry manure was near neutral (6.5) and the initial pH of different mixtures varied from 6.14 to 6.63, which after decomposition rapidly increased due to  $\text{NH}_3$  release (Table 4.5). The pH progressively increased up to 4 weeks, then stabilizing around pH 9 in aerobic and pH 8-8.4 in anaerobic conditions. These results are similar to those reported by Schefferle (1965), who observed a high pH in heaped poultry litter due to  $\text{NH}_3$  generation (refer Fig 2.1).

In anaerobic conditions the pH remained lower than in aerobic conditions at all stages of decomposition, suggesting that either less  $\text{NH}_3$  was released from the hydrolysis of uric acid and/or that more organic acids were produced under anaerobic conditions (Acharya, 1935a).

In aerobic conditions bedding materials had little influence on compost pH except for paper waste which increased pH at 4-12 weeks in manure alone from 8.1-8.4 to 8.7-9.0. The addition of  $\text{S}^0$  reduced manure pH considerably. As  $\text{S}^0$  undergoes oxidation it produces  $\text{H}_2\text{SO}_4$ , increasing the  $\text{H}^+$  ion concentration in the compost mixture and decreasing the pH. The type of bedding materials affected the extent of pH change caused by  $\text{S}^0$  addition under aerobic conditions. In aerobic composting, manure treated with paper waste plus  $\text{S}^0$  had lower pH than woodchip treated manure.

#### 4.4.5 Transformations of N during poultry manure decomposition

The net rate of conversion of organic N to  $\text{NH}_4^+$ -N (ammonification-nitrification) was greater under anaerobic conditions (Table 4.6). The net rate of conversion of  $\text{NH}_4^+$ -N to  $\text{NO}_3^-$ -N (nitrification-denitrification-immobilization) was greater under aerobic conditions (Table 4.7) indicating that while ammonification can proceed under aerobic and anaerobic conditions, nitrification requires oxygen. Initially the fresh poultry manure had only about 7% ( $1.26\text{mg g}^{-1}$ ) of N in the form of  $\text{NH}_4^+$ -N, whereas at the end of 12 weeks 15-77% (aerobic) and 33-95% (anaerobic) of the N appeared to be in the form of  $\text{NH}_4^+$ -N (Table 4.6). The presence of  $\text{NO}_3^-$  in anaerobic treatment indicates that oxygen must have entered the system when sampling.

**Table 4.5 Changes in pH at different periods during 12 weeks aerobic and anaerobic composting of poultry manure with different amendments**

Treatments	Initial	Aerobic			Anaerobic		
		4*	8*	12*	4*	8*	12*
1. Manure (m) alone	6.50	9.1	8.8	8.9	8.1	8.1	8.4
<b>(a). Bedding materials</b>							
2. m + woodchip (wc)	6.51	9.1	8.8	8.9	8.2	8.1	8.4
3. m + paper waste (pw)	6.49	9.0	8.9	9.0	9.0	8.9	8.7
4. m + straw	6.47	9.0	8.9	8.9	8.3	8.1	8.3
5. m + peat	6.35	9.0	8.8	9.0	8.2	7.9	8.4
<b>(b). Acidifying material</b>							
6. m + elemental sulphur (S°)	6.14	8.8	8.6	8.5	7.5	7.2	7.4
7. m + wc + S°	6.43	8.9	8.3	8.1	7.9	7.8	8.1
8. m + pw + S°	6.55	8.5	7.7	7.7	7.9	7.9	8.1
<b>(c). Adsorbents</b>							
9. m + zeolite	6.65	9.1	8.9	9.1	8.4	8.1	8.3
10. m + wc + zeolite	6.59	9.3	8.9	9.2	8.5	8.4	8.6
11. m + pw + zeolite	6.64	9.1	9.0	9.1	8.5	8.3	8.5
12. m + wc + soil	6.40	9.1	8.8	8.9	8.2	8.1	8.3
13. m + pw + soil	6.46	8.3	8.2	8.3	8.3	8.1	8.4
LSD (0.05)		0.1	0.1	0.15	0.07	0.06	0.25

\* weeks

**Table 4.6 Cumulative amounts of  $\text{NH}_4^+\text{-N}$  ( $\text{mg jar}^{-1}$ ) formed at different periods during 12 weeks aerobic and anaerobic composting of poultry manure with different amendments**

Treatments	Aerobic			Anaerobic		
	4*	8*	12*	4*	8*	12*
1. Manure (m) alone	158	115	425	321	265	719
<b>(a). Bedding materials</b>						
2. m + woodchip (wc)	194	180	435	489	428	994
3. m + paper waste (pw)	166	161	446	382	293	758
4. m + straw	208	165	375	603	414	1078
5. m + peat	363	263	257	638	391	1149
<b>(b). Acidifying material</b>						
6. m + $\text{S}^0$	403	327	146	304	243	511
7. m + wc + elemental sulphur ( $\text{S}^0$ )	483	583	1177	390	421	921
8. m + pw + $\text{S}^0$	678	886	1347	453	375	1011
<b>(c). Adsorbents</b>						
9. m + zeolite	341	297	490	554	393	838
10. m + wc + zeolite	374	347	617	541	464	877
11. m + pw + zeolite	388	281	609	624	412	1083
12. m + wc + soil	253	241	518	528	488	1124
13. m + pw + soil	444	327	402	536	408	1006
LSD (0.05)	56.3	64.1	64.5	97.4	55.2	171.7

\* weeks

**Table 4.7** Cumulative amounts of NO<sub>3</sub><sup>-</sup>-N (mg jar<sup>-1</sup>) formed at different periods during 12 weeks aerobic and anaerobic composting of poultry manure with different amendments

Treatments	Aerobic			Anaerobic**	
	4*	8*	12*	8*	12*
1. Manure (m) alone	0.18	0.71	1.52	0.41	0.62
<b>(a). Bedding materials</b>					
2. m + woodchip (wc)	0.23	0.84	1.99	0.46	0.78
3. m + paper waste (pw)	0.31	1.12	2.89	0.52	1.29
4. m + straw	0.34	0.93	2.03	0.53	0.88
5. m + peat	0.25	0.96	2.23	0.54	0.99
<b>(b). Acidifying material</b>					
6. m + elemental sulphur (S°)	0.20	0.69	1.52	0.34	0.45
7. m + wc + S°	0.41	1.19	3.21	0.61	0.83
8. m + pw + S°	0.55	1.24	1.91	0.78	0.87
<b>(c). Adsorbents</b>					
9. m + zeolite	0.41	1.05	1.34	0.51	0.80
10. m + wc + zeolite	0.56	1.24	2.37	0.73	0.94
11. m + pw + zeolite	0.34	1.29	1.61	0.64	1.01
12. m + wc + soil	0.48	1.14	2.88	0.65	0.84
13. m + pw + soil	0.48	1.39	1.69	0.79	0.98
LSD (0.05)	0.034	0.49	0.66	0.14	0.29

\* weeks

\*\* Negligible amounts of NO<sub>3</sub><sup>-</sup> were formed during the first 4 weeks of anaerobic incubation

In all treatments, at any stage, the  $\text{NH}_4^+\text{-N}$  content was higher (approximately 1000 times) than  $\text{NO}_3^-\text{-N}$  (Tables 4.6 and 4.7). According to Nodar *et al.*, (1990) nitrification may be slow, because the fresh poultry manure contains a high density of ammonifiers, which are responsible for the ammonification taking place continuously. However, it is known that the subsequent occurrence of nitrification from relatively immobile  $\text{NH}_4^+$  ions to mobile  $\text{NO}_3^-$  ions is affected by the concentration of  $\text{NH}_4^+$  ions present and the change in the pH of the compost solution to which nitrifiers are sensitive (Brameley and White, 1990). Continuous release of  $\text{NH}_3$  from the manure can also be toxic to nitrite oxidizing bacteria (Giddens and Rao, 1975). Calculation of the N mass balance for each jar (see later, section 4.4.6) suggests that some of the  $\text{NO}_3^-\text{-N}$  would have been lost through denitrification.

The C rich bedding materials had a significant effect on both ammonification and nitrification in aerobic systems (Tables 4.6 and 4.7). These easily decomposable N poor carbonaceous materials are capable of immobilizing inorganic  $\text{NH}_4^+$  ions into organic form reducing the potential for volatilization loss. The content of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  were higher in the presence of bedding materials than in their absence.

Apparent immobilization of N due to different bedding materials under aerobic systems was calculated as the difference in the N mineralization between manure alone and manure plus bedding materials (Table 4.8). Addition of peat and wheat straw immobilized more N than woodchip and paper waste. This is in consistent with the results of Kempainen (1987), and Kirchmann and Witter (1989).

The addition of  $\text{S}^0$  to poultry manure alone resulted in decreased ammonification (Table 4.6) but did not influence nitrification (Table 4.7). In the presence of either woodchip or paper waste, however, the rates of ammonification and nitrification increased. The compost with  $\text{S}^0$  plus paper waste recorded the highest  $\text{NH}_4^+\text{-N}$  content ( $22.9\text{mg g}^{-1}$ ) in the compost (Table 4.6).

The low level of  $\text{NH}_3$  volatilization in  $\text{S}^0$  treated manure, with no corresponding increase in either  $\text{NH}_4^+\text{-N}$  or  $\text{NO}_3^-\text{-N}$ , suggests that  $\text{S}^0$  addition inhibited the decomposition of uric acid or stimulated N immobilization. In the presence of the C sources, particularly

**Table 4.8 Apparent mineralization and immobilization of N in poultry manure during aerobic composting as affected by different bedding materials**

Treatments	NH <sub>3</sub> (vol) (mg g <sup>-1</sup> N)	NH <sub>4</sub> <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> (mg g <sup>-1</sup> N)		N <sub>min</sub> (m g <sup>-1</sup> N)	N <sub>imm</sub> (mg g <sup>-1</sup> N)
		t <sub>0</sub>	t <sub>end</sub>		
1. Manure alone (m)	285.9	74.1	874.1	1085.9	
2. m + woodchip	226.9	74.1	674.7	827.5	258.4
3. m + paper waste	247.2	74.1	711.2	884.3	201.7
4. m + straw	195.8	74.1	599.4	721.1	364.8
5. m + peat	212.2	74.1	412.9	550.9	534.9

1. NH<sub>3</sub>(vol) = volatilization loss of NH<sub>3</sub>
2. t<sub>0</sub> = initial
3. t<sub>end</sub> = at the end of experiment
4. N<sub>min</sub> = Nitrogen mineralization  
= [(NH<sub>4</sub> + NO<sub>3</sub>-N)<sub>t<sub>end</sub></sub> - (NH<sub>4</sub> + NO<sub>3</sub>-N)<sub>t<sub>0</sub></sub>] + NH<sub>3</sub>(vol)
5. N<sub>imm</sub> = Nitrogen immobilization  
= N<sub>min</sub> (manure alone) - N<sub>min</sub> (manure + bedding materials)

paper waste, greater microbial oxidation of  $S^0$  occurred, resulting in lower pHs and reduced loss of  $NH_3$ .

Addition of zeolite resulted in low levels of  $NH_4^+$ -N and  $NO_3^-$ -N and the addition of woodchip or paper waste to zeolite did change these results significantly (Tables 4.6 and 4.7). This may be due to the high exchange capacity and strong selectivity for  $NH_4^+$  ions by the zeolite, making it less available for both KCl extraction and nitrification. Further, the low rate of nitrification with zeolite treatment could be due to inaccessibility of strongly adsorbed  $NH_4^+$  ions to *Nitrosomonas* and *Nitrobacter* bacteria (Miner, 1984).

The addition of acid soil as a  $NH_3$  and  $NH_4^+$  adsorbent also had significant effect on ammonification and nitrification, significantly decreasing the  $NH_4^+$ -N, but increasing the  $NO_3^-$  content of the composts (Tables 4.6 and 4.7).

#### 4.4.6 Total N in the compost

Nitrogen mass balances were constructed from the amounts of total N initially present in composts,  $NH_3$  volatilized, N removed at each sampling time and total N remaining in composts after 12 weeks incubation (Table 4.9).

Generally, at the end of the incubation period, all treatments had higher total N under anaerobic than aerobic conditions which is consistent with the lower  $NH_3$  loss in anaerobic conditions. Under aerobic conditions  $NH_3$  volatilization accounted for most of the N loss when the manure was treated with bedding materials and  $S^0$ , or with paper waste and soil.

However, in all other treatments,  $NH_3$  volatilization loss accounted for only 3-41% of total N loss during aerobic and anaerobic composting, resulting in a large proportion of the N loss unaccounted for. For example, in the manure alone treatment the unaccounted losses of N were approximately 50 and 26% of the total initial N under aerobic and anaerobic conditions, respectively. It is suggested that the unaccounted N loss may probably be due to denitrification, a microbial process through which  $NO_3^-$  is reduced to nitrous oxide ( $N_2O$ ) and molecular nitrogen ( $N_2$ ) and lost (Firestone, 1982).

**Table 4.9 Amounts of total N (mg jar<sup>-1</sup>) remaining and NH<sub>3</sub> lost (mg jar<sup>-1</sup>) after 12 weeks composting of poultry manure with different amendments**

Treatments	Total N			NH <sub>3</sub> volatilization		Unaccounted losses	
	Initial	Final		Aerobic	anaerobic	Aerobic	Anaerobic
		Aerobic	Anaerobic				
1. Manure (m) alone	1711	845	1259	347	20	518	430
<b>(a). Bedding materials</b>							
2. m + woodchip (wc)	1726	1053	1366	276	17	397	342
3. m + paper waste (pw)	1711	783	1138	300	16	628	556
4. m + straw	1756	692	1468	238	16	826	272
5. m + peat	1778	449	1566	258	14	1071	198
<b>(b). Acidifying material</b>							
6. m + elemental sulphur (S <sup>o</sup> )	1711	995	1569	198	15	517	127
7. m + wc + S <sup>o</sup>	1834	1798	1748	152	15	-115	72
8. m + pw + S <sup>o</sup>	1819	1749	1665	105	14	-35	140
<b>(c). Adsorbents</b>							
9. m + zeolite	1711	833	1060	139	15	739	635
10. m + wc + zeolite	1726	913	1175	136	14	676	537
11. m + pw + zeolite	1711	815	1134	156	14	739	562
12. m + wc + soil	1834	1073	1424	210	15	552	396
13. m + pw + soil	1819	1968	1267	190	14	-338	538
LSD (0.05)		246	296				

## 4.5

## CONCLUSIONS

Composting biological wastes, with poultry manure can be an effective means of conserving the N in the manure. This not only improves the fertilizer value, but also reduces the potential for  $\text{NH}_3$  to contribute to environmental pollution. Reduction in N loss can be achieved using anaerobic rather than aerobic composting. When anaerobic composting is not feasible, the efficiency of aerobic composting to reduce N loss could be increased by using different easily available amendments. Amongst the bedding materials examined, cereal straw was found to be most effective in conserving  $\text{NH}_3$ .

Elemental  $\text{S}^0$  was as effective as zeolite in conserving N in poultry manure during composting by decreasing the compost pH, but there may have been additional processes occurring that prevented  $\text{NH}_3$  loss. In addition, it also enriches the compost with sulphur. Cheap sources of  $\text{S}^0$  are available from oil refinery and geo-thermal industries which could be utilized efficiently in reducing the  $\text{NH}_3$  loss during composting.

Even without carbonaceous materials, composting of poultry manure with zeolite was found to be more effective than soil in conserving the N. But, zeolite can be a costly material. The results further suggest that apart from  $\text{NH}_3$  volatilization, other processes of N loss, like denitrification, may also occur during composting of manure under aerobic and anaerobic conditions. A detailed study on the denitrification loss of N from poultry manure during composting is discussed in Chapter 5.

## CHAPTER 5

### LOSS OF NITROGEN THROUGH DENITRIFICATION DURING COMPOSTING OF POULTRY MANURE WITH DIFFERENT AMENDMENTS

#### 5.1 INTRODUCTION

Results in Chapter 4 indicate that the loss of nitrogen (N) through ammonia ( $\text{NH}_3$ ) volatilization during composting of poultry manure accounted for approximately 50% of total N loss. The remaining N loss is believed to be due to biological denitrification. Biological denitrification is the microbial reduction of nitrate ( $\text{NO}_3^-$ ) or nitrite ( $\text{NO}_2^-$ ) to either nitrous oxide ( $\text{N}_2\text{O}$ ) and (or) molecular nitrogen ( $\text{N}_2$ ). Evolution of nitric oxide (NO) is also possible (Burford and Bremner, 1975). Evolution of  $\text{N}_2\text{O}$  from natural sources like animal manure and compost, is of concern because  $\text{N}_2\text{O}$  is implicated in ozone destruction (Breitenbeck and Bremner, 1986).

Though the literature on denitrification loss from manure or compost is scarce, many researchers have recognised that biological denitrification together with  $\text{NH}_3$  volatilization could be a major pathway of N loss from manures (Giddens and Rao, 1975; Hadas *et al.*, 1983; Gale and Gilmour, 1986; Bitzer and Sims, 1988). As few direct measurements have been made on denitrification loss from manure or compost, the magnitude of loss has been deduced indirectly.

Using the mass balance approach, Kirchmann (1989) measured a 90% loss of  $^{15}\text{N}$  through denitrification during the storage of cattle manure. The presence of large numbers of denitrifying organisms, readily available carbon (C) and the existence of anaerobic microsites within the manure, are likely to favour denitrification during composting under aerobic conditions. However, there has been no direct measurement of denitrification loss from fresh manure or compost.

## 5.2 OBJECTIVES

The objectives of the experiment described in this chapter were: (i) to determine the denitrification loss of N from fresh poultry and animal manures, and from poultry manure during composting; and (ii) to examine the potential of different amendments to reduce the denitrification loss during composting.

## 5.3 MATERIALS AND METHODS

Biological denitrification results in the release of  $\text{N}_2\text{O}$  and  $\text{N}_2$  gases. While the high background concentration of  $\text{N}_2$  in the atmosphere makes it difficult to measure accurately the  $\text{N}_2$  released during denitrification, the release of  $\text{N}_2\text{O}$ , an intermediate product during denitrification, can be accurately measured. Amongst different methods used to measure the rate of denitrification in soils, acetylene ( $\text{C}_2\text{H}_2$ ) inhibition technique is found to be most useful and reliable (Ryden *et al.*, 1979; Firestone, 1982; Tiedje *et al.*, 1989; Aulakh *et al.*, 1991).

As  $\text{C}_2\text{H}_2$  inhibits the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  in soil (Yoshinari and Knowles, 1976), it is reasonable to expect that the quantity of  $\text{N}_2\text{O}$  produced by  $\text{C}_2\text{H}_2$  inhibited microorganisms in a short-term assay will be a direct measure of the total gaseous N produced without inhibition (Firestone, 1982; Tiedje *et al.*, 1989). In this study the  $\text{C}_2\text{H}_2$  inhibition technique was used to measure the denitrification rate during composting of poultry manure.

### 5.3.1 Experiment 1: Standardization of $\text{C}_2\text{H}_2$ inhibition technique

When measuring denitrification using the  $\text{C}_2\text{H}_2$  inhibition technique, it is important to allow sufficient time for  $\text{C}_2\text{H}_2$  to diffuse into reducing anaerobic zones within the manure sample in order to achieve maximum inhibition of the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$ . Prolonged exposure of manure to  $\text{C}_2\text{H}_2$  may affect other biological processes such as nitrification (Walter *et al.*, 1979), or reduce the efficiency of  $\text{C}_2\text{H}_2$  in inhibiting  $\text{N}_2\text{O}$  reduction (Yeomans and Beauchamp, 1982), and could underestimate the extent of denitrification (Ryden and Rolston, 1983). It is therefore necessary to determine the

maximum optimum time for  $C_2H_2$  contact in order to measure denitrification.

Samples of composted poultry manure (65% moisture content) were incubated with  $C_2H_2$  (10% v/v) in 125cm<sup>3</sup> Erlenmeyer flasks under aerobic and anaerobic conditions for different periods. Release of  $N_2O$  from a moist field soil was also examined for comparison. Gas samples were collected from the headspace of the flask after 1, 5, 8, 16 and 24h of incubation and the concentration of  $N_2O$  was measured as described in section 5.3.4.

### 5.3.2 Experiment 2: Denitrification in fresh poultry and animal manures and composted poultry manure

Fresh samples of poultry, dairy, sheep, pig and horse manure were collected. Firstly, the rate of denitrification in fresh manures was measured. Part of the poultry manure was used for composting using a range of amendments including, woodchip, wheat straw, elemental sulphur ( $S^0$ ) and zeolite (see Table 4.2). The amounts of amendments used were the same as in the experiment reported in Chapter 4.

Aerobic composting was carried out using glass preserving jars as previously described in Chapter 4 (section 4.3.3). In brief, fresh poultry manure (300g) was mixed thoroughly with an amendment and the mixture was incubated for 14 weeks in jars at room temperature (20-25°C). The moisture content of the mixture was adjusted to 68% (w/w) at weekly intervals. The oxygen was supplied through an air-inflated balloon. Periodically, the composts were thoroughly mixed, and 30g samples removed for denitrification measurements and other chemical analyses.

### 5.3.3 Experiment 3: Factors affecting denitrification

The effect of added  $NO_3^-$  on the denitrification potential of composts was examined by spiking compost samples obtained at the end of experiment 2 with  $KNO_3$  solution at a rate of 200µg  $NO_3^-$ -N g<sup>-1</sup> dry mixture. The samples were thoroughly mixed in 125cm<sup>3</sup> Erlenmeyer flasks and allowed to equilibrate for one hour. Then the samples were incubated anaerobically in an oxygen free  $N_2$  atmosphere in the presence of  $C_2H_2$  (10%,

v/v) and the concentration of  $\text{N}_2\text{O}$  measured after one hour.

To examine the effect of added  $\text{NO}_3^-$  on the rate of denitrification in fresh poultry manure, different levels of  $\text{KNO}_3$  solutions (0, 25, 50, 100 and  $200\mu\text{g NO}_3^- \text{-N g}^{-1}$  dry manure) were added to fresh poultry manure and mixed thoroughly. After one hour  $\text{C}_2\text{H}_2$  was introduced and the mixture incubated for one hour. Then the rate of  $\text{N}_2\text{O}$  release was determined.

Addition of manure to soil can enhance the rate of denitrification which is attributed mainly to the additional supply of C and  $\text{NO}_3^-$  (Burford and Bremner, 1975; Guenzi *et al.*, 1978; Christensen, 1985; Thompson and Pain, 1989). To examine the relative importance of C and  $\text{NO}_3^-$  on denitrification, measurements were made on soil after the addition of increasing amounts of poultry manure or glucose. The poultry manure or glucose was mixed with moist soil (coarse loamy mixed mesic *Dystric Eutrochrept*) at a rate equivalent to 4.6, 9.2, 18.4 and  $36.8\text{Mg C ha}^{-1}$  (dry weight basis; assuming 2cm depth, with a bulk density of  $1.0\text{g cm}^{-3}$ ). The rate of denitrification was measured at the end of two weeks incubation. To examine the effect of different manures on denitrification, the soil was also incubated with fresh poultry and animal manures at a rate of  $40\text{Mg ha}^{-1}$ . The denitrification was measured after two weeks of incubation.

#### 5.3.4 Denitrification measurements using $\text{C}_2\text{H}_2$ inhibition

About 20g moist sample (manure or compost) was placed in a  $125\text{cm}^3$  Erlenmeyer flask and uniformly spread on the surface to achieve maximum exposure to  $\text{C}_2\text{H}_2$ . Each flask was sealed with a two-septum seal stopper (suba seal No.49) and prepared for incubation under both aerobic and anaerobic conditions. For aerobic conditions,  $13.5\text{cm}^3$  of headspace was replaced with purified  $\text{C}_2\text{H}_2$  (obtained from the Department of Scientific and Industrial Research, Palmerston North), to produce a concentration of 10%  $\text{C}_2\text{H}_2$  (v/v) inside the flask, and flushed several times with the  $\text{C}_2\text{H}_2$  mixture to improve the diffusion of  $\text{C}_2\text{H}_2$  to all the potential sites of denitrification in manure. Ten per cent concentration of  $\text{C}_2\text{H}_2$  in the headspace has been found to be adequate for the inhibition of the reduction of  $\text{N}_2\text{O}$  to N in soil (Ryden *et al.*, 1979; Goulding and Webster, 1989).

For anaerobic conditions, the air inside the flask was flushed out with  $N_2$  using an air-compressor. This was repeated several times and the flask was filled with oxygen free  $N_2$  gas. Then,  $13.5\text{cm}^3$  of the headspace was replaced with  $C_2H_2$ . Both aerobic and anaerobic incubations were conducted at  $20^\circ\text{C}$ . After 1h, a gas sample from the headspace was collected into a  $15\text{cm}^3$  Becton Dickinson vacutainer using double sided needles.

The concentration of  $N_2O$  in the headspace was determined using a Hewlett model (5890 Packard Series II) Gas Chromatograph (1.5m column packed with Poropack QS and an electron capture detector operating at  $300^\circ\text{C}$ ) by injecting  $1\text{cm}^3$  gas sample. The rate of denitrification was calculated from the concentration of  $N_2O$ , the volume of the flask and the solubility of  $N_2O$  in manure solution, using the following equation (Eq 5.1):

$$DN_r = C_s * (V_h + (S_w * V_w)) * D_g * N_f * 24 \quad (5.1)$$

where,

$DN_r$	=	Denitrification rate ( $\text{mg } N_2O\text{-N kg}^{-1} \text{ day}^{-1}$ )
$C_s$	=	Concentration of $N_2O$ in the sample ( $\mu\text{L L}^{-1}$ )
$V_h$	=	Volume of headspace (L)
$S_w$	=	Solubility constant of $N_2O$ in manure solution (0.632 at $20^\circ\text{C}$ , Tiedje, 1982)
$V_w$	=	Volume of manure solution (L)
$D_g$	=	Gas density for $N_2O$ ( $1.83 \times 10^{-6} \text{ g } N_2O \text{ L}^{-1}$ )
$N_f$	=	Conversion factor for $N_2O$ to N (0.636)

### 5.3.5 Chemical analysis

The pH and mineral-N ( $NH_4^+\text{-N}$  and  $NO_3^-\text{-N}$ ) contents of the manure/compost sample were measured as described in Chapter 4 section 4.3.4.

5.4 RESULTS AND DISCUSSION

5.4.1 Release of N<sub>2</sub>O from poultry manure at different times of incubation with C<sub>2</sub>H<sub>2</sub>

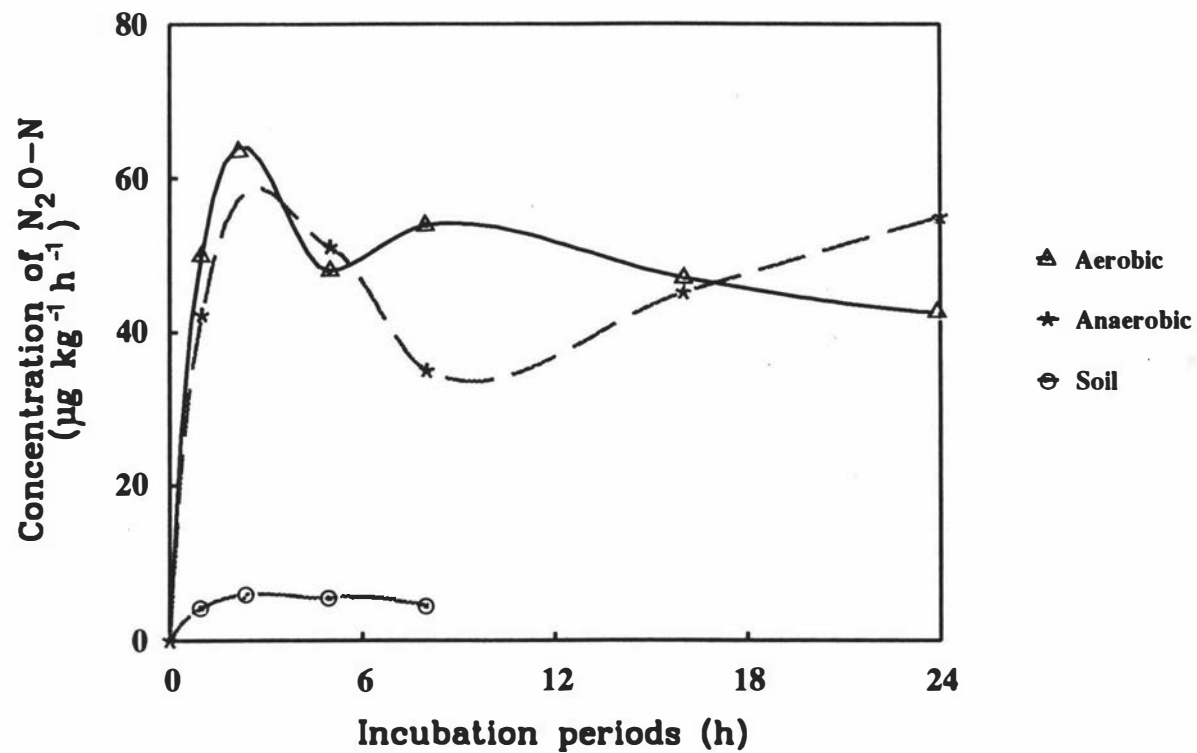
The release of N<sub>2</sub>O-N for various periods of C<sub>2</sub>H<sub>2</sub> incubation is presented in Figure 5.1a. The concentration of N<sub>2</sub>O-N released reached a maximum at 1h, after which it remained relatively constant. The rate of release of N<sub>2</sub>O-N (Fig 5.1b) indicates that both under aerobic and anaerobic conditions the rate of N<sub>2</sub>O-N released peaked after 1h incubation, but decreased sharply thereafter. For soil, the rate of denitrification followed a similar trend. There was no significant difference in the rate of N<sub>2</sub>O-N release between aerobic and anaerobic conditions.

It has often been observed that in soils the time required for maximum rate of denitrification is found to be generally higher (2 to 24h) than in manure. Smith *et al.* (1978) observed that denitrification rate increased within a few hours after the imposition of anaerobic conditions and they suggest that shorter assays are most likely to be representative of denitrification in soils.

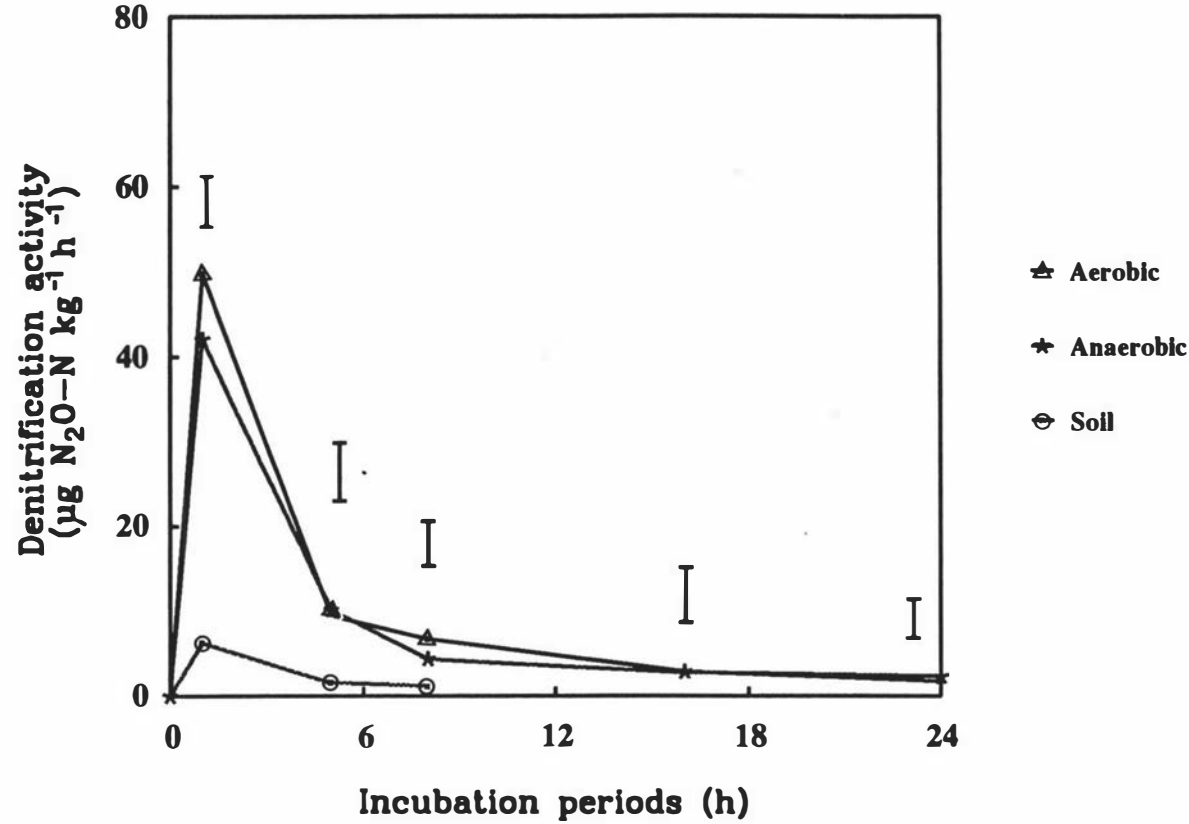
The short equilibrium period in poultry manure may be attributed to the greater availability of readily soluble C and high density of denitrifiers. To confirm this, in a separate experiment, denitrification in fresh manure was measured 1h or 16h after the addition of NO<sub>3</sub><sup>-</sup> (200µg NO<sub>3</sub><sup>-</sup>-N g<sup>-1</sup> fresh manure). The concentration of N<sub>2</sub>O-N in the headspace of fresh manure spiked with NO<sub>3</sub><sup>-</sup> was significantly higher at 1h after mixing than after 16h (Table 5.1).

Table 5.1 Rate of N<sub>2</sub>O release from fresh poultry manure at different times after NO<sub>3</sub><sup>-</sup> addition

Treatment	Rate of N <sub>2</sub> O formation (mg kg <sup>-1</sup> day <sup>-1</sup> )
1. Fresh manure (without NO <sub>3</sub> <sup>-</sup> )	0.08
2. Fresh manure with added NO <sub>3</sub> <sup>-</sup> (200µg g <sup>-1</sup> ). Denitrification measured after 1h	16.5
3. Fresh manure with added NO <sub>3</sub> <sup>-</sup> (200µg g <sup>-1</sup> ). Denitrification measured after 16h	0.19



**Fig 5.1a Release of  $N_2O-N$  from poultry manure compost and soil at different periods of incubation with acetylene**



**Fig 5.1b Denitrification activity in poultry manure compost and soil as measured by the rate of release of  $\text{N}_2\text{O-N}$  at different periods of incubation with acetylene. Vertical bars represent LSD (0.05)**

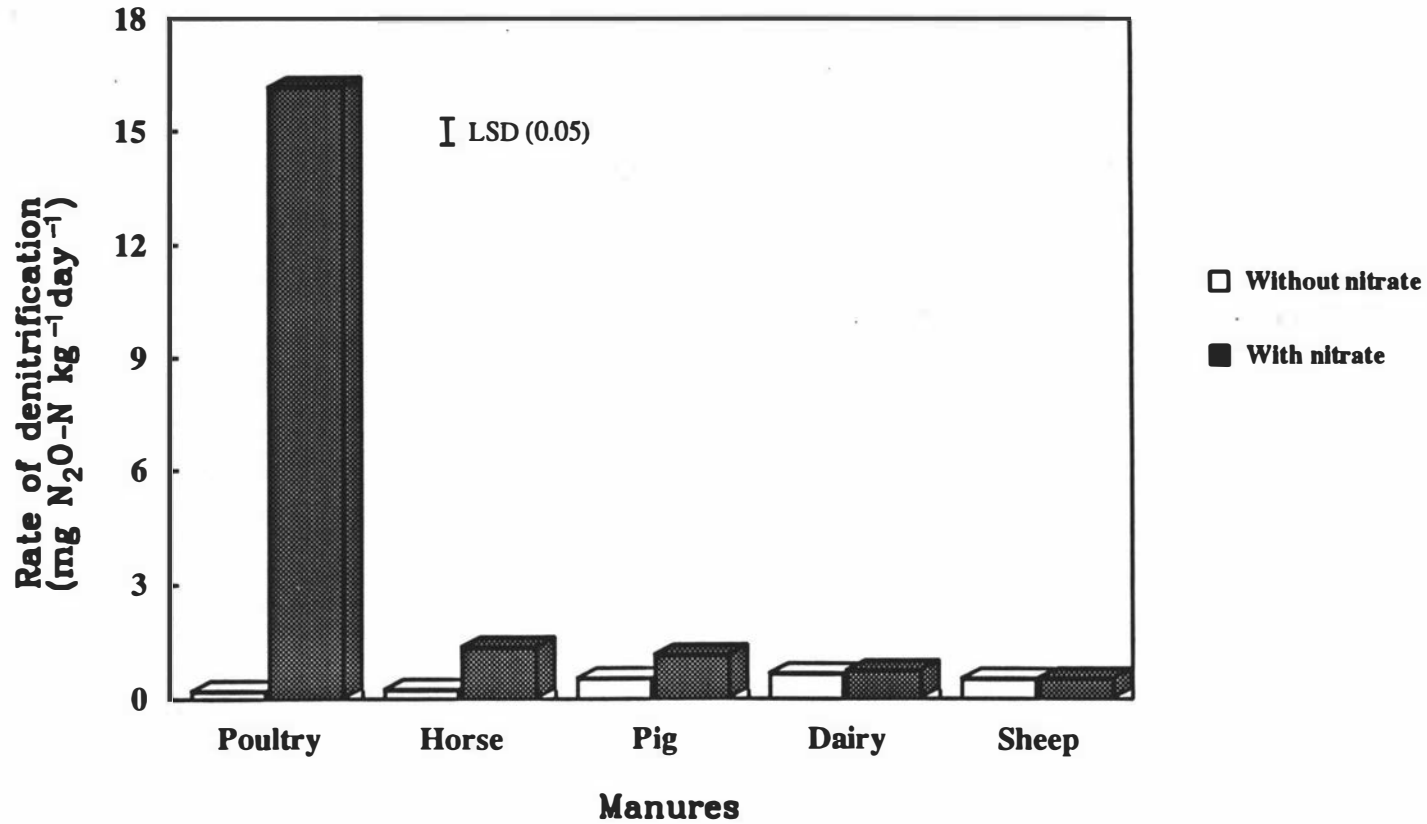
Measurement of  $\text{NO}_3^-$ -N in manure samples indicated that in the latter treatment most of the  $\text{NO}_3^-$  had disappeared already. This indicates that  $\text{NO}_3^-$  added to poultry manure is readily denitrified within a short period. Potential denitrification rates in poultry manure are high and appear to be partly limited by the availability of  $\text{NO}_3^-$ . Measures of denitrification loss from poultry manure should be made within 1h because  $\text{N}_2\text{O}$  release measured at longer periods after  $\text{NO}_3^-$  addition is likely to underestimate denitrification rates. Similarly, Smith *et al.* (1978), Ryden and Rolsten (1983) and Tiedje *et al.* (1989) suggest a short period of incubation with  $\text{C}_2\text{H}_2$  for the measurement of denitrification in soils.

Based on these results, denitrification in subsequent experiments was determined by measuring the concentration of  $\text{N}_2\text{O}$  in the headspace after 1h incubation with  $\text{C}_2\text{H}_2$ .

#### **5.4.2 Denitrification activity in fresh poultry and animal manures**

Using the 1h  $\text{C}_2\text{H}_2$  inhibition technique the rate of denitrification in fresh poultry and animal manures, both in the presence and absence of  $\text{NO}_3^-$  addition, was measured (Fig 5.2). In the absence of  $\text{NO}_3^-$  addition, the rate of denitrification losses from fresh manures was very low and there was no difference between the manure samples. Addition of  $200\mu\text{g NO}_3^-$ -N, however, increased the rate of denitrification with the effect more pronounced in poultry manure than in animal manures. The low rates of denitrification apparently resulted from the low content of  $\text{NO}_3^-$ -N ( $<1$  to  $7.4 \text{ mg kg}^{-1}$ ) in fresh manures.

For denitrification to occur, ammoniacal and urea N in fresh poultry and animal manures first needs to be oxidized to  $\text{NO}_3^-$ . Subsequent diffusion of  $\text{NO}_3^-$  to anaerobic zones in manure can result in denitrification. The difference in the rate of denitrification between the manures, in the presence of  $\text{NO}_3^-$ , may be related to the difference in the amounts of soluble C and population size of denitrifying microorganism (Guenzi *et al.*, 1978; Christensen, 1985).



**Fig 5.2** Rate of denitrification in fresh poultry and animal manures with and without nitrate addition

### 5.4.3 Denitrification during composting of poultry manure

The rate of denitrification during composting of poultry manure measured at different periods is presented in Figure 5.3. The loss of N through denitrification from the fresh poultry manure (1-3 days after dropping), was negligible (less than the background concentration of  $\text{N}_2\text{O}$ ) which could be attributed mainly to the very low  $\text{NO}_3^- \text{-N}$  ( $<1\mu\text{g g}^{-1}$ ) content in the manure.

The rate of denitrification increased steadily after 2 weeks of decomposition and reached a maximum of  $3.6\text{mg N}_2\text{O-N kg}^{-1} \text{ day}^{-1}$  at 10 weeks then remaining essentially constant. There was no significant difference in the  $\text{N}_2\text{O}$  formation by denitrification activity between aerobically and anaerobically incubated composts up to 10 weeks, after which the rate of denitrification was slightly higher in the former than in the latter condition.

In fresh poultry manure most N is present as uric acid and urea (refer Table 4.1). There is only a trace of  $\text{NO}_3^- \text{-N}$  ( $<1\mu\text{g g}^{-1}$ ) in the fresh poultry manure which may be the reason for the low level of denitrification. As the decomposition proceeds, the uric acid ( $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ ) and urea [ $(\text{CO}(\text{NH}_2)_2)$ ] are rapidly hydrolysed by microorganisms and lead to the formation of  $\text{NH}_4^+$  and  $\text{CO}_2$  (Eq 2.1 and 2.2). Subsequent oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  by nitrifiers (e.g. *Nitrosomonas* and *Nitrobactor*) results in the build up of  $\text{NO}_3^-$  which forms an essential substrate for denitrification. The increase in the rate of denitrification during the composting period could mainly be attributed to the increase in the  $\text{NO}_3^- \text{-N}$  in the manure compost (Fig 5.3).

A strong positive relationship between  $\text{NO}_3^-$  content of the composts and the rate of denitrification was observed both under aerobic ( $r=0.90$ ) and anaerobic ( $r=0.91$ ) conditions (Fig 5.4). The intercept of the regression line on the x axis gives the threshold concentration of  $\text{NO}_3^- \text{-N}$  below which there was no significant denitrification. In this study the threshold concentration for poultry manure was found to be  $3.6\text{mg NO}_3^- \text{ kg}^{-1}$  of dry manure/compost. Similarly, Blackmer and Bremner (1978) observed a concentration of  $5\text{mg NO}_3^- \text{-N kg}^{-1}$  below which there was no appreciable denitrification in soil.

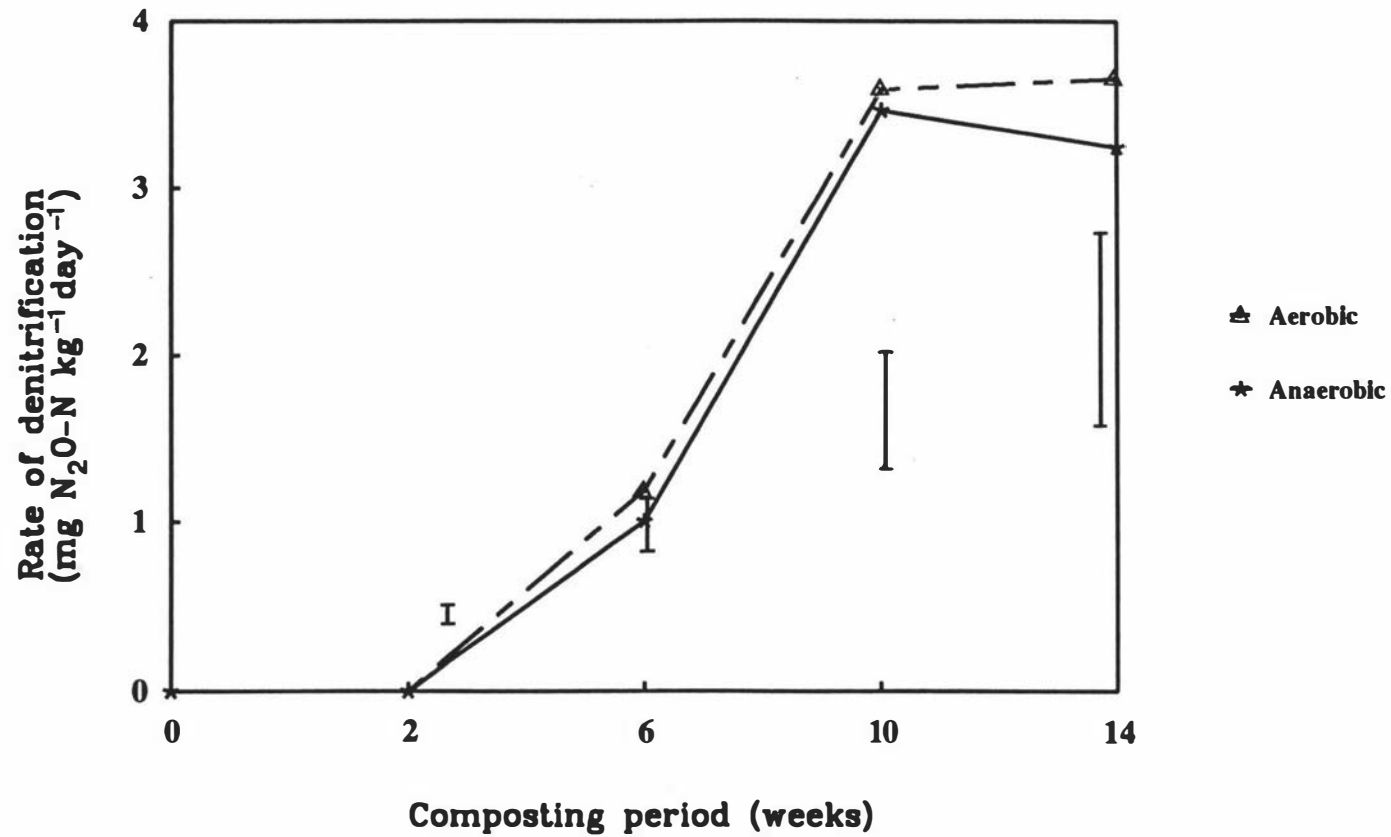
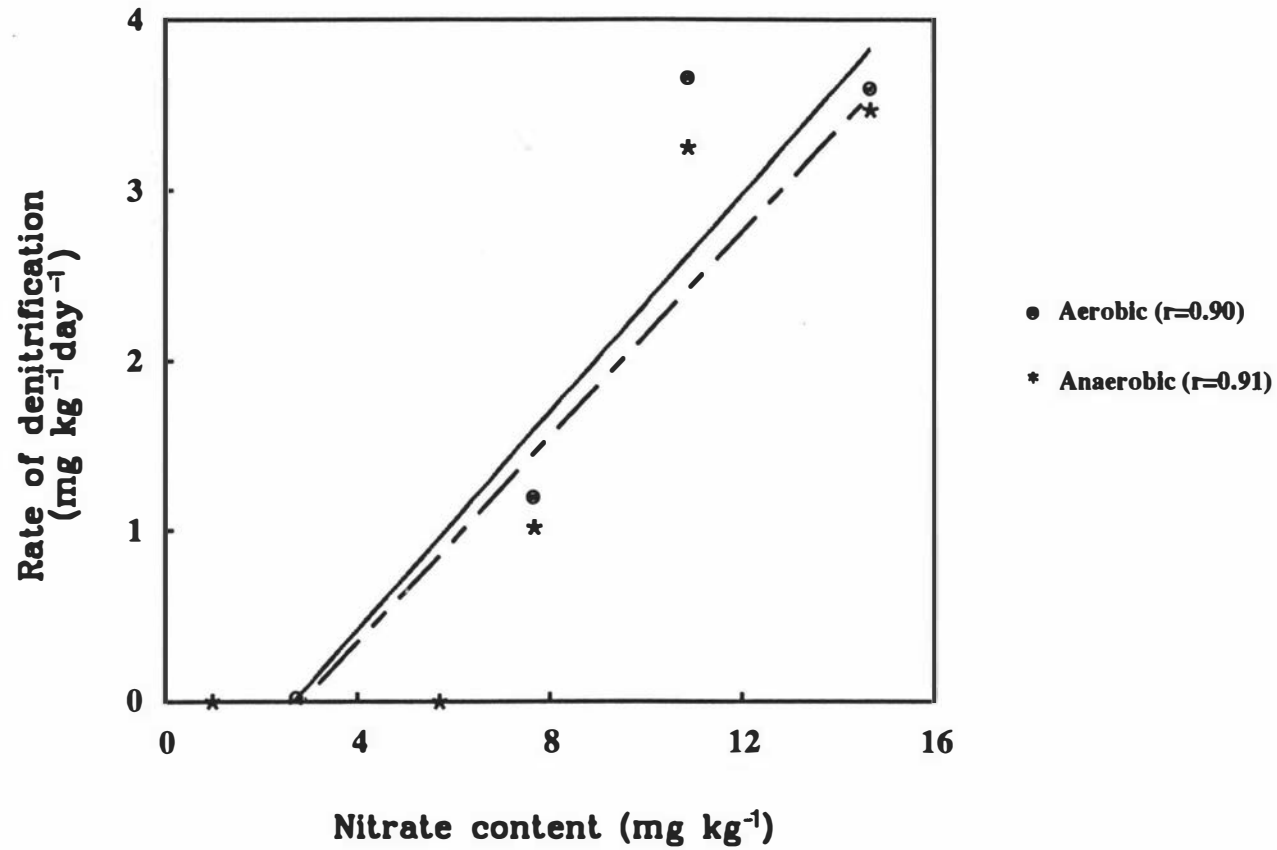


Fig 5.3 Rate of denitrification in poultry manure during composting. Vertical bars represent LSD (0.05)



**Fig 5.4** Relationship between nitrate content and rate of denitrification in poultry manure composts

Positive relationships between  $\text{NO}_3^-$  and denitrification have been reported by other researchers working with soils (Bowman and Focht, 1974; Stanford *et al.*, 1975). However, in soils, in addition to the  $\text{NO}_3^-$  content, the amount of soluble C also determines the rate of denitrification (Bremner and Shaw, 1958; Smid and Beauchamp, 1976; Knowles, 1982; Goulding and Webster, 1989). The increase in the population of denitrifying bacteria during composting may also contribute to the increase in denitrification rate under appropriate conditions (Thompson, 1989).

Though the ammonification of organic N was very rapid in the compost, the rate of nitrification appears to be very slow (Table 5.3), probably due to a smaller population of nitrifiers than ammonifiers (Nodar *et al.*, 1990), and restricted oxygen supply due to high biological oxygen demand and high moisture content (65-70%) limiting gaseous diffusion. The continuous release of free  $\text{NH}_3$ , which exists in chemical equilibrium with  $\text{NH}_4^+$  in manure solution, is toxic to nitrifiers (Giddens and Rao, 1975) and could reduce the rate of nitrification. Higher rates of denitrification are common in soils with high moisture content (Nommik, 1956; Bremner and Shaw, 1958; Bailey and Beauchamp, 1973).

From the amounts of  $\text{NO}_3^-$  present before and after denitrification measurements, the apparent loss of  $\text{NO}_3^-$  (manure  $\text{NO}_3^-$  plus added  $\text{NO}_3^-$ ) was calculated. The estimated loss of  $\text{NO}_3^-$ -N in manure alone treatment ranged from 23.8 to 33.7% (per day<sup>-1</sup>) during composting, showing a potential for  $\text{NO}_3^-$  to be lost through biological denitrification from poultry manure. As the different biological N transformation processes, such as ammonification, nitrification,  $\text{NH}_3$  volatilization, immobilization and denitrification, occur simultaneously, it is very difficult to quantify exactly the total loss of N through biological denitrification alone over a period of incubation.

Although denitrification in soils under apparently aerobic conditions has widely been reported (Burford and Bremner, 1975), several reasons could be attributed to the high rates of denitrification in manure under aerobic conditions. According to Paul and Beauchamp (1989) and Petersen *et al.*, (1991), the oxidation of volatile fatty acids during decomposition of manure depletes the gaseous oxygen supply and results in the use of  $\text{NO}_3^-$  as a terminal electron acceptor which initiates the denitrification process.

The denitrifying bacteria responsible for reduction of  $\text{NO}_3^-$  to gaseous forms of N are facultative anaerobes that have the ability to use both molecular oxygen ( $\text{O}_2$ ) and  $\text{NO}_3^-$  (or  $\text{NO}_2^-$ ) as electron acceptors (Burford and Bremner, 1975). The denitrifiers can grow under anaerobic conditions in the presence of  $\text{NO}_3^-$  or under partly anaerobic conditions in the presence of  $\text{O}_2$ . The presence of  $\text{O}_2$  has been shown to stimulate denitrification in soil (Gok and Ottow, 1988) presumably because nitrification is allowed to proceed.

The release of  $\text{N}_2\text{O}$  is known to occur not only during biological denitrification but also during nitrification of  $\text{NH}_4^+$  (Ryden *et al.*, 1979), and during the reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  (Yoshida and Alexander, 1970). The studies of Breitenbeck and Bremner (1986) showed substantial release of  $\text{N}_2\text{O}$  from well aerated soils treated with nitrifiable forms of fertilizer N. Similarly, Smith and Chalk (1980) concluded that decomposition of  $\text{NO}_2^-$  by chemical process also results in the release of NO,  $\text{N}_2\text{O}$  and  $\text{N}_2$ . But, according to Broadbent and Clark (1965), chemical denitrification of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  is not considered to be a major pathway of N loss from soil.

#### 5.4.4 Effect of different amendments on denitrification

Composting poultry manure with amendments (woodchip, straw,  $\text{S}^0$  and zeolite) resulted in significant reductions (60-80%) in the rate of denitrification (Table 5.2). Carbon rich bedding materials viz., woodchip and straw significantly decreased denitrification rate (Table 5.2). The reasons for this are unclear because presence of amendments did not markedly change  $\text{NO}_3^-$  levels (Table 5.3). But, Craswell (1978) reported reduction in denitrification from soil amended with wheat straw due to increased microbial immobilization of  $\text{NH}_4^+$ .

Addition of  $\text{S}^0$  decreased manure pH (Table 5.4) which was associated with a decreased rate of denitrification (Table 5.2). The oxidation of  $\text{S}^0$  results in the production of  $\text{H}_2\text{SO}_4$  which increases the acidity in the manure. Pain *et al.* (1987) and Thompson and Pain (1989) have shown that acidification of slurry reduces denitrification loss. The presence of anaerobic sites within the manure would have resulted in the reduction of  $\text{S}^0$  to hydrogen sulphide ( $\text{H}_2\text{S}$ ) which is toxic to denitrifiers. This agrees with the results of Sorensen *et al.* (1980) who reported a reduction in the denitrification activity due to

**Table 5.2** Rate of denitrification (mg N<sub>2</sub>O-N kg<sup>-1</sup> day<sup>-1</sup>) in poultry manure composts at different periods of composting

Treatments	10 weeks		14 weeks	
	Aerobic	Anaerobic	Aerobic	Anaerobic
1. Manure (m) alone	3.59	3.47	3.66	3.25
2. m + woodchip (wc)	0.92	0.63	0.68	0.68
3. m + straw	0.87	0.45	0.68	0.40
4. m + elemental sulphur (S <sup>o</sup> )	0.82	0.63	0.63	0.34
5. m + wc + S <sup>o</sup>	0.86	0.66	0.57	0.25
6. m + zeolite	0.67	0.48	0.41	0.10
7. m + wc + zeolite	0.44	0.29	0.48	0.16

**LSD (0.05)**

Treatments	0.20**	0.47**
Systems	0.11**	0.25**
Treatments * systems	NS	NS

**Table 5.3** Change in  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^+\text{-N}$  contents of poultry manure composts at different periods of aerobic composting

Treatments	$\text{NH}_4^+\text{-N}$ ( $\text{mg g}^{-1}$ )		$\text{NO}_3^+\text{-N}$ ( $\mu\text{g g}^{-1}$ )	
	10 weeks	14 weeks	10 weeks	14 weeks
1. Manure (m) alone	23.2	8.9	14.7	10.9
2. m + woodchip (wc)	35.6	17.8	12.8	17.8
3. m + straw	32.6	24.7	19.1	26.6
4. m + elemental sulphur ( $\text{S}^\circ$ )	39.1	18.6	8.2	12.8
5. m + wc + $\text{S}^\circ$	35.8	19.5	11.8	14.7
6. m + zeolite	17.4	12.6	10.4	10.8
7. m + wc + zeolite	13.7	15.2	9.5	13.9

**LSD (0.05)**

Treatments	4.42**	3.62**
Periods	2.36**	1.93**
Treatments * Periods	6.26**	NS

**Table 5.4 Change in pH of poultry manure composts at different periods of aerobic composting**

Treatments	pH (H <sub>2</sub> O)		
	Initial	10 weeks	14 weeks
1. Manure (m) alone	6.50	8.82	8.36
2. m + woodchip (wc)	6.51	8.83	9.13
3. m + straw	6.47	9.02	9.09
4. m + elemental sulphur (S°)	6.14	7.95	8.06
5. m + wc + S°	6.43	8.25	8.15
6. m + zeolite	6.65	9.02	9.26
7. m + wc + zeolite	6.59	9.25	9.27

**LSD (0.05)**

Treatments	0.98**
Periods	NS
Treatments * periods	0.14

H<sub>2</sub>S in soil. Also, the presence of sulphur compounds, especially sulphide, was reported to inhibit denitrification in soil (Myers, 1972; Knowles, 1982), specifically the reduction of NO and N<sub>2</sub>O to N<sub>2</sub> (Tam and Knowles, 1979; Sorensen *et al.*, 1980).

Although zeolite conserved relatively more N in the manure by strongly adsorbing NH<sub>4</sub><sup>+</sup> ions in the exchange sites, the availability of adsorbed NH<sub>4</sub><sup>+</sup> ions for nitrifiers is limited (Miner, 1984), which may be one of the reasons for the decrease in the denitrification.

In a separate experiment denitrification was measured after a fresh addition of exogenous NO<sub>3</sub><sup>-</sup> to the compost at a rate equivalent to 200mg NO<sub>3</sub><sup>-</sup>-N kg<sup>-1</sup>. Except in S<sup>o</sup> treated compost the denitrification rate was increased manyfold in all compost after the fresh addition of NO<sub>3</sub><sup>-</sup> (Fig 5.5). The highest rate occurred in zeolite (30.6mg kg<sup>-1</sup> day) followed by straw (22mg kg<sup>-1</sup> day<sup>-1</sup>) treated manure, while the lowest occurred in S<sup>o</sup> compost (0.7mg kg<sup>-1</sup> day<sup>-1</sup>). The S<sup>o</sup> was found to be very effective in preventing N<sub>2</sub>O formation in decomposing poultry manure.

Similarly, when the fresh poultry manure was spiked with different levels of NO<sub>3</sub><sup>-</sup>, the rate of denitrification increased linearly with increasing levels of NO<sub>3</sub><sup>-</sup> both under aerobic and anaerobic conditions showing a strong correlation (r=0.98)(Fig 5.6). This again suggests that the poultry manure has greater potential for N to be lost through denitrification, but is probably limited by NO<sub>3</sub><sup>-</sup> formation and availability.

#### **5.4.5 Effect of manure additions on the denitrification in soil.**

Addition of different manures to soil resulted in a substantial increase in denitrification (Fig 5.7). The rate of denitrification varied between the soil/manure mixtures and followed: pig >> dairy = horse = sheep > poultry manures = soil. Various reasons have been attributed to the increase in denitrification after the manure addition, including, promoting anaerobiosis (Stevens and Cornforth, 1974); increasing the activity of denitrifiers (Myrold and Tiedje, 1985; Thompson and Pain, 1989); increasing NO<sub>3</sub><sup>-</sup> content (Van den Abbeel *et al.*, 1989) and supply of C to denitrifying organisms (Guenzi *et al.*, 1978; Christensen, 1985; Goulding and Webster, 1989).

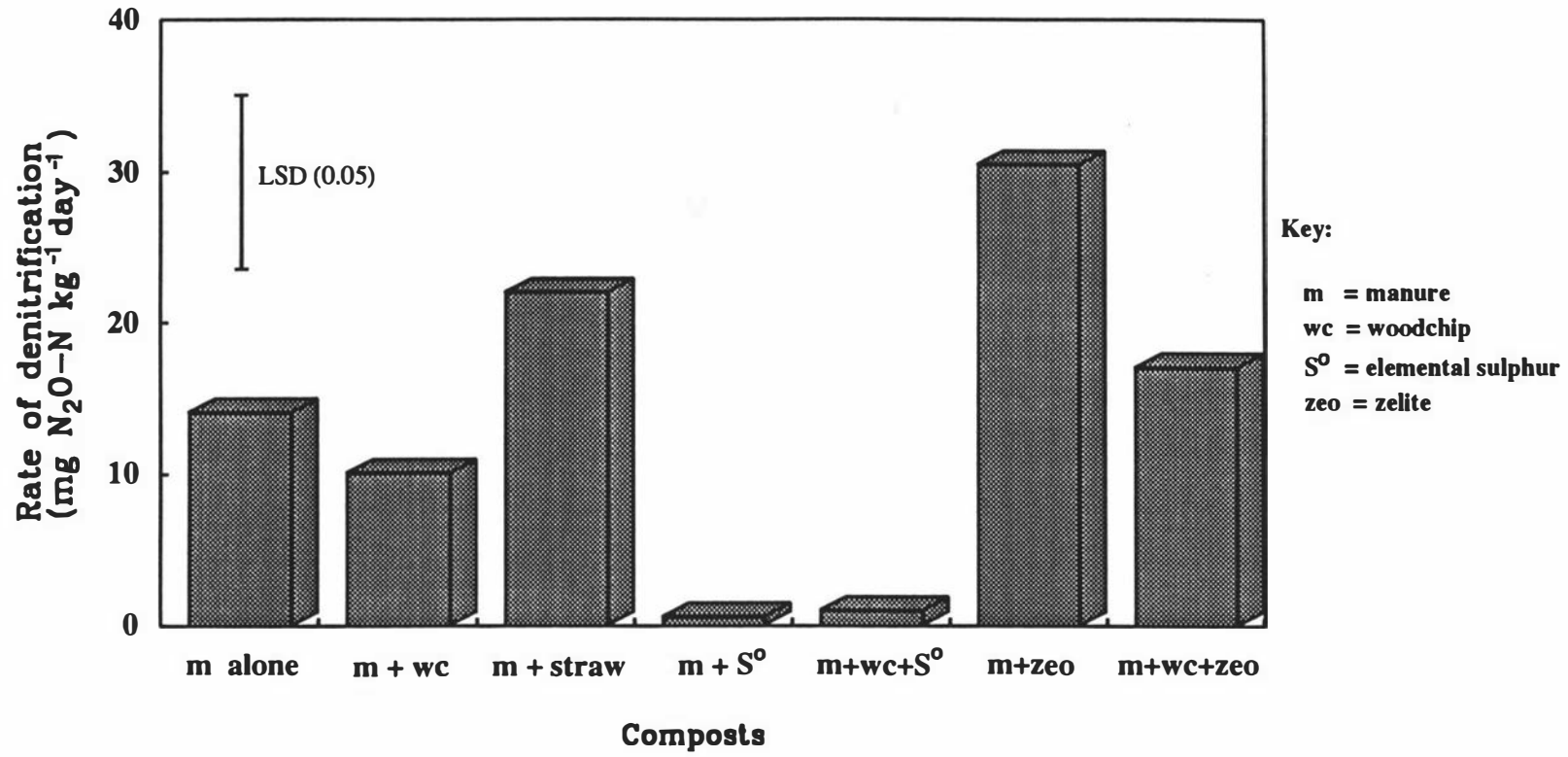
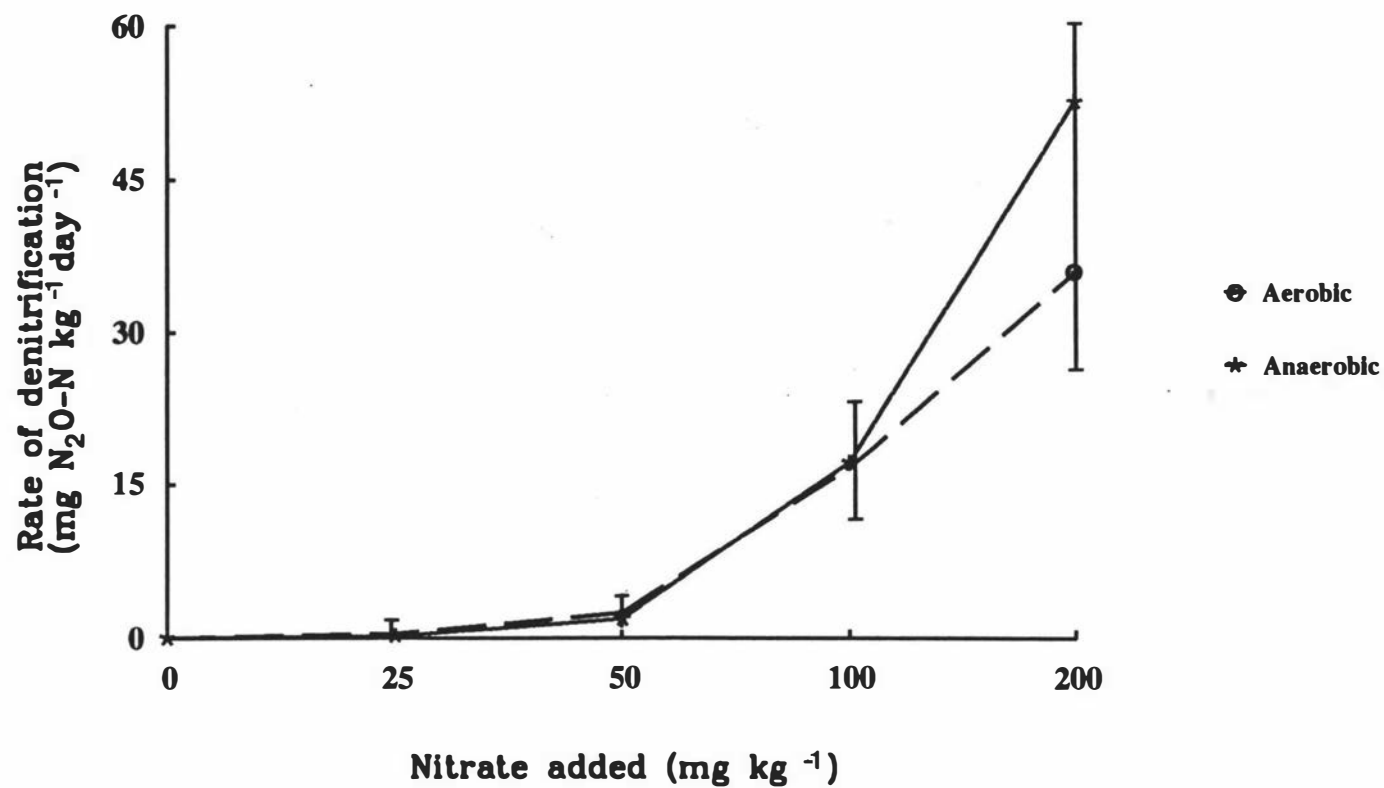
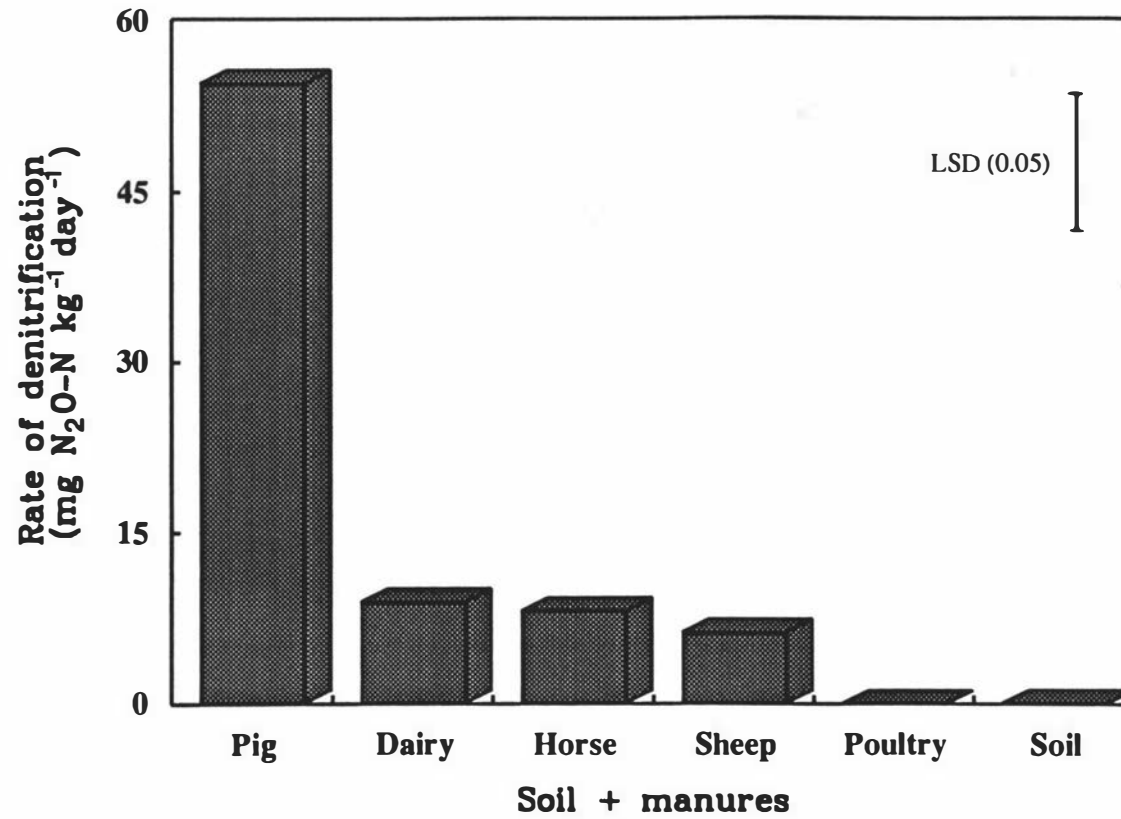


Fig 5.5 Rate of denitrification in poultry manure composts after a fresh addition of nitrate



**Fig 5.6 Effect of nitrate addition on the rate of denitrification in poultry manure.**  
**Vertical bars represent LSD (0.05)**



**Fig 5.7** Effect of manure addition on the rate of denitrification in soil

A strong correlation ( $r=0.78$ ) was observed between the  $\text{NO}_3^-$  content and the rate of denitrification in this study. In soils a close relationship was generally observed between denitrification rate and C content (Bremner and Shaw, 1958; Burford and Bremner, 1975; Smid and Beauchamp, 1976; Goulding and Webster, 1989). A low rate of denitrification in soil amended with poultry manure, at a rate equivalent to  $40\text{Mg ha}^{-1}$ , could be due to the high concentration of free  $\text{NH}_3$  released from poultry manure which is toxic to soil microorganisms.

#### **5.4.6 Effect of different levels of poultry manure and glucose on soil denitrification**

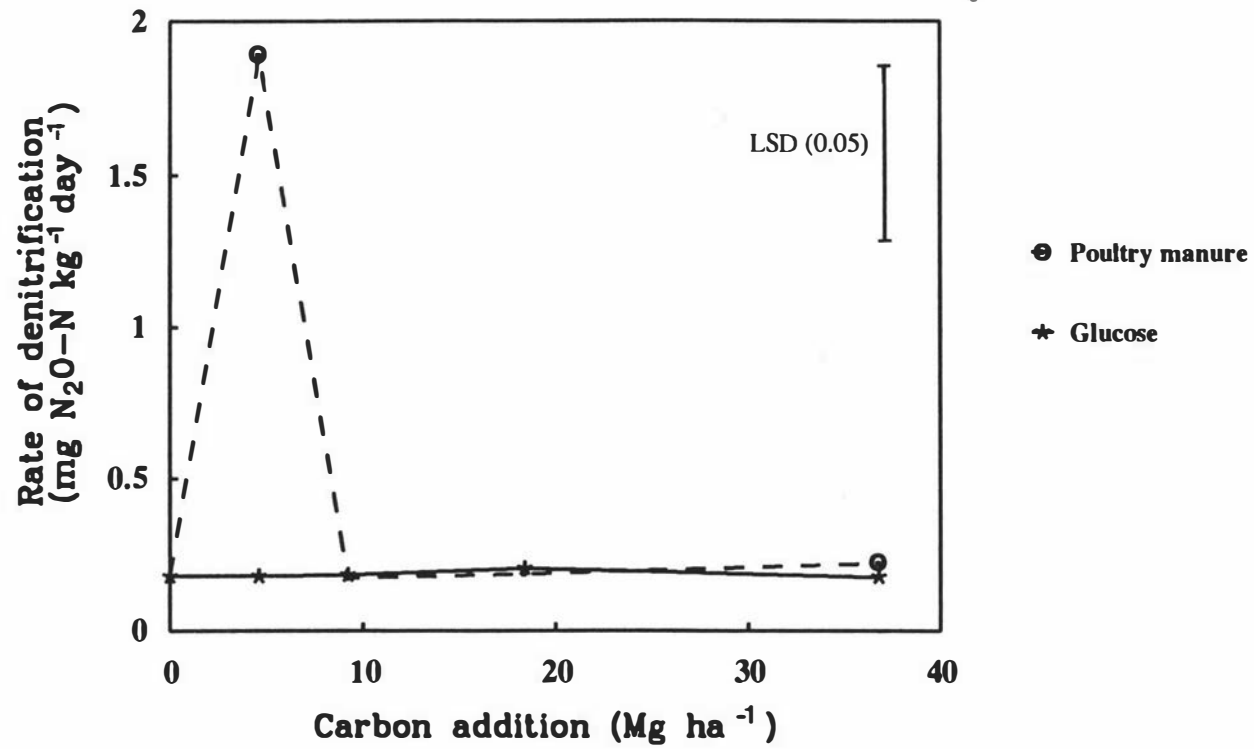
To examine the importance of C supply on soil denitrification, increasing amounts of poultry manure and glucose were added to the soil and the rate of  $\text{N}_2\text{O}$  formation was measured after 2 weeks incubation. There was no effect of C added through glucose on denitrification (Fig 5.8). Only a low rate of poultry manure, equivalent to  $4.6\text{Mg C ha}^{-1}$ , increased denitrification approximately 10 fold, but further increase in poultry manure levels had no effect on the rate of soil denitrification. This may be related to the high concentration of  $\text{NH}_3$  released from poultry manure which is found to be toxic to nitrifying and denitrifying organisms (Giddens and Rao, 1975).

Increased rate of C addition through glucose had no effect on denitrification loss from this soil. While the results of Bowman and Focht (1974) showed a strong dependency of denitrification from soil on  $\text{NO}_3^-$  and C, a very high concentration of C (1.8%, w/w), added as glucose, inhibited the denitrification. The data of Goulding and Webster (1989) also indicated that increased soil C does not always promote denitrification.

### **5.5 CONCLUSIONS**

The rate of denitrification, as measured by the rate of release of  $\text{N}_2\text{O}$  in the presence of  $\text{C}_2\text{H}_2$ , reached a peak value within 1h of incubation, showing a short time assay is important for measuring denitrification rates in manure or compost.

The loss of N from fresh poultry and animal manures through denitrification was



**Fig 5.8** Rate of denitrification in soil amended with different levels of carbon added through poultry manure and glucose

negligible and was associated with low content of  $\text{NO}_3^-$ -N in the manures. Increases in the  $\text{NO}_3^-$  concentration due to nitrification during 98 days of composting increased the denitrification activity up to  $3.7 \text{ mg N}_2\text{O-N kg}^{-1} \text{ day}^{-1}$  from poultry manure.

The addition of various amendments such as woodchip, wheat straw,  $\text{S}^0$ , and zeolite significantly reduced the rate of denitrification loss. The addition of woodchip and straw reduced the denitrification loss mainly by immobilizing the  $\text{NO}_3^-$ . While  $\text{S}^0$  reduced the loss by increasing the acidity of manure, zeolite reduced denitrification, probably by decreasing the availability of  $\text{NH}_4^+$  to nitrification and subsequently to denitrifying organisms.

Addition of animal manure to a soil increased the rate of denitrification in soil and followed: pig >> dairy = horse = sheep > poultry manures = soil. There was no effect of the addition of glucose as a C source on the denitrification loss from soil, suggesting addition of manure to soil increased denitrification mainly through the increase in the amounts of  $\text{NO}_3^-$  concentration in the soil. Increasing levels of poultry manure had no effect on the rate of denitrification probably due to the toxicity of  $\text{NH}_3$  to nitrifiers and denitrifiers. The results of these experiments showed that biological denitrification appears to be one of the major pathways of N loss during composting of poultry manure and in soils with surface application of manures. An attempt was made to estimate the N lost through denitrification during the 12 weeks composting of poultry manure in the earlier experiment (Chapter 4) in which  $\text{NH}_3$  volatilization was examined. The estimated denitrification loss ranged from 31 to  $126 \text{ mg N jar}^{-1}$ , which were much less than the amounts unaccounted for in the mass balance calculations (Table 4.9). It is important, however, to realize that as the different N transformation processes occur simultaneously it may be difficult to quantify the loss of N occur through these processes.

Composting of poultry manure with different amendments reduced the loss of N through both  $\text{NH}_3$  volatilization and denitrification. The  $\text{NH}_3$  conserved in manure releases protons ( $\text{H}^+$ ) during nitrification which can be used for the dissolution of phosphate rock (PR) added to compost. In Chapter 6 the dissolution of PR during composting is discussed.

## CHAPTER 6

### DISSOLUTION OF PHOSPHATE ROCK DURING COMPOSTING OF POULTRY MANURE WITH DIFFERENT AMENDMENTS

#### 6.1 INTRODUCTION

Composting of farm manure and biological waste material with phosphate rock (PR) has been practised widely as a low-input technology to improve the fertilizer value of manure (Seatz *et al.*, 1959; Mishra and Bangar, 1986; Singh and Amberger, 1991). It has been claimed that composting manure with PR enhances the dissolution of PR. Dissolution of PR can be increased by increasing the supply of protons ( $H^+$ ) and by the continuous removal of dissolved products, calcium (Ca) and phosphorus (P), from the zone of dissolution (Kirk and Nye, 1986a) (see Chapter 2, section 2.6.1.1). Various mechanisms have been proposed for the enhancement of PR dissolution during composting.

Firstly, different organic acids produced during the decomposition of manure can supply  $H^+$  and enhance the PR dissolution (Struthers and Sieling, 1950; Mishra and Bangar 1986; Singh and Amberger, 1991). Some organic acids may chelate Ca and thereby provide a sink for the Ca dissolved from PR (Dalton *et al.*, 1952; Sperber, 1958a,b; Chien, 1979).

Secondly, the  $H^+$  generated during the nitrification of ammonium ( $NH_4^+$ ) to nitrate ( $NO_3^-$ ) can increase the dissolution of PR (Chien, 1979; Apthorp *et al.*, 1987). More than 50% of the total nitrogen (N) in fresh poultry manure is in the form of uric acid (refer Table 4.1), which is decomposed rapidly by several aerobic bacteria to form ammonia ( $NH_3$ ) (Eq 2.1 and 2.2). The  $NH_3$  released may undergo volatilization loss and/or dissolve in the manure solution to form  $NH_4^+$  ions (Eq 2.3). Under aerobic conditions  $NH_4^+$  in manure is oxidized to  $NO_3^-$  by a variety of microorganisms. During this process of nitrification two  $H^+$  ions are produced per  $NH_4^+$  ion oxidized (Eq 2.15) which is likely to increase the dissolution of PR during composting (see Chapter 2, section 2.6.2.3).

Thirdly, it has been observed that during composting the concentration of inorganic P in manure solution decreases rapidly mainly due to the microbial immobilization. Very low solution P concentration will enhance the dissolution of PR, depending upon the pH and solution Ca concentration (Kirk and Nye, 1986a).

In most of the studies involving composting of PR with manure, the extent of PR dissolution has not been quantified. The effect of composting on PR dissolution has been inferred indirectly through increases in P extractable in various extractants, such as citric acid, water and  $\text{NaHCO}_3$  (Bangar *et al.*, 1985 and 1989; Mishra and Bangar, 1986; Singh and Yadav, 1986a; Singh and Amberger, 1991).

Changes in extractable P during composting may also result from the mineralization/immobilization of manure derived P. These changes interfere with the measurement of PR dissolution. The interference of native P with PR dissolution measurements may be overcome by the use of radioactive  $^{32}\text{P}$  labelled phosphate rock materials.

## **6.2 OBJECTIVES**

The overall objective of this study was to quantify the dissolution of PR during the composting of poultry manure. Firstly,  $^{32}\text{P}$  labelled synthetic francolite was used to evaluate the methods of measurements of PR dissolution in poultry manure compost. Subsequently, similar method with  $^{31}\text{P}$  was used to quantify the dissolution of North Carolina phosphate rock (NCPR) in poultry manure compost.

## **6.3 MATERIALS AND METHODS**

### **6.3.1 Compost samples**

The preincubated (12 weeks decomposed) poultry manure compost samples from a previous incubation experiment (Chapter 4) were used. The partly decomposed aerobic and anaerobic samples were freeze dried and ground (<2mm) to obtain a homogenised sample. Some characteristics of the compost samples used are given in Table 6.1. For

**Table 6.1 Important characteristics of poultry manure composts (pre-composted for 12 weeks) used in the francolite and NCPR incubations (freeze dried basis)**

**(a) Aerobic composts**

Treatments	pH (H <sub>2</sub> O)	Total N (%)	NH <sub>4</sub> <sup>+</sup> -N (g kg <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> -N (mg kg <sup>-1</sup> )	Total P (%)	C/P ratio	C/N ratio
1. manure (m)	8.9	2.95	14.86	53.23	1.95	21.2	14.0
2. m + woodchip + S°	8.1	3.01	19.73	53.77	1.07	24.8	8.8
3. m + woodchip + zeolite	9.2	1.68	11.41	43.93	0.78	21.7	10.1
4. m + paper waste + S°	7.6	2.97	22.95	42.47	1.04	22.1	7.7
5. m + paper waste + zeolite	9.1	1.52	11.36	29.96	0.72	19.1	9.8

S° = elemental sulphur

**(b) Anaerobic composts**

Treatments	pH (H <sub>2</sub> O)	Total N (%)	NH <sub>4</sub> <sup>+</sup> -N (g kg <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> -N (mg kg <sup>-1</sup> )	Total P (%)	C/P ratio	C/N ratio
1. manure (m)	8.4	4.1	23.13	20.1	1.91	23.8	11.2
2. m + woodchip (wc) + S°	8.1	2.8	14.52	13.0	0.84	36.7	11.0
3. m + woodchip (wc) + zeolite	8.6	2.2	14.98	16.1	0.76	29.8	10.4
4. m + paper waste + S°	8.1	3.1	16.00	13.8	1.21	26.7	10.7
5. m + paper waste + zeolite	8.5	2.0	18.59	17.4	0.62	30.8	9.8

the francolite experiment aerobic composts alone were used, while for the NCPR experiment both aerobic and anaerobic composts were used.

### 6.3.2 Soil extract

Fresh soil extract was used to enhance the nitrification process in the manure compost. About 50g of an unfertilised field-moist surface soil (Ramiha soil, NZ yellow-brown loam to yellow-brown earth intergrade, *Andic Dystrochrepts*) was mixed with 100cm<sup>3</sup> deionised water. After overnight equilibration, the supernatant solution was separated by centrifugation (2000rpm; 10min) and filtration (Whatman No. 42 filter paper).

### 6.3.3 <sup>32</sup>P labelled synthetic francolite

Reactive PR deposits are largely francolitic peloids composed mainly of carbonate fluorapatite. In this study a <sup>32</sup>P labelled synthetic francolite was used to examine the dissolution of PR in compost mixtures. Radioactive tracers have been used extensively to measure P uptake from PR (Murdock and Seay, 1955; Kucey and Bole, 1984). <sup>32</sup>P labelling has been used to measure the dissolution of partially acidulated PR (Harrison and Hedley, 1987).

Labelled (<sup>32</sup>P) PR can be obtained by neutron bombardment of natural PR (Murdock and Seay, 1955). Apart from being expensive, the neutron bombardment breaks some of the chemical bonds in the apatite structure, resulting in the partial processing of the rock (Kucey and Bole, 1984). Hence, in this study a <sup>32</sup>P labelled francolite was synthesized. Its chemical structure was close to that of the naturally occurring carbonate substituted fluorapatites. The specific objective of this experiment was to examine the potential use of radioactive labelled francolite to measure the dissolution of PR in poultry manure compost.

#### 6.3.3.1 Preparation of synthetic francolite

A technique developed by Ressler and Werner (1989) was used to prepare <sup>32</sup>P labelled carbonate fluorapatite (francolite type). The method involves precipitation of calcium

phosphate using  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  solutions in the presence of  $\text{Na}_2\text{CO}_3$  and  $\text{NaF}$  solutions. The precipitate was subsequently heated to various temperatures to obtain a desired solubility.  $^{32}\text{P}$  labelling of the product was achieved by adding a solution containing approximately 74MBq of carrier free  $^{32}\text{P}$  to  $\text{Na}_2\text{CO}_3$  and  $\text{NaF}$  solutions.

### 6.3.3.2 Reagents

#### (1) $\text{NH}_4\text{OH}$ 20% solution

To a 284cm<sup>3</sup> of  $\text{NH}_4\text{OH}$  (specific gravity 0.88; assay 33% w/w) 128cm<sup>3</sup> of deionised water was added. The pH of the solution was 13.5.

#### (2) Solution A

A sample of 61.336g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was dissolved in approximately 180cm<sup>3</sup> of 20%  $\text{NH}_4\text{OH}$  solution with a constant stirring.

#### (3) Solution B

- (a) A sample of 17.857g  $(\text{NH}_4)_2\text{HPO}_4$  was dissolved in 50cm<sup>3</sup> deionised water.
- (b) Samples of 5.3107g  $\text{Na}_2\text{CO}_3$  anhydrous and 2.4414g  $\text{NaF}$  were dissolved each in 75cm<sup>3</sup> deionised water with slight warming. Solutions (a) and (b) were mixed and the pH was adjusted to 10 using 20%  $\text{NH}_4\text{OH}$ .

#### (4) $^{32}\text{P}$ solution

An aqueous solution (13.7cm<sup>3</sup>) containing 74MBq carrier free  $^{32}\text{P}$  was mixed with solution B.

### 6.3.3.3 Synthesis

Solution B was added to solution A and stirred continuously for 2h. After 18h of standing, the calcium phosphate precipitate formed was filtered (Buchner funnel) using filter paper No.5. The precipitate was washed several times with deionised water to remove  $\text{NH}_4\text{NO}_3$ . The precipitate was then transferred into a silica crucible and heated at 100°C for 12h, 200°C for 2h, 400°C for 2h and at 600°C for 90min in a stepwise fashion to obtain the desired solubility. The heat treated francolite sample was ground in a ball mill and sieved through 160µm sieve. The X-ray diffraction pattern of the

synthetic francolite was similar to that of NCPR (Fig 6.1). Some important properties of the synthetic francolite are given in Table 6.2.

**Table 6.2 Important properties of the <sup>32</sup>P labelled synthetic francolite**

Properties	
1. Particle size (µm)	<160
2. Total P (% w/w)	16.1
3. Solubility in 2% citric acid (% total P)	35.2

**6.3.4 Phosphate rock**

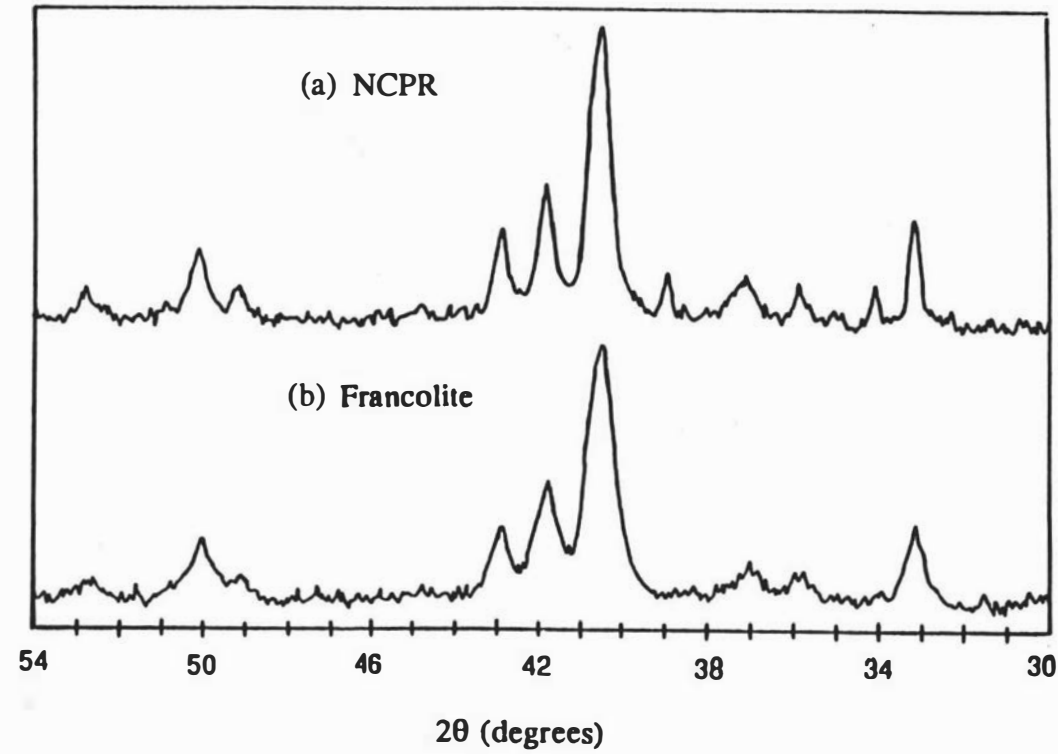
North Carolina phosphate rock (NCPR) with a particle size of 125-175µm was used. Important characteristics of the NCPR are given in Table 6.3.

**Table 6.3 Important properties of NCPR**

Properties	
1. Total P (% wt)	12.8
2. Total Ca (%wt)	34.7
3. Total CaCO <sub>3</sub> (% wt)	11.7
4. Extractable P (% total P w/w)	
Water	<0.01
Formic acid	57.5
Citric acid	30.2
5. Total Fe (%w/w)	0.41
6. Total Al (% w/w)	0.17

**6.3.5 Incubation with <sup>32</sup>P labelled francolite**

Synthetic francolite (labelled PR) was mixed with a 3g sample of 12 weeks predecomposed poultry manure compost (see Fig 6.2), at a rate of 5mg <sup>31</sup>P g<sup>-1</sup> compost (18.23kBq <sup>32</sup>P g<sup>-1</sup>) in a 20cm<sup>3</sup> plastic vial. The sample was moistened to 68% moisture



**Fig 6.1 X-ray diffractograms of powdered materials of (a) NCPR and (b) synthetic francolite**

(w/w) and thoroughly mixed. Approximately  $0.5\text{cm}^3$  of soil extract was added as an inoculum to provide a nitrifier population. Nine replicates of six treatments (see Table 6.1), including an unlabelled control treatment, were prepared giving a total of 54 samples which were randomly placed in a tray.

Three replicates from each treatment were used for initial analysis. The vials were covered with polyethylene sheets containing small pin-sized holes to permit aeration. The compost samples were incubated in an incubator at  $25\text{--}30^\circ\text{C}$  for 60 days. The moisture content was corrected at weekly intervals and maintained throughout the incubation. At the end of 30 and 60 days, 3 replicates from each treatment were removed from the incubator and analyzed for various P fractions. Protective clothing and perspex shields were used in all the operations involving radioactive materials.

#### **6.3.6 Incubation with NCPR**

North Carolina phosphate rock ( $125\text{mg P}$ ) was thoroughly mixed with  $25\text{g}$  poultry manure compost sample in a  $150\text{cm}^3$  plastic urine cup. From this triplicate sample mixtures ( $8\text{g}$  each) were transferred to other urine cups and deionized water was then added to bring the compost mixtures to 68% moisture (w/w). The compost mixture was then inoculated with  $0.5\text{cm}^3$  of soil extract, thoroughly mixed and the urine cups were closed with lids. For the aerobic system, the lid was loosely fitted, while for anaerobic conditions the urine cup lid was tightly closed and kept in a sealed polyethylene bag. The urine cups were then kept in a constant temperature room at  $25^\circ\text{C}$  for 120 days.

#### **6.3.7 Analysis and expression of results**

During the decomposition of manure, the weight loss due to carbon (C) and N release resulted in an increase in the P content. For example, if a  $5\text{g}$  manure sample, containing  $2.7\%$  ( $= 27\text{mg g}^{-1}$ ) total P (freeze dried basis) is allowed to decompose for 12 weeks, approximately  $2\text{g}$  weight may be lost due to C and N release. If expressed as ' $\text{mg g}^{-1}$ ' basis, this will give a final P content of  $4.5\%$  or  $45\text{mg g}^{-1}$  which may mislead the interpretation of results. However, if expressed as ' $\text{mg jar}^{-1}$ ' basis, the final total P content will not be changed. Under the closed incubation system the initial total P

content should equal the final total P content. As this factor is very significant for manure which undergoes rapid decomposition, the results are expressed as total  $^{32}\text{P}$  (kBq) or  $^{31}\text{P}$  (mg) per jar, which takes into account the weight loss of compost during incubation.

#### 6.3.7.1 *Fertilizer analysis*

The total P content of synthetic francolite and NCPR was analyzed by a tri-acid (concentrated  $\text{HNO}_3\text{:HCl:HClO}_4 = 5\text{:}5\text{:}7$ ) digestion (Johnson and Ulrich, 1959). The activity of  $^{32}\text{P}$  in the francolite was measured in the tri-acid digest using the Cerenkov counting method as described in section 6.3.7.4. The solubility of the fertilizer samples was measured by 2% citric acid extraction (Fertilizer Regulation, 1969; AOAC, 1975). The total Ca,  $\text{CaCO}_3$ , Fe and Al were determined by the methods described by O'Connor and Syers (1975) and the solubility in 2% citric and formic acids (OJEC, 1977).

#### 6.3.7.2 *Fractionation of P*

The P in the compost samples was fractionated following a modified method of Tambunan *et al.* (1993). The sequential fractionation procedure uses both acidic and alkaline reagents to extract different fractions of P. About 0.875g moist compost sample (0.35g dry wt basis) was shaken end-over-end with  $35\text{cm}^3$  of 1M NaOH (1:100 solid:solution ratio) for 16h in a  $50\text{cm}^3$  polypropylene centrifuge tube. The tubes were then centrifuged at 8000rpm for 20min and filtered through Whatman No.6 filter paper.

To the residue in the tube,  $35\text{cm}^3$  of 1M HCl was added and shaken for a further 16h period and then centrifuged and filtered (Apthorp *et al.*, 1987). The residue in the tube was carefully transferred to a  $150\text{cm}^3$  conical flask using a jet of water and dried in an oven. Ten  $\text{cm}^3$  of tri-acid ( $\text{HNO}_3 : \text{HCl} : \text{HClO}_4 = 5\text{:}5\text{:}7$ ) was added to the residue. The flask was heated slowly at  $260^\circ\text{C}$  for 45min, and then cooled before adding  $15\text{cm}^3$  of deionised water and again boiled for 2min. The digest was filtered (Whatman No.41) and the residue on the filter paper rinsed several times with water before the volume was made up to  $50\text{cm}^3$ .

The fractions of P in NCPR treated compost samples were analyzed as described above, except that the samples were pre-extracted with 0.5M NaCl plus Triethanolamine (TEA) to remove exchangeable Ca that prevents the formation of  $\text{Ca}(\text{OH})_2$  in the NaOH extracts, which could readsorb P or coprecipitate with extracted inorganic P (Pi) (Tambunan *et al.*, 1993). After pre-extraction with 0.5M NaCl/TEA, the compost sample was sequentially extracted with 1M NaOH followed by 1M HCl.

### 6.3.7.3 $^{31}\text{P}$ measurements

The  $^{31}\text{P}$  in the extract was measured according to the method of Murphy and Riley (1962). The total P in the NaOH extract was measured by digesting a sample ( $10\text{cm}^3$ ) of the extract with  $10\text{cm}^3$  of triacid. The organic P (Po) in the extract was calculated as the difference between total P and the Pi in NaOH (Bolan and Hedley, 1989).

### 6.3.7.4 $^{32}\text{P}$ measurements

The activity of  $^{32}\text{P}$  in various extracts was measured using Cerenkov system in a Beckman LS 3801 liquid scintillation counter. To measure the counting efficiency each sample solution was spiked with  $0.1\text{cm}^3$  of internal standard (carrier free  $^{32}\text{P}$  solution) recounted and an efficiency factor was estimated. All measurements of  $^{32}\text{P}$  activity were normalised for decay to a common date using a half-life of 14.29 for  $^{32}\text{P}$  according to the following equation:

$$A = A_0 \exp^{-kt} \tag{6.1}$$

where,

A	=	$^{32}\text{P}$ activity (Becquerels) remaining after time interval 't'
$A_0$	=	$^{32}\text{P}$ activity (Becquerels) present at time zero
t	=	Time interval elapsed since zero time (days)
k	=	Rate constant (0.693/14.29)

The percentage of P derived from francolite (%PdfF) extracted in NaOH and HCl was calculated as follows:

$$\%PdfF = (^{32}P_f / ^{32}P_a) * 100 \quad (6.2)$$

where,

$$\begin{aligned} ^{32}P_f &= \text{Activity of } ^{32}\text{P extracted in NaOH or HCl (kBq) per jar} \\ ^{32}P_a &= \text{Total activity of } ^{32}\text{P added as francolite (kBq) per jar} \end{aligned}$$

The absolute amount of PdfF extracted in NaOH (or HCl) was calculated as follows:

$$PdfF \text{ (mg)} = \%PdfF * (^{31}P_{fa}) \quad (6.3)$$

where,

$$^{31}P_{fa} = \text{The amount of } ^{31}\text{P added through francolite (mg jar}^{-1}\text{)}$$

The amount of  $^{31}\text{P}$  derived from poultry manure (PdfM) extracted in NaOH was calculated as follows:

$$PdfM \text{ (mg jar}^{-1}\text{)} = TP_{NaOH} - PdfF \quad (6.4)$$

where,

$$\begin{aligned} PdfF &= \text{(mg jar}^{-1}\text{)} \\ TP_{NaOH} &= \text{Total P in NaOH (mg jar}^{-1}\text{)} \end{aligned}$$

The amount of NaOH extractable P derived from francolite, expressed as a percentage of the total NaOH P (%PdfNaOH), was calculated from the amount of PdfF using the following equation:

$$\%PdfNaOH = (PdfF / TP_{NaOH}) * 100 \quad (6.5)$$

where,

$$\begin{aligned} PdfF &= \text{(mg jar}^{-1}\text{)} \\ TP_{NaOH} &= \text{Total P in NaOH (mg jar}^{-1}\text{)} \end{aligned}$$

### 6.3.8 Dissolution of PR

In soil systems the increase in NaOH extractable inorganic P (NaOH-Pi) in PR treated soil over the control soil provides a good estimate of the amount of P dissolved and retained by soil (Mackay *et al.*, 1986). As NaOH is an effective extractant of sorbed inorganic P (Williams *et al.*, 1967) it has been accepted as a good measure of PR dissolution in incubated soils. But, in organic manure where immobilization of dissolved P is likely to occur, this method is unsuitable. However, the measurement of total  $^{32}\text{P}$  extracted in NaOH may give a better measure of dissolution as it may include recently immobilized  $^{32}\text{Po}$ . The extent of dissolution of  $^{32}\text{P}$  labelled francolite was measured from the increase in the activity of  $^{32}\text{P}$  in NaOH (Eq 6.6):

$$\%DF = ([^{32}\text{P}_t - ^{32}\text{P}_0] / ^{32}\text{P}_a) * 100 \quad (6.6)$$

where,

- $\%DF$  = Dissolution of francolite (%)
- $^{32}\text{P}_t$  = Activity of  $^{32}\text{P}$  measured in NaOH at time 't'(kBq jar<sup>-1</sup>)
- $^{32}\text{P}_0$  = Activity of  $^{32}\text{P}$  measured in NaOH at time 'zero'(kBq jar<sup>-1</sup>)
- $^{32}\text{P}_a$  = Total activity of  $^{32}\text{P}$  added (kBq jar<sup>-1</sup>)

The dissolution of NCPR was measured by the increases in the soluble plus adsorbed P (Eq 6.7):

$$\%DPR = ([P_{fr} - P_{fc}] / P_a) * 100 \quad (6.7)$$

where,

- $\%DPR$  = Dissolution of NCPR (%)
- $P_{fr}$  = Increase in P extracted in NaCl/TEA + total P in NaOH for NCPR treated compost during 120 days incubation (mg jar<sup>-1</sup>)
- $P_{fc}$  = Increase in P extracted in NaCl/TEA + total P in NaOH for compost alone (control) during 120 days incubation (mg jar<sup>-1</sup>)
- $P_a$  = NCPR-P added (mg jar<sup>-1</sup>)

### 6.3.9 Measurement of pH and mineral N

The pH and the mineral N content ( $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$ ) in compost samples were determined as described in Chapter 4, sections 4.3.4.2 and 4.3.4.6.

### 6.3.10 Statistical analysis

The treatment means were analyzed by analysis of variance using a SAS package (SAS, 1985).

## 6.4 RESULTS AND DISCUSSION

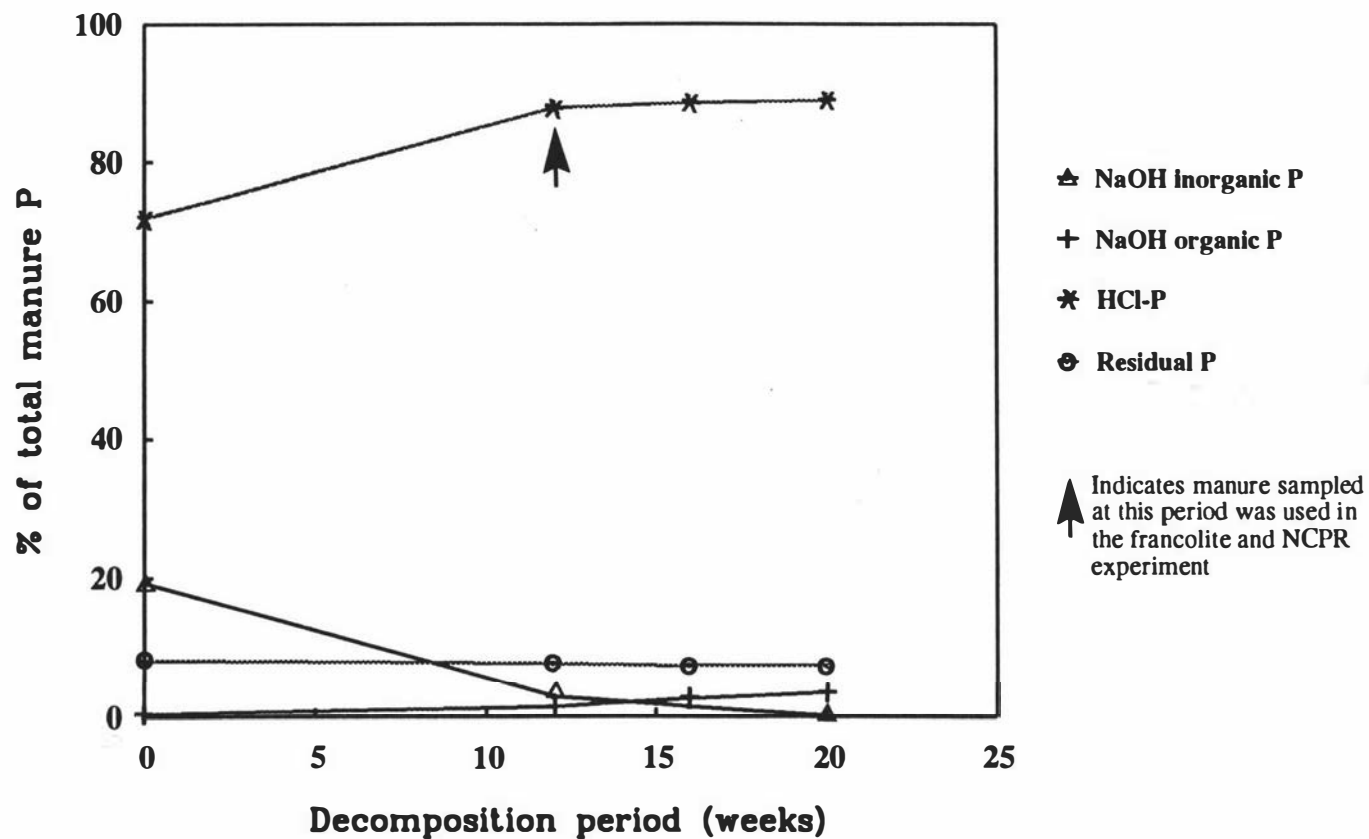
### 6.4.1 Characteristics of compost samples

The  $\text{pH}_{\text{water}}$  of different composts used in the francolite and NCPR incubations ranged from 7.6 to 9.2 for aerobic composts, and 8.1 to 8.6 for anaerobic composts (Table 6.1). The  $\text{S}^\circ$  compost had a lower pH and higher N contents compared to the compost containing zeolite. The C/N and C/P ratio of composts ranged from 7.7 to 14.0 and from 19.1 to 24.8, respectively. The anaerobic composts had relatively higher C/P ratios than aerobic composts.

### 6.4.2 Transformation of P in poultry manure

The amount of P extracted by various extractants during the decomposition of poultry manure are presented in Figure 6.2. Fresh poultry manure contained large amounts of P (2.7% P, freeze dried basis), which was due to poultry feed containing high phosphate. Approximately 20% of total manure P was NaOH extractable (NaOH-P), of which 98% was in inorganic form (NaOH-Pi, solution plus adsorbed P) and about 2% in organic form (NaOH-Po). Approximately 72% of total manure P was acid extractable P (HCl-P). Similar values were reported by Peperzak *et al.* (1959) for poultry manure.

During the decomposition of manure, the NaOH-Pi decreased rapidly at first followed by a gradual decrease (Fig 6.2). This was mostly due to physico-chemical



**Fig 6.2** Changes in the forms of phosphorus (P) during the decomposition of poultry manure

immobilization of P (adsorption, precipitation) into acid soluble forms. A small increase in NaOH-Po during the course of decomposition indicates a small amount of microbial immobilization of P. In addition, after 20 weeks NaOH-Pi decreased to 9% of NaOH total P (solution plus adsorbed P), while the proportion of NaOH-Po increased to >90% of NaOH extractable total P. Both results are in accordance with the result of Gerritse and Zugec (1977) who reported large microbial immobilization of inorganic P in pig slurry within 10 to 20 weeks. In the present study, the increase in NaOH-Po was small and did not account for the decrease in NaOH-Pi.

Acid extractable P in manure continued to increase during decomposition as NaOH-Pi decreased. This probably suggests that physico-chemical immobilization of Pi has occurred. However, 1M HCl may extract a portion of microbially immobilized Po. According to Fordham and Schwertmann (1977a,b), precipitation of inorganic phosphate, particularly struvite ( $\text{NH}_4\cdot\text{MgPO}_4\cdot 6\text{H}_2\text{O}$ ), a mineral species generally found in poultry manure, was largely responsible for the decrease in phosphate from manure solution during storage.

Microbially immobilized P is more likely to be extracted as NaOH-Po. Strong alkaline reagents (NaOH) have generally been used to extract most of the Po in soil (Halstead and Anderson, 1970; Anderson and Malcolm, 1974). Hedley (1978) has shown that in systems where there is a rapid microbial immobilization, NaOH extracted 50-80 % of the Po.

A complication may exist with fractionating P in Ca rich media like poultry manure. In soils containing large amounts of solution Ca, it has been suggested that extraction with NaOH results in the formation of  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$  precipitate during extraction, which may adsorb or coprecipitate the dissolved P (Bolan and Hedley, 1989). The adsorbed/coprecipitated P is removed during the subsequent extraction with HCl.

It is possible that part of the increase in the HCl-Pi fraction is caused by this phenomena. However, because the chemical fractionation procedure remained constant while HCl-Pi increased with incubation time, the results most probably indicate an increase in an acid soluble P form caused by reactions in the manure and not in the

extract. To overcome this potential problem in the P fractionation, a pre-extraction with NaCl/TEA (Tambunan *et al.*, 1993) has been introduced for fractionating the samples composted with NCPR (section 6.3.7.2).

Phosphorus not extracted either in alkali or acid (residual-P) formed only 8% of total manure P which remained unchanged during the decomposition of the poultry manure (Fig 6.2).

The large amount of HCl-P in manure samples, together with its increasing trend during decomposition, makes it difficult to measure accurately any change in HCl-P due to the dissolution of PR during composting. This problem can partly be overcome by using  $^{32}\text{P}$  labelled francolite to quantify the dissolution of PR.

### **6.4.3 Experiment with $^{32}\text{P}$ labelled francolite**

#### **6.4.3.1 Transformation of $^{32}\text{P}$**

Compost withdrawn from the main experiment (Chapter 4) after 12 weeks decomposition was mixed (zero time for this experiment) and incubated with  $^{32}\text{P}$  labelled francolite (refer Fig 6.2). At time zero, only a small fraction of the added  $^{32}\text{P}$  (0.33-0.39%) was extracted in NaOH (Table 6.4). Using a synthetic apatite Cano and Talibudeen (1957) have shown that <1% of the total P in apatite is in exchangeable form (surface P) which is extracted in NaOH.

During incubation the activity of  $^{32}\text{P}$  extracted by 1M NaOH and the estimate of per cent P derived from francolite (%PdfF) increased with time (Table 6.4). This indicates the probable dissolution of labelled francolite. In manure alone samples the physico-chemical reactions that increased HCl-Pi may have continued from 12 weeks (zero time for this experiment) period (Fig 6.2). Therefore, the fate of dissolved  $^{32}\text{P}$  is likely to be similar to that of manure P. Some dissolved  $^{32}\text{P}$  may have been reprecipitated as HCl-Pi in the manure.

Addition of amendments had a significant effect on NaOH- $^{32}\text{P}$  activity. The activity was

**Table 6.4  $^{32}\text{P}$  activities in 1M NaOH fraction at different periods (days) of incubation**

Francolite plus treatment	$^{32}\text{P}$ activities in 1M NaOH (kBq jar <sup>-1</sup> )			% PdfF		
	0	30	60	0	30	60
1. manure (m)	0.21	5.75	8.86	0.38	10.52	16.20
2. m + woodchip + S°	0.20	8.66	10.92	0.37	15.83	19.96
3. m + woodchip + zeolite	0.18	7.28	6.84	0.33	13.64	12.50
4. m + paper waste + S°	0.20	5.23	10.16	0.37	9.93	18.57
5. m + paper waste + zeolite	0.21	4.29	3.77	0.39	8.23	6.88

**LSD (0.05)**

Treatments	0.49**	0.90**
Days	0.38**	0.70**
Treatments * Days	0.86**	1.56**

higher with S° compost both in the presence of woodchip (10.9kBq) and paper waste (10.2kBq) than other composts. Zeolite composts had low activities. The data on %PdfF indicates that only between 7 and 20% of the added  $^{32}\text{P}$  has been transformed into NaOH extractable form.

At time zero approximately 97 to 111% of added  $^{32}\text{P}$  was recovered in HCl. Consistent with  $^{32}\text{P}$  in NaOH, the activity of  $^{32}\text{P}$  in HCl decreased by 7 to 20% during incubation and showed a significant variation between different composts (Table 6.5). The decrease in the activity of HCl- $^{32}\text{P}$  further confirms the dissolution of francolite.

The activity of  $^{32}\text{P}$  not extracted either in alkali or acid varied from 1.7 to 6.9% of added francolite between compost samples, but there was not much change during incubation, except a slight increase at 60 days (Table 6.6).

#### 6.4.3.2 *Transformation of $^{31}\text{P}$ in francolite/composts mixtures*

Initially the NaOH-Pi was high in all the treatments due to P derived from poultry manure, which decreased during decomposition (0 to 30 days, Table 6.7). The changes in the concentration of different fractions of  $^{31}\text{P}$  with incubation showed different trends to those of  $^{32}\text{P}$  activity. This is expected because labelled PR is the only source of  $^{32}\text{P}$ , whereas both PR and manure form the source of  $^{31}\text{P}$ .

Irrespective of treatments, the Pi extracted in the NaOH extract continues to decrease with time (Table 6.7) which is consistent with trends in manure Pi as shown in Figure 6.2. Similar results were reported by Singh *et al.* (1983) and Singh and Amberger (1991).

Explanation for the decrease in Pi were discussed in section 6.4.2. Brown and Warner (1917) reported a very significant decrease in the plant available P during six weeks decomposition of manure, and attributed this to the assimilation of P by microorganisms in the early stage of decomposition. But, according to Blair and Boland (1978) and White and Ayoub (1983), the decrease in available P during early stages of decomposition of green manure in soil was due to physico-chemical immobilization of

Table 6.5 <sup>32</sup>P activities in 1M HCl fraction at different periods (days) of incubation

Francolite plus treatment	<sup>32</sup> P activities in 1M HCl (kBq jar <sup>-1</sup> )			% PdfF		
	0	30	60	0	30	60
1. manure (m)	54.2	48.7	44.1	99.0	89.0	80.7
2. m + woodchip + S°	60.7	51.5	49.3	110.9	94.2	90.2
3. m + woodchip + zeolite	60.8	53.4	53.2	111.1	97.5	97.3
4. m + paper waste + S°	52.8	47.84	41.4	96.5	87.5	75.7
5. m + paper waste + zeolite	53.5	50.2	49.8	97.8	91.8	91.0

LSD (0.05)

Treatments	4.47**	8.18**
Days	3.46**	6.34**
Treatments * Days	7.75*	14.17*

**Table 6.6  $^{32}\text{P}$  activities in residue fraction (after NaOH and HCl extractions) at different periods (days) of incubation**

Francolite plus treatment	Residual $^{32}\text{P}$ activities (kBq jar $^{-1}$ )			% PdfF		
	0	30	60	0	30	60
1. manure (m)	2.38	2.30	3.76	4.4	4.2	6.9
2. m + woodchip + S $^{\circ}$	2.27	2.97	2.91	4.2	5.4	5.3
3. m + woodchip + zeolite	1.21	1.36	2.13	2.2	2.5	3.9
4. m + paper waste + S $^{\circ}$	1.90	1.60	3.31	3.5	2.9	6.0
5. m + paper waste + zeolite	1.93	0.92	2.08	3.5	1.7	3.8

**LSD (0.05)**

Treatments	0.33**	0.59**
Days	0.25**	0.46**
Treatments * Days	0.57**	1.04**

**Table 6.7 Changes in  $^{31}\text{P}$  fractions (as % of total manure P) at different periods (days) of incubation**

**(a) Day 0**

Francolite plus treatments	NaOH extractable P		HCl-P	Residual P
	Pi	Po		
1. manure (m)	3.64	0.73	89.50	6.17
2. m + woodchip + S°	3.04	1.93	87.29	7.72
3. m + woodchip + zeolite	3.20	0.78	88.45	7.56
4. m + paper waste + S°	1.40	1.49	90.62	6.49
5. m + paper waste + zeolite	2.48	2.01	86.02	9.48
6. manure alone (unlabelled)	2.96	1.52	87.85	7.67
LSD (0.05)	0.39**	0.79*	1.51**	0.74**

**(b) Day 30**

Francolite plus treatments	NaOH extractable total P		HCl-P	Residual P
	Pi	Po		
1. manure (m)	1.56	1.03	93.06	4.35
2. m + woodchip + S°	2.25	0.52	92.87	4.36
3. m + woodchip + zeolite	2.04	0.71	94.82	2.44
4. m + paper waste + S°	1.63	0.52	93.62	4.23
5. m + paper waste + zeolite	1.93	0.41	94.77	2.89
6. manure alone (unlabelled)	1.54	2.61	88.48	7.36
LSD (0.05)	0.36**	0.44**	1.52**	1.56**

**(c) Day 60**

Francolite plus treatments	NaOH extractable P		HCl-P	Residual P
	Pi	Po		
1. manure (m)	0.98	1.55	91.12	6.35
2. m + woodchip + S°	1.35	1.60	91.17	5.89
3. m + woodchip + zeolite	0.96	1.52	95.18	2.34
4. m + paper waste + S°	0.85	1.19	94.68	3.28
5. m + paper waste + zeolite	0.81	1.28	96.03	1.90
6. manure alone (unlabelled)	0.35	0.71	92.90	6.03
LSD (0.05)	0.11**	0.44*	2.55**	2.40**

P. Increases in the HCl-Pi fraction in this experiment also support these latter observations. Bangar *et al.* (1985, 1989) also observed a decrease in water soluble P content during composting farm manure with PR, and related this to the reaction of soluble P with PR compounds.

The NaOH-Po also decreased initially, probably due to remobilization, but increased slightly at 60 days due to microbial immobilization transforming approximately 0.5% of total manure P (Table 6.7).

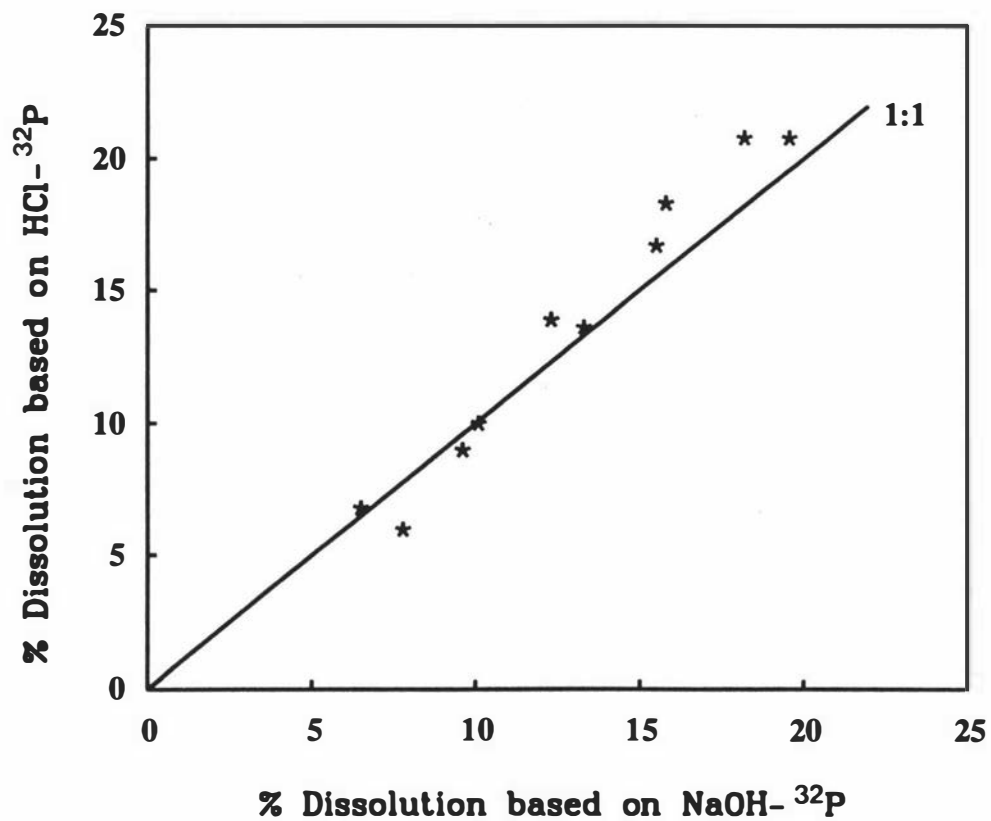
The per cent of HCl extractable  $^{31}\text{P}$  increased during incubation and varied significantly between the composts (Table 6.7). As already mentioned this suggests that part of the P dissolved from francolite or manure P may have been chemically precipitated or HCl may have extracted large portions of Po. Ames and Richmond (1917) and Bangar *et al.* (1985) have shown results of increase in acid soluble (HCl) or apatite P due to a transformation of organic to inorganic P during decomposition.

The residual  $^{31}\text{P}$  showed a similar trend to that of residual  $^{32}\text{P}$  (Table 6.6), but there was no significant change during incubation.

#### 6.4.3.3 *Dissolution of $^{32}\text{P}$ labelled francolite*

The dissolution of labelled francolite was measured both from increase in the activity of  $^{32}\text{P}$  in NaOH ( $\Delta\text{NaOH-}^{32}\text{P}$ ) and a decrease in the activity of  $^{32}\text{P}$  in HCl ( $\Delta\text{HCl-}^{32}\text{P}$ ) according to equation 6.6. A very close relationship was obtained between these two methods (Fig 6.3).

In the presence of physico-chemical precipitation of P in the francolite-compost mixtures it is likely that some of the dissolved  $^{32}\text{P}$  (labile form) extractable in NaOH may be in isotopic equilibrium with relatively stable form of HCl- $^{32}\text{P}$ . Therefore, the method of measuring francolite dissolution based on  $\Delta\text{NaOH-}^{32}\text{P}$  is likely to reflect net dissolution of francolite. Absolute francolite dissolution cannot be measured if  $^{32}\text{P}$  is reprecipitated and extracted as a secondary acid soluble (HCl) P fraction.



**Fig 6.3 Relationship between dissolution of francolite based on increase in NaOH-<sup>32</sup>P and decrease in HCl<sup>32</sup>P**

The calculated amount of P in NaOH derived from manure (PdfM) was high initially (Table 6.8), but decreased with time, as explained in section 6.4.2. The NaOH-P derived from francolite expressed as per cent NaOH P (%PdfNaOH) increased progressively with time due to the release of P from the dissolution of francolite. With time, most of the P extracted in NaOH in the francolite treated compost originated mainly from francolite dissolution.

The net dissolution of francolite based on  $\Delta\text{NaOH-}^{32}\text{P}$  increased with time (Fig 6.4). Except for S° plus paper waste compost, the initial (up to 30 days) dissolution was rapid, after which only a small increase was observed. There was slightly less dissolution with zeolite compost which did not increase from 30 to 60 days. In general, only about 7.8 to 19.6% of added  $^{32}\text{P}$  in francolite was found to be dissolved in compost over 60 days.

Dissolution of PR in manure compost is achieved through various processes. The organic acids produced during the decomposition may be implicated in the dissolution of francolite (Sperber, 1958a,b; Alexander, 1967; Bangar *et al.*, 1985; Singh and Amberger, 1991). Substances like humic acid, produced during the decomposition, could solubilize PR, possibly by chelating  $\text{Ca}^{2+}$  (Sperber, 1958a,b; Chien, 1979; Mishra *et al.*, 1984). Further,  $\text{CO}_2$  produced during decomposition of organic matter dissolves in manure water, forming carbonic acid which may also dissolve PR partially (Dalton *et al.*, 1952; Singh and Amberger, 1991). Protons ( $\text{H}^+$ ) generated during nitrification in compost also may contribute to dissolution, which will be discussed later in this Chapter.

In general, very low levels of PR dissolution were observed during composting of poultry manure. Various reasons could be attributed for the low levels of PR dissolution.

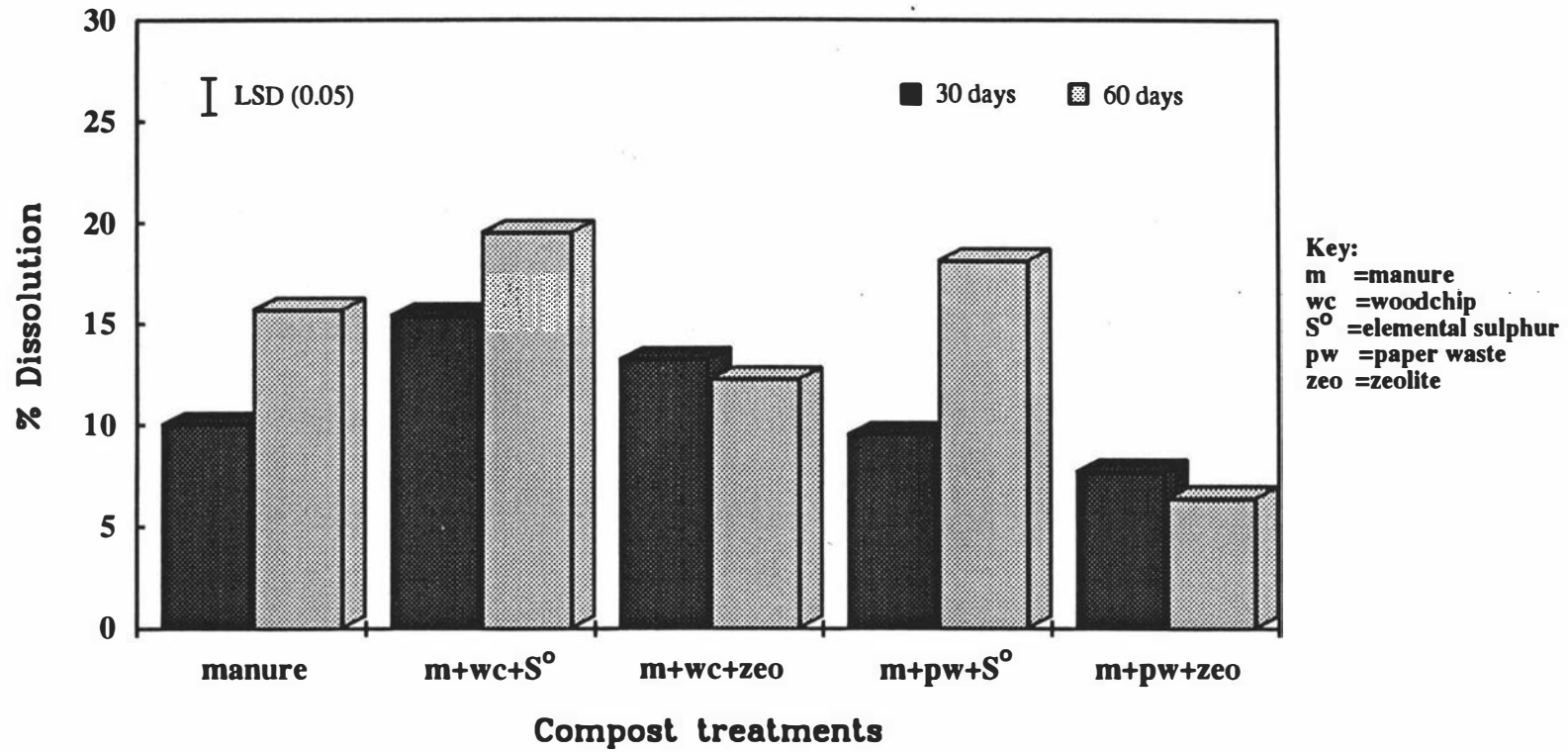
One important factor which may be responsible for the low dissolution is the high initial concentration of P and  $\text{Ca}^{2+}$  in manure solution. Further, the concentration of P and Ca in manure solution increases during the decomposition. This is likely to reduce the size of sink for removal of  $\text{H}_2\text{PO}_4^-$  and  $\text{Ca}^{2+}$  ions released during the dissolution of francolite, and may affect the solubility.

**Table 6.8 Absolute amount of PdfF and %PdfNaOH calculated for different periods (days) of incubation**

Francolite plus treatment	Absolute amount of PdfF (mg jar <sup>-1</sup> )			PdfM (mg jar <sup>-1</sup> )			%PdfNaOH		
	0	30	60	0	30	60	0	30	60
1. manure (m)	0.06	1.58	2.43	3.68	0.94	0.16	1.5	62.8	94.4
2. m + woodchip + S°	0.05	2.38	2.99	3.68	-0.30	-0.78	1.5	114.3	135.7
3. m + woodchip + zeolite	0.05	2.05	1.88	2.44	-0.33	-0.32	2.0	122.6	122.2
4. m + paper waste + S°	0.06	1.49	2.79	1.78	-0.11	-1.26	3.0	108.2	186.0
5. m + paper waste + zeolite	0.06	1.24	1.03	2.15	-0.09	0.01	2.8	108.3	103.6

**LSD (0.05)**

Treatments	0.21**	0.33**	19.5**
Days	0.17**	0.25**	15.12**
Treatments * Days	0.37**	0.57**	33.8**



**Fig 6.4** Dissolution of  $^{32}\text{P}$  labelled francolite during incubation with poultry manure composts

The presence of high levels of  $\text{Ca}^{2+}$  has been shown to inhibit the dissolution of PR in the soil (Mackay and Syers, 1986; Khasawneh and Doll, 1978). Wilson and Ellis (1984), Mackay and Syers (1986), and Robinson and Syers (1990) also suggested that the  $\text{Ca}^{2+}$  ion activity in soil solution may be an important factor controlling the rate and extent of dissolution of PR.

In closed incubation systems, it has often been shown that PR dissolution reached an equilibrium within a short time (Syers and Mackay, 1986; Kanabo and Gilkes, 1987), which is attributed to the limited size of sinks for the dissolution products,  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$ . To confirm the equilibration it was decided to incubate the NCPR treated compost for a longer period (120 days).

Poultry manure also contains large amounts of  $\text{CaCO}_3$  (Bril and Salomons, 1990). It is likely that any organic acids produced during composting may have been neutralised by  $\text{CaCO}_3$ , limiting the availability of acids for PR dissolution (Sperber, 1958a). The presence of  $\text{CaCO}_3$  has been shown to inhibit the dissolution of PR in soil (Mackay *et al.*, 1984; Bolan and Hedley, 1989) due to both a Ca-common ion effect and an increase in pH caused by carbonate dissolution.

The high pH in the manure, due to ammonification and aerobic degradation of volatile fatty acids and other organic compounds, also plays a crucial role in the precipitation and dissolution processes (Japenga and Harmsen, 1990). Indirectly, the pH also influences the concentration of organic acid anions with chelating properties in the manure solution, and the concentrations of Ca and P.

#### 6.4.3.4 *Effect of amendments on francolite dissolution*

The effect of different composts on the net dissolution of francolite during incubation is shown in Figure 6.4. Significantly high dissolution was obtained with  $\text{S}^0$  both in the presence of woodchip (19.6%) and paper waste (18.2%), followed by manure alone treatment (15.8%). The high dissolution with  $\text{S}^0$  compost is possibly due to the acidity produced. As the  $\text{S}^0$  is oxidized to  $\text{H}_2\text{SO}_4$  by *Thiobacillus spp.* there is a parallel increase in acidity (Alexander, 1967) in the compost. This would enhance the

dissolution of labelled francolite. Similar results with NCPR experiment also confirm this, as is discussed later in section 6.4.4.2.

Less dissolution was obtained with zeolite compost. This could be attributed to (i) the restricted supply of  $H^+$  at high pH; (ii) the  $H^+$  produced should have been neutralized by the high  $CaCO_3$  content of zeolite, and (iii) adsorption of  $NH_4^+$  by zeolite may have restricted nitrification.

#### 6.4.4 Experiment with NCPR

##### 6.4.4.1 *Changes in Pi and Po during 120 days incubation with NCPR*

Irrespective of compost, the amount of Pi (extracted in NaCl/TEA and NaOH) and Po (extracted in NaOH) markedly increased during 120 days incubation both under aerobic and anaerobic conditions (Table 6.9). The net increase was more pronounced under aerobic than anaerobic conditions. At first this result seems to contradict earlier observations with  $^{32}P$  labelled francolite, where the  $^{31}P$  content decreased with time, which is probably due to physico-chemical precipitation. It should be noted that the physico-chemical precipitation which increased HCl-Pi mostly completes after 12 weeks incubation (Fig 6.2). As 12-week-old compost was incubated with NCPR, it is likely that most of the Pi (dissolved from both manure P and NCPR) was not precipitated and remained alkali extractable.

The prolonged incubation (120 days) facilitates further dissolution of P which should have exceeded the rate of immobilization (physico-chemical or microbial). Similar results were reported with composting paddy straw and PR (Mathur *et al.*, 1986; Singh and Yadav, 1986b), and composting cattle urine/straw with PR (Singh and Amberger, 1991).

The amounts of NaOH-Pi and Po were higher with manure alone compost and  $S^o$  compost, both under aerobic and anaerobic conditions. Lower values were observed with zeolite compost. The increased amount of Po indicates that approximately 23% (for manure+PR) to 26% (for manure alone) of net Pi ( $\Delta Pi$ ) had been microbially

**Table 6.9 Changes in the inorganic and organic P content of poultry manure composts during 120 days aerobic and anaerobic incubation with NCPR**

NCPR plus treatment	Aerobic (mg jar <sup>-1</sup> )				Anaerobic (mg jar <sup>-1</sup> )			
	Inorganic P		Organic P		Inorganic P		Organic P	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
1. manure (m)	4.56	27.57	0.85	7.69	16.80	24.57	1.26	4.99
2. m + woodchip + S°	5.66	27.11	2.29	5.65	7.15	17.14	1.36	2.12
3. m + woodchip + zeolite	5.28	9.41	0.46	3.19	10.04	11.89	2.10	2.34
4. m + paper waste + S°	1.34	24.86	2.02	7.87	7.13	16.57	1.08	2.20
5. m + paper waste + zeolite	1.95	9.99	1.19	2.83	7.32	10.98	0.86	2.58
6. manure alone (absolute control)	6.61	20.44	0.97	5.89	16.97	22.71	0.43	4.18
LSD (0.05)	0.29**	2.86**	0.80**	2.34**	1.28**	3.08**	NS	NS

immobilised into Po under aerobic conditions, whereas the increase ranged from 37% (for manure+PR) to 41% (for manure alone) under anaerobic conditions.

Higher rates of microbial immobilization were recorded both under aerobic and anaerobic conditions for manure alone plus PR treatment, probably due to relatively higher content of soluble C available for microorganisms. As the P demand for microbes is increased during decomposition, due to increase in the microbial activity soluble inorganic P is immobilized into Po (Alexander, 1967; Singh and Singh, 1986).

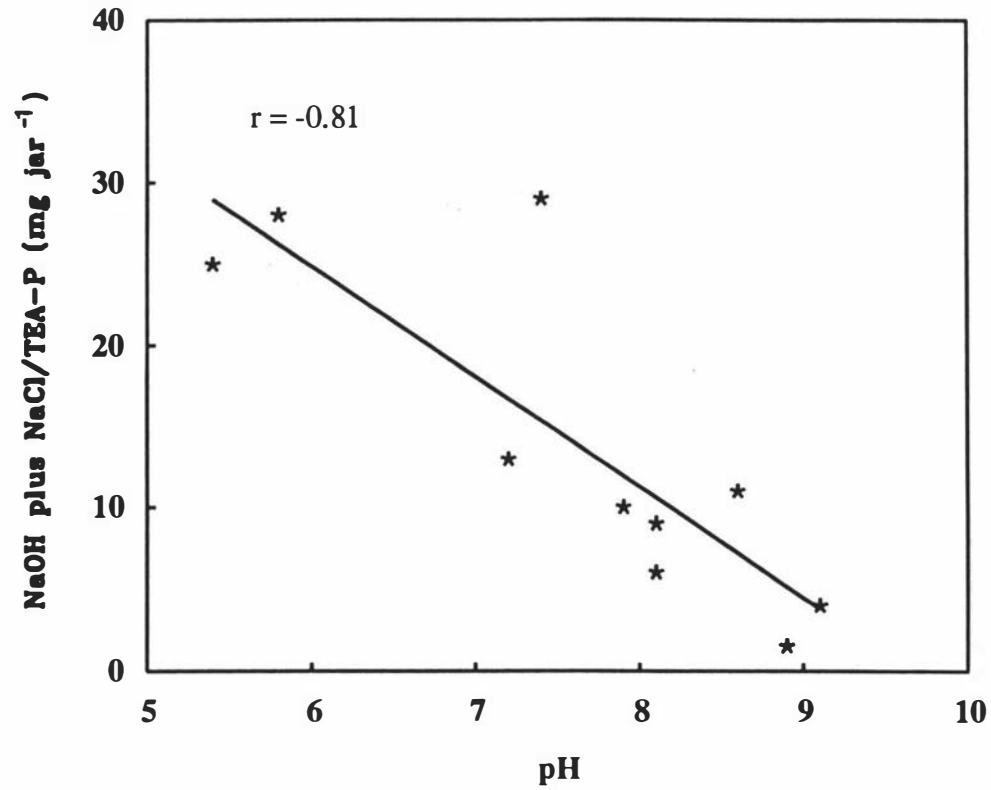
#### 6.4.4.2 *Dissolution of NCPR*

As discussed earlier, the high amount of HCl-Pi in the poultry manure sample and its increase with incubation due to physico-chemical precipitation of Pi makes it difficult to measure any changes in HCl-P due to NCPR dissolution. However, the P extracted by NaOH in manure decreases with time due to immobilization reaction which completes after 12 weeks of decomposition, the NaOH-P fraction becomes small and therefore, it is possible to measure increases in this fraction due to the dissolution of PR.

A significant negative correlation (Fig 6.5) was observed between the pH of different composts and the amount of Pi (NaOH plus NaCl/TEA-P) measured after 120 days. The increases in Pi, with a decrease in pH, probably results from both the dissolution of acid soluble manure (HCl) P and from the dissolution of NCPR.

In poultry and animal manures several P components such as struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ), trimagnesium phosphate ( $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), octacalcium phosphate ( $\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 3\text{H}_2\text{O}$ ), dicalcium phosphate ( $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ) have been identified in the solid phase (Fordham and Schwertmann, 1977a,b,c; Bril and Salomons, 1990). In spite of its strong buffering action, the mineral struvite in manure dissolves at a pH range of 8.9 to 7.0 (Fordham and Schwertmann, 1977b) and could have contributed to the increase in NaOH-Pi with decreased pH in the composts.

The relationship between the pH and the increase in Pi (Fig 6.5) shows the effect of different amendments. Since the pH of the manure alone and manure alone plus NCPR



**Fig 6.5 Relationship between pH and increase in NaOH plus NaCl/TEA extractable P in poultry manure composts after 120 days incubation with NCPR**

was not significantly different, it was assumed that the transformation of manure P both in the presence and absence of NCPR is essentially same.

The net dissolution of NCPR was calculated only for manure alone plus NCPR treatment, from the increases in the amount of P extracted by NaCl/TEA plus NaOH extractable  $P_i$  and  $P_o$  (Eq 6.7). Manure composted alone was used as a control for manure plus NCPR samples. In the manure alone plus NCPR compost the net dissolution was found to be significantly higher under aerobic (27.5%) than anaerobic (6.6%) conditions. This observation closely agrees with that of  $^{32}P$  results, where about 16% dissolution of francolite was recorded in the same treatment during 60 days of aerobic incubation.

Since appropriate control for other treatments have not been included in this experiment, it is not possible to show the effect of different amendments on NCPR dissolution. However, as the method based on  $\Delta P_i$  (NaOH plus NaCl/TEA- $P_i$ ) appears to give a good estimate of NCPR dissolution, the effect of different amendments on the increase in  $P_i$  with time may throw some light on their effect on NCPR dissolution.

The addition of  $S^o$  appreciably increased the amount of  $P_i$ , mainly through increasing the acidity of compost. A marked reduction in pH (from 8.1 to 5.4 and 7.7 to 5.8, with woodchip and paper waste, respectively) was observed with the  $S^o$  compost. This may be one of the reasons for higher amount of  $P_i$  under aerobic conditions. Under anaerobic conditions, the oxidation of  $S^o$  was negligible (due to restricted oxygen supply), but there was no significant effect of  $S^o$  addition on  $P_i$  increase.

This result suggests that only by increasing the acidity of poultry manure compost, can the amount of soluble  $P_i$  be increased. This occurs through the dissolution of both manure and PR-P. The addition of  $S^o$ , a cheap source for acidity, to compost is therefore found to be effective in achieving this.

#### 6.4.5 N transformation

The changes in  $NH_4^+$ -N and  $NO_3^-$ -N contents of compost during 60 days incubation are

given in Table 6.10 and 6.11. In general, irrespective of compost, the  $\text{NH}_4^+\text{-N}$  decreased at 30 days and thereafter slightly increased. The decrease in  $\text{NH}_4^+\text{-N}$  at 30 days might be due to volatilization loss of  $\text{NH}_3$ , nitrification and microbial immobilization of  $\text{NH}_4^+$  ions. At a later period continuous mineralization of organic N from manure increased the  $\text{NH}_4^+\text{-N}$  content. Initially (30 days) the  $\text{NO}_3^-\text{-N}$  content of the compost decreased due to denitrification (see Chapter 5) which exceeded nitrification, but increased due to the activation of nitrifiers after longer periods of incubation (Table 6.11).

#### 6.4.6 N transformation and dissolution of PR

Based on the  $\Delta\text{NH}_4^+\text{-N}$  contents (initial - final), the amounts of  $\text{H}^+$  generated during the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  were calculated, assuming 2moles of  $\text{H}^+$  are produced per mole of  $\text{NH}_4^+$  oxidized (Eq 2.15). As  $\text{NH}_4^+$  is subjected to volatilization loss, it was assumed only 50% of  $\Delta\text{NH}_4^+$  were involved in nitrification process. The result showed that more than 86% of PR-P added at the rate of  $5\text{mg g}^{-1}$  could be dissolved if all the  $\text{H}^+$  ions were consumed in the dissolution process (Table 6.10). In contrast, a similar calculation based on  $\Delta\text{NO}_3^-\text{-N}$  accumulation indicates that no dissolution of francolite could have been achieved due to nitrification process (Table 6.11).

Though the nitrification of ammonium salts was reported to have increased the dissolution of PR in soil (Chien, 1979; Apthorp *et al.*, 1987) and in compost (Alexander, 1967), it was not possible to demonstrate such effect in this experiment. This may be due to the following:

(1) As the processes of  $\text{NH}_3$  volatilization (proton generating) and denitrification (proton consuming) occur simultaneously and continuously, the measurement of  $\Delta\text{NH}_4^+\text{-N}$  and  $\Delta\text{NO}_3^-$  is unlikely to give accurate estimate of amounts of  $\text{H}^+$  produced during nitrification.

(2) As discussed in Chapters 4 and 5, the lower population of nitrifiers in manure and the toxicity of high concentration of  $\text{NH}_3/\text{NH}_4^+$  to nitrifiers, may be responsible for the low rate of nitrification. The calculated amount of  $\text{NH}_4^+\text{-N}$  oxidized to  $\text{NO}_3^-$  based on  $\Delta\text{NO}_3^-$  was found to be negligible, <1% (Table 6.11). However, large amounts of  $\text{NO}_3^-$

**Table 6.10 Changes in  $\text{NH}_4^+\text{-N}$  content ( $\text{mg jar}^{-1}$ ) of poultry manure composts during 30 and 60 days incubation with francolite and predicted level of francolite dissolution due to protons produced during nitrification**

Francolite plus treatments	Initial	After 30 days	After 60 days	$\Delta\text{NH}_4^+\text{-N}^*$	Calculated amount of protons ( $\text{H}^+$ ) produced (m moles)**	Expected level of P dissolution due to $\text{H}^+$ *** ( $\mu\text{g P}$ )***
1. manure (m) alone	44.6	29.2	29.9	14.7	0.82	12710
2. m + woodchip + $\text{S}^\circ$	59.2	34.9	41.9	17.3	0.96	14880
3. m + woodchip + zeolite	34.2	12.7	16.3	17.9	0.99	15345
4. m + paper waste + $\text{S}^\circ$	68.8	46.1	46.3	22.5	1.24	19220
5. m + paper waste + zeolite	34.1	9.5	11.5	22.6	1.26	19530
LSD (0.05)	7.5	1.6	4.8	7.9		

\* For 60 days and assuming 50% loss of  $\text{NH}_4^+$  due to  $\text{NH}_3$  volatilization

\*\* assuming 2 moles of  $\text{H}^+$  produced for one mole of  $\text{NH}_4^+$  oxidized (Eq 2.15)

\*\*\* assuming 2 moles of  $\text{H}^+$  required for one mole of P released,  
= ( $\text{H}^+$  m moles/2)\*31\*1000 (Eq 2.6)

**Table 6.11 Changes in  $\text{NO}_3^-$ -N content ( $\mu\text{g jar}^{-1}$ ) of poultry manure composts during 30 and 60 days incubation with francolite and predicted level of francolite dissolution due to protons produced during nitrification**

Francolite plus treatments	Initial	After 30 days	After 60 days	$\Delta\text{NO}_3^- \text{-N}^*$ ( $\mu\text{g}$ )	Amount of $\text{NH}_4^+ \text{-N}$ oxidized to $\text{NO}_3^- \text{-N}$ (%)	Predicted dissolution based on $\Delta\text{NO}_3^-$ ( $\mu\text{g P}$ )
1. manure (m) alone	159.7	109.8	183.2	23.5	0.16	12
2. m + woodchip + $\text{S}^\circ$	161.3	75.3	245.6	84.3	0.49	42
3. m + woodchip + zeolite	131.8	85.9	113.5	-18.3	-0.10	-9
4. m + paper waste + $\text{S}^\circ$	127.4	80.9	259.9	132.5	0.59	66
5. m + paper waste + zeolite	89.9	74.3	112.3	22.4	0.10	11
LSD (0.05)	49.4	21.3	37.9	42.0		

formed during nitrification may have been lost through denitrification, a process more active in poultry manure because of the relatively higher population of denitrifiers (Nodar *et al.*, 1990).

(3) It is also possible that most of the  $H^+$  released during nitrification may involve in reactions other than PR dissolution. Faurie and Fardeau (1990) reported that acidification due to nitrification does not transform soil/added P into a readily available P form.

## 6.5 CONCLUSIONS

The high levels of P in poultry manure and the immobilization of dissolved P into HCl-Pi (physico-chemical immobilization) or Po (microbial immobilization) make it difficult to measure any changes in the amount of P due to the dissolution of PR during short term incubation. The use of  $^{32}P$  labelled francolite was found to be successful in allowing net PR dissolution to be measured.

The measurement of dissolution of  $^{32}P$  labelled francolite both by  $\Delta NaOH-^{32}P$  and  $\Delta HCl-^{32}P$  methods closely agreed and gave a reasonable estimate of net dissolution. The results suggest that due to precipitation reactions and active microbial immobilization reducing NaOH-Pi amounts in compost to low levels, the measurement of total alkali extractable P (Pi plus Po in NaOH extract) is likely to give reasonably good estimates of PR dissolution.

The experiments involving both  $^{32}P$  labelled francolite and NCPR show low levels of dissolution of PR in poultry manure composts, which could be attributed to (i) high concentration of P and Ca in manure solution (see section 6.6), (ii) low rates of nitrification and (iii) neutralization of organic acids and  $H^+$  by  $CaCO_3$  and buffering reactions. However, the dissolution was found to increase with the addition of  $S^0$  and long term incubation. A significant negative correlation between the pH of composts and the increase in Pi suggests that the use of materials which acidify the compost may be helpful in the dissolution of both manure-P and PR-P or PR should be added to mature compost with a low pH.

There is no evidence of protons released during nitrification of  $\text{NH}_4^+$  in poultry manure compost contributing to the dissolution of PR. One of the reasons attributed was the high concentration of  $\text{Ca}^{2+}$  in manure solution which inhibits the dissolution.

Based on this study it can be reasonably concluded that the use of  $^{32}\text{P}$  labelled francolite can be successfully used to measure the net dissolution of PR during composting with organic manure. As the dissolution of PR in poultry manure compost is small, short term incubation of such mixtures are unlikely to enhance the fertilizer value of PR. The addition of materials like  $\text{S}^0$ , and long-term composting are found to be potentially effective in increasing the plant available P through the dissolution of manure and PR-P.

## 6.6 EPILOGUE

### 6.6.1 Introduction

In the previous sections of this Chapter, the low amount of dissolution of both labelled PR (francolite) and NCPR was attributed mainly to the high concentration of  $\text{Ca}^{2+}$  in manure solution. Therefore, it was decided to measure Ca and P concentrations in manure solution and examine the effect of Ca concentration on PR dissolution using solubility product relationship.

### 6.6.2 Methods

Manure solution from the compost sample was obtained following a modified centrifugation technique of Tambunan (1992). The extraction unit consisted of two centrifuge tubes placed one inside the other. The inner tube contained the moist (68%, w/w) compost and had a small opening at the base.

The tube was centrifuged at 8000rpm for 15min. Most of the solution formed a supernatant just above the compost sample in the inner tube, with only a small amount obtained in the outer tube. Therefore, the manure solution was collected both from the

inner and outer tubes. The solution was filtered through 0.2 $\mu$ m filter paper. A soil sample (Ramiha) was also included for comparison.

The concentration of  $\text{Ca}^{2+}$  and P in the manure and soil solutions was measured. Calcium was measured in the presence of strontium as an ionization suppressant, using an atomic absorption spectrophotometer. Measurement of phosphate followed Murphy and Riley (1962) method.

### 6.6.3 Results and discussion

The concentration of Ca and P in manure and soil solution is presented in Table 6.12.

**Table 6.12 Concentration of  $\text{Ca}^{2+}$  and P in manure and soil solutions**

Material	$\text{Ca}^{2+}$ (mol L <sup>-1</sup> )	P (mol L <sup>-1</sup> )
1. Poultry manure compost	$4.8 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$
2. Soil	$1.6 \cdot 10^{-3}$	$2.0 \cdot 10^{-6}$

The concentration of  $\text{Ca}^{2+}$  and P in the manure solution ( $4.8 \cdot 10^{-2}$ ,  $2.0 \cdot 10^{-3}$  mol L<sup>-1</sup>, respectively) was much higher than those in soil solution ( $1.6 \cdot 10^{-3}$ ,  $2.0 \cdot 10^{-6}$  mol L<sup>-1</sup>, respectively). The high  $\text{Ca}^{2+}$  and P concentrations in manure solution can be attributed to a high Ca and P content of poultry feed.

As  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$  form the main dissolution products (refer Eq 2.6), high concentrations of these ions in manure solution is expected to affect PR dissolution (Kirk and Nye, 1986a). To examine the effect of  $\text{Ca}^{2+}$  ion concentration on PR dissolution, the equilibrium concentration of  $\text{Ca}^{2+}$  maintained during the dissolution of a carbonate substituted PR at different pHs and at two P concentration was computed according to the following equation (6.8) given by Kirk and Nye (1986b)

$$8.7p\text{Ca} + 4.5p\text{H}_2\text{PO}_4 - 12p\text{H} = -18.96 \quad (6.8)$$

where,  $pCa$ ,  $pH_2PO_4$  and  $pH$  are the negative logarithms of the activities of the respective ions. The relationship between  $pH$  and the equilibrium  $Ca^{2+}$  concentration maintained through PR dissolution at two P concentrations is illustrated in Figure 6.6. The P concentrations used to calculate the equilibrium  $Ca^{2+}$  concentration were those maintained in the equilibrium solutions of Ramiha soil and poultry manure. Also included in the figure are the initial  $Ca^{2+}$  concentrations in solutions of the soil sample and poultry manure in the absence of PR addition.

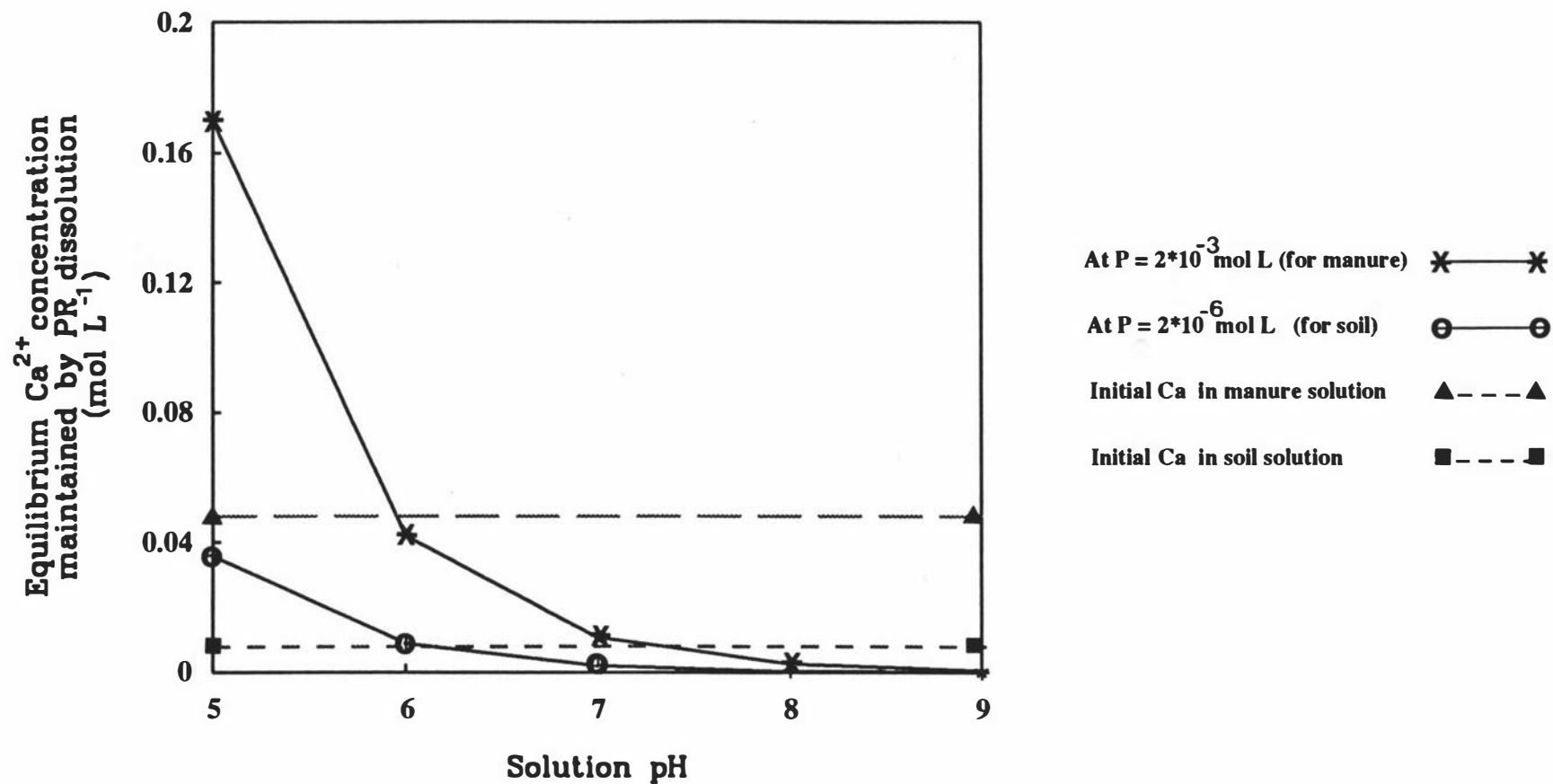
As anticipated, the dissolution of PR decreased with increasing  $pH$  resulting in a decrease in  $Ca^{2+}$  concentration. At a given  $pH$  the  $Ca^{2+}$  concentration maintained by PR dissolution was higher at lower solution concentrations of P. This suggests that as long as one of the dissolution products ( $Ca^{2+}$ ,  $H_2PO_4^-$ ) is removed from the site of dissolution, the PR dissolution continues to occur in the presence of an adequate supply of protons.

In soil, when the P concentration is  $2 \times 10^{-6} \text{ mol L}^{-1}$ , the initial  $Ca^{2+}$  concentration ( $1.6 \times 10^{-3} \text{ mol L}^{-1}$ ) exceeds the  $Ca^{2+}$  concentration maintained by PR dissolution only above  $pH$  6.5. In poultry manure, when the P concentration is  $2 \times 10^{-3} \text{ mol L}^{-1}$ , the initial  $Ca^{2+}$  concentration ( $4.8 \times 10^{-2} \text{ mol L}^{-1}$ ) exceeds the  $Ca^{2+}$  concentration maintained by PR dissolution above  $pH$  6.

This suggests that at  $pH$  below 6.5, dissolution of PR in soil continues to occur as long as the concentration of  $Ca^{2+}$  and P is kept below  $1.6 \times 10^{-3}$  and  $2 \times 10^{-6} \text{ mol L}^{-1}$ , respectively, in the zone of dissolution. In poultry manure, however, unless the  $pH$  is lowered below 6, the initial  $Ca^{2+}$  concentration is too high (exceeds solubility product) to cause any dissolution of PR. This explains why the dissolution of PR in poultry manure compost is very low. As the addition of  $S^0$  lowered the  $pH$  it enhanced the dissolution of PR.

#### 6.6.4 Conclusion

The results demonstrate that the high  $Ca^{2+}$  ion activity in manure solution is mainly responsible for the low dissolution of PR during the composting of poultry manure. It further suggests that to accomplish a desirable level of PR dissolution during



**Fig 6.6 Relationship between pH and equilibrium  $\text{Ca}^{2+}$  concentration maintained by PR dissolution at two solution P concentrations (computed from Eq 6.8)**

composting, a reduction in pH is essential. This can be achieved through acidification of compost using cheaply available  $S^0$ .

The inhibitory effect of manure Ca on PR dissolution can be overcome by physically separating the manure from the PR. An incubation system developed to achieve this is discussed in Chapter 7.

## CHAPTER 7

### ABSORPTION OF AMMONIA RELEASED FROM POULTRY MANURE IN BARK AND SOIL MATERIALS AND THE USE OF ABSORBED AMMONIA IN THE DISSOLUTION OF PHOSPHATE ROCK

#### 7.1 INTRODUCTION

Composting phosphate rock (PR) with poultry and animal manures has been recommended as a low-input technology to enhance the dissolution of PR (Mishra and Bangar, 1986). The organic acids produced during composting and the protons ( $H^+$ ) generated during the oxidation of ammonium ( $NH_4^+$ ) to nitrate ( $NO_3^-$ ) through nitrification process, are considered to increase PR dissolution.

Results in Chapter 6, however, have demonstrated that if PR is incubated with poultry manure, low levels of dissolution (<16%) are obtained because of the high concentrations of calcium ( $Ca^{2+}$ ) ions in the manure solution which inhibit the dissolution of PR through the  $Ca^{2+}$  common-ion effect.

The inhibitory effect of  $Ca^{2+}$  in manure solution on the dissolution of PR may be overcome by trapping the ammonia ( $NH_3$ ) released from poultry manure using absorbents. The  $H^+$  produced during the oxidation of the absorbed  $NH_3$  may subsequently be used in the dissolution of PR. Biological waste materials such as bark and cereal straw can be used as absorbents.

In the past many processes have been investigated for the removal of nitrogen (N) from waste water and polluted streams (Reeves, 1972). Amongst them air stripping of  $NH_3$  was found feasible and attractive because of its economy and efficiency (O'Farrell *et al.*, 1972). In this Chapter, two different methods to achieve efficient  $NH_3$  removal from poultry manure in order to dissolve the PR are examined.

## 7.2 OBJECTIVES

The objectives of this experiment were to investigate: (1) methods for absorbing  $\text{NH}_3$  released from decomposing poultry manure using bark and soil materials; and (ii) the potential use of  $\text{H}^+$  produced during the nitrification of absorbed  $\text{NH}_3$  in the dissolution of PR. Two systems, one with bark and soil covers and another with bark and soil columns using forced aeration, were investigated and will be discussed separately in this Chapter.

## 7.3 MATERIALS AND METHODS

### 7.3.1 Poultry manure

Fresh poultry manure (31.5% solid matter) was collected from the Poultry Research Centre at Massey University. Some characteristics of the manure are given in Table 7.1.

**Table 7.1 Important characteristics of poultry manure, bark and soil materials**

Characters	Poultry manure	Bark**	Soil**
1. Type	<i>Layer bird</i>	<i>Pinus radiata</i>	<i>Andic Dystrochrepts</i>
2. pH	6.5	4.7	5.2
3. Carbon (%)	46.1	51.2	7.6
4. Nitrogen (%)	5.4	0.3	0.7
5. C/N ratio	8.5	170.0	11.0
6. CEC (cmol (+) $\text{kg}^{-1}$ )	-	56.0	34.0
7. Exchangeable acidity (cmol (+) $\text{kg}^{-1}$ )	33.3	80.5	20.8
8. Exchangeable Ca (cmol (+) $\text{kg}^{-1}$ )	-	7.3	6.0
9. Total P (%)	2.71	0.20	0.13

\* Freeze dried basis    \*\* air dried basis

### 7.3.2 Bark and soil materials

Bark (*Pinus radiata*) obtained from Levin Horticultural Research Centre (MAF) and a surface soil (Ramiha soil, a NZ yellow-brown loam to yellow-brown earth intergrade, *Andic Dystrochrepts*) were used for the absorption of  $\text{NH}_3$ . The bark and soil were air dried and sieved to less than 2mm. Some of the important characteristics of bark and soil are presented in Table 7.1.

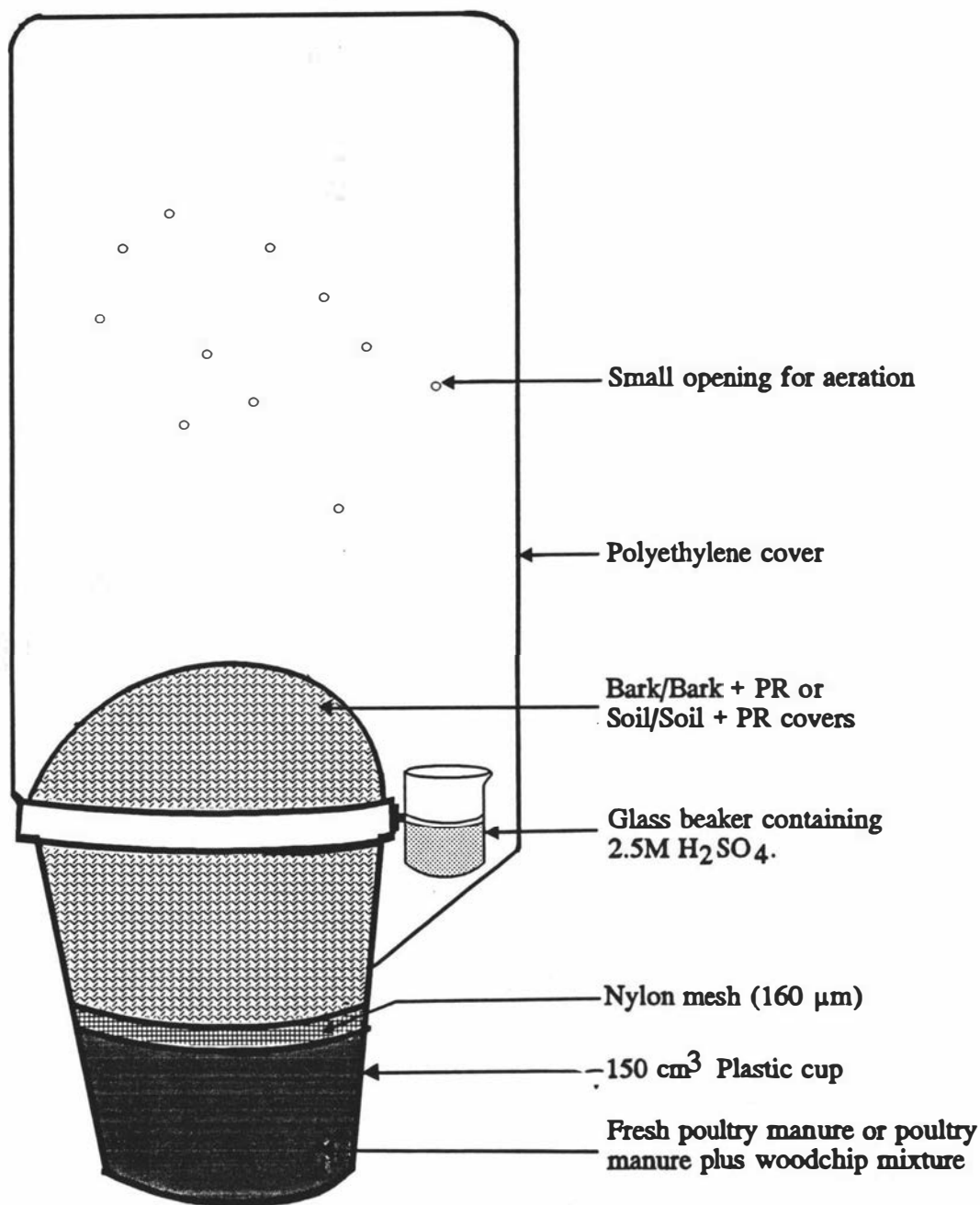
### 7.3.3 Phosphate rock

The important characteristics of North Carolina phosphate rock (NCPR, 125-175 $\mu\text{m}$ ) used in the experiment have already been given in Table 6.2 (Chapter 6).

### 7.3.4 Experiment I: Bark and soil covers to absorb $\text{NH}_3$

Triplicate samples of fresh poultry manure (50g) were placed in a 150 $\text{cm}^3$  polyethylene urine cups and covered with a nylon mesh (160 $\mu\text{m}$  pore size) as shown in Figure 7.1. A layer (approximately 8cm height) of either bark (30g) or soil (40g) mixed with or without NCPR at a rate equivalent to 1000 $\mu\text{g P g}^{-1}$ , was placed over the manure. The bark and soil materials were moistened to a gravimetric water content of 0.6 (g/g) prior to placement. A 5 $\text{cm}^3$  glass beaker containing 3 $\text{cm}^3$  of 2M  $\text{H}_2\text{SO}_4$  was tied to the urine cup using rubber bands, to trap the unabsorbed  $\text{NH}_3$  escaping from the bark and soil. The urine cup was covered with a polyethylene bag to minimise the loss of moisture and  $\text{NH}_3$ . The urine cup was kept in a dark room at 20°C-25°C for 12 weeks. At weekly intervals, the  $\text{H}_2\text{SO}_4$  was replaced and the moisture content of bark and soil covers was corrected. At the end of 12 weeks, the bark and soil were carefully removed and separated into approximately two equal layers, representing top and bottom layers of the covers. The bark and soil samples were airdried before analysis.

In a parallel experiment, the NCPR was incubated with bark and soil samples in the absence of poultry manure and the dissolution of NCPR measured.



**Fig 7.1** Experimental set-up used to absorb NH<sub>3</sub> released from poultry manure using bark and soil covers mixed with and without North Carolina phosphate rock (Experiment I)

### 7.3.5 Experiment II: Bark and soil columns to absorb $\text{NH}_3$ using forced aeration

#### 7.3.5.1 $\text{NH}_3$ absorption stage

The  $\text{NH}_3$  absorption apparatus used in the experiment was constructed as shown in the Figure 7.2. It consists of (1) air source, (2) incubation jar, (3) reaction chamber and (4) gas collection system. Glass preserving jars with an internal diameter of 110mm and a capacity of one litre were used for incubation. The head space of the jar was modified to have a lid fitted with a Terumo Venoject rubber insert to permit the introduction of two syringe needles, one for the inlet of the air stream and other for the outlet of gases.

The outlet of the jar was connected to the inlet of the reaction chamber, which consisted of a polyethylene tube (i.d. 3.5cm) containing a bark or soil bed supported by nylon mesh (160 $\mu\text{m}$ ). About 40g of bark or soil was thoroughly mixed with NCPR at a rate of 1000 $\mu\text{g P g}^{-1}$  and placed in the tube. The moisture content of the mixtures was adjusted to a gravimetric water content of 0.6 (g/g). Both ends of the reaction chamber were sealed with rubber stoppers fitted with glass tubing. The outlet of the reaction chamber was attached in series to an empty test tube followed by test tubes containing 1M  $\text{H}_3\text{BO}_3$  and 2.5M NaOH to absorb  $\text{NH}_3$  and  $\text{CO}_2$ , respectively.

Triplicate samples of fresh poultry manure (100g) were placed into the incubation jars and incubated at 20°C-25°C for 8 weeks. A wet  $\text{CO}_2$ - and  $\text{NH}_3$ -free airstream was pumped into the incubation jar at a rate of 204 $\text{cm}^3 \text{ h}^{-1}$  using a peristaltic pump and prebubblers containing 6M NaOH and acidified water. The  $\text{NH}_3$  released from the decomposing manure was carried in this airstream through the bark and soil columns. Ammonia and  $\text{CO}_2$  leaving the bark and soil columns were trapped in  $\text{H}_3\text{BO}_3$  and NaOH, respectively. After 8 weeks, the bark and soil columns were dismantled, carefully sectioned at 2cm intervals and analyzed for pH, mineral N and dissolution of PR.

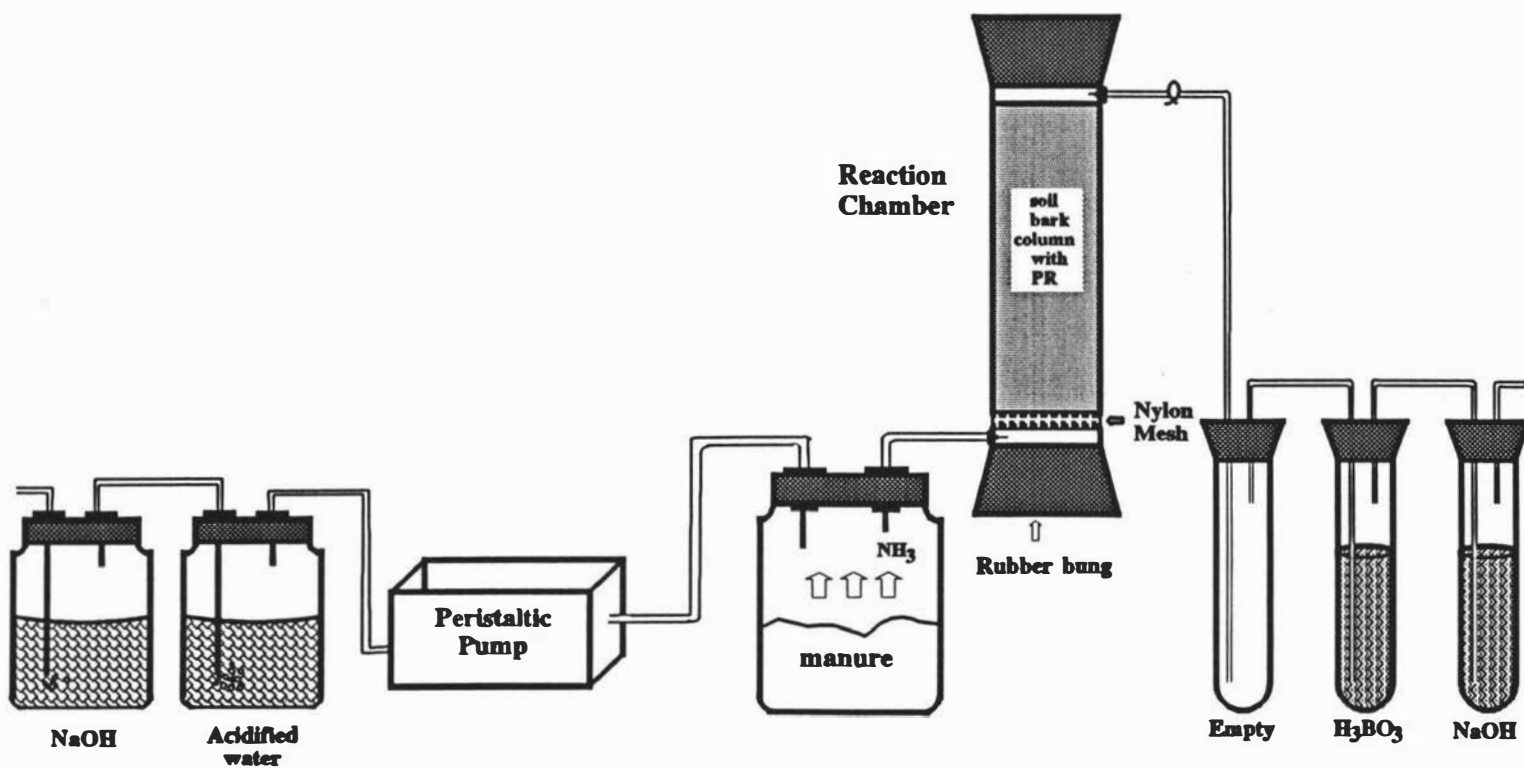


Fig 7.2 Experimental set-up used to absorb  $\text{NH}_3$  released from poultry manure using bark and soil columns mixed with and without North Carolina phosphate rock (Experiment II)

### 7.3.5.2 *Reincubation stage*

During the 8 weeks  $\text{NH}_3$  absorption stage there was an increase in the amounts of  $\text{NH}_4^+$ -N in the bark and soil columns resulting from the absorption of  $\text{NH}_3$  from the manure. But, there was no evidence of nitrification of the absorbed  $\text{NH}_4^+$ . Therefore, at this stage, subsamples of the bark and soil sections were re-inoculated with nitrifiers using a water extract of fresh soil and reincubated for 6 weeks. At the end of the incubation period the samples were analyzed for pH, mineral N and PR dissolution.

### 7.3.6 *Chemical analysis*

#### 7.3.6.1 *pH and N (mineral N and total N)*

The pH of the bark and soil samples was measured in water at a solid:water ratio of 1:2.5 after an equilibrium period of 1h and 16h, respectively.

The mineral N ( $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N) content of the bark and soil samples was measured by extracting subsamples with 2M KCl at a soil:solution ratio of 1:10 and determining the concentration of  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N in the extracts by the methods of Technicon (1976) and Downes (1978).

Total Kjeldahl N (TKN) and total N content of the bark and soil samples were determined as outlined in Chapter 4 (section 4.3.4.4).

#### 7.3.6.2 *Cations*

The concentrations of  $\text{Ca}^{2+}$  and potassium ( $\text{K}^+$ ) in NaCl/TEA (at a solid:solution ratio of 1:40), and magnesium ( $\text{Mg}^{2+}$ ) in 2M KCl (at a solid:solution ratio of 1:10) extracts of the bark and soil samples, were measured after adding an appropriate ionization suppressor using an atomic absorption spectroscopy (for Ca and Mg) and emission spectroscopy (for K).

#### 7.3.6.3 *Exchangeable acidity and cation exchange capacity (CEC)*

Exchangeable (titratable) acidity of the bark and soil cover samples before and after incubation was measured according to a modified method given by Blakemore *et al.* (1987). The CEC was measured after leaching the bark and soil with neutral 1M ammonium acetate (Blakemore *et al.*, 1987). The Ca sink size for bark and soil was estimated as the difference between total CEC and exchangeable Ca (Robinson *et al.*, 1992).

#### 7.3.6.4 *Dissolution of NCPR*

The extent of NCPR dissolution in the bark and soil covers and in the sectioned columns was determined by either measuring increases in the amounts of soluble and adsorbed P or from the decreases in the residual apatite P remaining as undissolved PR (HCl extractable P).

In the first experiment with bark and soil covers, the amount of soluble and adsorbed P was measured in 0.5M NaCl/TEA followed by NaOH extractions (Tambunan *et al.*, 1993). In the second experiment with bark and soil columns, the soluble and adsorbed P was measured using resin strips and NaOH extractions. The resin extraction was introduced to determine the readily plant available P content in the bark and soil materials.

For the measurement of resin extractable P, the bark or soil was shaken in a 50cm<sup>3</sup> polypropylene tube first with deionised water in the presence of anion exchange resin (AER) strips at a solid:solution ratio of 1:30, on an end-over-end shaker for 16h. The AER strip was removed and washed with deionised water to remove adhering bark/soil particles and fine roots. The P from the resin strip was determined as described by Sagger *et al.* (1990).

After the resin extraction, the bark or soil residue was shaken with 1M NaOH for 16h at a solid:solution ratio of 1:40 (MacKay *et al.*, 1986). After centrifuging at 8000rpm

for 20min, the supernatant solution was filtered using Whatman No. 6 filter paper. To the residue in the tube 1M HCl was added (solid:solution ratio of 1:40), shaken for a further 16h, centrifuged and filtered (Hedley *et al.*, 1982). The P concentration in neutralized filtered extracts was determined by the method of Murphy and Riley (1962).

### 7.3.7 Statistical analysis

Significant differences between treatment means were tested using the analysis of variance procedure (SAS, 1985).

## 7.4 RESULTS AND DISCUSSION

### 7.4.1 Experiment I: Bark and soil covers (Fig 7.1)

#### 7.4.1.1 Absorption of $\text{NH}_3$ in bark and soil covers

The amount of  $\text{NH}_3$  volatilized from poultry manure and subsequently retained by the bark and soil covers can be estimated from the increases in the total N and  $\text{NH}_4^+\text{-N}$ . The total Kjeldahl N (TKN) content of the bark and soil covers increased during the 12 weeks incubation with poultry manure (Table 7.2). Top layers of the bark and soil cover showed a slightly higher values of TKN than the bottom layers. The total increase in TKN was found to be 3 to 6 times higher in bark covers than in soil covers.

Data on total N (TKN plus  $\text{NO}_3^-\text{-N}$ ) content of the bark and soil covers indicates that varying amounts of N originated from poultry manure. In the bark covers about 48% to 49% (416 to 423mg) of manure N was retained as against only 9 to 16.2% (75 to 138mg) in soil covers (Table 7.3).

The 2M KCl extractable  $\text{NH}_4^+\text{-N}$  contents in the bark and soil covers markedly increased due to the absorption of  $\text{NH}_3/\text{NH}_4^+$  from poultry manure during 12 weeks incubation. The increase (final - initial) in  $\text{NH}_4^+\text{-N}$  content in the bark and soil covers is shown in Figure 7.3. Consistent with the TKN, the  $\text{NH}_4^+\text{-N}$  content was significantly higher in

**Table 7.2 Changes in total Kjeldahl N (TKN) content of bark and soil covers during 12 weeks incubation with poultry manure**

Treatments		Total Kjeldahl N			
		Initial (mg g <sup>-1</sup> )	After 12 weeks incubation		Total increase in TKN (mg) <sup>§</sup>
			Top <sup>@</sup> (mg g <sup>-1</sup> )	Bottom <sup>@</sup> (mg g <sup>-1</sup> )	
1.	Manure covered with bark	4.02	16.45	16.15	368.4
2.	manure covered with bark plus NCPR	3.98	17.67	16.54	393.8
3.	manure covered with soil	7.91	12.37	10.12	133.4
4.	manure covered with soil plus NCPR	7.51	10.54	8.86	87.6
5.	manure + woodchip mixture covered with soil	7.91	10.17	8.46	56.2
6.	manure + woodchip mixture covered with soil plus NCPR	7.51	9.67	8.78	68.6

**LSD (0.05):**  
Treatments                    1.83\*\*  
Layers                         1.06\*  
Treatment\*Layers        NS

<sup>@</sup>        representing top and bottom layers of bark and soil covers

<sup>s</sup>        calculated as the difference between initial and final for the total amounts of bark or soil in a system

**Table 7.3 Total N derived from poultry manure and different fractions of N in bark and soil covers**

Treatments	Total N <sup>1</sup> derived from poultry manure (mg)	Exchangeable <sup>2</sup> NH <sub>4</sub> <sup>+</sup> -N (%)	Fixed or immobilized NH <sub>4</sub> <sup>+</sup> -N <sup>3</sup> (%)	NO <sub>3</sub> <sup>-</sup> form <sup>4</sup> (% TN)	AAR <sup>5</sup>
1. Manure covered with bark	416.3	41.9	46.6	11.5	20.4-34.5
2. manure covered with bark plus NCPR	423.9	47.4	45.5	7.1	19.9-36.2
3. manure covered with soil	137.8	69.4	27.4	3.2	7.4-19.2
4. manure covered with soil plus NCPR	90.9	82.9	13.4	3.7	4.4-12.5
5. manure + woodchip mixture covered with soil	75.0	69.6	5.3	25.1	3.8-8.7
6. manure + woodchip mixture covered with soil plus NCPR	86.4	49.8	29.6	20.6	3.5-5.9

<sup>1</sup> = Total N (TN) derived from manure (mg) =  $\Delta$ Total Kjeldahl N (TKN) +  $\Delta$ NO<sub>3</sub><sup>-</sup>-N

<sup>2</sup> = (Exchangeable NH<sub>4</sub><sup>+</sup> extractable in 2M KCl/ $\Delta$ TN)\*100

<sup>3</sup> = Fixed NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>-N (%) =  $[(\Delta$ TKN -  $\Delta$ NH<sub>4</sub><sup>+</sup>-N)/ $\Delta$ TN]\*100

<sup>4</sup> = % Nitrified = ( $\Delta$ NO<sub>3</sub><sup>-</sup>-N/ $\Delta$ TN)\*100

<sup>5</sup>AAR = Ammonium adsorption ratio  
(the values are for bottom [lowest] and top [highest] layers)

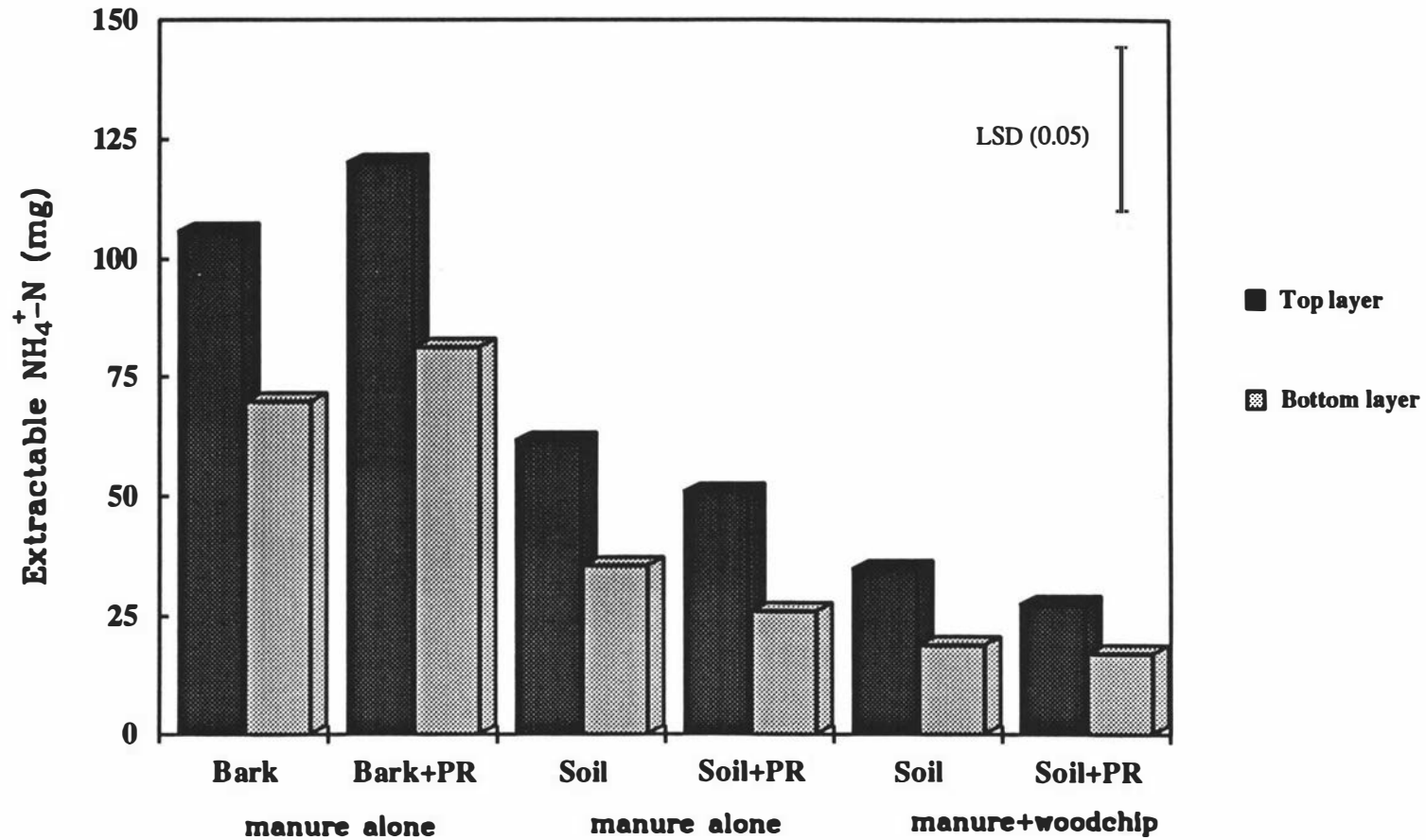


Fig 7.3 Increases in  $\text{NH}_4^+\text{-N}$  content of bark and soil covers after 12 weeks incubation with poultry manure

the bark than in the soil cover.

A linear relationship ( $R^2 = 99\%$ ) was obtained between the increases in TKN and  $\text{NH}_4^+$ -N contents. This shows that the increase in TKN content of the bark and soil mainly originated from poultry manure. Apart from  $\text{NH}_3$  release, considerable amounts of  $\text{NH}_4^+$  formed during the partial aerobic/anaerobic decomposition of the manure may have diffused from manure to bark/soil covers. This was possible since the bark and soil covers were kept in physical contact with the manure.

The low amount of N in the soil cover may possibly be due to the loss of considerable amounts of N through  $\text{NH}_3$  volatilization from soil surface, or it may be that the soil cover reduced the oxygen supply to the manure resulting in less  $\text{NH}_3$  production. Because of the coarse texture, the bark cover could have favoured higher  $\text{NH}_3$  release from manure. The higher levels of N recovered in the bark covers can be attributed to the high absorption of  $\text{NH}_3$  and  $\text{NH}_4^+$  in the bark due to its higher initial exchangeable acidity ( $80.5\text{cmol (+) kg}^{-1}$ ) and CEC ( $56\text{cmol (+) kg}^{-1}$ ) than the soil.

While it is estimated that approximately 50 to 83% of total N (TKN plus  $\text{NO}_3^-$ -N) in the soil covers was in an exchangeable form (as extracted in KCl), only 42 to 47% was found to be in an exchangeable form in the bark (Table 7.3). Mixing manure with woodchip resulted in a slight decrease in the amount of  $\text{NH}_4^+$ -N and TKN contents in the soil cover. This may be probably due to the reduction in  $\text{NH}_3$  volatilization from poultry manure in the presence of woodchip.

The  $\text{NH}_4^+$  ion is adsorbed onto the cation exchange sites mostly by replacing  $\text{H}^+$  ions. As the pH rises, due to the release of  $\text{OH}^-$  ions, more effective cation exchange sites are created in the bark and in soil containing high organic matter, and the predominant reaction for  $\text{NH}_3$  retention would be  $\text{NH}_4^+$  exchange. When all effective cation exchange sites are saturated and the solution pH rises above 9, free  $\text{NH}_4^+$  ions in the solution are likely to form  $\text{NH}_3$  (Eq 7.1) which moves through upward gaseous diffusion in the bark or soil covers resulting a gradient in  $\text{NH}_4^+$  distribution.



The amount of N, fixed or immobilized as organic N in the bark and soil, was calculated as the difference between  $\Delta\text{TKN}$  and  $\Delta 2\text{M KCl extractable NH}_4^+\text{-N}$  (Sohn and Peech, 1958; Nyborg, 1969) and expressed as a % of  $\Delta$  total N (Table 7.3). The amount of N, fixed or immobilized, was several times greater in the bark than soil. It has been generally reported that organic materials have a greater capacity for fixing or immobilising  $\text{NH}_3$  than soil (Sohn and Peech, 1958; Nyborg, 1969). Irrespective of the manure mixtures, low fixation or immobilization of N occurred in the soil. Low fixation of N by soil may be due to low pH, since according to Nommik and Nilsson (1963) and Nyborg (1969) large amounts of  $\text{NH}_3$  are fixed only when soil pH is above 8.

To examine the relative activity of  $\text{NH}_4^+$  in exchange reactions, the ammonium adsorption ratio (AAR) for bark and soil was calculated (Lance, 1972) using the following equation (Eq 7.2):

$$\text{AAR} = \frac{[\text{NH}_4^+]}{(1/2[\text{Ca}^{2+}] + 1/2[\text{Mg}^{2+}]^{1/2})} \quad (7.2)$$

where, AAR is the ammonium adsorption ratio and the ionic concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  are expressed in  $\text{cmol (+) kg}^{-1}$  bark or soil material. The AAR of bark was significantly higher than soil (Table 7.3) suggesting that most of the exchange sites in the bark can be occupied by  $\text{NH}_4^+$  ions.

Guedes de Carvalho *et al.* (1991) observed a considerable increase in the  $\text{NH}_4^+\text{-N}$  holding capacity of bark during composting which could be attributed to the high exchangeable acidity and availability of exchangeable sites (CEC) in bark. Bark contains a high proportion of phenolic ( $>\text{-OH}$ ) compounds, (eg. tannins and lignin) (Markham and Porter, 1973), and also carboxylic ( $-\text{COOH}$ ) compounds. Dissociation of active  $\text{H}^+$  ions at high pH ( $>7$ ) from the carboxyl and phenolic functional groups

creates cation exchange sites and resulting in the retention of  $\text{NH}_4^+$ .

#### 7.4.1.2 $\text{NO}_3^-$ in bark and soil covers

During the 12 weeks incubation oxidation of absorbed  $\text{NH}_4^+$  to  $\text{NO}_3^-$  (nitrification) had occurred in bark and soil covers. The total  $\text{NO}_3^-$ -N content was significantly higher in bark than in soil covers (Fig 7.4). Soil covers with poultry manure and woodchip mixture had relatively higher content of  $\text{NO}_3^-$ -N than soil with manure alone.

Higher  $\text{NO}_3^-$ -N levels in bark covers were associated with the higher amounts of  $\text{NH}_3/\text{NH}_4^+$ . While better aeration within bark covers, due to its relatively coarse particle size, favoured more nitrification, under soil covers, finer particles have reduced the porespace and restricted the aeration, creating more anaerobic pockets within the soil cover and manure. This resulted in less  $\text{NH}_3$  release from poultry manure under the soil cover.

#### 7.4.1.3 pH of bark and soil covers

The pH of the bark and soil covers measured at the end of 12 weeks incubation is shown in Figure 7.5. In the bark and soil covers the change in pH is a function of the absorption of  $\text{NH}_3$  which tends to increase the pH and the oxidation of  $\text{NH}_4^+$  which tends to decrease the pH.

The  $\text{NH}_3$  released from manure is physically sorbed in the bark and soil materials and then acquires  $\text{H}^+$  to form stable  $\text{NH}_4^+$  resulting in an increase in pH. The subsequent nitrification of  $\text{NH}_4^+$  produces  $\text{H}^+$  and decreases the pH in bark and soil covers. Higher nitrification in the bark results in relatively lower pHs in bark than in soil.

Invariably the pHs of bottom layers of the bark and soil close to the manure surface were lower than top layers. This may suggest that while more  $\text{NH}_4^+$  diffused into the bottom layer, most N entered as  $\text{NH}_3$  gas and raised the pH of the top layer.

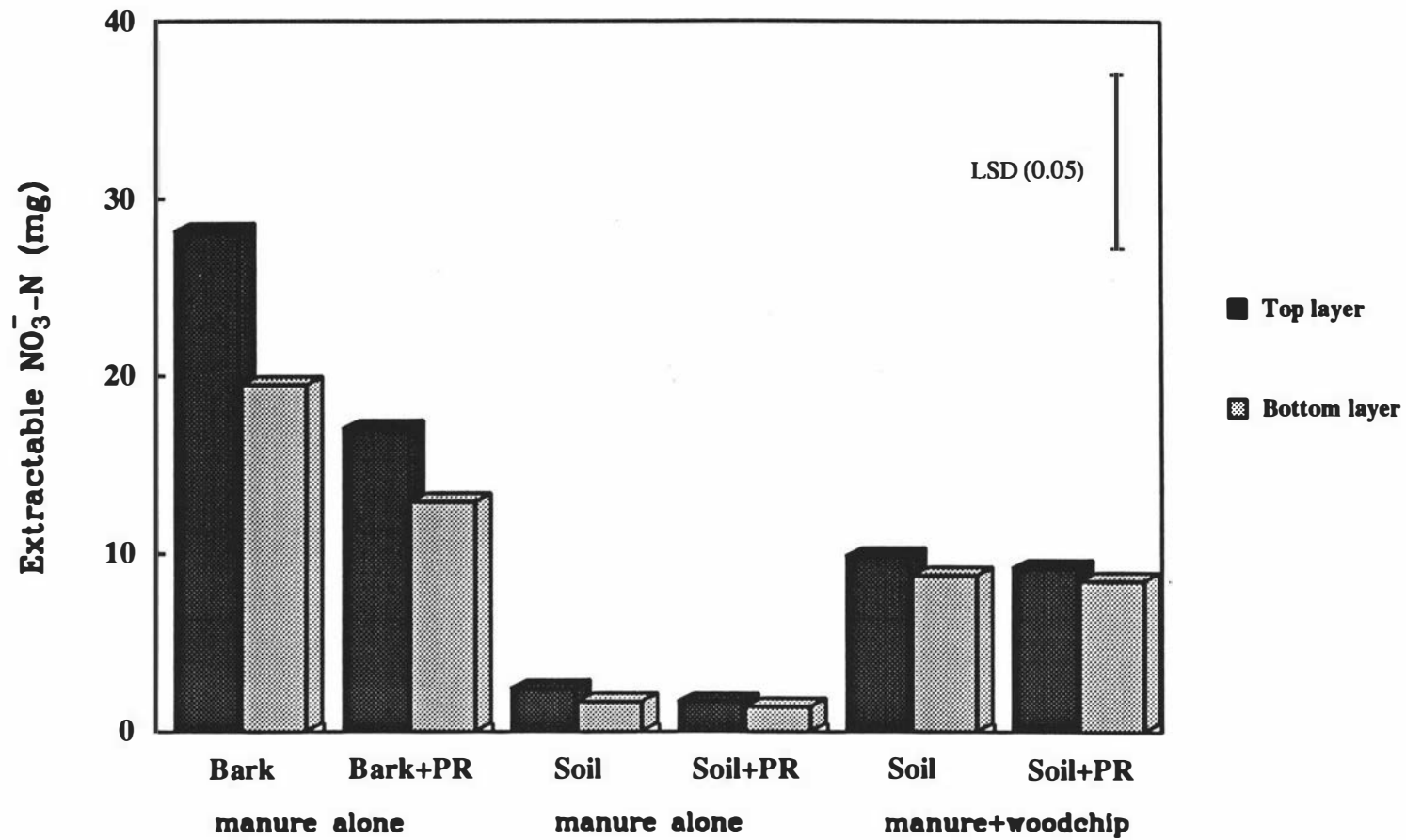
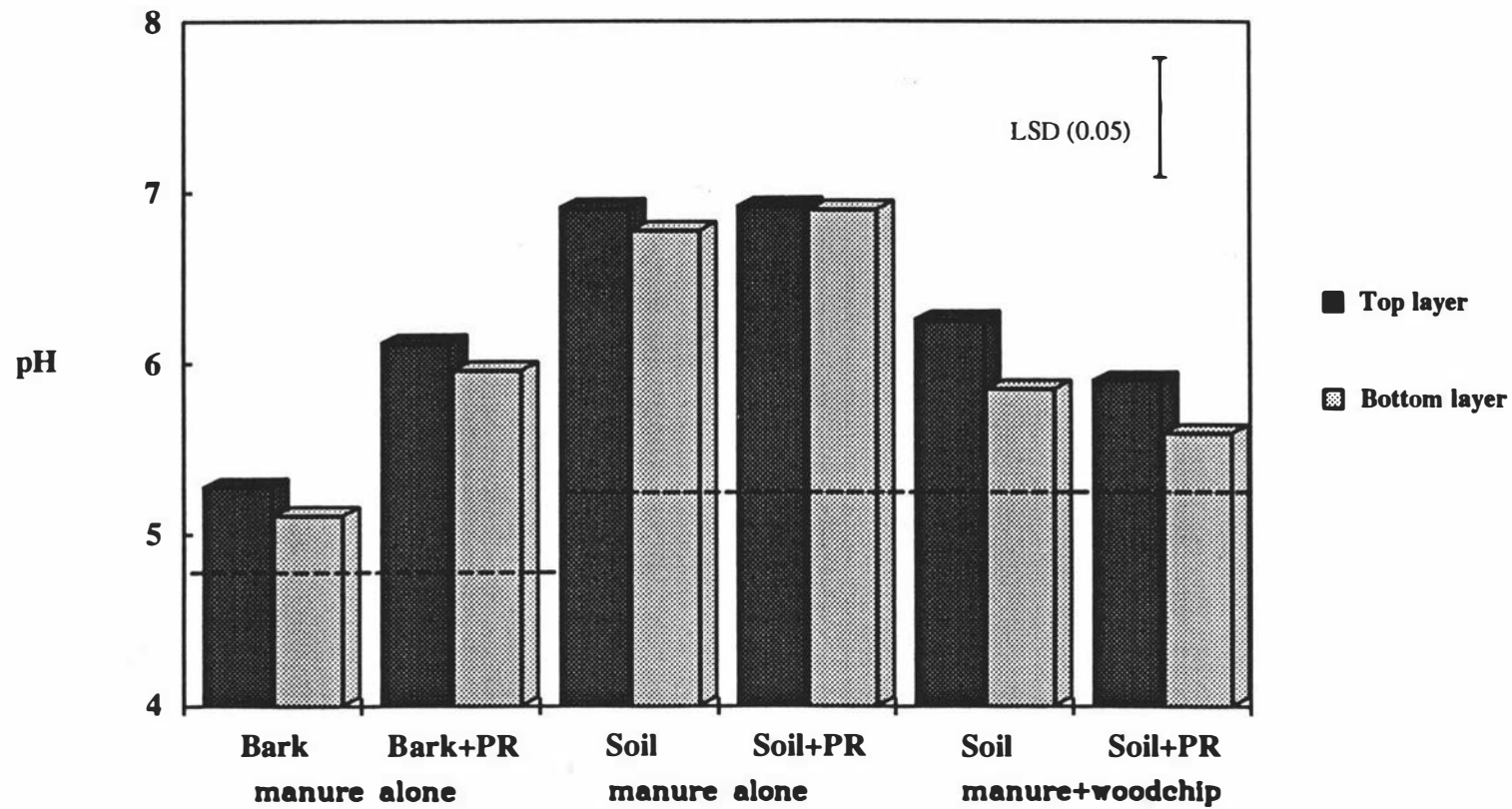


Fig 7.4 Increases in  $\text{NO}_3\text{-N}$  content of bark and soil covers after 12 weeks incubation with poultry manure



**Fig 7.5 pH values of bark and soil covers after 12 weeks incubation with poultry manure. Dotted lines represent initial pHs**

**7.4.1.4      *Exchangeable cations and CEC***

The concentration of some exchangeable cations were measured in the composite samples of the bark and soil covers (without NCPR) to examine whether diffusion of cations from poultry manure to the bark and soil covers had occurred. It is interesting to note that the concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$  in the bark and soil covers increased considerably during the incubation with poultry manure (Table 7.4).

**Table 7.4    Changes in the concentration of some exchangeable cations and CEC in the bark and soil covers**

Cations	Bark cover		Soil cover	
	Initial	Final	Initial	Final
1. $\text{Ca}^{2+}$	7.3	17.4	6.0	10.2
2. $\text{Mg}^{2+}$	3.2	6.9	2.2	4.0
3. $\text{K}^{+}$	1.7	26.2	0.9	10.1
4.CEC	56.1	117.3	34	51.3

Cations and CEC are expressed in  $\text{cmol (+) kg}^{-1}$

Further, the increase in cations concentration was found to be more with bark than soil covers, similar to the trend observed with  $\text{NH}_4^{+}\text{-N}$  content. As already pointed out, it is likely that the physical contact between bark/soil covers and poultry manure enabled the diffusion of cations and anions across the bark and soil covers. Correspondingly, the CEC also increased in the bark and soil covers. While the CEC increased from 56 to  $116\text{cmol (+) kg}^{-1}$  in bark, it increased only from 34 to  $51.3\text{cmol (+) kg}^{-1}$  in soil, which explains why the AAR and the concentration of  $\text{NH}_4^{+}\text{-N}$  were lower in the soil than in the bark.

**7.4.1.5      *Dissolution of NCPR in bark and soil covers***

The dissolution of NCPR in the bark and soil covers was determined from the increases in NaCl/TEA extractable P plus NaOH extractable P (Eq 7.3).

$$\%DPR = (\Delta P / P_a) * 100 \quad (7.3)$$

where,

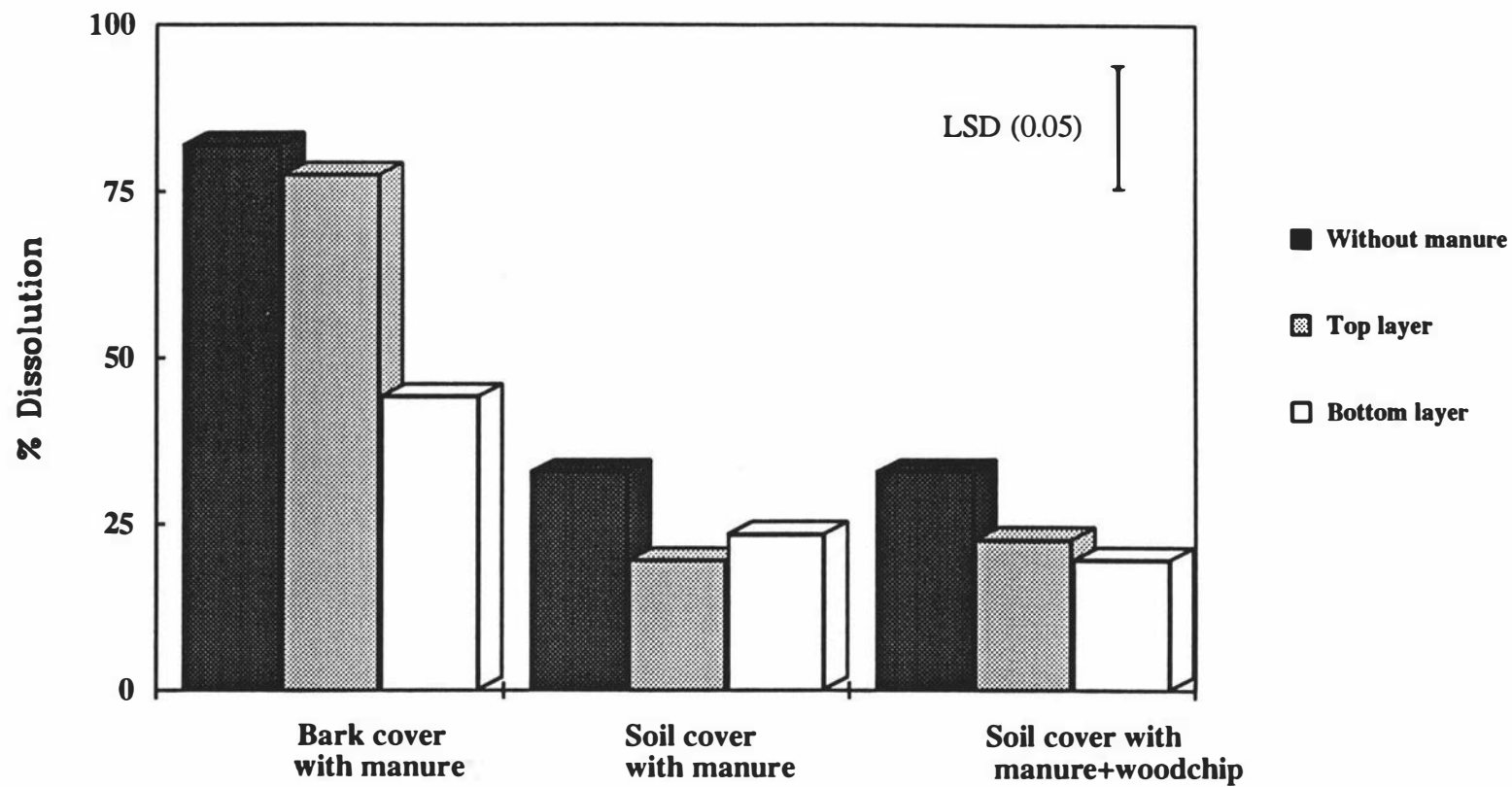
%DPR	=	Dissolution of NCPR (% added)
$\Delta P_i$	=	Increase in NaCl/TEA extractable P plus NaOH extractable P due to NCPR
	=	(NaCl/TEA-Pi+NaOH-Pi in NCPR treatment) - (NaCl/TEA-Pi + NaOH-Pi in control) ( $\mu\text{g g}^{-1}$ bark/soil)
$P_a$	=	P added ( $1000\mu\text{g g}^{-1}$ bark/soil)

In the absence of poultry manure, incubation of NCPR with bark and soil resulted in about 82% and 33% dissolution, respectively. With the manure- $\text{NH}_3$  absorption-system, the dissolution of NCPR was found to be slightly decreased both in the bark and soil (Fig 7.6).

Only between 44% (bottom layer) to 78% (top layer), and 20% (bottom layer) to 24% (top layer) dissolution of added P in bark and soil covers, respectively, occurred during 12 weeks incubation in the presence of manure (Fig 7.6). The dissolution of NCPR was, however, significantly higher in bark covers than in soil covers.

The higher exchangeable acidity, the availability of large Ca sink size and the higher amounts of  $\text{H}^+$  generated during the nitrification of  $\text{NH}_4^+$  could be attributed for the higher levels of dissolution of NCPR in bark than in soil.

A small reduction in the dissolution of NCPR under the manure- $\text{NH}_3$  absorption-system may be attributed to the following reasons. The exchangeable acidity ( $\text{H}^+$ ) available in bark and soil may have reduced during the transformation of  $\text{NH}_3$  to  $\text{NH}_4^+$ , as one mole of  $\text{NH}_3$  essentially requires one mole of  $\text{H}^+$  to form  $\text{NH}_4^+$ . Probably, this may have reduced the  $\text{H}^+$  availability for PR dissolution. Further, the measurements of exchangeable Ca in the bark and soil covers showed evidence for the diffusion of Ca from manure (Table 7.4). Accumulation of Ca and P in bark and soil solutions in the presence of poultry manure may also be another reason for the reduction in PR dissolution.



**Fig 7.6** Dissolution of NCPR in bark and soil covers during 12 weeks incubation with poultry manure

## 7.4.2 Experiment II: Bark and soil columns (Fig 7.2)

### 7.4.2.1 *NH<sub>3</sub> absorption stage*

#### 7.4.2.1.1 Absorption of NH<sub>3</sub> in bark and soil columns

In this experiment the NH<sub>3</sub> released from poultry manure was allowed to pass through bark and soil columns using a forced aeration technique (see Fig 7.2). During 8 weeks incubation the NH<sub>4</sub><sup>+</sup>-N content significantly increased both in the bark and soil columns (Table 7.5) as a result of the absorption of NH<sub>3</sub> released from poultry manure. In both cases the content of NH<sub>4</sub><sup>+</sup>-N decreased as the distance from the NH<sub>3</sub> inlet increased (Fig 7.7).

Soil columns contained less NH<sub>4</sub><sup>+</sup>-N than bark columns. This probably resulted from greater chemical fixation and organic immobilization of NH<sub>4</sub><sup>+</sup>-N in the soil columns. All NH<sub>3</sub> released from the poultry manure was trapped in the bark and soil columns and no NH<sub>4</sub><sup>+</sup>-N was detected in the H<sub>3</sub>BO<sub>3</sub> acid trap.

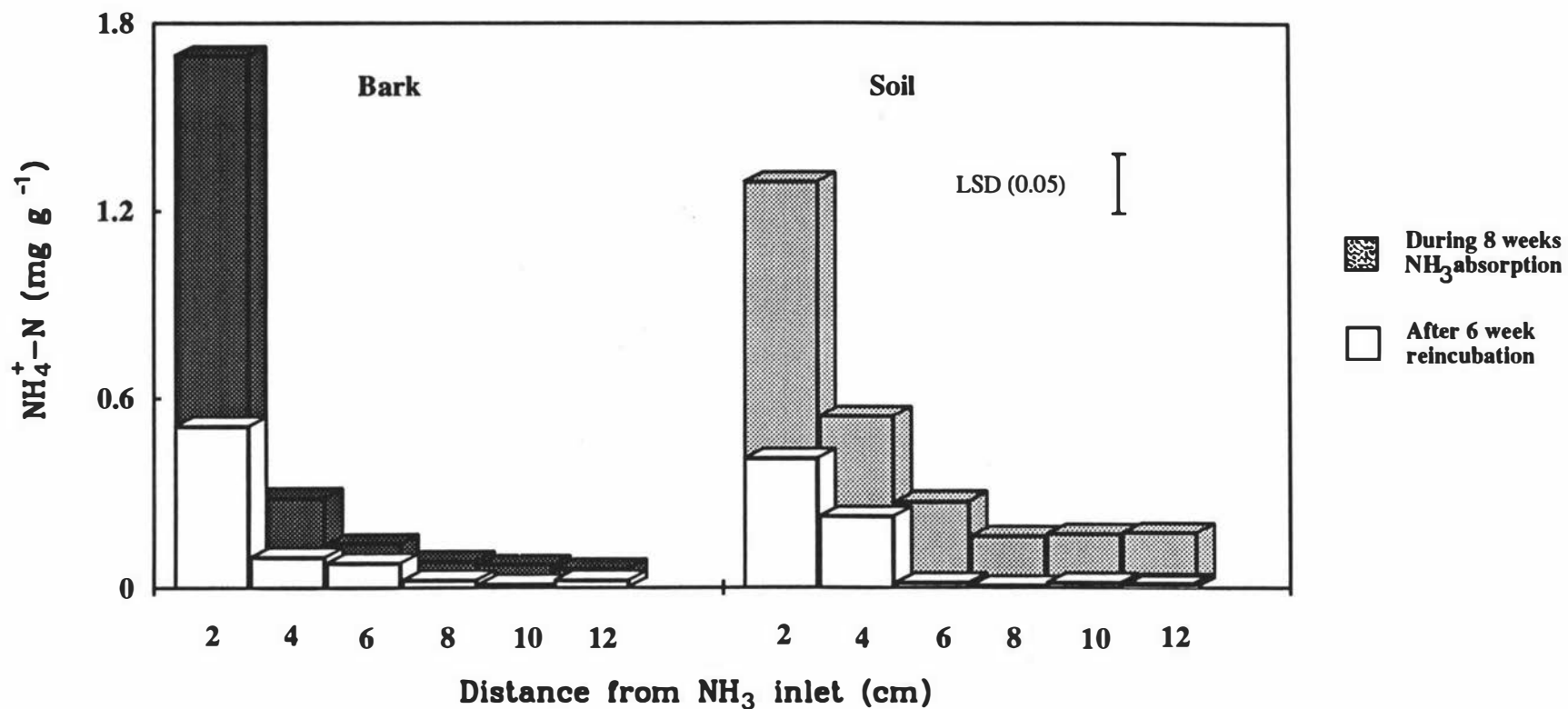
A shortage of the bark and soil samples made it impossible to determine the total N increase after NH<sub>3</sub> absorption. In the experiment I, the changes in total N content of bark and soil covers accounted for 22 to 48% of the total N volatilized from poultry manure (see section 7.4.1.1). In an earlier experiment (Chapter 4), similar to this experimental design, the effluent gases, continuously removed from the incubation jar, were found to contain only about 17% of manure N volatilized.

In this experiment, increase in the amount of KCl extractable NH<sub>4</sub><sup>+</sup>-N in bark and soil columns accounted for only 1% of the total N in the poultry manure, which is obviously far less than that obtained with bark and soil covers. As has already been discussed in the experiment I, with covers, the absorption of NH<sub>3</sub> and diffusion of NH<sub>4</sub><sup>+</sup> from manure to the bark and soil covers resulted in marked increases in N content (section 7.4.1.1). In this experiment the increase in NH<sub>4</sub><sup>+</sup>-N in the bark or soil columns resulted from the absorption of gaseous NH<sub>3</sub> only.

**Table 7.5** Changes in  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  ( $\mu\text{g g}^{-1}$ )\* content of bark and soil columns during  $\text{NH}_3$  absorption and reincubation

Material	$\text{NH}_4^+\text{-N}$		$\text{NO}_3^-\text{-N}^{**}$
	After $\text{NH}_3$ absorption	After reincubation	After reincubation
1. Bark	334.3	118.8	152.7
2. Bark + NCPR	345.9	79.1	194.6
3. Soil	360.9	54.7	471.0
4. Soil + NCPR	382.2	35.8	522.5
LSD (0.05)	183.5	69.5	66.2

- \* Mean of six sections with three replicates and denote net change in  $\text{NH}_4^+\text{-N}$  or  $\text{NO}_3^-\text{-N}$  (final-initial).
- \*\* The concentrations of  $\text{NO}_3^-\text{-N}$  were very low ( $<0.1 \mu\text{g g}^{-1}$ ) before reincubation



**Fig 7.7** Amounts of  $\text{NH}_4^+-\text{N}$  in the sections of bark and soil columns 8 weeks after  $\text{NH}_3$  absorption and 6 weeks after reincubation with fresh soil inoculum

#### 7.4.2.1.2      NO<sub>3</sub><sup>-</sup>-N in bark and soil columns

The content of NO<sub>3</sub><sup>-</sup>-N in the bark and soil columns at the end of 8 weeks NH<sub>3</sub> absorption period was <1 µg g<sup>-1</sup> (Table 7.5). This may suggest that either the oxidation of the absorbed NH<sub>4</sub><sup>+</sup> has not occurred or that some of the NO<sub>3</sub><sup>-</sup> produced has been immobilized into organic N. As the free NH<sub>3</sub> released from poultry manure is considered to be toxic to nitrite oxidizing bacteria (Giddens and Rao, 1975), it may probably have suppressed the nitrification in bark and soil.

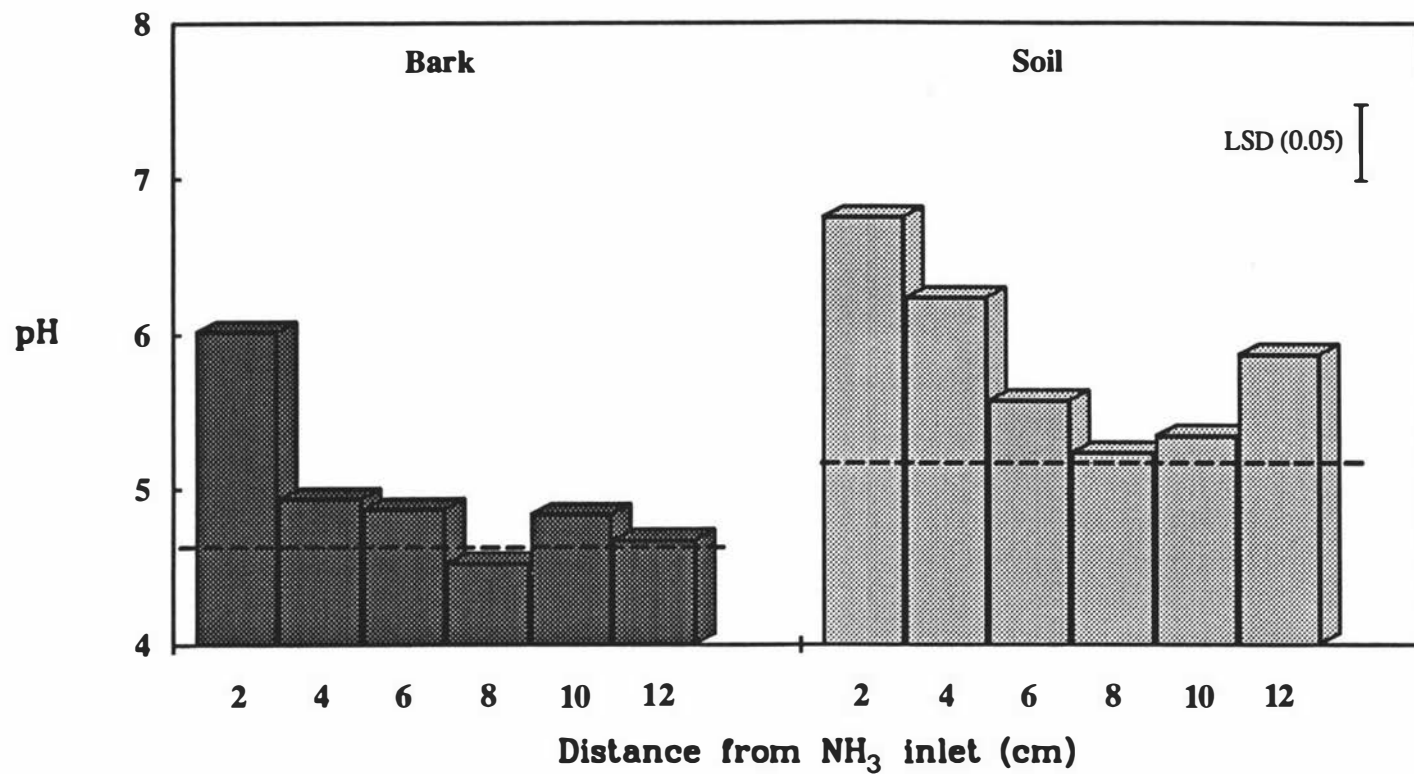
#### 7.4.2.1.3      pH of bark and soil columns

As the NH<sub>3</sub> is chemisorbed forming NH<sub>4</sub><sup>+</sup>, the concentration of OH<sup>-</sup> ions increased, which increased the pH of the bark and soil. The changes in pH corresponded to the NH<sub>4</sub><sup>+</sup>-N distribution in bark and soil columns (Fig 7.8). Similar to earlier observation with covers, the pH increased from 4.8 to 6.0 in bark, while it increased from 5.2 to a maximum of 6.8 in soil columns. In both cases the pH generally decreased as the distance from the NH<sub>3</sub> inlet increased (Fig 7.8) and the increase in pH was highly correlated ( $r=0.99$  and  $0.96$ , for bark and soil, respectively) with the amount of absorbed NH<sub>4</sub><sup>+</sup>.

#### **7.4.2.2      *Reincubation after NH<sub>3</sub> absorption stage***

After 6 weeks of reincubation, the NH<sub>4</sub><sup>+</sup>-N in the sectioned samples of bark and soil decreased by >50% (Fig 7.7). The decrease in the NH<sub>4</sub><sup>+</sup>-N was attributed to the oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>. Although the increase in NO<sub>3</sub><sup>-</sup>-N content after reincubation correlated with the decrease in NH<sub>4</sub><sup>+</sup>-N content, a 1:1 relationship was not obtained.

It was observed that in the sections of bark and soil close to the NH<sub>3</sub> inlet the increase in NO<sub>3</sub><sup>-</sup>-N during reincubation were lower than the decrease in NH<sub>4</sub><sup>+</sup>-N. In the other sections, as the distance from the inlet increased, the increase in NO<sub>3</sub><sup>-</sup>-N was higher than the decrease in NH<sub>4</sub><sup>+</sup>-N. This implies that while in the former samples some of the NO<sub>3</sub><sup>-</sup> might have been immobilised into the microbial cells, in the latter samples the



**Fig 7.8** pH values of the sections of bark and soil columns after 8 weeks  $\text{NH}_3$  absorption. Dotted lines show the initial pH values

mineralization of the organic N may have increased  $\text{NO}_3^-$  content. Alternatively, free  $\text{NH}_3$  could have been volatilized during the preparation of sections having the highest pH and  $\text{NH}_4^+$ -N content.

When the bark and soil column samples were reincubated with fresh soil inoculum, the  $\text{NO}_3^-$ -N increased substantially indicating the occurrence of nitrification (Table 7.5). The highest content of  $\text{NO}_3^-$ -N were observed in the bark and soil samples which were nearest to the  $\text{NH}_3$  entry point and the content decreased rapidly with increasing distance from the inlet (Fig 7.9).

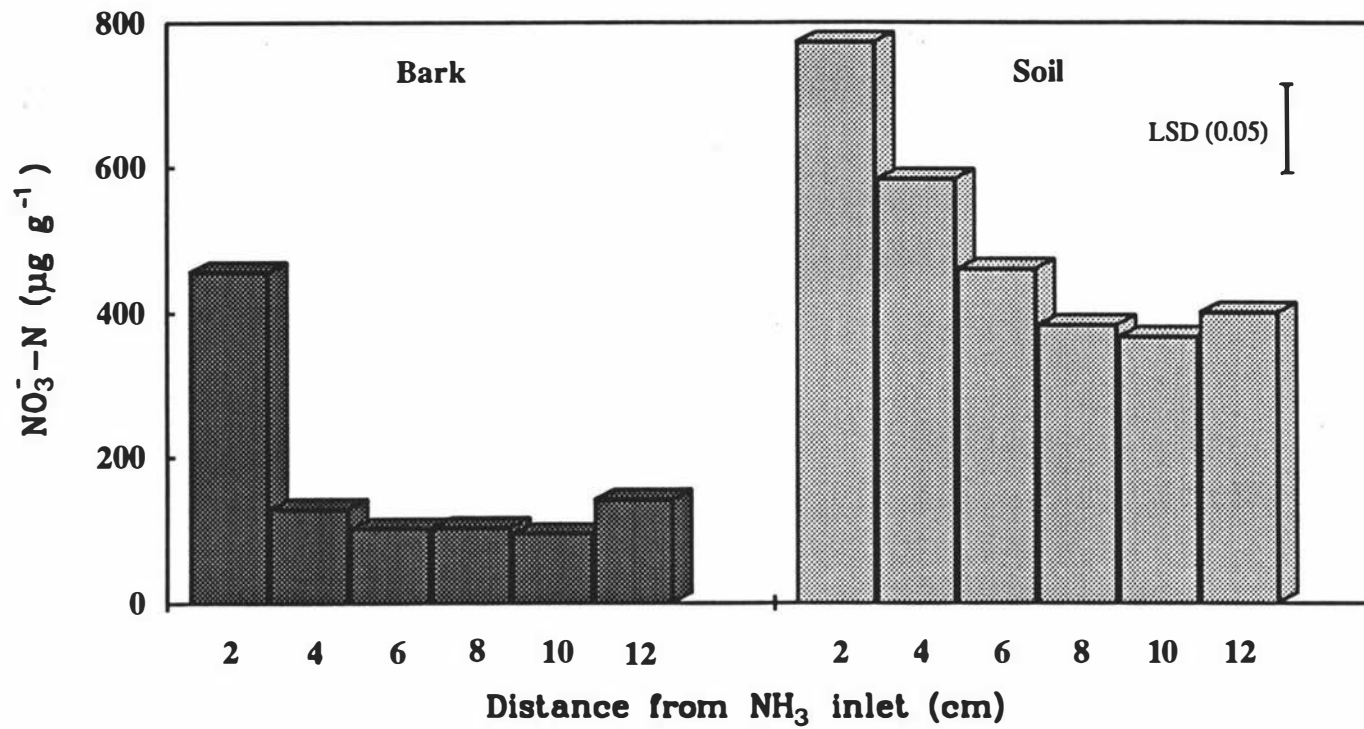
Although the bark contained higher amounts of  $\text{NH}_4^+$ -N, the rate of nitrification was observed to be lower in bark than in soil which may be due to the deficiency of nitrifying organisms and lower pH in the bark. Also high  $\text{NH}_4^+$  levels inhibit nitrification (Alexander, 1967).

After 8 weeks  $\text{NH}_3$  absorption, reincubation of bark and soil samples with fresh soil inoculum resulted in substantial decreases in pH (from 6.03 to 4.20 and 6.76 to 4.54 in bark and soil, respectively), which was attributed to the release of  $\text{H}^+$  during the subsequent oxidation of the absorbed  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . The pH of the bark and soil closely followed the increase in the  $\text{NO}_3^-$ -N content during reincubation.

#### 7.4.2.3 *Dissolution of NCPR in bark and soil columns*

Dissolution of NCPR in bark and soil columns after 8 weeks  $\text{NH}_3$  absorption, and after 6 weeks of reincubation, was determined from the increases in the amount of soluble and adsorbed P (resin plus NaOH extractable P) and from the decreases in the amount of residual apatite P (HCl extractable P) (Eq 7.4).

$$\%DPR = (\Delta P/P_0) * 100 \quad (7.4)$$



**Fig 7.9** Distribution of  $\text{NO}_3^- \text{N}$  in the sections of bark and soil columns after 6 weeks reincubation with fresh soil inoculum

where,	
%DPR	= Dissolution of NCPR (% P added)
$\Delta P_i$	= Increases in the amount of $P_i$ due to NCPR (as extracted in resin plus NaOH) or decreases in the amount of residual P due to NCPR (as extracted in HCl)( $\mu\text{g g}^{-1}$ bark/soil)
$P_a$	= P added ( $1000\mu\text{g g}^{-1}$ bark/soil)

There was a close relationship between these two methods (Fig 7.10). However, in soil, the former method slightly underestimated the extent of PR dissolution. This suggests that some of the dissolved P has been transformed into organic P which was not included in the measurement.

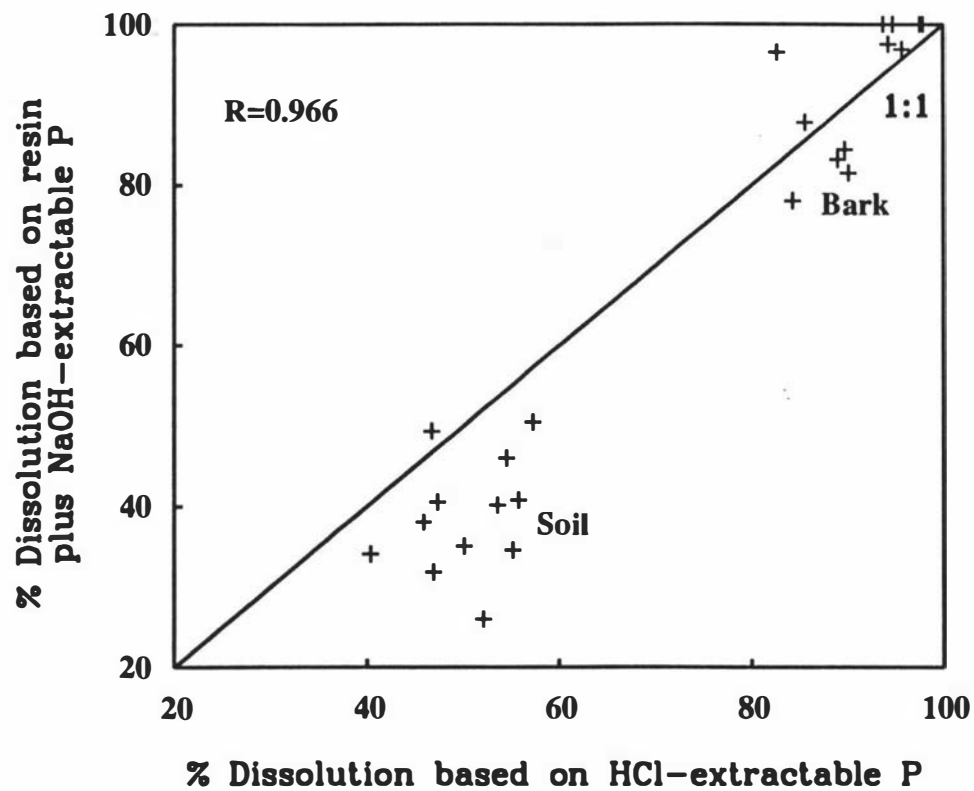
The dissolution of NCPR in bark and soil in the absence and presence of  $\text{NH}_3$  absorption and after the subsequent reincubation is given in Table 7.6 and Figure 7.11. Under all three situations, the dissolution of NCPR was higher in bark than in soil which may be attributed to the higher levels of exchangeable acidity ( $80.5\text{cmol (+) kg}^{-1}$ ) and Ca sink size ( $82.7\text{cmol (+) kg}^{-1}$ ) in the bark than in the soil ( $20.8$  and  $28\text{ cmol (+) kg}^{-1}$ , respectively), (Bolan *et al.*, 1990; Robinson *et al.*, 1992).

The extent of NCPR dissolution during the initial  $\text{NH}_3$  absorption was not significantly different from that in the absence of  $\text{NH}_3$  absorption (Fig 7.11). However, the subsequent reincubation of soil and bark materials with fresh addition of soil inoculum significantly (in bark) and slightly (in soil) increased the NCPR dissolution (Table 7.6).

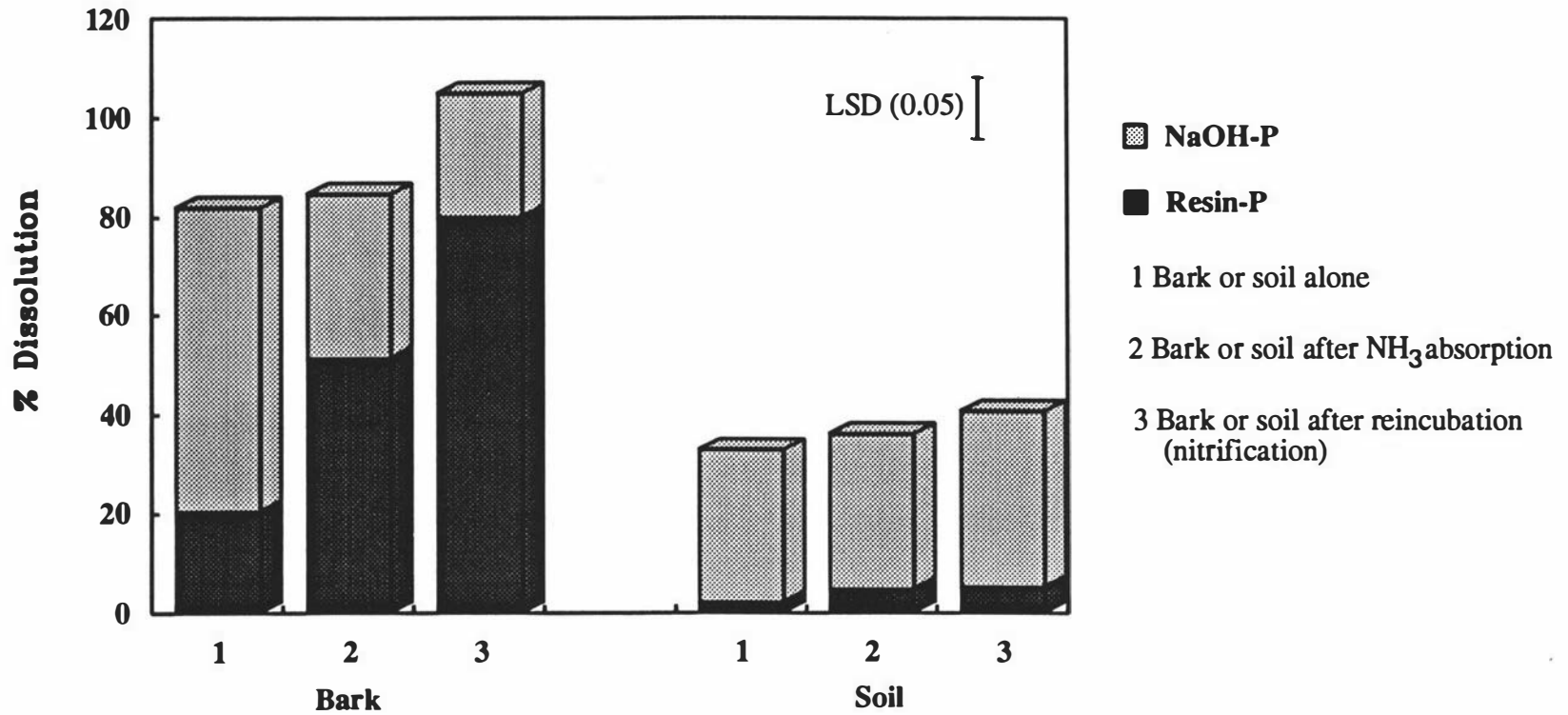
During the initial  $\text{NH}_3$  absorption there was no evidence for nitrification as the pH remained high which may be the reason for the absence of any effect on PR dissolution. Subsequent reincubation of the samples caused nitrification of the absorbed  $\text{NH}_4^+$  ions resulting in the release of protons and thereby inducing PR dissolution. The amount of resin extractable P showed that about 80% and 5% of the dissolved P were in the readily available form in bark and soil, respectively (Fig 7.11).

#### 7.4.2.4 Nitrification vs NCPR dissolution

Nitrification of ammoniacal fertilizers in soils has been shown to increase the dissolution



**Fig 7.10 Relationship between PR dissolution based on the residual apatite P (HCl-extractable P) and the resin plus NaOH-extractable P**



**Fig 7.11** Dissolution of NCPR as measured from the increases in resin plus NaOH extractable P in bark and soil columns in the presence and absence of  $\text{NH}_3$  absorption and after reincubation

of both the added and residual P (Chien, 1979; Apthorp *et al.*, 1987). Increased PR dissolution has mostly been attributed to the release of  $H^+$  during the nitrification process. The availability of  $H^+$  ions release during nitrification for the dissolution of PR depends on the pH buffering capacity of the soil. An attempt was made to predict the amount of NCPR dissolved from the quantity of  $H^+$  ions released during nitrification. It was assumed that 2 moles of  $H^+$  are consumed per mole of dissolved P (Eq 2.6).

Ammoniacal N decreased approximately from 345 to 79  $\mu\text{g N g}^{-1}$  and from 382 to 36  $\mu\text{g N g}^{-1}$  in bark and soil, respectively (Table 7.5). Assuming that the decrease in  $\text{NH}_4^+\text{-N}$  resulted from the nitrification, it can be calculated from equation 2.6 (Chapter 2) that approximately 38 and 49  $\mu\text{mol H}^+ \text{ g}^{-1}$  are produced in the bark and soil, respectively. If all these  $H^+$  are involved in the dissolution of NCPR, it can cause an additional dissolution of approximately 59% and 76% of added NCPR in the respective systems (Table 7.6).

A similar calculation using the increased amounts of  $\text{NO}_3^-\text{-N}$  indicates that approximately 43% and 115% of NCPR dissolution in bark and soil, respectively, can be achieved by the  $H^+$  released from nitrification (Table 7.6). The measured increase in dissolution, resulting from the nitrification during the reincubation, were approximately 15% and 5% in bark and soil systems, respectively, which were much less than those calculated from the extent of nitrification.

The above calculations indicate that in bark systems more than 50% of the  $H^+$  released is probably involved in PR dissolution, while in soil systems only a fraction (5-10%) of the  $H^+$  released is involved in PR dissolution. Apthorp *et al.* (1987) have observed that in an incubation experiment the addition of acidifying N fertilizers, urea and ammonium sulphate, caused 19% and 33% increases in the dissolution of Sechura phosphate rock over the control soil. However, calculation of the amounts of  $H^+$  released through nitrification indicated that only approximately 5% of the protons are involved in the dissolution of PR.

**Table 7.6** Dissolution of NCPR in bark and soil columns in the absence (-) and presence (+) of  $\text{NH}_3$  absorption and during the reincubation

Materials	Measured dissolution of NCPR (%) based on $\Delta\text{Pi}$ (Resin + NaOH-P)			Predicted* Dissolution (%)	
	In the absence of $\text{NH}_3$ absorption	In the presence of $\text{NH}_3$ absorption	Reincubation	Based on $\Delta\text{NH}_4^+\text{-N}$	Based on $\Delta\text{NO}_3^-\text{-N}$
1. Bark	82.3	85.2	106.3	59.0	43.0
2. Soil	33.2	36.6	41.0	76.9	115.0

**LSD (0.05)**

Materials	6.14**
Incubation	6.14*
Materials * Incubation	8.66*

\* Increases in the dissolution based on the changes in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  and the production of  $\text{H}^+$  from nitrification. It assumes all  $\text{H}^+$  produced are involved in PR dissolution.

It is evident that most of the  $H^+$  released during nitrification was involved in reactions buffering soil pH or solution  $Ca^{2+}$  increased preventing PR dissolution. At the pH range 4-6 in this experiment the major pH buffering reactions in the soil would be reactions of Al and Fe hydrous oxides and protonation of organic functional groups. At pH's above 6, metal carbonates may be involved (Faurie and Fardeau, 1990). Bark, therefore, appears to be a better medium than soil in which to conserve protons for PR dissolution.

## 7.5 CONCLUSIONS

These laboratory experiments have shown that  $NH_3$  released from poultry manure can be absorbed either by covering the manure heaps with a layers of bark or soil or by passing the  $NH_3$  through a column containing these materials.

The results show that the materials were enriched with N which also resulted in an increase in cation exchange capacity due to the pH increase from  $NH_3$  absorption. Comparing the two methods for efficient absorption of  $NH_3$ , bark and soil covers appear to be less expensive to install than columns with forced aeration. In both systems, bark was found to be more effective in absorbing  $NH_3$  than soil.

The dissolution of NCPR, with and without  $NH_3$  absorption, was higher in bark due to the high exchangeable acidity and large Ca sink size. With bark more than 80% of the dissolved P remained in a readily plant available form. When the manure heap was covered with bark or soil, accumulation of Ca in the bark or soil inhibited the dissolution of PR. The inhibitory effect of Ca on PR dissolution was overcome by physically separating the bark/soil from manure.

Both in the bark and soil, only a small fractions of the protons released during the oxidation of absorbed  $NH_3$  are involved in the dissolution of PR; most of the protons are involved in pH buffering reactions of bark and soil. The results show that the exchangeable acidity in bark can be regenerated by absorbing  $NH_3$  from manure which, upon nitrification, produces  $H^+$ .

If large volumes of bark or similar products are available, it is possible to enrich these biological wastes with both N and P nutrients using poultry manure and PR, which could be used as fast release organic fertilizers in agricultural and horticultural systems.

## CHAPTER 8

### AGRONOMIC EFFECTIVENESS OF POULTRY MANURE COMPOSTS

#### 8.1 INTRODUCTION

Results of the laboratory experiment discussed in Chapter 6 show that only <16% of phosphorus (P), added through phosphate rock (PR) was dissolved during composting with poultry manure. Several studies have shown that PR either composted with organic manure, or applied together with organic manure, increased the yield and uptake of P by crops which is attributed mainly to the increase in the availability of P from PR (see Chapter 2, section 2.6.2). Under field conditions it is likely that the plant uptake of P and calcium (Ca) and the availability of exchange sites provide sinks for PR dissolution products ( $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$ ), enhancing the dissolution of PR.

The addition of elemental sulphur ( $\text{S}^0$ ) to poultry manure/synthetic francolite and poultry manure/North Carolina phosphate rock compost resulted in increased amounts of inorganic P ( $\text{Pi}$ ) due to PR dissolution (Chapter 6). The  $\text{S}^0$  was also found to be very effective in reducing the N loss from manure both through  $\text{NH}_3$  volatilization (Chapter 4) and denitrification (Chapter 5). Also, addition of  $\text{S}^0$  to the compost is likely to meet the crop's requirement of sulphur (S).

Two types of compost, sulphocompost (a blend of poultry manure with woodchip,  $\text{S}^0$  and PR) and phosphocompost (a blend of poultry manure with woodchip and PR) were prepared. Fresh manure mixtures were also prepared using similar combinations. The agronomic effectiveness of composts and fresh manure mixtures was tested under field conditions using winter cabbage and summer maize as test crops.

#### 8.2 OBJECTIVES

The objective of these experiments was to evaluate the agronomic effectiveness of poultry manure composts and fresh manure mixtures under field condition.

8.3 MATERIALS AND METHODS

8.3.1 Collection of poultry manure

Fresh poultry manure was collected from under cage batteries at the Poultry Research Centre, by scrapping the top layer of recently deposited droppings. Any feathers and coarse materials including feed materials in the manure were carefully removed by hand. The characteristics of the manure are given in Table 4.1. The manure was immediately mixed with woodchip and a soil inocula containing PR and S° for composting, as described below (section 8.3.3.1.2). For fresh manure mixtures, fresh manure was collected at the time of field application.

8.3.2 Phosphate rock

In this study, a sample of Sechura phosphate rock (SPR), a reactive PR, was used to prepare the enriched composts. Some basic characteristics of the SPR sample are given in Table 8.1.

Table 8.1 Some characteristics of Sechura phosphate rock used in the study

Characteristics	
1. Particle size (µm)	>180
2. Reactivity*	High
3. Total P (% wt)	13.5
(a) water extractable P (% of total P)	0.01
(b) 2% citric acid extractable P (% of total P)	42.4
4. Total CaCO <sub>3</sub> (% wt)	9.0
5. Total Ca (% wt)	33.4

\* Based on the solubility in 2% citric acid

### 8.3.3 Preparation of composts

Two types of compost (a) *sulphocompost* (blending poultry manure with woodchip, S° and PR) and (b) *phosphocompost* (blending poultry manure with woodchip and PR) were prepared.

#### 8.3.3.1 *Sulphocompost*

##### 8.3.3.1.1 Soil/PR inoculum

2.46kg of SPR and 320g of commercial grade S° were thoroughly mixed with about 2.5kg of moist field soil (Karapoti fine sandy loam, *Dystic Eutrochrept*) and kept in a plastic bucket for 4 weeks prior to blending with manure. The moisture content of the mixture was maintained at field capacity which facilitated oxidation of S° prior to composting with manure.

##### 8.3.3.1.2 Composting

Poultry manure from the broiler (meat) industry is generally a combination of excreta and litter, usually consisting of woodchip, paper waste or sawdust. For this reason woodchip was used in the preparation of composts and manure mixtures.

About 34kg of airdried woodchip (*Pinus spp.*) were spreaded on heavy grade plastic sheets, moistened to 68% (w/w) with tap water, covered and allowed to soak for one week. About 58kg of fresh poultry manure was thoroughly blended with the soil-PR mixture and then mixed with 34kg of woodchip to obtain a C/N ratio of about 25, which, according to Gotaas (1956) and Gray and Biddlestone (1981), is considered to be ideal C/N ratio for composting. The ratio of manure, S° and PR in each mixture were calculated based on the N,S and P requirements of a winter cabbage crop (300, 100, 100kg ha<sup>-1</sup> N,S,P, respectively).

After mixing, a small compost heap of approximately 1.5m<sup>3</sup> was prepared by stacking the mixture in the open and immediately covering it with thick heavy grade polyethylene

sheet to conserve the heat and reduce the loss of moisture and  $\text{NH}_3$ . A windrow type composting was carried out for 5 weeks. On alternate days the compost heap was mixed thoroughly then recompressed by treading.

#### **8.3.3.2      *Phosphocompost***

The phosphocompost was prepared in the same way as described above, but without  $\text{S}^\circ$ . About 58kg of fresh poultry manure was blended with 2.5kg of PR which was preincubated with 2.5kg of moist field soil 4 weeks prior to blending. Finally, 34kg of moistened woodchip was added to the mixture and composted as described above.

#### **8.3.4      *Fresh manure mixtures***

Fresh manure mixtures were prepared by blending the same quantities of manure, PR, woodchip with and without  $\text{S}^\circ$ . These mixtures were thoroughly hand mixed and immediately applied to the field.

#### **8.3.5      *Treatments***

Details of the fertilizer treatments and rates are shown in Table 8.2. There were six treatments comprising two compost, two fresh manure mixtures, one urea treatment, and an absolute control. Treatments were applied by hand and incorporated into the soil using a rotovator.

#### **8.3.6      *Field experiment I***

A field experiment using winter cabbages (*Brassica oleracea* var. capitata cv. Winter Pride) was conducted to evaluate the agronomic effectiveness of the manure compost and fresh manure mixtures compared to inorganic fertilizer (urea).

The soil at the experimental site was a Karapoti fine sandy loam (coarse loamy mixed mesic *Dystic Eutrochrept*), which is suitable for horticultural crops (Fig 8.1a). Some characteristics of the soil (0-15cm depth) are given in Table 8.3.

**Table 8.2 Treatment details for the field experiments**

Treatments	Total amount added (kg plot <sup>-1</sup> )	Amount of materials in the composts or manure mixtures (kg or g plot <sup>-1</sup> )					Total supply of nutrients (kg ha <sup>-1</sup> )			
		PM <sup>1</sup> (kg)	WC <sup>2</sup> (kg)	S <sup>3</sup> (g)	PR <sup>4</sup> (g)	Soil <sup>5</sup> (g)	N <sup>6</sup>	P <sup>7</sup>	K <sup>8</sup>	S <sup>9</sup>
1. Sulphocompost	23.63	14.12	8.47	80	615.4	350	300	209	81.5	100
2. Phosphocompost	23.55	14.12	8.47	-	615.4	350	300	209	81.5	-
3. Fresh manure mixture (Fmm) (manure + wc + S <sup>3</sup> + PR)	23.28	14.12	8.47	80	615.4	-	300	209	81.5	100
4. Fresh manure mixture (Fmm) (manure + wc + PR)	23.20	14.12	8.47	-	615.4	-	300	209	81.5	-
5. Urea + S <sup>3</sup> + PR	1.22			80	615.4	-	300	100	81.5	100

Treatments 1,2,3 applied 3 days before transplanting and treatments 2 & 3 applied 15 days before transplanting.

<sup>1</sup> PM = poultry manure contained 1.71% N; 0.62% P; 0.46% K (fresh weight basis)

<sup>2</sup> wc = woodchip

<sup>3</sup> S<sup>3</sup> = elemental sulphur

<sup>4</sup> PR = Sechura phosphate rocks (13.1% P)

<sup>5</sup> Soil added as an inoculum

<sup>6</sup> Total N

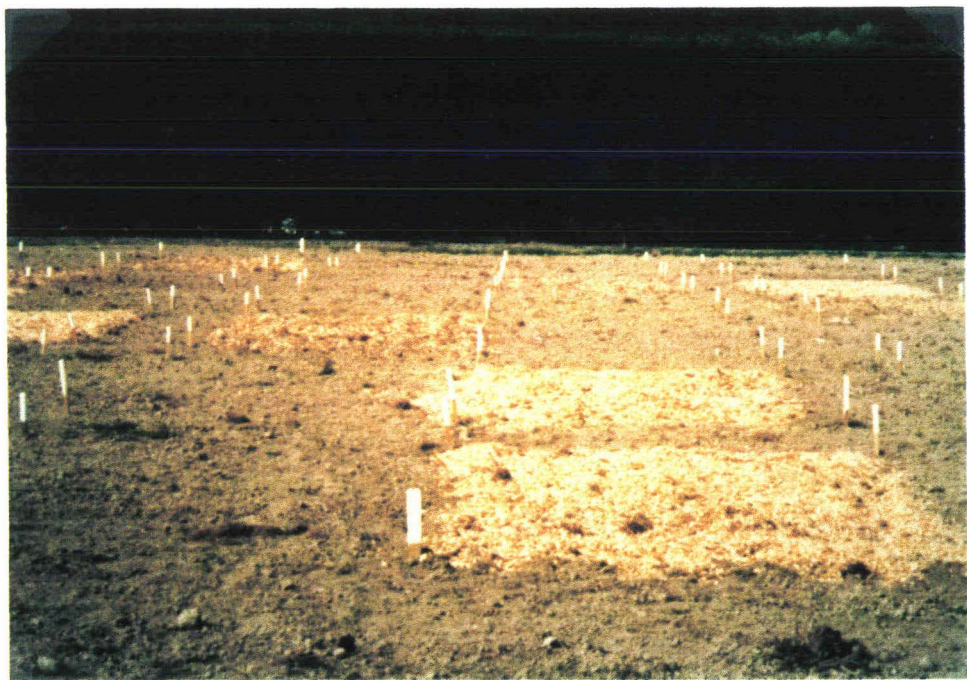
<sup>7</sup> Total P

<sup>8</sup> Total K

<sup>9</sup> Total S



**Fig 8.1a General view of the experimental field**



**Fig 8.1b Experimental field immediately after compost and fertilizer application**

**Table 8.3 Characteristics of soil (0-15cm depth) prior to planting winter cabbage**

Properties	
1. pH (H <sub>2</sub> O)	5.5
2. Total Carbon (%)	3.9
3. CEC (cmol (+) kg <sup>-1</sup> )	24
4. Total N (mg kg <sup>-1</sup> )	90.0
5. NH <sub>4</sub> -N (mg kg <sup>-1</sup> )	38.5
6. NO <sub>3</sub> -N (mg kg <sup>-1</sup> )	22.3
7. Olsen P (mg kg <sup>-1</sup> )	36.9
8. SO <sub>4</sub> -S (mg kg <sup>-1</sup> )	3.4
9. NH <sub>4</sub> OAc-K (mg kg <sup>-1</sup> )	0.47

The soil pH was 5.5, which is almost near the pH requirement range of cabbage (5.5-6.5). The soil is low in P retention capacity (MAF, 1986) with an Olsen soil test P level of 36.9mg kg<sup>-1</sup> soil. The potassium (K) was also well above the target soil test K value for a sandy loam soil (MAF, 1986).

The experimental plot size was 3.2 \* 2.5m (8m<sup>2</sup> ) and the treatments were replicated four times in a completely randomised block design. All the plots received 100kg K ha<sup>-1</sup> (as KCl) before planting. Compost and inorganic fertiliser were applied to the field plots 3 days prior to planting, whereas fresh manure mixtures were applied 2 weeks prior to planting (Fig 8.1b) and immediately incorporated into the soil using a rotovator.

Seedlings of winter cabbages were transplanted on 14 May 1990 into a freshly rotovated seedbed, with a spacing of 50\*80cm. The general view of the crop, photographed 120 days after transplanting (DAT) is shown in Figure 8.2. The cabbage plants were harvested on 2 November, 1990, by cutting just below the node of the first leaf. Fresh and dry weight of samples were recorded at harvest.

Meteorological data for the experimental period was obtained from the DSIR Meteorological Station situated about 300m from the experimental site. The predicted daily net drainage was calculated using the following water balance equation (Eq 8.1).



**Fig 8.2** General view of winter cabbage in the field



**Fig 8.3** General view of summer maize in the field

$$D = R - E_t + W - W_{fc} \quad (8.1)$$

where,

D	=	Net drainage (mm)
R	=	Daily rainfall (mm)
E <sub>t</sub>	=	Daily potential evapotranspiration (mm), calculated according to Priestly and Taylor (1972)
W	=	Depth of water for soil (mm)
W <sub>fc</sub>	=	Depth of water for the soil at field capacity (mm)

### 8.3.7 Field experiment II

To examine the residual effect of different manure and fertilizer treatments, summer maize (*Zea mays* L. cv Honey) was grown on the same plots without further application of nutrients after ploughing and rotovating. Using a tractor drawn seed drill the maize seeds were sown adopting a spacing of 20\*15cm on 30 November, 1990 (summer). The general view of the crop, photographed 3 months after sowing is shown in Figure 8.3. After tasselling, representative samples were collected on 7 February 1991 by cutting entire plants just above the ground and recorded green yields.

### 8.3.8 Soil and plant sampling

Soil cores (0-60cm) were collected at 60 and 120 DAT cabbage in order to examine the leaching of fertilizer N. Plant samples were collected at harvest from the inner rows leaving the guard rows. The plants were dried at 70°C and ground to pass a 0.425mm screen using a stainless steel Wiley Mill.

### 8.3.9 Analysis

The NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N contents of the soil were measured by extracting soil samples with 2M KCl at a soil:solution ratio of 1:10. The NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N concentrations in the extracts were determined by autoanalyzer methods (Technicon 1976; Downes, 1978). The total Kjeldahl N and P contents of plant were determined by digesting the samples with 4cm<sup>3</sup> Kjeldahl digest mixture and determined by the autoanalyzer method (Twine and Williams 1971; Technicon 1976).

### 8.3.10 Calculations

The agronomic effectiveness of compost and fresh manure mixtures relative to urea (RAE) was calculated using the following equation:

$$RAE = [\Delta Y_t / \Delta Y_u] * 100 \quad (8.2)$$

where,

RAE	=	Relative agronomic effectiveness in terms of yield (Mg ha <sup>-1</sup> )
$\Delta Y_t$	=	Yield increase with compost or fresh manure mixtures over control (Mg ha <sup>-1</sup> )
$\Delta Y_u$	=	Yield increase with urea (plus S° and PR) over control (Mg ha <sup>-1</sup> )

The nitrogen use efficiency (NUE), in terms of yield produced per unit applied N for compost, and fresh manure mixtures, was calculated as follows:

$$NUE = [T_y - C_y] / N_a \quad (8.3)$$

where,

$T_y$	=	Yield obtained with compost or fresh manure mixtures or urea treatments (Mg ha <sup>-1</sup> )
$C_y$	=	Yield obtained with absolute control (Mg ha <sup>-1</sup> )
$N_a$	=	Applied N (kg ha <sup>-1</sup> )

The apparent N recovery (ANR), in terms of % N recovered, was calculated using the following equation:

$$ANR = ([TN_{\text{uptake}} - CN_{\text{uptake}}] / N_a) * 100 \quad (8.4)$$

where,

$TN_{\text{uptake}}$	=	N uptake with treatments (kg ha <sup>-1</sup> )
$CN_{\text{uptake}}$	=	N uptake with absolute control (kg ha <sup>-1</sup> )
$N_a$	=	Added N (kg ha <sup>-1</sup> )

### 8.3.11 Statistical analysis

Analysis of variance was used to compare treatment means. The least significant difference (LSD) between means was calculated according to SAS (1985). The LSD was used in conjunction with Duncan's multiple-range test.

## **8.4 RESULTS AND DISCUSSIONS**

### **8.4.1 Temperature in the compost piles**

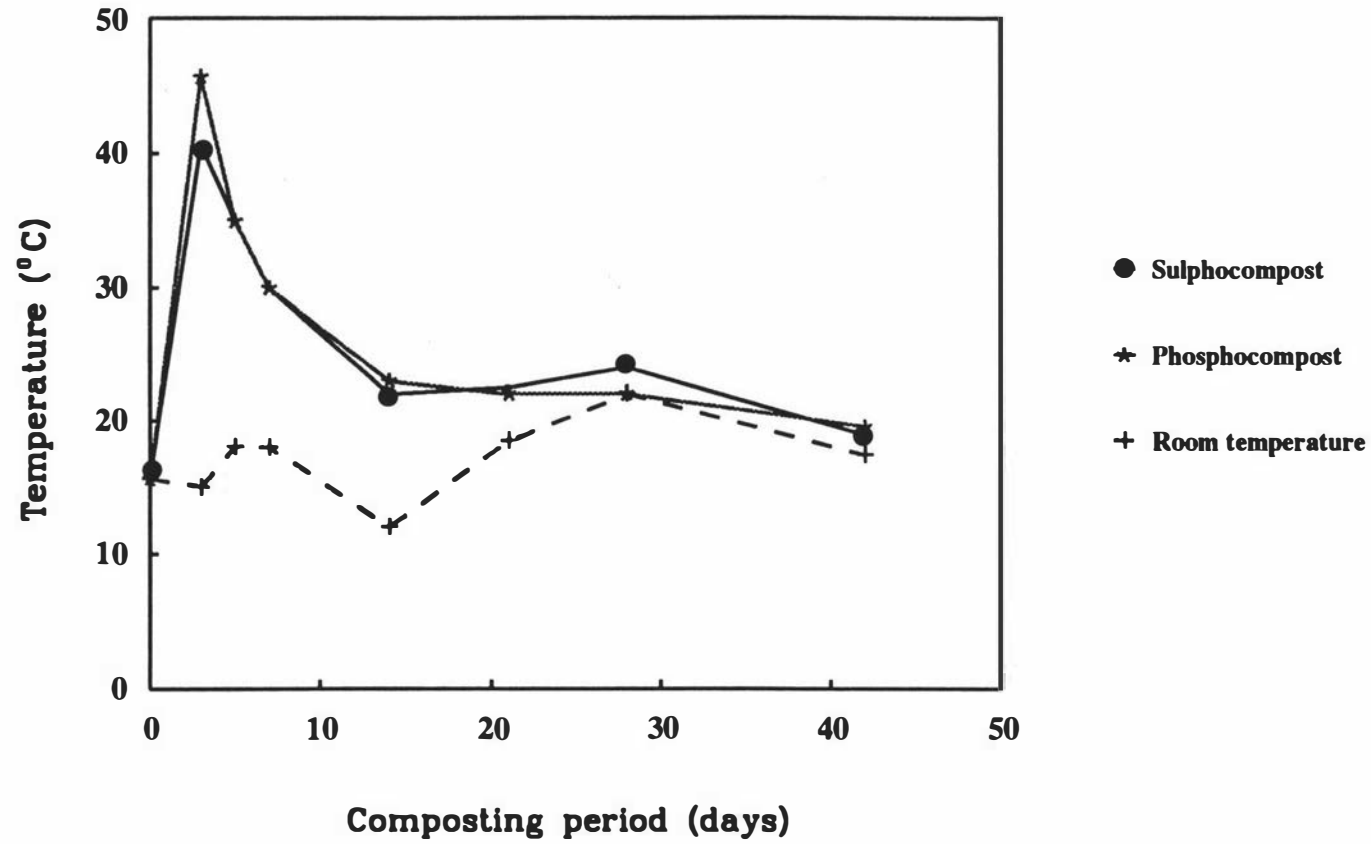
The temperature variation observed in the compost piles during composting is shown in Figure 8.4. It followed a typical trend of an initial sharp increase followed by a decrease finally attaining more or less constant value. The temperature reached a maximum of 47°C within 3 days of composting due to thermophilic microorganisms and then decreased. After 3 or 4 weeks the temperature reached the ambient temperature and remained constant. However, the temperature in the compost piles did not rise above 47°C probably due to the lack of an easily decomposed carbon source and due to cold weather which prevailed over the composting period, May-June, 1990.

### **8.4.2 Rainfall and drainage during the crop growth**

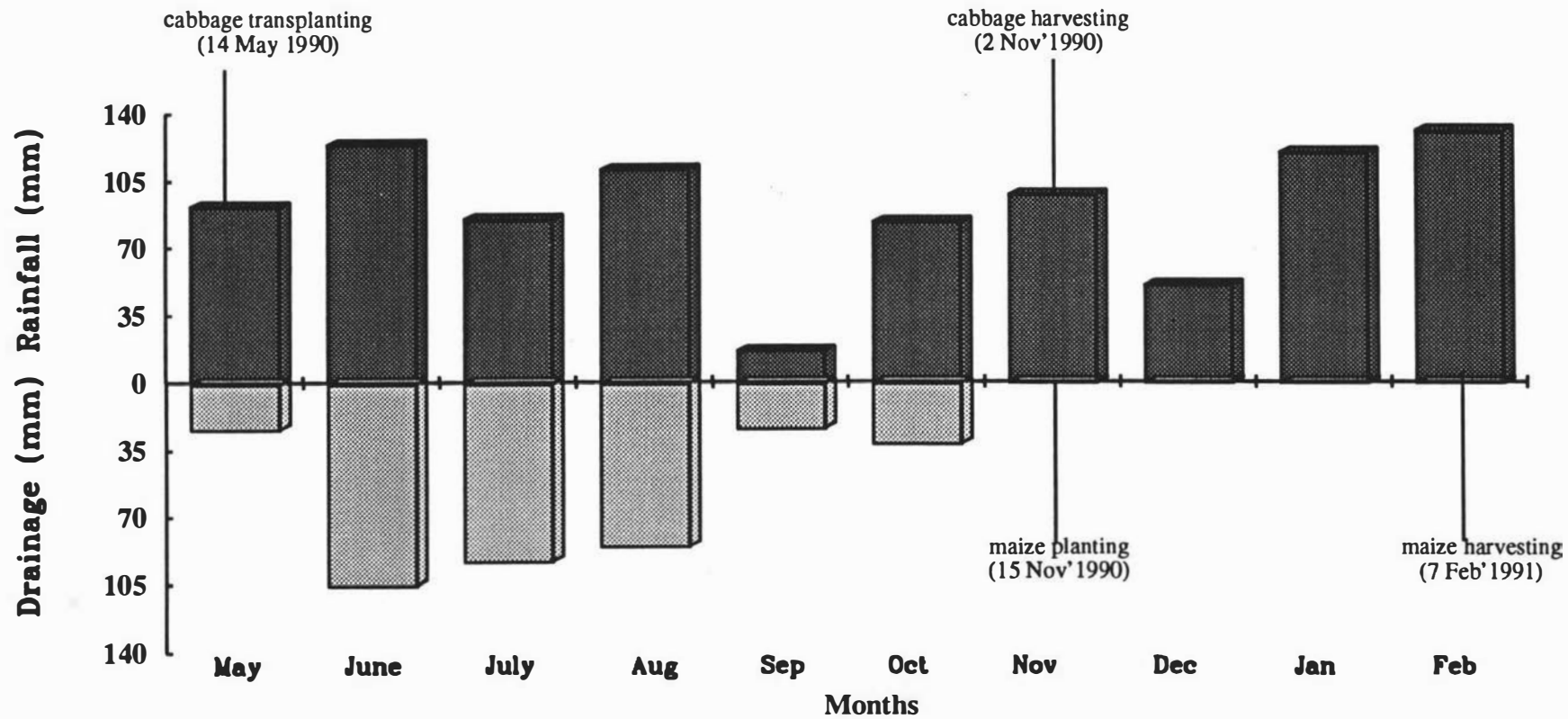
The average annual rainfall at the trial site is 920mm. The pattern of the monthly rainfall and predicted amount of net drainage (Eq 8.1) for the experimental period are shown in Figure 8.5. A total rainfall of 340mm and a cumulative drainage of 310mm were calculated from cabbage transplanting, 14 May 1990, to harvesting, 2 November 1990, which may have had a significant effect on leaching and the movement of nutrients in the soil profile.

### **8.4.3 Effect of composts and fresh manure mixtures on cabbage yield**

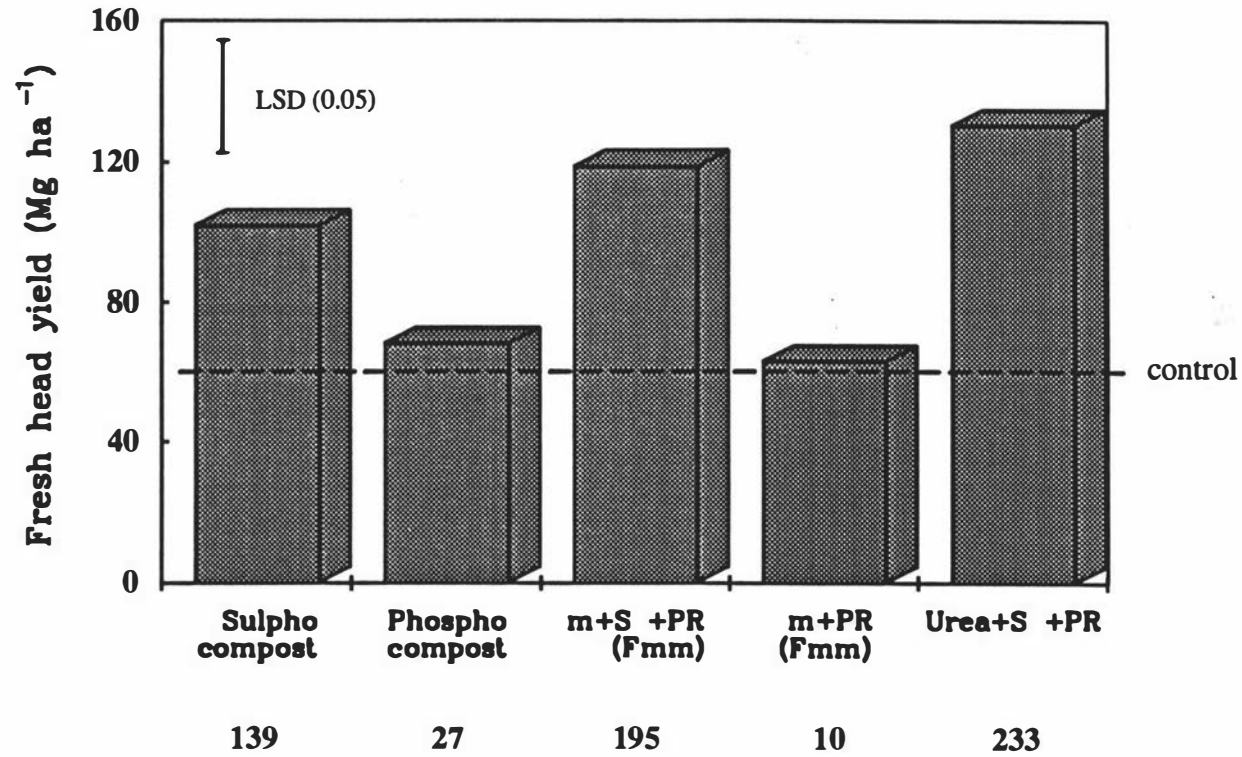
The addition of composts, fresh manure mixtures and urea had a significant effect on the fresh head yield of cabbage (Fig 8.6). Although the highest yield (130Mg ha<sup>-1</sup>) was obtained with the application of urea in combination with S° and PR, it was not significantly different from the yield obtained with sulphocompost (102.2Mg ha<sup>-1</sup>) or fresh manure mixture amended with S° and PR (119.2Mg ha<sup>-1</sup>). The addition of S° both to the compost and fresh manure mixture significantly increased the cabbage yield above the absolute control and treatments not containing S° (LSD<sub>0.05</sub>=39.2Mg ha<sup>-1</sup>). Yield increase with the addition of phosphocompost or fresh manure mixture amended with PR alone was not significant over control.



**Fig 8.4** Changes in temperature in the compost piles during composting



**Fig 8.5 Monthly rainfall and predicted net drainage for the experimental period (May 1990-February 1991)**



**Fig 8.6 Effect of composts, fresh manure mixtures (Fmm) and urea on yield of cabbage and nitrogen use efficiency (NUE)**

A maximum fresh head yield of  $130.6 \text{ Mg ha}^{-1}$  was achieved with an application of  $300 \text{ kg N ha}^{-1}$  as urea with  $\text{S}^{\circ}$  and PR. This maximum yield was equivalent to  $11.9 \text{ Mg dry matter yield (DMY) ha}^{-1}$ , which was far above the values reported by Greenwood *et al.* (1980b) and Bonoan (1990) who obtained 5.1 and  $5.5 \text{ Mg DMY ha}^{-1}$ , respectively, with an optimum N level ( $281 \text{ kg N ha}^{-1}$ ) applied to winter cabbages. The high yields obtained are probably associated with the larger number of degree growing days to harvest in this experiment. Further, the cultivar, Winter Pride, produces very large size cabbages.

The net yield increase over control was markedly higher with the addition of sulphocompost than phosphocompost (Fig 8.6). A visual observation of the cabbages at 60 days after transplanting is shown in Figure 8.7. Cabbage growth was found to be more vigorous and relatively sturdy with sulphocompost than with phosphocompost and control. The measured harvest data support the visual observations. Similarly, in the case of fresh manure mixtures the cabbage yield was significantly ( $p < 0.05$ ) higher in the presence than in the absence of  $\text{S}^{\circ}$  addition (Fig 8.6).

The calculated RAE (Eq 8.2) in terms of cabbage yield showed that the fresh manure mixture containing  $\text{S}^{\circ}$  and PR was about 84% as effective as urea (plus  $\text{S}^{\circ}$  and PR), while sulphocompost was found to be 60% as effective as urea treatment. Phosphocompost and fresh manure mixture with PR alone were only 12% and 4%, respectively, as effective as urea treatment.

Varying levels of agronomic efficiency of manure have been reported. While Azevedo and Stout (1974) reported that poultry manure was about one-half as effective as ammoniacal N fertilizers, Adolph *et al.* (1969) reported that poultry manure applied to a N and P deficient soil performed equally to that of inorganic fertilizers. Methods of manure application, cultivation practices and type of plants grown also affect the efficiency of manure N.

The nitrogen use efficiency (NUE) calculated in terms of fresh head yield produced per kg N applied (Eq 8.3) was also higher (refer Fig 8.6) with sulphocompost (139) and fresh manure mixture containing  $\text{S}^{\circ}$  plus PR (195) than phosphocompost (27) and



**Fig 8.7** Difference in the growth of cabbage in the control (1), phosphocompost (2) and sulphocompost (3) treated plots at 60 days after transplanting

manure mixture containing PR alone (10). It can be seen that the effectiveness of  $S^0$  was found to be higher with fresh manure mixture than compost. Immediate incorporation of fresh manure mixture with  $S^0$  and PR resulted in relatively higher yield and NUE than its respective compost.

It is often reported that fresh manure is more effective in increasing yield and uptake by crops than composted manures (Brinton, 1985; Kirchmann, 1989). During composting the N availability is reduced (Castellanos and Pratt, 1981) because some of the potentially available forms of N such as  $NH_3$ , amines, and urea have been diminished or have been transformed chemically and biologically to more stable polymerized humic compounds (Golueke, 1972) or in organic forms (Kirchmann, 1985b) and, therefore, may release N slowly during decomposition in soil (Castellanos and Pratt, 1981).

The result clearly demonstrates the beneficial effect of  $S^0$  in the compost as well as in fresh manure mixtures. The higher cabbage yield and NUE obtained with sulphocompost and manure mixture containing  $S^0$  plus PR can be attributed to either an increase in the availability of manure N resulting from improved conservation of  $NH_3$  when  $S^0$  is added, or to improved S nutrition of the cabbage leading to increased N uptake. The importance of an N\*S interaction in cabbage growth needs further investigation.

Another possibility is that the production of  $H_2SO_4$  during the oxidation of  $S^0$  may have dissolved the PR and therefore increased the P availability. Bangar *et al.* (1989) found that composting paddy straw with PR and iron pyrite increased the yield of wheat crops more than superphosphate addition, attributing this to the enrichment of both N and P in compost achieved through the addition of pyrite. In general, phosphocompost and fresh manure plus PR mixture were less effective than sulphocompost and fresh manure plus  $S^0$  and PR mixture.

#### 8.4.4 Uptake of N

The N content of cabbages varied from 1.8 to 2.4%. Urea treatment resulted in the

highest N content (2.44%) in plants, but there were only small differences in N content between treatments. In general, the N content observed with organic and inorganic sources in this experiment was below the critical level of 3-4% for cabbage crop as reported by Geraldson *et al.* (1973), MAF (1986) and Piggott (1986). However, a linear increase ( $r=0.668$ ) in yield with increasing N content in cabbage was observed.

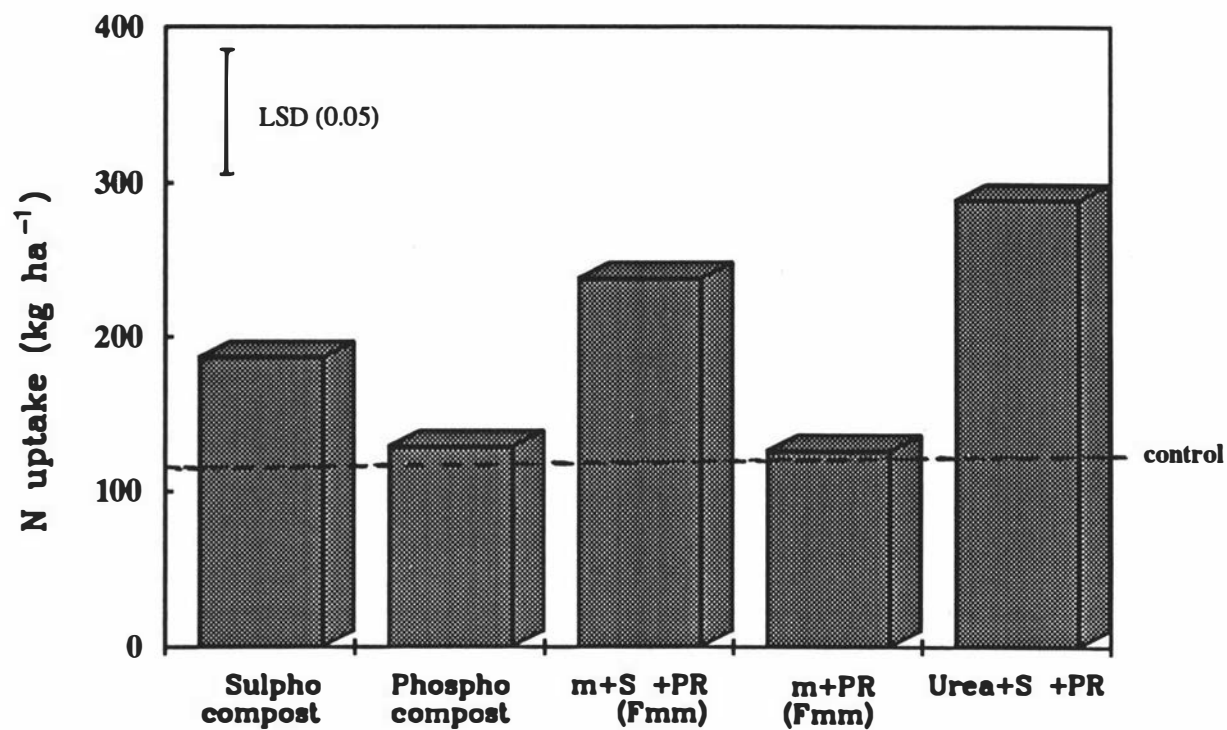
The plant uptake of N (Fig 8.8) closely followed the trend in cabbage yields (Fig 8.6) and, therefore, showed a strong correlation between N uptake and fresh head yield (Fig 8.9). Amongst the treatments, the S° and PR containing fresh manure mixtures and sulphocompost resulted in a significant increase in N uptake over the control treatment (Fig 8.9).

Though not significant at the  $P=0.05$  level, N uptake was also higher with sulphocompost than phosphocompost. Similar results were obtained with the respective manure mixtures (+S°, -S°). In this study the plant N uptake with the use of sulphocompost and fresh manure mixture with S° and PR were 188 and 239kg ha<sup>-1</sup>, respectively, which were higher than those reported for inorganic fertilizers by Greenwood *et al.* (1980b) and Bonoan (1990).

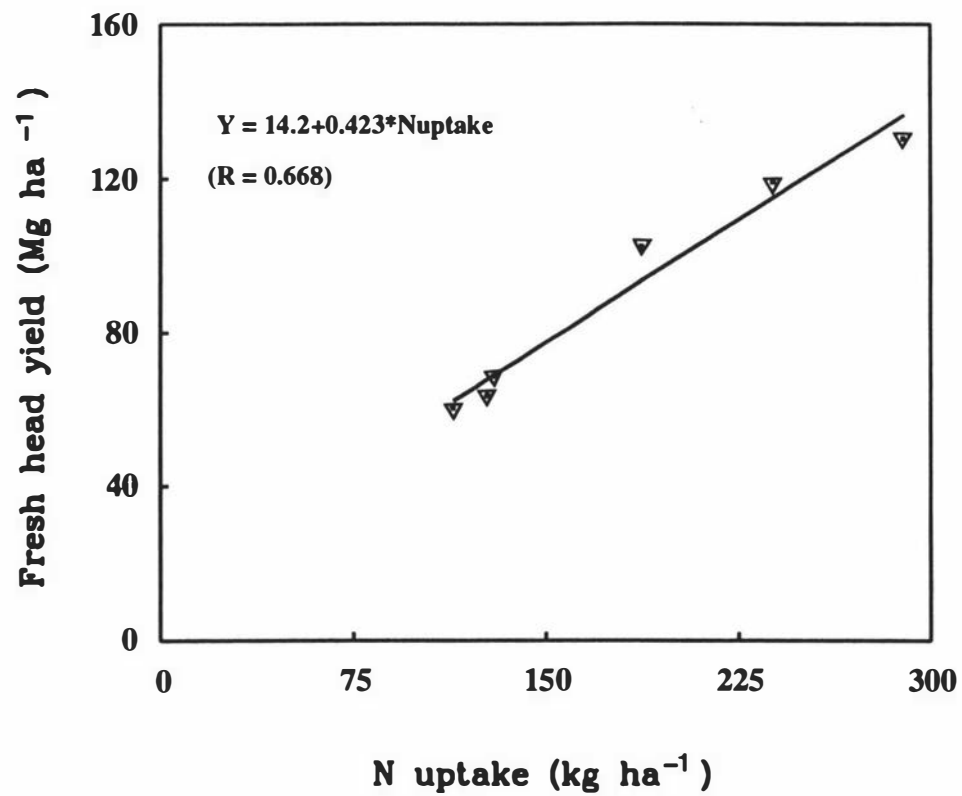
The results of apparent nitrogen recovery (ANR), calculated as a % of total N added (Eq 8.4), showed that the efficiency of N for urea treatment is about 58.6%, while for composts and fresh manure mixtures it ranged from 5.3 to 24.7% and 4.5 to 41.7%, respectively (Table 8.4). Within the manure treatments, the N recovery was higher with sulphocompost (24.7%) and the manure mixture containing S° plus PR (41.7%).

Brinton (1985) reported that the calculated efficiency of N utilization followed: urea (46%) > fresh manure (28%) > compost (9.2%). The higher values obtained in this experiment may be attributed to the longer growth period and the increase in the efficiency of both urea, and fresh and composted manure due to the addition of S° and PR.

The ANR values were also higher than the recovery level (38%) measured by Greenwood *et al.* (1980b) for their optimum N rate with inorganic sources. However,



**Fig 8.8** Effect of composts, fresh manure mixtures (Fmm) and urea on N uptake by cabbage



**Fig 8.9 Relationship between N uptake and fresh head yield of cabbage**

these values were relatively low compared to those obtained by Tinsley and Nowakowski (1959b) who reported about 75% recovery of N from poultry manure-straw compost for spinach beet.

**Table 8.4 A comparison of net yield, N uptake and apparent N release under different treatments**

Treatments	Net yield increase (Mg ha <sup>-1</sup> )	Net N uptake (kg ha <sup>-1</sup> )	ANR (% of total N added)	Apparent N release* (% of total N added)
1. Sulphocompost	41.7	73.9	24.7	42.2
2. Phosphocompost	8.2	16.0	5.3	9.1
3. Fresh manure mixture (manure+woodchip+S°+PR)	58.7	125.1	41.7	71.1
4. Fresh manure mixture (manure+woodchip+PR)	23.7	13.5	4.5	7.7
5. Urea + S° + PR	70.0	175.8	58.6	

\* assuming 58.6% efficiency

If it is assumed that the efficiencies of uptake of N mineralized from manure as well as urea N are the same (Brinton, 1985), then the fraction of total N mineralized in the fresh manure mixtures and compost ranges from 7.7 to 71.7% and 9.1 to 42.2%, respectively, (Table 8.4). Brinton (1985) reported 20% and 62% for compost and fresh manure, respectively.

The apparent N release (as % of total N added; Table 8.4) for fresh manure mixture (with S° and PR) and sulphocompost closely agrees with the results of Kirchmann (1990) who reported that approximately 82% of the total N can be released as inorganic N from fresh poultry manure within 10 days after application to soil. The results are also in agreement with Castellanos and Pratt (1981) who reported higher efficiency of fresh manure due to higher N contents and higher rate of mineralization than composted manure.

#### 8.4.5 Uptake of P

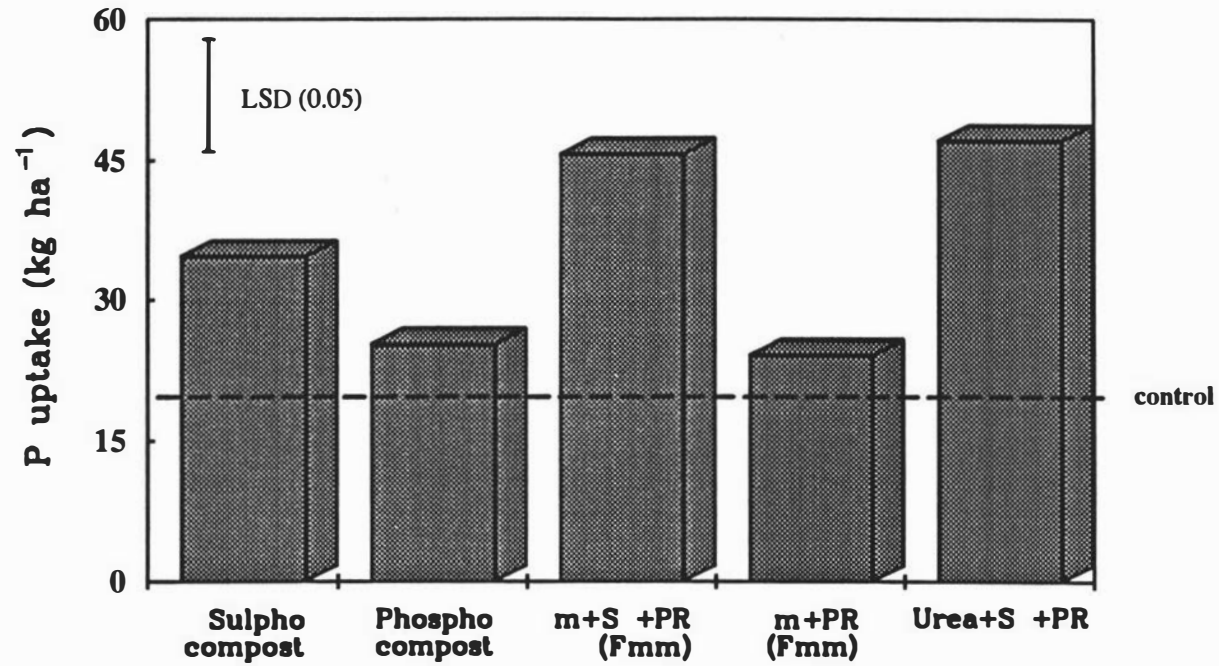
Only a small increase in P uptake was obtained with the application of phosphocompost or manure mixture containing PR alone, than control (Fig 8.10). The P content in cabbages in this experiment ranged from 0.35 to 0.41% and was not significantly different between treatments. The content of P, in general, was below the critical level of 0.6% as reported by Piggott (1986) for cabbage at final harvest; however, P did not appear to be yield limiting.

Generally, it is reported that the application of P fertilizers do not appreciably increase yields of cruciferae crops including cabbages (Greenwood *et al.*, 1980a). However, the fresh manure mixture containing S° plus PR, and sulphocompost, resulted in higher P uptake than fresh manure with PR alone and phosphocompost, a trend similar to yield and N uptake which was probably due to an increase in the availability of P in the compost and fresh manure mixtures.

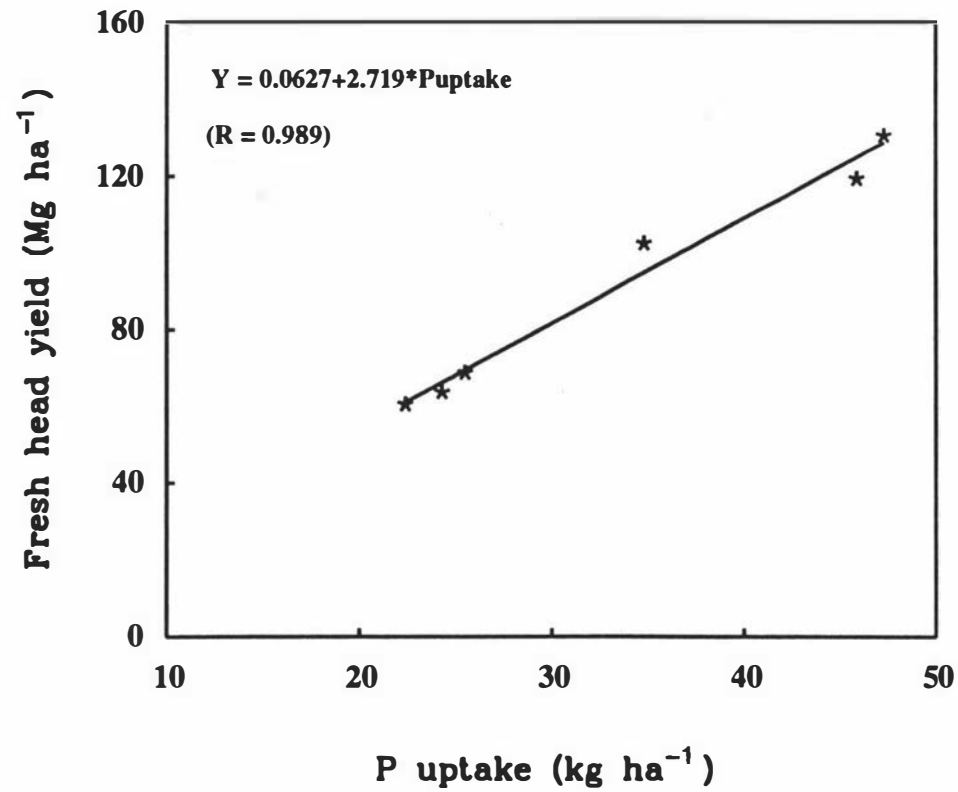
Similar to the N uptake, the P uptake correlates significantly ( $r=0.989^{**}$ ) with the fresh head yield of cabbage (Fig 8.11). A significant correlation ( $r=0.981^{**}$ ) was also obtained between the uptake of N and P (Fig 8.12). Oxidation of S° produces protons ( $H^+$ ) which partly dissolve not only PR-P, but also struvite-P (a mineral phosphate) of poultry manure (see Chapter 6, section 6.4.3.4) and thereby could have increased the P availability. Furthermore, the oxidation of the  $NH_4^+$  in the manure or compost to  $NO_3^-$  produces protons which also may have enhanced the dissolution of manure-P and PR-P. Such effect is more visible with fresh manure mixture than compost. Cogranulation of PR with an ammoniacal-N fertilizer has been shown to increase the plant available P in soil (Apthorp *et al.*, 1987). It is not clear, however, whether this effect was due to increased P release from the compost or improved S and N nutrition of the cabbage.

#### 8.4.6 Nitrate leaching in soil

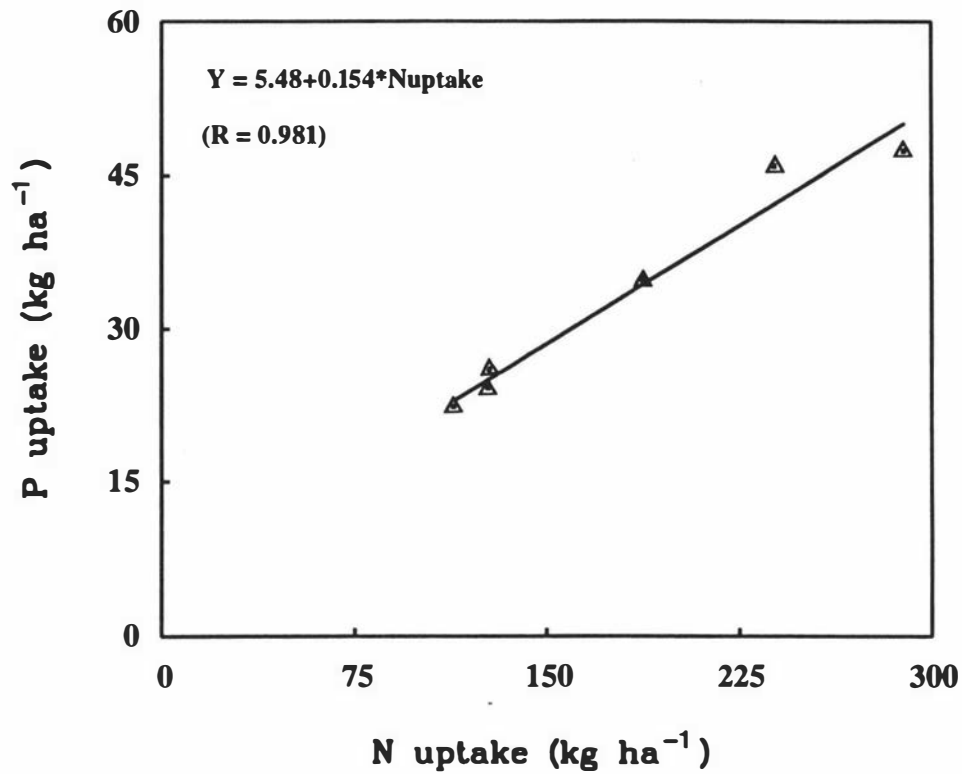
With winter grown crops there is a risk that application of soluble fertilizer N are likely to increase the amounts of  $NO_3^-$  moving to groundwater. Approximately 185mm of accumulated drainage water was predicted from 346mm of rainfall which occurred up



**Fig 8.10** Effect of composts, fresh manure mixtures (Fmm) and urea on P uptake by cabbage



**Fig 8.11 Relationship between P uptake and fresh head yield of cabbage**



**Fig 8.12 Relationship between N and P uptake by cabbage**

to 60 DAT. This resulted in considerable leaching of mineral N through the soil profile with fertilized plots compared to the unfertilized control (Fig 8.13).

Distribution of mineral N ( $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$ ) at various soil depths measured at 60 and 120 DAT for selected treatments is shown in Figure 8.13. At 60 DAT soil  $\text{NH}_4^+\text{-N}$  in the top 30cm was much higher with urea application than other treatments, but below that depth there was not much variation in  $\text{NH}_4^+\text{-N}$  between the treatments. However, at 120 DAT,  $\text{NH}_4^+\text{-N}$  had decreased in the urea treatments, whereas it increased with manure treatments due to continuous release of  $\text{NH}_4^+\text{-N}$  through mineralization. The decrease in  $\text{NH}_4^+\text{-N}$  in urea treatment may be attributed to the oxidation of most of the  $\text{NH}_4^+\text{-N}$  to  $\text{NO}_3^-\text{-N}$ . At 120 DAT soil contained slightly more  $\text{NH}_4^+\text{-N}$  in the manure treatment than urea treatment (Fig 8.13a).

At both soil sampling dates the application of urea increased the  $\text{NO}_3^-\text{-N}$  content at all soil depths due to vertical movement of  $\text{NO}_3^-$  or urea (Fig 8.13b). Manure addition also increased the soil  $\text{NO}_3^-\text{-N}$  content up to 60 DAT, but showed much reduction at 120 DAT.

It has often been shown that a greater downward movement of mineral N occurs from inorganic fertilizers than from manures (Sutton *et al.*, 1986). However, it has been reported that excessive rates of manure application result in loss of highly mobile  $\text{NO}_3^-$  due to leaching (Kofoed and Klausen, 1986).

#### 8.4.7 Residual effects

The yield response of summer maize, grown after the main cabbage crop, to different treatments is shown in Figure 8.14. The maize yield was higher in the fertilized plots than in the control. There were no yield differences between manure and urea fertilized plots. Interestingly, the relative agronomic effectiveness (Eq 8.2) of compost and fresh manure mixtures over urea treatment were markedly increased during maize crop (Fig 8.15), the increase being more significant with phosphocompost and fresh manure mixture with PR alone.

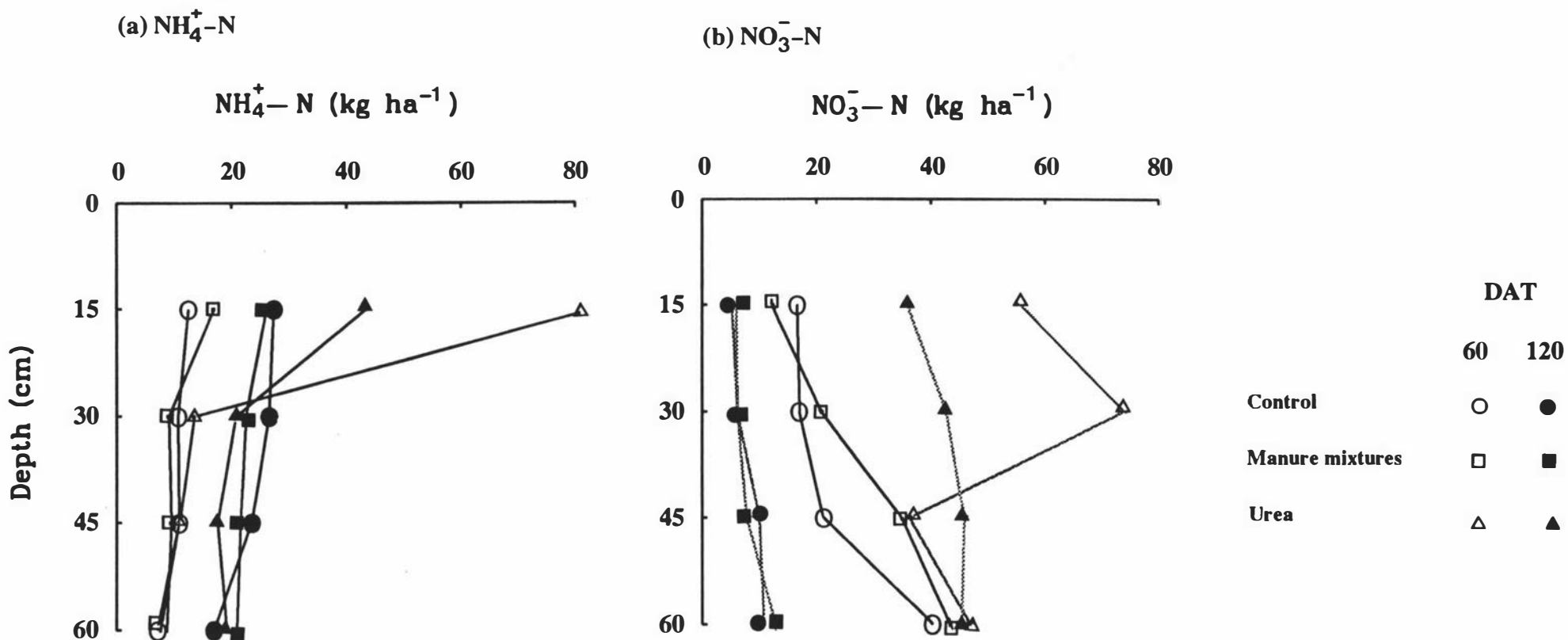
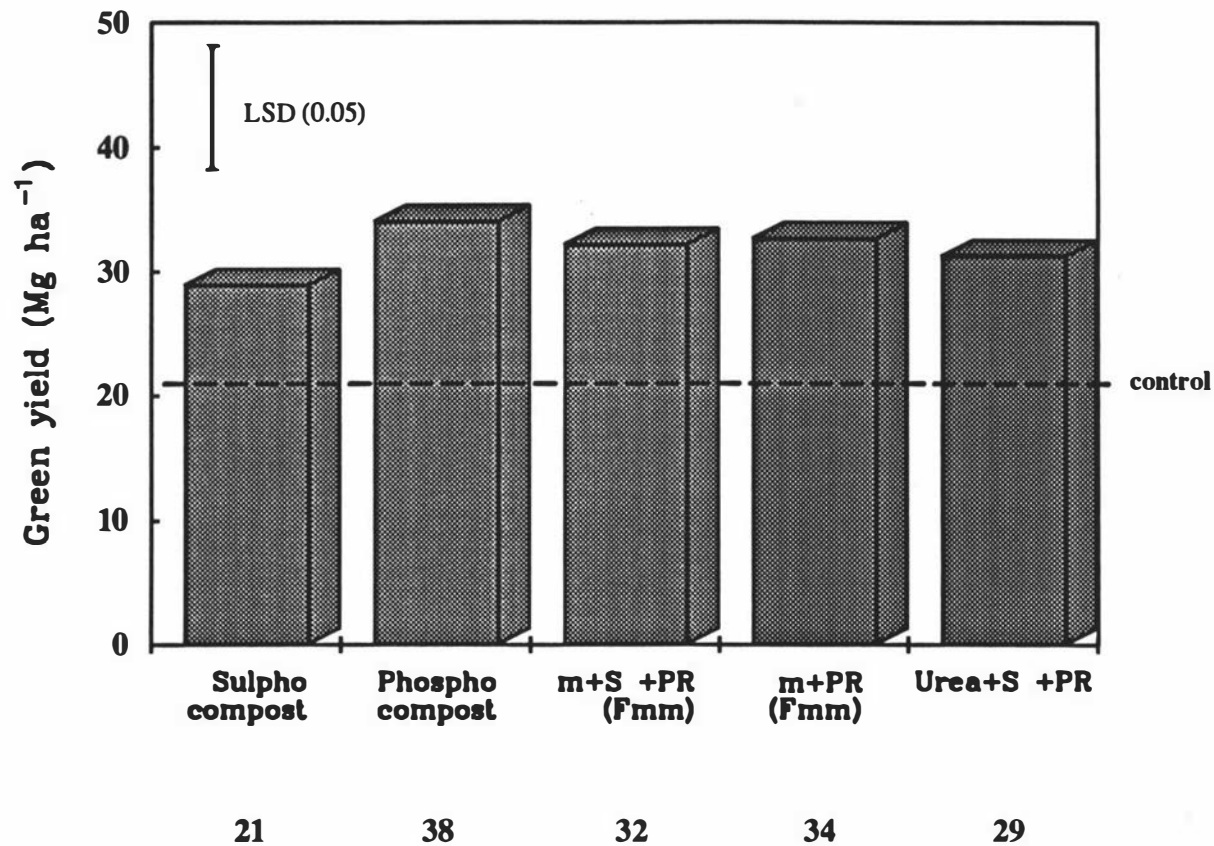
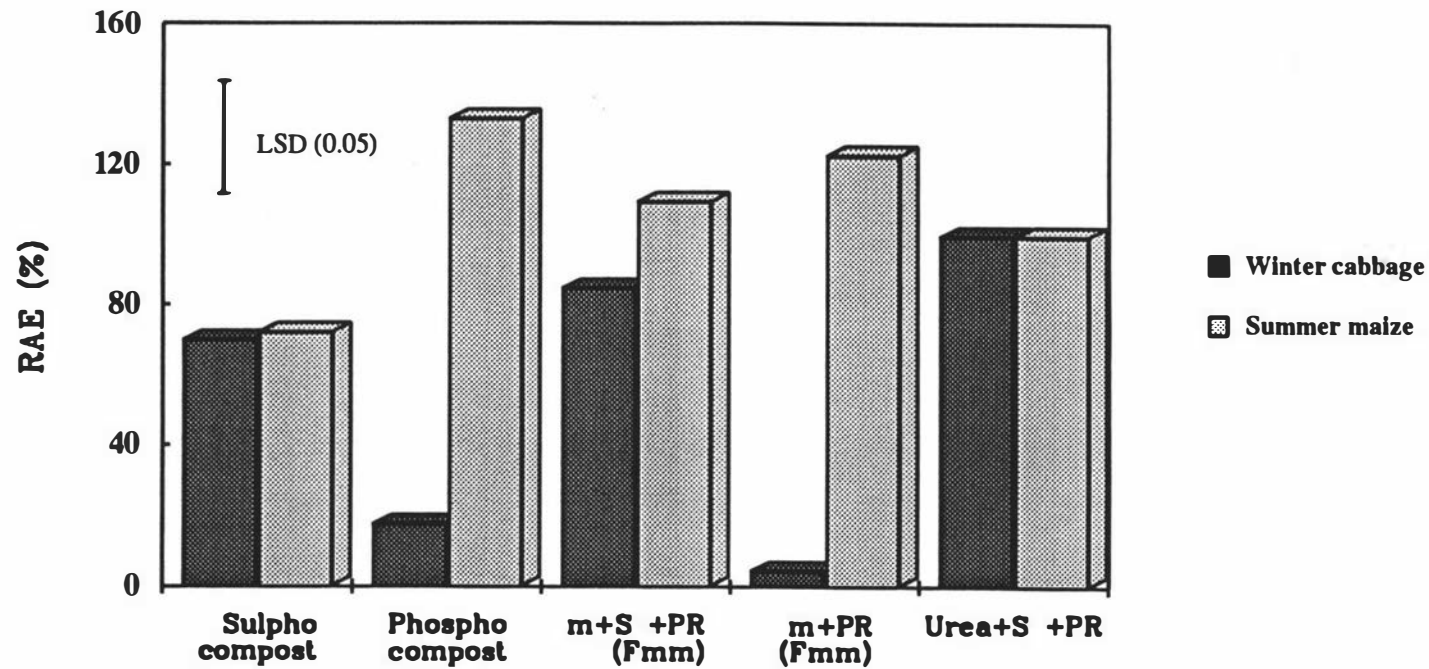


Fig 8.13 Distribution of (a)  $\text{NH}_4^+\text{-N}$  and (b)  $\text{NO}_3^-\text{-N}$  in the soil profile at 60 and 120 days after transplanting (DAT)



**Fig 8.14 Effect of composts, fresh manure mixtures (Fmm) and urea on green yield of maize and nitrogen use efficiency (NUE)**



**Fig 8.15 Relative agronomic effectiveness (RAE) of composts and fresh manure mixtures (Fmm) over urea application**

A few researchers have observed residual effects of fresh manure or compost, although it is not always clear whether the residual effects can be attributed to nutrient residues or to the improvements in soil physical properties associated with manure application. Singh and Yadav (1986a) observed a marked increase in the availability of soil P in the residual crop, due to the addition of phosphated compost. The residual effect from a low grade Mussoorie phosphate rock composted with manure and pyrite is reported to be far higher than superphosphate (Vishwanath *et al.*, 1986). Improved residual value is attributed to the slow release of P by the action of organic acids produced during the decomposition of organic matter on PR dissolution.

Several studies have shown that PR fertilizers have higher residual values than soluble P fertilizers in a range of soils and crops (Mackay *et al.*, 1984; Gregg *et al.*, 1988; Rajan *et al.*, 1991). This may be one of the reasons for improved residual efficiency with phosphocompost which contains more residual PR.

The presence of woodchip or cereal straw either in the compost or after application to soil is expected to temporarily immobilize the N in the compost or in the soil. Since both the manure mixtures and the compost contain large amounts of woodchip, it is expected that part of N may have been immobilized initially and, therefore, may have reduced the N availability to cabbage.

However, during maize growth, remineralization of immobilized N may have occurred which may be one of the reasons for the improved residual efficiencies with compost and fresh manure mixtures. The results of Buchanan and Gliessman (1991) and Bitzer and Sims (1988) show that remineralization of immobilized N could contribute significantly to the residual N value. However, using cattle manure Kirchmann (1985a) observed a very low residual N effect from a single application.

## 8.5 CONCLUSIONS

Addition of S<sup>o</sup> to poultry manure-PR compost increased the yield of winter cabbage. In the season of application the agronomic effectiveness of sulphocompost was higher than that of phosphocompost. For winter cabbage the phosphocompost and

sulphocompost were approximately 12% and 60% as effective as urea, and both composts were as effective as urea for the second season's maize crop.

The NUE in terms of yield produced per kg of added N and apparent N recovery were higher with the addition of fresh manure mixture in the presence of  $S^0$ . But, adding PR alone to fresh manure mixture was found to be less effective.

It is unclear whether the increase in the agronomic effectiveness of sulphocompost and fresh manure mixture (with  $S^0$  and PR) was due to improved N use efficiency only, or due to the effect of S addition on crop nutrition, or due to a cumulative effect. Major benefits of  $S^0$  addition to fresh manure and compost include: (1) conservation of N, (2) dissolution of PR, and (3) enrichment of S nutrient.

Though fresh manure mixture amended with  $S^0$  and PR was found to have higher agronomic effectiveness, field application of fresh manure may not be always feasible. Therefore, composting appears to be an efficient method of manure management.

Distribution of  $NO_3^-$ -N in the soil profile of field plots indicates greater potential for winter leaching of N from urea than poultry manure, which may be the reason for the improved residual value of the manure reflected in summer maize yields.

The results of field experiments show that composting poultry manure with  $S^0$  and PR may be beneficial which could not only reduce environmental pollution associated with manure application, but also increase the agronomic effectiveness of manure.

## CHAPTER 9

### SUMMARY

The work presented in this thesis may be summarised as follows:

#### 9.1 Review of literature

Animal and poultry manures are rich in nitrogen (N). The fertilizer value of manure is reduced by the loss of N through ammonia ( $\text{NH}_3$ ) volatilization, and denitrification. Gaseous loss of N can also be a potential atmospheric pollutant.

Information on N loss during storage or composting of manure is scarce, because most studies have examined the N loss after the field application of manure. Moreover, studies on N loss during storage or composting may help in designing feasible technologies to improve the fertilizer value of manure. Further, one of the requirements in the Resource Management Regulations of many countries is to develop environmentally sound manure management practices to avoid atmospheric and water pollution.

Though several biological and chemical methods were examined in the past, it appears that no single method is effective in conserving N in manure. Therefore, in this study combinations of biological and chemical approaches were examined to develop effective means of N conservation.

Composting not only conserves N in manure, but also enriches the manure with phosphorus (P) if composted with phosphate rock (PR). Several biological processes occurring during composting may enhance the dissolution of PR, and may increase the plant availability of P in compost. Therefore, the overall objective of this study is to examine the potential of composting poultry manure in relation to N conservation and PR dissolution.

## 9.2 Measurement of N in poultry and animal manures

Different methods were evaluated in order to identify a suitable procedure for preserving and measuring the total N more accurately in animal and poultry manures. Since routine Kjeldahl digestion does not include nitrate ( $\text{NO}_3^-$ )-N, pretreatment of the sample with a strong oxidising agent to reduce the  $\text{NO}_3^-$ -N is required prior to routine Kjeldahl digestion. Amongst various pretreatments tested, oxidation with potassium permanganate ( $\text{KMnO}_4$ ) prior to Kjeldahl digestion achieved a complete recovery of  $\text{NO}_3^-$ -N. Alternatively the  $\text{NO}_3^-$ -N may be determined separately after extraction with 2M KCl.

Compared to airdrying and oven drying, freeze drying of manure causes minimum loss of N through  $\text{NH}_3$  volatilization. This suggests that fresh poultry and animal manures can be stored for N analysis by freeze drying.

## 9.3 $\text{NH}_3$ volatilization loss from poultry manure

Using incubation experiment, the N loss through  $\text{NH}_3$  volatilization during aerobic and anaerobic composting of poultry manure, and the efficiency of different amendments to reduce such losses, were investigated. The amendments included, four carbon (C) rich bedding materials (woodchip, paper waste, cereal straw and peat), one acidifying material (elemental sulphur-  $\text{S}^0$ ) and two adsorbents (zeolite and soil).

The N loss through  $\text{NH}_3$  volatilization during aerobic decomposition of poultry manure was approximately 17% of total manure N. This was reduced by 90-95% by anaerobic composting conditions. The percent loss of N by  $\text{NH}_3$  volatilization measured in this experiment was less than that measured under open systems in poultry houses. This illustrates the limitation of controlled incubation systems for measuring the  $\text{NH}_3$  loss.

When anaerobic composting/storage is not feasible, the effectiveness of aerobic composting to reduce N loss could be increased by using different easily available amendments. Amongst the bedding materials examined, wheat straw, which contains readily decomposable C, was found to be most effective in conserving N.

Loss of  $\text{NH}_3$  was reduced 60% by amending manure with  $\text{S}^0$  both in the presence and absence of the bedding materials. The microbial oxidation of  $\text{S}^0$  produced  $\text{H}_2\text{SO}_4$  which neutralised the ammonium carbonate produced in the manure, and reduced the loss of  $\text{NH}_3$ . Zeolite was a more effective  $\text{NH}_3$  (or  $\text{NH}_4^+$ ) adsorbent than soil, reducing the  $\text{NH}_3$  loss by 60%.

The measurement of total N in the manure mixtures at the end of the incubation period showed some evidence for the loss of large amounts of N through denitrification. Therefore, the extent of denitrification and some factors affecting denitrification in poultry and animal manures were examined in the subsequent experiments.

#### **9.4 Denitrification loss from poultry manure**

The widely used acetylene inhibition technique for denitrification measurement was standardised to obtain an estimate of denitrification rate from poultry and animal manures.

Fresh poultry and animal manures lost negligible amounts of N through denitrification, which is attributed to the low amounts of  $\text{NO}_3^-$ -N in the manure. Increases in the  $\text{NO}_3^-$  content through nitrification during aerobic decomposition of poultry manure or through fresh addition of  $\text{NO}_3^-$  increased the denitrification activity in poultry manure. Significant reductions in denitrification loss (60-80%) were achieved through the addition of various amendments such as woodchip, wheat straw,  $\text{S}^0$  and zeolite to poultry manure, which is attributed mainly to decreases in  $\text{NO}_3^-$ -N content in manure. The addition of  $\text{S}^0$  greatly reduced the denitrification loss mainly by increasing the acidity of the manure.

Incorporation of manure into soil greatly increased the rate of denitrification. Addition of manure to soil is likely to supply C, increase the activity of denitrifiers, and promote anaerobiosis in the short term, all of which may contribute to the increase in the denitrification if  $\text{NO}_3^-$  is present.

The denitrification rate was found to be higher in soil amended with pig manure

followed by dairy manure and poultry manure. However, it was shown that high levels of poultry manure decreased the rate of denitrification. This was attributed to the release of  $\text{NH}_3$  which is toxic to nitrifiers and denitrifiers.

The results demonstrated that biological denitrification is also one of the major pathways of N loss from poultry and animal manures.

## 9.5 Dissolution of PR during composting

Microbial and chemical immobilization, and transformation of P in manure makes it difficult to measure accurately the extent of PR dissolution during composting of manure. To accurately measure the dissolution of PR during composting with poultry manure, a radioactive  $^{32}\text{P}$  labelled PR (francolite) was synthesised and used. The results show that the use of  $^{32}\text{P}$  labelled francolite proved very successful in measuring the net dissolution of francolite by overcoming several interferences associated with manure.

In manure systems, PR dissolution can be measured more accurately from increases in NaOH extractable P ( $\Delta\text{NaOH-P}$ ) than from decreases in HCl extractable P ( $\Delta\text{HCl-P}$ ) in the PR treated manure over the control. The dissolution measured by  $\Delta\text{NaOH-}^{32}\text{P}$  showed that only about 8 to 20% of added  $^{32}\text{P}$  in francolite was found to be dissolved in various manure compost during 60 days incubation. Further, the results provide no evidence for nitrification of  $\text{NH}_4^+$  in poultry manure providing protons ( $\text{H}^+$ ) involved in PR dissolution.

The experiments with  $^{32}\text{P}$  labelled francolite and North Carolina phosphate rock (NCPR) showed low levels of dissolution of PR in poultry manure compost, which was attributed mainly to the high concentration ( $4.8 \times 10^{-2} \text{ mol L}^{-1}$ ) of  $\text{Ca}^{2+}$  in manure solution. Measurement of Ca and P concentrations in the manure solutions indicated that when the P concentration is  $2 \times 10^{-3} \text{ mol L}^{-1}$ , the initial  $\text{Ca}^{2+}$  concentration ( $4.8 \times 10^{-2} \text{ mol L}^{-1}$ ) in manure solution exceeds the  $\text{Ca}^{2+}$  concentration maintained by PR dissolution above pH 6. This suggests that in manure, unless the pH is lowered below 6, the initial  $\text{Ca}^{2+}$  concentration is too high (exceeds solubility product) to cause any dissolution of PR. This explains why the dissolution of PR in poultry manure compost is very low.

Addition of  $S^0$  lowered the pH which enhanced the dissolution of PR.

## 9.6 Absorption of $NH_3$ released from poultry manure to dissolve PR

To overcome the inhibitory effect of manure  $Ca^{2+}$  on the dissolution of PR and to examine the use of  $NH_3$  released from poultry manure in the dissolution of PR, two methods of composting were examined. The  $NH_3$  released from poultry manure was absorbed either by covering the manure heaps with layers of bark or soil materials, or by passing the  $NH_3$  through a column containing these materials. The materials were enriched with N and as this occurred cation exchange capacity increased due to  $NH_3$  absorption. The exchangeable acidity in bark and soil was also regenerated by absorbing  $NH_3$  from manure which upon nitrification produces  $H^+$ . Bark and soil covers were more suited to field practice than columns with forced aeration. In both systems, bark was more effective in absorbing  $NH_3$  than soil.

When mixed with PR higher PR dissolution (82.3%) occurred in bark than in soil (33.2%), and more than 80% of the dissolved P in bark remained in a form readily available to plants. A high exchangeable acidity and large Ca sink size in bark were the cause of the large PR dissolution.

Under the composting system, in which the manure was covered with bark or soil, Ca accumulated in the coverage material due to the diffusion of Ca from the manure and therefore, inhibited the dissolution of PR. The absorption of  $NH_3$  in the bark and soil columns, and the subsequent nitrification, caused only a small increase in the dissolution of PR. Most of the  $H^+$  released during the nitrification is involved in pH buffering reactions in the bark and soil materials.

Bark provides a high CEC material suited to removing  $NH_3$  from poultry manure and shed atmosphere. The results of this study may contribute significantly to the efficient utilization of bark materials. If large volumes of bark, or similar products are available, it is possible to enrich these cheaply available wastes with both N and P nutrients which could be used as 'fast release' organic fertilizers in agricultural and horticultural systems.

## 9.7 Agronomic effectiveness of poultry manure composts

The use of  $S^0$  proved beneficial in conserving N and enhancing PR dissolution in poultry manure, and was used for formulating a manure compost. Two types of composts, sulphocompost (blending poultry manure with woodchip,  $S^0$  and PR) and phosphocompost (blending poultry manure with woodchip and PR), were prepared and the agronomic effectiveness evaluated through field experiments.

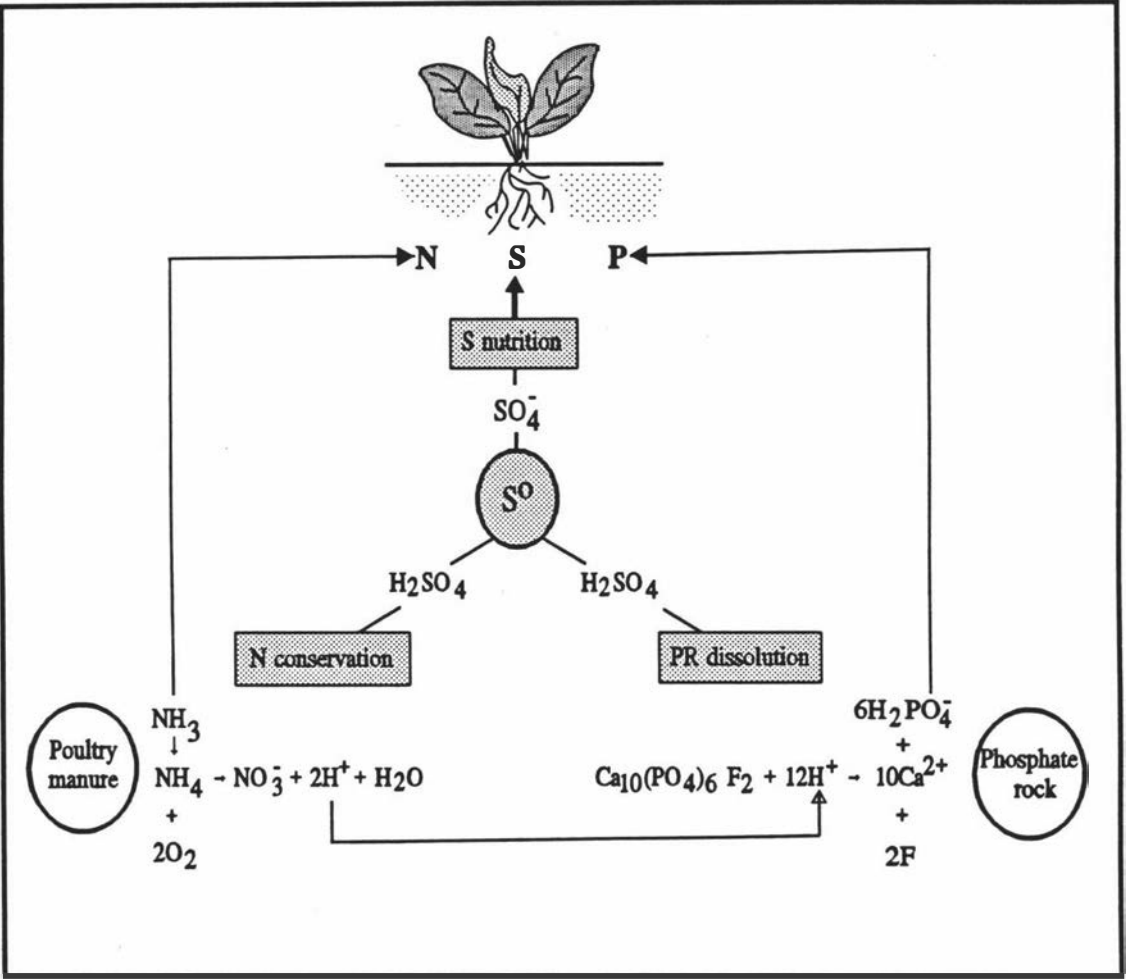
In the season of application winter cabbage yields indicate that the agronomic effectiveness of sulphocompost was higher than that of phosphocompost. For winter cabbage the phosphocompost and sulphocompost were approximately 12% and 60% as effective as urea (plus  $S^0$  and PR). However, both composts were as effective as urea (plus  $S^0$  and PR) for the second season's maize crop. The benefit of adding  $S^0$  was clearly seen both in fresh poultry manure mixtures and in compost. Adding PR alone to fresh manure mixtures made a less effective fertilizer.

Distribution of  $NO_3^-$ -N in the soil profile of field plots indicated greater potential for winter leaching of N from urea than poultry manure (applied at the same rate of N), which may be the reason for the improved residual value of the manure reflected in summer maize yields.

As illustrated in Figure 9.1, it is evident that the addition of  $S^0$  to poultry manure not only conserves N and increases PR dissolution, but also enriches the compost with S achieving a better nutrient balance. The increase in the agronomic effectiveness of sulphocompost and fresh manure mixture (with  $S^0$  and PR) may be attributed to one or more of the following effects: (i) improved N use efficiency; (ii) increased PR dissolution; (iii) improved S nutrition of crop (Fig 9.1).

## 9.8 Suggestions for future research

Ammonia volatilization in this study is limited to the incubation system under controlled conditions. Further research is needed to measure the loss of  $NH_3$  under open systems, perhaps using a poultry shed environment.



**Fig 9.1** Role of elemental sulphur ( $S^0$ ) in improving the agronomic effectiveness of poultry manure composts

Cereal straw with high C/N ratio was found to be effective in reducing the N loss. Its use as a bedding material should be further examined under poultry shed conditions. This will have some practical implications, because surplus amounts of cereal straw are being produced worldwide, and could be utilized extensively as a bedding material for chicken production.

The amounts and type of organic acids produced during the decomposition of poultry manure were not examined in this study. Further research is required to quantify the organic acid produced during composting, and to identify the methods necessary to achieve desired levels of production, particularly using anaerobic composting methods.

Bark appears to have several unique properties including high cation exchange capacity, exchangeable acidity and Ca sink size. The phytotoxic effect of bark often limits its use as a mulch or soil amendment. However, some published reports show that composting reduces the phytotoxic effect of bark on plants. Composting of bark in combination with PR and manure needs further research, which may lead to the development of a nutrient rich compost suitable for organic farming and nursery industries.

S<sup>0</sup> has been found to be very effective in not only reducing N loss, but also enhancing PR dissolution during composting. Research is needed to examine the oxidation of S<sup>0</sup> during composting, the factors affecting oxidation and the amount of S<sup>0</sup> needed to achieve a desirable level of PR dissolution in compost. The production of toxic hydrogen sulphide associated with S<sup>0</sup> usage during composting needs thorough investigation.

Studies are needed to determine the nutrient interactions (especially N, P and S), and their availability in compost (enriched with P or S<sup>0</sup>) under different soil, climatic, and cropping conditions, for developing more efficient and effective methods of utilizing animal and poultry manures in agriculture and horticulture.

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