IMMOBILIZATION AND FIXATION OF N^{15}-LABELLED AMMONIUM SULPHATE AS AFFECTED BY STRAW APPLICATION AND METHOD OF FERTILIZER PLACMENT

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GOTTFRIED PAUL MSUMALI

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ABSTRACT

The extent of biological immobilization and fixation of fertilizer nitrogen as affected by method of placement was studied in a Newdale clay loam soil. Two laboratory incubation experiments were conducted in which N^{15}-labelled ammonium sulphate was either mixed with the soil or banded in the soil. The effects of amount of nitrogen added, presence of straw and its mode of placement (mixing with the soil or banding in the soil) and the effect of a nitrification inhibitor (N-Serve) were studied.

Immobilization or fixation of nitrogen as measured by percent recovery of mineral nitrogen (ammonium, nitrate and nitrite) was increased when straw was added. Fertilizer placement, mode of straw placement, amount of nitrogen mixed with the soil and addition of N-Serve did not affect percent recovery of added mineral nitrogen.

Immobilization or fixation of N^{15} banded in the soil was about one half of that when the nitrogen was mixed with the soil. Straw application at 1% of soil weight doubled immobilization for both nitrogen mixed with the soil and for nitrogen banded in the soil although percent nitrogen immobilized was greater in all instances where the nitrogen was mixed with the soil. Straw placement did not alter percent nitrogen immobilized. N-Serve increased immobilization.

Immobilization as measured by recovery of mineral nitrogen was not consistent with the results obtained from N^{15} data. Soil-fertilizer interactions which may have been responsible for this discrepancy are discussed.

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1. INTRODUCTION

1.1 General

The most important forms of nitrogen readily absorbed by plant roots are the mineral forms: nitrate (NO_3^-) ammonium (NH_4^+) and to a very little extent, nitrite (NO_2^-). Yet only a very small fraction of the total soil nitrogen occurs in the inorganic available form. The greater portion of soil nitrogen occurs in the organic form. This organic form can only be used by plants after it is broken down by heterotrophic microorganisms to release the nitrogen in inorganic form, a process called mineralization. But only about 2 to 4 percent of the organic nitrogen is mineralized each year. As a result of this slow rate of mineralization, modern agriculture cannot depend on this supply of nitrogen only. Yet nitrogen is the soil nutrient which plants require in greatest quantity. Therefore, in order to attain high crop yields, there must be a liberal addition of nitrogen to the soil to supplement the supply from mineralization and the amounts already present in the inorganic form.

The purpose of nitrogen fertilizer addition is to increase the supply of nitrogen to the plant. Nitrogen fertilizer applications have to be made at the proper stage of plant growth and placed such that plant roots can easily absorb it in order to attain efficient use of the fertilizer.

The efficiency of utilization of nitrogen fertilizers by crops depends not only on the method and time of application but also on the nitrogen requirement of the crop and its rooting habit, the chemical form in which the fertilizer is applied (NH_4^+-N or NO_3^--N), the amount of potentially mineralizeable nitrogen in the soil and amounts of inorganic nitrogen in the soil profile. Only about 40 to 60 percent of the fertilizer nitrogen added to a nitrogen-deficient soil is recovered by crops. The remainder is rendered unavailable or lost from the soil environment by some physical, chemical and biological processes. The addition of carbonaceous crop residues and the method of fertilizer application influence such losses.

1.2 Problem Analysis

Studies on fertilizer placement conducted by the Department of Soil Science, University of Manitoba, indicated that placing nitrogen fertilizers in a band (35 cm. spacing and 6 to 7 cm. depth) was superior, as measured by grain yields, to equal amounts of fertilizer mixed throughout the surface 5 to 7 cm. depth of soil. This indicated relatively more fertilizer nitrogen was lost from the soil or rendered unavailable when it was mixed throughout the soil as compared to nitrogen placed in a band. There are various ways by which nitrogen is rendered unavailable to crops. These include:

(a) Immobilization of nitrate and ammonium forms of nitrogen by soil microorganisms during the decomposition of crop residues low in nitrogen content. Immobilized nitrogen is temporarily unavailable to plants.

(b) Entrapment in between lattices of expanding silicate clays. (Ammonium fixation).

(c) Loss of the nitrate form of nitrogen in drainage water when it rains or when soil is irrigated, a process called leaching.

(d) Volatilization of gaseous products such as ammonia when ammonium fertilizers are placed on the soil surface or not properly incorporated.

(e) Loss of gaseous products such as molecular nitrogen or oxides of nitrogen in poorly drained soils, or in conditions that favour nitrite accumulation (denitrification).

1.3 Objectives

This study was conducted to determine the proportion of applied nitrogen which is rendered unavailable by ammonium fixation and microbial immobilization when ammonium sulphate fertilizer is mixed throughout the soil as compared to placed in a band. A nitrification inhibitor, 2-chloro-6-(trichloromethyl) pyridine (N-Serve) was included in some of the treatments to study the extent of ammonium fixation and microbial immobilization when nitrogen is retained in the ammonium form for a long period of time. The effect of crop

residues (wheat straw) and the method of placement of the straw in the soil on biological immobilization was also studied. This study consisted of two laboratory experiments in which the treated soils were incubated at field capacity moisture content for periods up to 12 weeks at 20 to 25 C. The stable isotope N^{15} was used to enrich the ammonium sulphate fertilizer in order to determine the fate of the nitrogen fertilizer.

II. LITERATURE REVIEW

2.1 Fate of Chemical Sources of Nitrogen in the Soil

Inorganic sources of nitrogen are by far the most important of fertilizer nitrogen compounds. Most inorganic nitrogen fertilizers are ammonia derivatives such as anhydrous ammonia, aqua ammonia, ammonium chloride, ammonium nitrate, ammonium sulphate and urea. Nitrate sources are used to a lesser extent than ammoniacal fertilizers. Since all the ammoniacal nitrogen fertilizers provide the ammonium ion (NH_4^+) as the main initial product in the soil and since these are important sources of fertilizer nitrogen, most chemical, physical and biological interactions in the soil begin with the ammonium ion. The reactions which determine the fate of fertilizer nitrogen are discussed in the following sections.

(A) Crop Uptake

When nitrogen fertilizer is introduced into the soil it is exposed to plant roots for absorption. This is the intended fate for which the fertilizer is added. However, soil constituents (inorganic and organic fractions or the soil microflora) also react with fertilizer nitrogen. This has a great influence on the availability of the added fertilizer to plants. Usually considerable loss occurs. Unpublished data (Dept. of Soil Science, University of Manitoba) showed that annual crops recovered about 20 to 60 percent of fertilizer nitrogen applied. Allison (1966), in

his review of work on the fate of nitrogen in soils, showed fertilizer recoveries in crops varied widely with growth conditions and cropping systems, but were not likely to be greater than 50 to 70 percent even under the best field conditions. Zamyatina (1969) using N^{15}- labelled fertilizer, showed that only about 30 to 70 percent of applied nitrogen was taken up by plants. Seven to 45 percent was immobilized and the rest was unaccounted for. Chalk *et al.* (1975) in their study of crop recovery and nitrification of fall and spring-applied anhydrous ammonia showed that although crop recovery of applied nitrogen depended on soil type and rate of application, at most 40 percent was recovered. Thus, the findings of these researchers, among others, indicated that it is almost inevitable that some fraction of fertilizer nitrogen is rendered unavailable to crop plants. Only by proper agronomic practices can these losses be minimized.

(B) Biological Immobilization of Inorganic Nitrogen

(1) The immobilization-mineralization cycle

Microorganisms and higher plants absorb and assimilate inorganic nitrogen into cellular organic nitrogenous compounds. Under normal soil conditions, inorganic nitrogen is formed from organic nitrogen also. So, the processes of immobilization and mineralization occur simultaneously (Biological interchange of nitrogen). The net effect of these processes depends on the energy supplied

to the microorganisms among other soil factors. In the presence of an abundant energy supply in the form of carbonaceous material, microorganisms multiply rapidly with a consequent vigorous synthesis of protoplasm. This process requires nitrogen. Microbial protoplasm contains from 3 to 12 percent nitrogen (Harmsen and Kolenbrander 1965). This is usually higher than the nitrogen content of most decomposing substrates. It is common practice to leave crop residues on the soil after harvest which are exposed to microbial decomposition. In their decomposition, the nitrogen they contain is released and re-absorbed by the decomposing microflora. If the nitrogen content of the decomposing residue is less than microbial demand, the additional nitrogen must be supplied by the soil reserves of inorganic nitrogen. Therefore, there will be a net immobilization of inorganic nitrogen initially present in the native soil, or, applied as fertilizer. Net mineralization occurs if the decomposing substrate contains more nitrogen than the microbial demand in which case inorganic nitrogen accumulates in the soil.

Net immobilization and mineralization can sometimes be predicted from the C:N (carbon to nitrogen) ratio of the residue added. Net mineralization usually occurs when the C:N ratio of the decomposing residue is below 20 to 25. At ratios greater than this in the residue

net immobilization usually occurs, (Pinck *et al.* 1946; Allison and Klein 1962). However, some substrates which are highly lignified are resistant to microbial breakdown and despite their wide C:N ratio, may not cause net nitrogen immobilization. On the other hand, stable humus, whose C:N ratio has been reduced to 10 to 15 will not degrade any further and therefore its narrow C:N ratio does not imply a ready release of nitrogen (Harmesen and Kolenbrander 1965). The degradability of a substrate rather than its C:N ratio *per se* is important in predicting the fate of mineral nitrogen in the soil. Allison and Klein (1961), studied the comparative rates of decomposition of wood and bark of ten different species of softwoods incubated in the soil at two levels of nitrogen for 53 to 800 days, and measured CO_2 evolution as an index of decomposition. They showed that these substrates were resistant to decomposition, the resistance varying for different tree species. Due to the slow rates of decompostion, the soil itself was able to furnish adequate available nitrogen for maximum rates of decomposition and supplemental nitrogen was not needed. Supplemental nitrogen at times reduced the decomposition rate. The authors suspected the supplemental nitrogen was in excess of microbial demand and inhibited microbial activity by the salt effect.

Iritani and Arnold (1960) studied the release

of nitrogen during the incubation of 11 vegetable crop residues as related to their chemical composition. Multiple and simple correlation and regression analysis were conducted between the chemical composition of the residue and the accumulation of mineral nitrogen in the soil. The authors showed that although the amount and decomposability of the carbon and nitrogen was important in affecting nitrogen release, the characteristics of the nitrogen were also important. For example, total nitrogen in the residue influenced mineralization but water-soluble nitrogen in the residue was twice as effective as the insoluble fraction in affecting nitrogen release. Net mineralization of nitrogen occured when the residue contained at least 1.66 to 1.89 percent nitrogen. Total nitrogen plus water-soluble nitrogen was more highly correlated with the accumulation of mineral nitrogen than just total nitrogen and total carbon.

Pinck *et al.* (1946) indicated that organic substances high in lignin were likely to have a lower nitrogen requirement per unit dry weight than materials low in lignin. In connection with this Agarwal *et al.* (1972) studied the effects of different carbon sources on nitrogen transformations. In all 5 soils studied, mineral nitrogen was found to decrease with the addition of carbon substrates. Sucrose, a readily available energy source accelerated immobilization of added and native nitrogen more than

sugar cane bagasse, a slowly available form; but without any energy source treatment, the immobilization of added nitrogen was related to the C:N ratio of the native soil organic matter. Winsor and Pollard (1956), in a similar problem, studied the effects of sucrose on the immobilization of NH_4^+-N and showed that maximum immobilization occurred in 2 days for sucrose instead of 40 days as observed by Allison and Klein (1961) for straw. After 16 days one third of the immobilized nitrogen was released in the sucrose-treated soil. In the straw-treated soil of Allison and Klein, 40 days passed after maximum immobilization before the nitrogen re-mineralized. At maximum immobilization, sucrose caused immobilization of nitrogen equal to 3.7 percent of the weight of the sugar added as compared to 1.7 percent for straw.

(2) Amounts of inorganic nitrogen immobilized and factors affecting immobilization.

The amounts of nitrogen immobilized cannot be specified because these differ depending on soil conditions. Apart from the availability of easily decomposable organic residues that cause immobilization of inorganic nitrogen, other reactions must be considered. Ammonium fixation when ammoniacal fertilizers are used and the reaction of ammonia with soil organic matter to form a stable resistant complex, increase losses of plant-available nitrogen. These reactions

make it difficult to interpret the extent of biological interchange, (Tyler and Broadbent 1958; Broadbent and Tyler 1962). Jansson (1963) studied this problem also. Using a sandy loam subsoil, he grew oats and N^{15}-labelled $(NH_4)_2SO_4$ and $NaNO_3$ were added. After one year, 56.5 percent of the added nitrogen remained in the soil for $(NH_4)_2SO_4$, whereas 32.0 percent remained in the soil for $NaNO_3$. After six years, the amount remaining in the soil was 42.9 percent for $(NH_4)_2SO_4$ and 25.5 percent for $NaNO_3$. The author explained the difference was caused by ammonium fixation or a preferential utilization of NH_4^+ to NO_3^- by the soil microflora. But since this was a subsoil, ammonium fixation was probably a dominant factor. Depending on the capacity of a soil to fix ammonium, the amount of biologically immobilized nitrogen can at times be overestimated. The following factors affect the amount of inorganic nitrogen immobilized.

(a) Amount of nitrogen added

The amount of nitrogen immobilized has been shown by some workers to increase with increase in amount of nitrogen fertilizer added. Legg and Allison (1959) showed immobilized N^{15} increased 4 or 5 times as nitrogen addition increased from 37.5 mg to 600 mg of $(NH_4)_2SO_4$ per pot. However, the amount mineralized was constant with rate of addition. Jansson (1958) and Cady and Bartholomew (1960)

also observed an increase in the amount of mineral nitrogen immobilized by soil under greenhouse conditions with an increase in the amount of nitrogen added. Harmsen and Lindenbergh (1949) noted that large quantities of soluble nitrogen appear to depress mineralization probably due to the salt effect. Jansson (1958) explained the reduction in mineralization by suggesting that the high concentration of soluble nitrogen stimulated immobilization, giving an impression of reduced mineralization. These findings were noted at soluble nitrogen concentrations of 100 to 200 ppm or greater. The increase in net immobilization of available nitrogen was most noted in situations where nitrogen was limiting to the development of heterotrophic microflora, (Allison 1955; Bartholomew 1955; and Kuo 1955). In such cases, increasing the supply of nitrogen increases immobilization.

(b) Presence of growing plants versus fallow

The amount of nitrogen immobilized is also influenced by the presence of plants growing in the soil. Absorption of mineral nitrogen by plants is another type of biological immobilization since the inorganic form of nitrogen is converted to an organic form. However, this is the intended route of the nitrogen that is applied to the soil, so it is not regarded as a loss. But plants have other effects that influence nitrogen immobilization by microorganisms.

Broadbent and Norman (1946) found mineralization of native soil organic matter to be accelerated by the increase in microbial activity attending the decomposition of a readily available energy source in the soil. This led to the belief that increased microbial activity may serve to accelerate biological interchange. Plant roots secrete various organic substances that stimulate microbial multiplication and hence activity, (rhizosphere effect). It has generally been observed that nitrogen immobilization is greater in cropped than in fallow soils. Goring and Clark (1948) noted higher bacterial numbers in cropped than in fallow soils. Also, net increase in mineral nitrogen was lower in cropped than in fallow soils even when nitrogen uptake by the crop was accounted for. Hiltbold *et al.* (1951) showed that the presence of oat plants increased microbial immobilization of nitrogen to values 2 to 4 times greater than that in fallow soils. Plhak and Vicherkova (1970) emphasized that many higher plants excrete organic compounds into the soil solution, with hemicellulose-like compounds being liberated in relatively larger quantities. Therefore, the decrease in mineral nitrogen under cropping may be brought about by the development of a rhizosphere flora containing cellulolytic organisms. These same workers however, observed that peas and timothy grass roots increased the accumulation of nitrate. This observation was not explained by the authors. The rhizosphere

effect in increasing immobilization of nitrogen may be partially responsible for the observed low levels of inorganic nitrogen in grassland soils, varying from a trace to about 5 ppm (Harmsen and Kolenbrander 1965). This rhizosphere effect is increased by the extensive root system in soils under grass. Although it is generally accepted that immobilization of nitrogen by the rhizosphere effect is higher in cropped than in soils under fallow, the extent of immobilization depends on the plant species, rate of growth of plants and the stage of growth of the plants (Allison 1966).

The degree of immobilization of nitrogen, increased by the rhizosphere effect, can sometimes be overestimated if the disappearance of inorganic nitrogen is taken as a measure of immobilization (even when plant uptake is accounted for). Some of the root exudates and sloughed off tissues may be easily degradable by microorganisms, a process which increases the biochemical oxygen demand in the soil. Therefore, any available nitrate may be used as an alternative terminal electron acceptor in the respiration of facultative anaerobic bacteria(Craswel and Martin 1975). The level of organic nitrogen is thus lowered by the reduction of nitrate to gaseous products.

(c) Nitrogen source

Extensive work has been done to study the effect

of nitrogen source on the immobilization of nitrogen in the soil. Jansson *et al.* (1955) studied nitrate and ammonium sources of nitrogen in the decomposition of oat straw and showed the ammonium form was used preferentially to nitrate. This is because the utilization of nitrate as a nitrogen source requires energy to reduce it to the ammonium form, the only form in which nitrogen is incorporated into carbon skeletons in amino acid synthesis. Nightingale (1948) and Winsor and Pollard (1956) also showed the preferential utilization of NH_4^+ versus NO_3^- by heterotrophs. Jansson *et al.* (1955), therefore, regarded the NO_3^- form of nitrogen as being "passive" and unimportant in biological interchange. However, Stojanovic and Broadbent (1956); Allison and Klein (1962), and Broadbent and Tyler (1962) did not agree with this view and regarded both NH_4^+-N, and NO_3^--N as sources of nitrogen for immobilization. Allison (1966) emphasized that where NO_3^- was the most abundant source of nitrogen, there was no doubt that this was the readily available source. Besides, under normal soil conditions nitrification takes place so quickly that NH_4^+-N does not persist for a long period of time unless it is placed at high concentrations in bands where nitrification is slowed down.

The relative rates at which NH_4^+-N or NO_3^--N is immobilized is probably related to the pH of the soil environment. Broadbent and Tyler (1965) studied the effect

pH had on nitrogen immobilization and noted that NH_4^+ was assimilated by microorganisms more rapidly under acid than alkaline conditions (pH 5.3). The absolute quantities of nitrogen utilized were higher for NH_4^+ than for NO_3^- at all pH values but quantities of NH_4^+ immobilized decreased with pH. The reverse was observed for NO_3^-. The authors suggested the results seem to be related to the physiological acidity or alkalinity of the nitrogen source; the NH_4^+ source being physiologically acidic, the NO_3^- source being physiologically alkaline.

Overrein (1970) studied the effects of temperature and incubation time on the interchange of N^{15}-labelled urea, nitrate and ammonium in forest raw humus. His results suggested immobilization took place faster from urea than from other sources at all temperatures; therefore, the nitrogen carrier affected biological interchange. However, the author pointed out that the apparently higher immobilization of urea may have been associated with direct reactions of urea with some specific sites on the humus fraction. Broadbent and Nakashima (1970) showed that in the presence of rice straws of different nitrogen contents immobilization was higher when nitrogen was supplied as glycine rather than ammonium sulphate. No explanation for the observed difference was given by the authors.

(d) Position of carbonaceous residues in the soil

The presence of carbonaceous residues influence biological interchange of soil nitrogen. The position of the residues in the soil is known to affect the rate of the immobilization process. After harvest, crop residues may be removed from the field, left in the field on top of the soil or incorporated into the soil in the cultivation process.

Residues left on the surface of the soil get dehydrated and become more resistant to microbial breakdown, (Parker *et al.* 1957). For this reason, surface mulch low in nitrogen or with a wide C:N ratio does not significantly increase immobilization of nitrogen in the soil. In contrast buried residues are not only protected from dehydration but are also in direct contact with the added nitrogen and therefore are easily degradable and increase immobilization.

(e) Temperature, soil pH and moisture content

Low temperature and suboptimal moisture generally slow down biological activity and hence the immobilization-mineralization process. There is a slight tendency to slower decomposition under acid than neutral or slightly alkaline conditions (Norman 1931). This, however, is not necessarily the case since there is a wide variety of microorganisms in the soil that can withstand extreme environmental factors of pH, temperature and moisture. Broadbent and Nakashima (1970) indicated that immobilization of nitrogen occurred to a con-

siderable extent even in anaerobic soils under flooding.

(3) Availability of immobilized nitrogen

Immobilization is regarded as a loss of plant-available nitrogen only from the point of view of immediate needs by plants. It does not represent a net loss of this nutrient from the soil system in which it is held as a reserve. But it is important to know how useful this reserve is to future crop needs. Bremner (1955) indicated that a large fraction of the organic nitrogen taken up by microorganisms is synthesized into protein, with a smaller fraction being in the form of amino sugars. Microbial tissue, like animal and plant protein,is susceptible to enzymatic hydrolysis releasing nitrogen into the inorganic form (Bartholomew 1965). However, in the formation of humus, microbial nitrogenous compounds combine with resistant products of decomposition from plant residues to form a stable complex which protects the nitrogen from further decomposition. Tyler and Broadbent (1958); Broadbent and Tyler (1962) and Broadbent and Nakashima (1970) indicated that although immobilization is a rapid process, the immobilized nitrogen resists mineralization for a long period of time. Immobilized nitrogen was released at the rate of about 2 to 4 percent each year. Jansson (1963) found net mineralization rates of only 3.0 to 4.7 percent per year for immobilized nitrogen. The availability of immobilized nitrogen decreased progressivley with time as

the newly-immobilized nitrogen compounds changed to substances of increasing biological stability. Wojcik-Wojtkowiak (1969) considered immobilization as a way of preventing nitrogen loss because she observed large losses of nitrogen when straw was not added to the soil. This was true for soils of a high nitrifying capacity where the soil conditions were conducive to considerable loss of nitrate by leaching. She noted, however, that the coefficient of ultilization of fertilizer nitrogen was possibly reduced by immobilization.

The period of time during which immobilized nitrogen remains stable or resistant to decomposition is largely unknown (Broadbent and Tyler 1962). However, Hallam and Bartholomew (1953) and Stotzky and Mortensen (1955) noted that fresh organic materials promoted decomposition of native organic matter. Chu and Knowles (1966) also noted this "priming effect" of raw black spruce humus on the mineralization of stable humus. This priming effect is believed to increase the development of an active and violent microbial population that is able to attack stable humus. The reactions occurring to give a priming effect are difficult to comprehend. As it was already pointed out by Tyler and Broadbent (1958) immobilized nitrogen becomes progressively unavailable with time due to the formation of compounds of increasing biological stability. Broadbent

and Tyler (1962) and Gasser *et al.* (1967), using N^{15} as a tracer, showed that in instances where there was an increase in mineralization following the amendment of the soil with N^{15}, the release of inorganic nitrogen was more from the non-tracer nitrogen of soil humus than from the recently immobilized tracer nitrogen. Therefore, the actual reactions responsible for the priming effect probably await further clarification.

(C) Ammonium Fixation

(1) Mechanism of ammonium fixation

Another reaction of mineral nitrogen is ammonium fixation in which expanding clays with a 2:1 lattice entrap ammonium in between the interlayer spaces. The mechanism by which ammonium ions are fixed by expanding clay lattices was understood from studies of potassium fixation and the mechanism is believed to be the same. The entrapment of potassium or ammonium in the facing ditrigonal holes of expanding 2:1 layer silicates (lattice hole theory) makes these ions fit tightly in the interlayer spaces and renders them inaccessible to replacing cations because the crystal lattice is contracted. In this way, the NH_4^+ is rendered temporarily unavailable to microorganisms or plants. Unlike biological immobilization, this is purely a physical phenomenon.

The concentration of the ammonium ion in the soil solution is usually low and is in equilibrium with the

exchangeable and fixed forms (Bartholomew and Janssen 1931).

i.e. $NH_4^+ \rightleftharpoons NH_4^+ \rightleftharpoons NH_4^+$

(in soil solution) (exchangeable) (fixed)

In a well-aerated soil, ammonium is quickly oxidized to nitrate by nitrifying microorganisms. NH_4^+ is also a ready source of nitrogen for plants and heterotrophic microflora. The above reactions account for the low concentrations of NH_4^+-N in soil solution. However, the concentration can be high immediately after the addition of ammonium fertilizers and after hydrolysis of urea. The position of the equilibrium given above will, therefore, depend on the concentration of the ion in soil solution.

(2) Factors affecting ammonium fixation

(a) Influence of potassium on ammonium fixation

It has been pointed out that the mechanism of potassium fixation is similar to that of ammonium fixation. Saturation of vermiculite, illite and montmorillonite with K^+ or NH_4^+ results in the contraction of the mineral crystal lattice when these ions are trapped in between the lattices. For this reason, the presence of K^+ influences the behaviour of the ammonium ion to such an extent that the equilibrium given above is modified to be as follows: (Nommik 1957).

$(K^+ + NH_4^+) \rightleftharpoons (K^+ + NH_4^+) \rightleftharpoons (K^+ + NH_4^+)$

(in soil solution) (exchangeable) (fixed)

Thus the soils which are impoverished in potassium fix more

ammonium than soils rich in potassium (Ghildyal and Singh 1961). Stanford and Pierre (1947) and Bower (1950) showed that ammonium fixation increased when potassium was added simultaneously in equivalent amounts and that fixation of ammonium was reduced by potassium applied prior to ammonium application. Even in soils with equal fixation capacity, the degree of ammonium fixation differed with soil horizon. Surface soils fixed equal amounts of ammonium and potassium whereas ammonium fixation was greater than potassium fixation in subsoils. No explanation was given for the differences in fixation. Nielsen (1972) also noted that the two cations were fixed in similar proportions but that potassium was fixed preferentially to ammonium when the two were added together. He also noted that maxiumum fixation in surface soil was 20 to 30 percent of the applied ammonium and potassium whereas 50 to 80 percent of the added potassium and ammonium was fixed by subsoil. Nommik (1957), however, noted the simultaneous addition of potassium and ammonium gave variable results of the extents of fixation depending on the type of fixing material, concentration and ratio of the concentration of ammonium to potassium. For example, potassium and ammonium added at low concentrations but in equivalent amounts to a hydrogen-saturated montmorillonite resulted in more potassium being fixed than ammonium. However, more ammonium than potassium was fixed when the concentrations of both cations

were high.

(b) Presence of other ions

Some investigations have shown that other ions which do not necessarily cause a contraction of lattice spacing in silicate clays can influence the amount of ammonium fixed. Divalent and trivalent ions have a higher replacing power than the NH_4^+ ion and therefore reduce the concentration of NH_4^+ on exchange sites. Thus soils pre-treated with iron and aluminium salts fix less NH_4^+ than soils not treated (Reiteimer 1951 and Stanford 1948). The anion associated with the ammonium ion may influence the fixation of the latter. Leggett (1958) pointed out that anions such as phosphate which tend to be absorbed strongly to the soil tend to increase ammonium fixation. Ammonium fixation was greater for diammonium phosphate when compared to different ammonium salts. The work of Malquori and Radaelli (1960), however, did not agree with the above findings.

(c) Concentration of ammonium

It has been shown that soluble NH_4^+ is in equilibrium with the exchangeable and fixed forms. Thus the amount of ammonium fixed increases with amounts added; however, the percent of applied NH_4^+ which is fixed decreases with increasing amounts of NH_4^+ added (Leggett and Moodie 1962).

(d) Temperature

Ammonium fixation is a rapid process and rate of fixation depends on rate of diffusion of the NH_4^+ ions. Rate of fixation is greatest immediately after addition of the ammonium salt and decreases slowly as equilibrium is reached. Harada and Katsuna (1954) showed that about 60 to 90 percent of added NH_4^+ was fixed within 6 hours after addition. Since the rate of fixation depends on the rate of diffusion and since the latter process is determined by temperature, within 0 to 60C the rate of fixation increases with temperature. However, the absolute magnitude of fixation at equilibrium is temperature independent (Aomine and Wada 1952).

(e) Soil moisture content

The amount of ammonium fixed by expanding clays depends on how tightly the crystal lattice remains contracted. The lattice of 2:1 clays expands in the presence of moisture and the capacity of soils to fix ammonium is lower under moist than dry conditions (Allison *et al.* 1951). For dilute solutions of ammonium, drying increased the concentration of ammonium which increased both the rate and magnitude of fixation. This effect was mostly noted with vermiculite and illite and not observed where the concentration of ammonium was initially high (Allison *et al.* 1951). Alternate wetting and drying of soil increases ammonium fixation

(Jansson 1958; Walsh and Murdock 1960; and Stojanovic and Broadbent 1960).

(f) Particle size, clay content and soil pH

Fixation of ammonium increases with clay content particularly for 2:1 clay types. Kaolinitic clay-dominated soils show less tendency to fix ammonium. Sandy soils would be expected to show less tendency for ammonium fixation. However, it has been observed that even silt and fine sand soils often fix considerable ammonium (Jansson and Ericsson 1962). Vermiculite and illite fix more ammonium than montmorillonite.

The accessibility to a fixed NH_4^+ ion decreases with increase in size of the particle of the fixing minerals. Grinding the soil to reduce the particle size is accompanied by the exposure of internal surfaces and this facilitates the replacement of absorbed ammonium ions (McDonnell *et al.* 1959 and Barshad 1954).

Ghildyal and Singh (1961) observed that ammonium fixation in a hydrogen-saturated clay was negligible probably because the high replacing power of the hydrogen ion enabled it to dominate the exchange sites on the clays, or hydrogen caused the expansion of the lattice and rendered interlattice ammonium more accessible to replacing cations. Liming the soil increased ammonium fixation because of removal of

exchangeable hydrogen, iron and aluminium (Rich 1960). However, some Scandanavian soils with free calcite showed a low ammonium fixation capacity (Karlsson 1952).

(g) Presence of non-exchangeable aluminium and other ions

The presence of non-exchangeable aluminium is known to decrease ammonium fixation. Non-exchangeable aluminium can occur in the interlayer lattice and the mineral cannot contract even in the presence of K^+ or NH_4^+ ions. Filling of the interlayer lattice space with hydroxy-aluminium groups was observed to reduce the collapsibility of the lattice thus reducing ammonium fixation (Rich 1960). Other ions with approximately the same radii as potassium or ammonium, such as rubidium and cesium are also fixed by expanding clay minerals. Their presence reduces ammonium fixation through competition for fixation sites.

(h) Influence of organic compounds on ammonium fixation

Organic compounds can interfere with ammonium fixation. Porter and Stewart (1970) pre-treated subsoils and vermiculite with organic compounds including sucrose, hexadecanol, citric acid, gelatin, acetic acid, lysine, cysteine and glycine and then added ammonium chloride. Their results demonstrated that some of these substances reduced ammonium fixation. The reduction of ammonium fixation by substances containing amino groups was considerable. Glycine reduced fixation of ammonium by 78 percent

but organic acids had very little effect.

(3) Plant availability of fixed ammonium

Data on the availability of fixed ammonium to field crops is inconclusive. Most of the information was obtained using pot experiments in greenhouses where the root to soil volume ratio was too artificial to suit field extrapolation. Information under field conditions is complicated by such factors as uncontrolled precipitation and temperature regimes which determine the fixation and release process through contraction and expansion of clay minerals. Also, the general vigour of plants influence its ability to utilize fixed ammonium. In spite of this, the studies still provide some useful information. Bower (1951), using barley seedlings, showed that the availability of fixed ammonium was increased 14 to 25 percent when the soil was inoculated with nitrifying bacteria. Allison *et al.* (1953) demonstrated that millet could only recover 7 to 12 percent of fixed ammonium. Aomine and Higashi (1953) showed that the availability of fixed ammonium to wheat depended on the nature of the fixing material. Nommik (1957) showed that the oat plant utilized up to 80 percent of ammonium in a high fixing capacity vermicullite heavy clay. Legg and Allison (1959) showed the uptake of ammonium by Sudan grass was the same in 2 different types of subsoils with a high ammonium fixing capacity and in non-fixing surface soils.

Axley and Legg (1960) showed, however, that the uptake of nitrogen by plants from a direct ammonium source or from urea was not affected by the capacity of the soil to fix ammonium unless there was sufficient potassium to block the release of the fixed ammonium. It was concluded that ammonium should not be applied simultaneously with potassium to soils with a high fixing capacity.

Plant species differ in their ability to utilize fixed ammonium. Cereals have roots with a low cation exchange capacity and are more able to absorb monovalent cations such as K^+ and NH_4^+. Dicotyledon roots with a high cation exchange capacity cannot readily absorb monovalent ions from solutions and minerals (Drake *et al.* 1951). This view was disputed by Evans and Attoe (1948) who showed that clover removed more ammonium from soils with a high fixing capacity than oats. The ability of a plant to utilize fixed ammonium is not only dependent on the species but on other such factors as rate of growth, rooting habit and the potassium requirement. But the removal of potassium is an absolute condition for complete release of fixed ammonium (Nommik 1965).

Most surface soils of arable land do not fix very high levels of ammonium, unlike subsoils. Thus, the agronomic significance of ammonium fixation on the availability of fertilizer nitrogen may sometimes be overestimated. Moreover, fixation and release processes are in equilibrium

and therefore it should be expected (and is found to be the case) that once the exchangeable and solution ammonium are depleted, ammonium is released from the fixed portion, even though not all the fixed ammonium participates in the equilibrium reaction (Nommik 1965).

(4) Influence of microbial activity on availability of fixed ammonium.

Microbial activities probably aid in the release of fixed ammonium. Nitrifiers can oxidize to nitrate about 10 to 28 percent of fixed ammonium (Bower 1951; Allison *et al.* 1951; and Nommik 1957). Work by Aomine and Higashi (1953) showed that 40 to 75 percent of the fixed ammonium was available to nitrifiers after incubating the soil for 11 weeks. However, the availability of fixed ammonium to nitrifiers is generally low. This is difficult to explain if the equilibrium reaction of solution, exchangeable and fixed ammonium is operating. Other factors, particularly the concentration of potassium interfere with the release of fixed ammonium since Nommik (1965) noted that in potassium-free vermiculite soils, all the added ammonium was recovered as nitrate. The low ability of nitrifiers to utilize fixed ammonium could also be accounted for by the fact that nitrifiers have a low requirement for potassium, (Welch and Scott 1959). Therefore, oxidation of ammonium to nitrate by the nitrifiers increases the K^+/NH_4^+ ratio

and this may further hinder the release of fixed ammonium. In contrast, heterotrophic microorganisms require both NH_4^+ and K^+, and therefore, would be more able to utilize fixed NH_4^+ provided there was a sufficient energy supply in the form of an easily degradable organic substrate. Since the presence of an energy supply reduces both K^+ and NH_4^+ in solution through uptake by heterotrophs, the release of fixed NH_4^+ is thus favoured. However, it was noted in some cases that nitrifiers seemed to be more effective in utilizing fixed ammonium than heterotrophs (Jannson 1958). For both heterotrophs and nitrifiers, it appears the level of K^+ in the soil has a greater influence on the availability of fixed NH_4^+ to both groups of microorganisms than merely their relative efficiencies in utilizing it.

(D) Fixation of Ammonia by Soil Organic Matter

Soil organic matter can combine with ammonia to form a stable complex that is resistant to microbial enzyme hydrolysis. Since it is ammonia and not the ammonium ion that is involved in the fixation, this reaction becomes important only when aqueous ammonia is used as a fertilizer or when ammonia is formed under alkaline pHs from the application of ammonium fertilizers. Urea could be lost in this manner after hydrolysis.

Ammonia fixation increased above pH 7 (Broadbent

et al. 1961). Above pH 7 autooxidation of organic substances occurs, particularly those with aromatic compounds and phenolic groups, resulting in the fixation of ammonia. The fixing capacity increases with an increase in the lignin content of the organic matter (Jansson 1960). Jansson (1960) postulated ammonia was initially bound to phenolic groups to form aminophenols which were further oxidized to unstable quinonoimine rings which joined to form a stable heterocyclic ring structure in which ammonia was stabilized from chemical and biological action. Since this is an oxidative process, it would be expected that molecular oxygen was an absolute requirement for ammonia fixation. Such was found to be the case for pure phenols but not with phenolic groups of soil organic matter which fixed ammonia even under anaerobic conditions (Broadbent *et al.* 1961). The presence of O_2, however, tends to increase ammonia fixation.

Ammonia-lignin complexes were resistant to microbial decomposition and stable to acid treatment (Bremner and Shaw 1957). Digestion of ammonia-treated beach leaf humus with 4N HCl for 24 hours removed only 10 percent of fixed ammonia although 2N NaOH removed nearly 50 percent (Mattson and Koutler-Anderson 1942). Sudan grass utilized only 4.29 percent of fixed ammonia (Burge and Broadbent 1961). With time the resistance of fixed ammonia

to microbial attack and plant availability increased (Nommik 1965).

(E) Precipitation of Ammonium as Taranakites

Soil constituents other than those discussed previously react with NH_4^+ and reduce the effectiveness of nitrogen fertilizers. Tamini *et al.* (1963) noted that hydrous oxides of iron and aluminium which fix phosphorous, also react with ammonium to form insoluble compounds such as ammonium taranakite, $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$. The prerequisite for the formation of these complexes was the presence of NH_4^+, aluminium, phosphorous, water and an acid environment. The higher the PO_4:NH_4 ratio in the fertilizer, the higher the proportion of added ammonium fertilizer that is precipitated as taranakite. This reaction may contribute to considerable losses of ammonium fertilizers in highly weathered tropical soils if ammonium phosphate fertilizers are used.

(F) Leaching

The ammonium ion, due to its positive charge, is held by the negatively charged exchange materials; silicate minerals and organic matter in the soil. Therefore, the downward movement of NH_4^+ is only possible if it is displaced by another cation of a higher displacing power or of the same displacing power but present in large quantities in the soil. This cation exchange reaction depends on the cation exchange capacity of the soil (Harmsen and Kolenbrander

1965). Ammonium losses might be of considerable importance in sandy soils. Soils with a high cation exchange capacity retain most of the applied ammonium.

The quantity of ammonium held by soil colloids is usually low since the ion is subject to various alternative reactions such as: ammonium fixation, immobilization by heterotrophic microflora, absorption by higher plants and oxidation to nitrate by nitrifying microflora. The nitrate produced, being negatively charged, is not held by soil colloids and is susceptible to loss by drainage water from rainfall or irrigation. Large losses are likely to occur in course-textured soils and in climatic areas with intense rainfalls. NO_3^--N moved to relatively deep depths in soils even under semi-arid climatic condition prevailing over some prairie regions of Western Canada. Doughty *et al.* (1954) showed substantial amounts of NO_3^--N in subsurface horizons of a heavy clay soil. Leaching losses are usually not serious in soils with a high water table since nitrate can move up and down the soil profile with water movement. Field-Ridley (1975) noted upward and downward movement of nitrate occurred in response to changes in the environment. Evapotranspiration, by causing an upward movement of water, may aid some upward displacement of any nitrates leached beyond the root zone. The presence of plants not only absorbs the available nitrate but also increases the upward

movement of water by transpiration. Therefore, leaching losses are less in cropped than fallow soil.

(G) Denitrification

(a) Biological denitrification

Similar to leaching, denitrification losses involve NO_3^--N. The conversion of NH_4^+ to NO_3^- makes the former susceptible to loss when the latter is reduced to gaseous products. Unlike the other reactions already discussed, denitrification causes a net loss of nitrogen from the soil-plant system. Nitrate can serve as a terminal electron acceptor in the respiration of some facultative anaerobic bacteria. It was generally thought that denitrification accurred only where the facultative anaerobic population was faced with a condition of inadequate O_2 supply in poorly drained soils in the presence of large quantities of nitrate. However, Russell (1961) and Broadbent and Clark (1965) suggested that denitrification occurred even in well-aerated soils. Its occurrence depended on the biochemical oxygen demand (BOD) of the soil system. When easily decomposable materials are added to the soil the O_2 present may not be sufficient to provide for the BOD so nitrate becomes a supplemental terminal electron acceptor. Under such conditions, the microenvironment of the bacterial cell may be completely anaerobic in an otherwise well-aerated soil. This condition prevails in fine-textured soils and inside large soil aggregates where the

diffusion of O_2 is slow particularly at the centre of the aggregate. As such, denitrification is a continuous process, the magnitude of which depends primarily on the BOD of the soil. Greenland (1962) noted that nitrification, an absolutely aerobic process occured simultaneously with denitrification.

Denitrification can result in a significant loss of nitrogen in some soils because temporary anaerobiosis can occur after heavy rains or irrigation. The presence of a crop may increase denitrification losses from root exudates and sloughed off tissues which increase the BOD of the soil solution (Bremner and Shaw 1958). As such, soils under fallow denitrify less nitrogen than soils under crops. Since denitrification is a metabolic process, it is favoured by mesophilic temperatures; therefore; cold soils have less denitrification losses than warm soils. The small, continuous losses of nitrogen by denitrification occurring in well-aerated soils, in small pockets of microbial activity or in soils with large aggregates may be serious losses in all soils and may account for losses of 10 to 15 percent of the total annual mineral nitrogen inputs (Broadbent and Clark 1965). In his review of the fate of nitrogen added to the soil, Allison (1966) pointed out that under common field conditions biological denitrification is probably second only to leaching as the cause of

poor recoveries of nitrogen.

(b) Chemo-denitrification

Dissimilatory nitrate reduction by facultative anaerobes could not adequately explain all the gaseous nitrogen losses from the soil when a nitrate source and an ammonium source were added to the same well-aerated fallow soil. More nitrogen was recovered from the nitrate than from the ammonium source (Broadbent and Clark 1965). This was noted as gaseous losses of nitrogen chiefly as N_2 in situations where nitrite or nitrous acid accumulated. The following pathways were suggested to be responsible for chemo-denitrification.

(1) Loss of nitric oxide under acid conditions

$$3HNO_2 \longrightarrow 2NO\uparrow + HNO_3 + H_2O$$

(2) Reaction of nitrous acid with amino acids (Van Slyke reaction)

$$R\text{-}NH_2 + HNO_2 \longrightarrow R\text{-}OH + H_2O + N_2\uparrow$$

The importance of these reactions in explaining gaseous nitrogen losses was doubtful because the soil pH must be below 5 for the above reactions to take place, a pH range which does not favour appreciable accumulation of nitrite.

(3) Reaction of ammonia or ammonium with nitrous acid and subsequent decomposition of ammonium nitrite

$$NH_3 + NHO_2 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

This reaction probably explained most of the gaseous losses

of nitrogen by chemo-denitrification (Allison 1963). Broadbent and Clark (1965), however, did not agree with the significance of losses of nitrogen through the formation and breakdown of ammonium nitrite.

Since the above reactions could not explain the occurrence of chemo-denitrification in neutral soils or soils of less than pH 5 it was thought that other factors in the soil accounted for nitrite instability. Clark and Beard (1960) noted that nitrate instability was greater in the presence of organic matter than in its absence. Pretreatment of the soil with hydrogen peroxide to destroy the organic matter resulted in less nitrogen gaseous losses involving nitrite. Clark (1962) proposed that there were probably organic-reducing compounds of microbial origin that accelerated nitrite dismutation. Wullstein *et al.* (1963) proposed that exchangeable cations, particularly heavy metals, in addition to organic reducing substances, could be involved in volatile losses of nitrogen in the soil.

(H) Volatilization of Ammonia

Loss of nitrogen as ammonia arises from the use of anhydrous or aqua ammonia in dry soils, use of high concentrations of urea which is readily hydrolyzed by urease to ammonia, and the use of ammonium fertilizer on alkaline soils (Allison 1966). Losses of nitrogen were noted to be high when ammonium fertilizers were applied on the surface of

alkaline soils and they were noted to increase with concentration of NH_4^+, soil temperature, pH and inversely related to soil moisture and cation exchange capacity (Carefoot 1971; McGill 1971; and Toews 1971).

2.2 Minimizing Nitrogen Fertilizer Losses from the Soil-Plant System

(a) Minimizing nitrogen losses by control of nitrification

Leaching and denitrification losses of ammonium occur after the ammonium is oxidized to nitrate. The nitrification process is not always a desirable one. In addition to increasing the mobility of nitrogen and thus making it susceptible to loss by leaching, it results also in increasing soil acidity. Since the nitrate form is easily moved below the crop root zone in high rainfall areas, it is necessary to apply nitrogen fertilizers in split applications to insure a continuous supply of nitrogen to plants. Also, a delay or inhibition of nitrification would be desirable in certain instances. This is based on the assumption that NH_4^+-N is as good a source of nitrogen for plants as is NO_3^--N. A chemical inhibitor, 2-chloro-6-(trichloromethyl) pyridine has been tested under laboratory and to a lesser extent, under field conditions (Goring and Hamaker 1972). This chemical, also known as N-Serve, has been shown to control nitrification by *Nitrosomanas* but not by heterotrophic nitrifiers. In the field, the bene-

fits from the use of N-Serve were not consistent. Swezey and Turner(1962)obtained greater yield increases of cotton, corn and sugar beets with the use of ammonium fertilizers treated with N-Serve than with fertilizers not treated. Huber *et al.* (1969) showed N-Serve inhibited nitrification and prevented the movement of fertilizer nitrogen below 30.5 cm. The treatment also increased wheat yield as much as 42 percent more than a $Ca(NO_3)_2$ treatment. Jaiswal *et al.* (1972) showed that some nitrification inhibitors, including N-Serve, increased the yield of millable cane sugar,dry matter synthesis and nitrogen uptake as compared to control treatments without nitrification inhibitors. In contrast, other workers did not obtain benefits from nitrification inhibitors. Gasser *et al.* (1967) found the nitrification inhibitor reduced losses of nitrogen but decreased the yield of wheat by changing the proportions of NO_3^- to NH_4^+ in the soil. Lewis and Stefanson (1973) also found N-Serve did not significantly increase grain yields. The difference in these results is probably caused by the difference in tolerance of plants to NH_4^+ and NO_3^- nutrition. Although plants can effectively absorb both the NH_4^+ and NO_3^- forms, the assimilation of each of these forms depends on the species, age of the plant and environmental factors. Rice plant utilizes NH_4^+ more effectively than NO_3^- at all stages of growth whereas cotton utilizes NH_4^+ more readily

at early stages than at later stages of growth (Scarsbrook 1965). Rhoads (1972) obtained better leaf yields and quality of cigar wrapper tobacco with a nitrate than with an ammonium source of nitrogen. In contrast, Forsyth (1971) obtained equal yields of peaches with NO_3^- and NH_4^+ sources although the NO_3^- source resulted in larger fruit size and higher leaf nitrogen. It is uncommon to find a plant in a well-aerated soil, growing better at all times on NH_4^+ than on NO_3^- . Prolonged exposure to ammonium results in toxicity in many plant species (Jasson and Volk 1966). This toxicity arises in cases where plants fail to synthesize amides and other soluble organic compounds and the ammonium accumulates in the tissues. This happens when the photosynthetic activity of the plant is impaired and insufficient carbon skeletons are supplied for amino acid synthesis.

Another attempt to minimize nitrogen losses by leaching and denitrification was to use slow-release nitrogen fertilizers. Attempts were made to apply fertilizers which would release nitrogen at a slow rate and at the time when the nitrogen would be required by the crop. These fertilizers include soluble materials with coatings to reduce solubility, materials of limited water solubility (eg. magnesium ammonium phosphate) and materials which are slowly decomposed by microorganisms. The evaluation of slow-release materials has been mainly limited to laboratory and

greenhouse studies. At times slow release materials gave slightly higher yield, about 5 percent more than soluble materials (Hauck and Koshino 1971), but often at nutrient levels that were too low to sustain intensive crop production. However, slow release materials have been found to produce a better seasonal distribution of growth particularly for grasses. Hauck and Koshino (1971) noted that little information is available on the large-scale use of such materials in practical agriculture. Thus more information on the relationship between nutrient release and plant needs is required to assess the efficiency of slow release nitrogen fertilizers.

(b) Effect of fertilizer placement on the effectiveness of nitrogen fertilizers

Nitrogen fertilizers are applied in various ways. A fertilizer may be localized in a band, mixed throughout the soil or broadcast on the soil surface. The method used depends on the ease of handling which in turn depends on the physical form of the fertilizer; solids (such as salts) or liquids (such as aqueous ammonia). Other factors that determine the method of application are the type of crop, the amount of fertilizer to be added and soil characteristics.

The effectiveness of a fertilizer is affected by the method of application as the physical, biological and

chemical interactions of soil constituents with applied nitrogen depends on the method of placing the fertilizer in the soil. The method of fertilizer application can reduce some of the losses already discussed. Mixing the fertilizer throughout the soil increases the physical contact with clay minerals and organic matter. These processes enhance ammonium fixation and biological immobilization. Placing ammonium fertilizer in a band makes the salt concentration within the band very high and microbial growth is inhibited (Pesek *et al.* 1971). Such inhibition maintains the nitrogen in the NH_4^+ form in which it is less susceptible to denitrification and leaching. Nyborg (unpublished data 1975) showed banding nitrogen fertilizers to be more effective in increasing grain yields than nitrogen mixed throughout the soil. Nommik (1965) noted that band application of ammonium fertilizers and use of granulated materials reduced ammonium fixation and increased fertilizer effectiveness. Legg and Allison (1959) found nitrogen uptake by Sudan grass was greater from banded $NaNO_3$ and $(NH_4)_2SO_4$ than from $(NH_4)_2SO_4$ uniformly mixed with the soil. The difference was entirely ascribed to less fixation when the NH_4^+ source was banded. Van Uyen (1971) found that placement of $(NH_4)_2SO_4$ reduced nitrogen losses from a water-logged soil and produced rice yields that were 20 to 25 percent higher than from broadcasting the $(NH_4)_2SO_4$. Donald *et al.* (1963), in their

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review of nitrogen studies, concluded that the greatest efficiency of applied nitrogen results when a small portion of the total fertilizer was placed in a band in close proximity to the seed row.

Work by others, however, has indicated results contrary to the above. Burns and Dean (1964) in their study of the factors affecting movement of nitrate in the soil, indicated that under certain conditions a large portion of nitrate present in bands in the soil could move down very rapidly when the moisture content was above field capacity. Banding of fertilizers such as aqueous ammonia and urea increases the pH of the localized environment. At this high pH and high levels of ammonium, *Nitrobacter* spp. activity is inhibited (Alexander 1961) while ammonium oxidation remains unaffected. Under these conditions, nitrite accumulates which is toxic to plants and can be lost by chemo-denitrification as already described. Jones and Hedlin (1970) also noted these same effects in some Manitoba soils. A localized placement of urea increased the risk of ammonia fixation by organic matter because urea hydrolysis yields ammonium carbonate which in turn can decompose to yield ammonia. Wittich (1961) showed that applying ammonia by uniform incorporation resulted in less fixation by organic matter than when it was banded by a special applicator.

Losses occurring due to ammonia volatilization

could be reduced by properly incorporating aqueous ammonia, urea or other ammoniacal fertilizer deep enough in a calcareous soil. The soil should also be moist so that any ammonia that tends to escape is dissolved and remains in the soil (Fenn 1975 and Watkins *et al.* 1972).

III. MATERIALS AND METHODS

(A) Materials

(1) Soil

The soil used in these investigations was a Newdale clay loam with the following characterics:

pH:	8.2	(soil/water 1:10)
% total N:	0.37	
% Organic carbon:	3.5	
Inorganic C(%CO_3):	0.4	
C.E.C.:	29.6	(NH_4 Ac. displacement method)

(2) N^{15}-labelled $(NH_4)_2SO_4$

N^{15}-labelled $(NH_4)_2SO_4$ was used in order that the fate of added fertilizer could be determined. The fertilizer used in this study was prepared from N^{15}-enriched $(NH_4)_2SO_4$ with an isotopic abundance of 54.1 percent N^{15} excess supplied by Vebberline-Chemie: Berlin-Adlershof. The $(NH_4)_2SO_4$ with an N^{15} abundance of 54.1 percent was mixed with reagent grade $(NH_4)_2SO_4$ to obtain various levels of N^{15} excess depending upon the amount of fertilizer added to the soil.

These were:

21.70 percent excess N^{15} for the 200 ppm treatments,

10.63 percent excess N^{15} for the 400 ppm treatments and

3.26 percent excess N^{15} for the 800 and 1600 ppm treatments.

The N^{15} abundance of each of the above was first determined by mass spectrometry.

(3) N-Serve

A nitrification inhibitor, 2 chloro-6-[tricholoro-methyl] pyridine (N-Serve), supplied by Dow Chemical Co. Ltd., contained 22 percent active ingredient. It was added in two of the treatments to determine the fate of nitrogen fertilizers when it was maintained in the NH_4^+ form for a long period of time.

(4) Straw

The straw, obtained from wheat stubble, was finely ground and contained 0.30 percent total nitrogen. This was included in some of the treatments to determine the effect of carbonaceous residues on immobilization of inorganic nitrogen.

(5) Incubation plastic cylinders

Each cylinder was 10 cm long and 2.5 cm wide (internal diameter).

(B) Methods

Two laboratory incubation experiments were conducted.

Experiment 1 - Effects of Straw, Fertilizer Placement, N-Serve and Amount of Nitrogen on Fixation or Immobilization of Added Nitrogen

An experiment was designed to study the immobilization and fixation of nitrogen from $(NH_4)_2SO_4$ as affected by placement. Nitrogen fertilizer was either banded into the soil or thoroughly mixed with the soil. The effect of the amount of nitrogen added on immobilization and fixation was also studied. Straw was added to some of the treatments to assess the effects of application of carbonaceous residues on immobilization. N-Serve was included in two of the treatments to study the effect of maintaining nitrogen in the NH_4^+ form on immobilization and fixation. N^{15}-labelled $(NH_4)_2SO_4$ was used to trace the fate of nitrogen as affected by different treatments. This experiment consisted of ten treatments each replicated twice. The treatments were broadly divided into 2 groups.

(a) Nitrogen fertilizer mixed with the soil

(i) 0 ppm N

(ii) 200 ppm N as $(NH_4)_2SO_4$

(iii) 400 ppm N as $(NH_4)_2SO_4$

(iv) 800 ppm N as $(NH_4)_2SO_4$

(v) 1600 ppm N as $(NH_4)_2SO_4$

(vi) 400 ppm N as $(NH_4)_2SO_4$ plus 1% straw (w/w basis mixed with the soil)

(vii) 400 ppm N as $(NH_4)_2SO_4$ plus 20 ppm N-Serve (w/w mixed with the fertilizer)

(b) Nitrogen fertilizer banded in the soil

(i) 400 ppm N as $(NH_4)_2SO_4$

(ii) 400 ppm N as $(NH_4)_2SO_4$ plus 1% straw (w/w soil basis)

(iii) 400 ppm N as $(NH_4)_2SO_4$ plus 20 ppm N-Serve (w/w soil basis)

The fertilizer treatments were prepared as follows:

(a) Nitrogen Fertilizer Mixed with the Soil

Sixty grams of soil were thoroughly mixed with the respective amounts of fertilizer to ensure uniform distribution of the fertilizer throughout the soil. The N-Serve, where included, was mixed with the fertilizer prior to incorporation into the soil. The treated soils were placed into plastic cylinders the bottoms of which were sealed with a double layer of paraffin coated paper. The soil was moistened to field capacity moisture content (28 percent) and this moisture regime was maintained throughout the duration of the incubation by adding water as required. The soils were incubated at 20 to 25C. A sufficient number of samples were prepared to provide duplicate samples for each incubation period and treatment.

(b) Nitrogen Fertilizer Banded in the Soil

The plastic cylinders (10 cm length) were cut into 3 cm and 7 cm portions and rejoined with masking tape.

The opening of the 3 cm portion of the cylinder was then sealed with paraffin coated paper. N^{15}-labelled $(NH_4)_2SO_4$ fertilizer was placed into the cylinder and uniformly distributed on the paraffin coated paper. Sixty grams of soil were then added to the cylinders. The 0 to 3 cm portion of the cylinder, subsequently referred to as 0 to 3 cm from the band contained approximately 17 g of soil whereas the 3 to 10 cm portion of the cylinder (3 to 10 cm from the band) contained approximately 43 g of soil. The moisture regime and incubation temperature were maintained as described for the treatments where nitrogen was mixed with the soil. The amounts of N-Serve and straw added and method of application were similar to those described previously.

Sampling

The soil was sampled at 0,2,4,8 and 12 weeks of incubation. In treatments where the nitrogen fertilizer was mixed with the soil, the duplicate incubation samples were composited and stored at -20C. For the banded treatments, the portion of soil near the fertilizer band (0 to 3 cm from the band) was sampled separately from the remainder of the soil. Duplicate incubation samples were composited and stored at -20. The samples were stored in tight plastic bags to avoid changes in moisture content during storage.

Sample Analysis

(i) Moisture Content

In order to express the concentrations of NH_4^+, NO_2^-, NO_3^- and total nitrogen on oven-dry basis, 2.0 g of soil was dried at 100C for 24 hours. The loss in weight was obtained and the moisture content of the samples expressed on an oven-dry weight basis.

(ii) Nitrate and Nitrite

Two and one half grams of moist soil were used for these determinations. Nitrate and nitrite determinations were done on a Technicon Auto-Analyzer (Technicon Controls Inc. Chaneey, N.Y.) and the procedure was as outlined by Kamphake *et al*. (1966). The concentrations of both NO_3^- and NO_2^- were expressed on an oven-dry weight basis.

(iii) Ammonium Nitrogen and Total Nitrogen

Ten grams of moist soil were shaken with 30 ml 2N KCl for 1 hour. The suspension was filtered and the soil transferred to the filter paper. The soil was then leached with several 10 ml portions of 2N KCl. The solutions were brought to volume (100 ml). The soil residue was saved for N^{15} excess and Kjeldahl determinations.

Ammonium-Nitrogen

The concentration of ammonium nitrogen in the filtrates was determined by using an Ammonia Electrode (Model 95-10) in conjunction with an Ionalyzer Model 801/ digital pH meter. Twenty-five milliliters of the total filtrate were treated with strongly alkaline NaOH and the

ammonium nitrogen converted to ammonia gas. The concentration of ammonia gas was determined using an ammonia electrode as outlined by Mertensens *et al.* (1975).

Total Nitrogen and N^{15} Excess Determinations

The soil residue that was saved after extraction with 2N KCl was used for these determinations. Total nitrogen was determined by the regular macro-Kjeldahl procedure as outlined by Bremner (1965a) without including nitrite and nitrate. After digesting the soil in concentrated H_2SO_4 followed by alkaline distillation of the digest, the liberated ammonia was collected in excess standard H_2SO_4 and the excess acid was back titrated with standard NaOH solution. From this the total nitrogen was calculated. The resulting ammonium sulphate solution was acidified with 1 to 2 drops of concentrated H_2SO_4 and evaporated by heating to a volume of about 7 ml. The concentrated $(NH_4)_2SO_4$ solution was used to determine the abundance of N^{15} in the samples as described by Bremner (1965b). The ammonium sulphate solution was oxidized with alkaline sodium hypobromite to yield N_2 gas. The gas was collected in completely pre-evacuated gas tubes for mass spectrometry analysis. The N^{15} abundance in the gas samples was determined using a Micromass 602 mass spectrometer (V.G. Micromass Ltd., Winsford, England.).

Experiment 2 - Effect of Placement of Nitrogen Fertilizer and Straw on Immobilization of Added Nitrogen

This experiment was set up to study the effect of straw placement on nitrogen immobilization. Results of the first experiment indicated a significant effect of straw on nitrogen immobilization. The present experiment was intended to study further the effects of straw placement (mixing with the soil versus banding in the soil) on the immobilization of nitrogen.

The same soil as that used in the first experiment was used. Only one rate of nitrogen (400 ppm) was used for all treatments with an isotopic composition of 10.63 percent excess N^{15}. Incubation plastic cylinders, temperature and moisture regime were identical to the first experiment. Incubation time and sampling intervals were also the same. The straw used was the same as that in the first experiment, and the same weight of soil (60 g) per cylinder was used.

Nitrate, nitrite, ammonium nitrogen, total nitrogen and N^{15} excess determinations were as described previously. This experiment consisted of 8 treatments as described below, each replicated twice.

(i) No straw, no nitrogen

(ii) No straw, 400 ppm NH_4-N mixed with the soil

(iii) No straw, 400 ppm NH_4-N banded in the soil

(iv) 1% straw mixed with the soil, no nitrogen

(v) 1% straw banded in the soil, no nitrogen

(vi) 1% straw mixed with the soil, 400 ppm NH_4-N mixed with the soil

(vii) 1% straw mixed in the soil, 400 ppm NH_4-N banded in the soil

(viii) 1% straw banded in the soil, 400 ppm NH_4-N banded in the soil

Where both straw and fertilizer were banded in the soil, the fertilizer was first applied evenly on the bottom of the cylinder. The straw was then placed on top of the fertilizer; the soil was then added to the incubation vessel. Thus, the straw was placed as a band between the soil and the fertilizer band. All other treatments were prepared as described for Experiment 1.

(C) Calculations

(a) Percent N^{15} Excess

The mass spectrometer measures the ratio of intensities of the ion currents produced by the two isotopic beams (Bremner 1965b). For nitrogen, the measured ratio (R) is that of the ion currents corresponding to mass 28 ($N^{14}N^{14}$) and mass 29 ($N^{14}N^{15}$).

$$R = \frac{[N^{14}N^{14}]}{[N^{14}N^{15}]}$$

Atom percent N^{15}, (A), is defined as:

$$A = \frac{\text{Number } N^{15} \text{ atoms}}{\text{Number } N^{14} \text{ atoms} + \text{Number } N^{15} \text{ atoms}} \times 100$$

$$= \frac{100}{2R + 1} \quad \text{(Bremner 1965b)}$$

where R is the measured peak heights (in cm) corresponding to the N^{14} and N^{15} isotopes on the mass spectrometer scanning sheets. The N^{15} excess in the sample was calculated by subtracting 0.366 (background percent N^{15}) from the value of A obtained for each sample.

(b) Nitrate as a Percent of Total Extractable Mineral Nitrogen

For both experiments, the nitrate nitrogen as a percent of total mineral nitrogen was calculated as follows:

(i) Nitrogen mixed with the soil

$$NO_3^-\text{-N as \%} = \frac{\left[(NO_3^-\text{-N in treated soil})_{(ppm)} - (NO_3^-\text{ in control})_{(ppm)}\right]}{\left[NH_4^+\text{-N (ppm) in treated soil} - NH_4^+\text{ (ppm) in control}\right] + \left[NO_3^-\text{-N (ppm) in treated soil} - NO_3^-\text{-N (ppm) in control}\right] + \left[NO_2^-\text{-N (ppm) in treated soil} - NO_2^-\text{-N (ppm) in control}\right]} \times 100$$

(ii) Nitrogen banded in the soil

Since the fertilizer was placed in a band, and the soil was sampled in two separate portions, the calculation in this case was made separately on each portion of the soil. There was 17 g of soil in the portion of soil next to the fertilizer band and 43 g of soil in the 3 to 10 cm portion of the incubation cylinder.

$$NO_3^-\text{-N as \%} = \frac{\left[(\text{mg } NO_3^-\text{-N in 0-3 cm portion} + \text{mg } NO_3^-\text{-N in 3-10 cm portion})\right] - \left[(\text{mg } NO_3^-\text{-N in control})\right]}{\left[\text{mg } NH_4^+\text{-N in 0-3 cm portion} + \text{mg } NH_4^+\text{-N in 3-10 cm portion} - \text{mg } NH_4^+\text{-N in control}\right] + \left[\text{mg } NO_3^-\text{-N in 0-3 cm portion} + \text{mg } NO_3^-\text{-N in 3-10 cm portion} - \text{mg } NO_3^-\text{-N in control}\right] + \left[\text{mg } NO_2^-\text{-N in 0-3 cm portion} + \text{mg } NO_2^-\text{-N in 3-10 cm portion} - \text{mg } NO_2^-\text{-N in control}\right]} \times 100$$

(c) Percent Recovery of Mineral Nitrogen

(i) Nitrogen mixed with the soil

$$\text{\% Recovery} = \frac{\text{ppm}\left[NO_3^-\text{-N} + NO_2^-\text{-N} + NH_4^+\text{-N}\right]_{\text{in treated soil}} - \text{ppm}\left[NO_3^-\text{-N} + NO_2^-\text{-N} + NH_4^+\text{-N}\right]_{\text{in control}}}{\left[\text{ppm } NH_4^+\text{-N added}\right]} \times 100$$

(ii) Nitrogen banded in the soil

$$\% \text{ Recovery} = \frac{\left[\begin{array}{l}\text{mg } NO_3^- \text{-N in 0-3 cm portion + 3-10 cm portion} \\ + \text{mg } NH_4^+ \text{-N in 0-3 cm portion + 3-10 cm portion} \\ + \text{mg } NO_2^- \text{-N in 0-3 cm portion + 3-10 cm portion}\end{array}\right] - \left[\begin{array}{l}\text{mg } NO_3^- \text{-N in control} \\ + \text{mg } NH_4^+ \text{-N in control} \\ + \text{mg } NO_2^- \text{-N in control}\end{array}\right]}{\left[\text{mg } NH_4^+ \text{-N added}\right]} \times 100$$

(d) Percent N^{15} Immobilized or Fixed (Using N^{15} data)

$$= \frac{\text{g of } N^{15} \text{ excess in soil residue}}{\text{g of } N^{15} \text{ added}} \times 100$$

$$= \frac{\%N^{15} \text{ Excess} \times \% \text{ Kjeldahl N} \times \text{weight of soil used}}{\%N^{15} \text{ Excess in Fertilizer} \times \text{g of N added}} \times 100$$

(i) Nitrogen mixed with soil

$$\%\ N^{15} \text{ immobilized or fixed} = \frac{\left[\frac{\%N^{15} \text{ Excess in Residue}}{100} \times \frac{\% \text{ Kjeldahl N} \times 60}{100}\right]}{\left[\frac{\%N^{15} \text{ Excess in Fertilizer}}{100} \times \text{g of N added}\right]} \times 100$$

(ii) Nitrogen banded in the soil

$$\%\ N^{15} \text{ immobilized or fixed} = \frac{\left[\begin{array}{l}\frac{\%N^{15} \text{ Excess}}{100} \text{ in Residue (0-3 cm portion)} \times \frac{\% \text{ Kjeldahl N} \times 17}{100} \\ + \frac{\%N^{15} \text{ Excess}}{100} \text{ in Residue (3-10 cm portion)} \times \frac{\% \text{ Kjeldahl N} \times 43}{100}\end{array}\right]}{\left[\%N^{15} \text{ Excess in fertilizer} \times \text{g of N added}\right]} \times 100$$

IV. RESULTS

Experiment 1

Effects of Straw, Fertilizer Placement, N-Serve and Amount of Nitrogen on Immobilization or Fixation of Added Nitrogen

(A) Nitrate-Nitrogen Content

Nitrate concentration increased with time of incubation (tables 1 and 2). The concentration of nitrate increased with amounts of $(NH_4)_2SO_4$ added (table 1), except for the N-Serve treatment. N-Serve inhibited nitrification in all treatments. The concentration of nitrate when straw was added was slightly less than when no straw was added. This was evident for both banded treatments and when nitrogen was mixed with the soil (tables 1 and 2). The nitrate content of the soil in the portion of the cylinder away from the fertilizer band (3 to 10 cm portion) increased with incubation time. This was due to an upward movement of nitrate by diffusion as a result of establishment of a chemical potential gradient.

(B) Nitrite-Nitrogen Content

The concentration of nitrite-nitrogen in the soil was very low for all treatments at all times (tables 3 and 4). The greatest concentration of nitrite-nitrogen obtained was 2.3 ppm.

Table 1. Nitrate concentration (ppm N) when fertilizer was mixed with the soil. - Experiment 1.

Amounts of $(NH_4)_2SO_4$ added (ppm N)

Incubation Period (wk)	0	200	400	400 + Straw	400 + N-Serve	800	1600
0	6	7	6	7	7	6	7
2	50	171	161	141	9	186	130
4	49	251	300	248	10	322	311
8	68	252	457	337	16	695	730
12	71	241	383	275	20	785	751

Table 2. Nitrate concentration (ppm N) when fertilizer was banded in the soil. - Experiment 1.

Amount of $(NH_4)_2SO_4$ added (ppm N) and soil sampled

Incubation Period (wk)	400		400 + Straw		400 + N-Serve	
	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	6	6	7	7	7	7
2	110	66	78	9	10	8
4	227	131	163	37	7	11
8	553	227	424	159	7	5
12	430	322	353	173	12	19

Table 3. Nitrite concentration (ppm N) when fertilizer was mixed with the soil. - Experiment 1.

Amounts of $(NH_4)_2SO_4$ added (ppm N)

Incubation Period (wk)	0	200	400	400 + Straw	400 + N-Serve	800	1600
0	1.2	1.5	0.7	0.9	0.8	0.7	0.6
2	0.4	0.5	0.4	0.7	0.3	0.7	0.6
4	0.7	0.5	0.8	0.5	0.6	0.5	0.7
8	0.9	1.0	0.9	1.1	1.1	1.0	0.9
12	0.1	0.5	0.5	0.3	0.3	0.4	0.2

Table 4. Nitrite concentration (ppm N) when fertilizer was banded in the soil. - Experiment 1.

Amount of $(NH_4)_2SO_4$ added (ppm N) and soil sampled

Incubation Period (wk)	400		400 + Straw		400 + N-Serve	
	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	1.2	1.2	0.8	0.8	0.5	0.5
2	0.7	0.4	0.7	1.1	0.5	0.4
4	0.7	0.4	0.9	1.1	0.9	0.7
8	1.4	1.2	1.6	2.3	2.3	0.6
12	0.3	0.3	0.3	0.5	0.4	0.4

(C) KCl-Extractable Ammonium-Nitrogen Content

A general decrease in the concentration of KCl-extractable ammonium-nitrogen occurred with time (tables 5 and 6). There was a noticeable and sharp decrease in the concentration of ammonium-nitrogen during the second to the fourth week of incubation. N-Serve maintained high levels of ammonium-nitrogen at all times (table 5). A noticeable decrease in the concentration of ammonium-nitrogen occurred after eight weeks of incubation in the soil treated with N-Serve. As would be expected, the concentration of ammonium-nitrogen increased with the amounts of fertilizer added. About 600 ppm NH_4^+-N was present even at the twelfth week sampling for the soil treated with 1600 ppm NH_4^+-N (table 5). Virtually all the added ammonium had disappeared by the eighth week (except for the N-Serve treatment) when 400 ppm NH_4^+-N was added. Almost all the added ammonium had disappeared by the fourth week when 200 ppm NH_4^+-N was added. The concentration of ammonium-nitrogen during the zero to four-week incubation period was lower in the straw-treated soil than in soil not treated with straw (table 5). The trend of a lower content of ammonium-nitrogen in the presence of straw was not evident where the fertilizer was banded (table 6). The concentration of ammonium-nitrogen decreased after eight weeks of incubation for the N-Serve treated soil (tables 5 and 6). Except for the N-Serve treated soil (table 5), virtually all the added

Table 5. Concentration of KCl-extractable ammonium (ppm N) when fertilizer was mixed with the soil. Experiment 1.

Incubation Period (wk)	Amounts of $(NH_4)_2SO_4$ added (ppm N)						
	0	200	400	400 + Straw	400 + N-Serve	800	1600
0	18	24	377	408	388	766	1635
2	7	66	278	167	412	608	1309
4	6	10	89	30	470	390	1104
8	5	3	3	3	474	99	994
12	6	4	4	24	328	21	611

Table 6. Concentration of KCl-extractable ammonium (ppm N) when fertilizer was banded in the soil. Experiment 1.

Incubation Period (wk)	Amount of $(NH_4)_2SO_4$ added (ppm N) and soil sampled					
	400		400 + Straw		400 + N-Serve	
	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	1267	18	1267	27	1267	19
2	1135	12	1041	11	1105	62
4	781	16	814	3	1251	98
8	368	3	312	4	1035	84
12	152	3	151	7	630	175

ammonium-nitrogen had disappeared by the end of the incubation, when the fertilizer was mixed with the soil but not when it was placed in a band at 400 ppm NH_4^+-N (table 6).

(D) Nitrate as a Percent of Total Mineral Nitrogen

Nitrate, as a percent of total mineral nitrogen, when fertilizer was mixed with the soil and when it was banded in the soil, is shown in tables 7 and 8, respectively. This parameter measures the relative appearance of nitrate-nitrogen or disappearance of ammonium-nitrogen. Nitrate as a percent of total mineral nitrogen increased to 100% after 4 to 8 weeks of incubation, particularly when 200 and 400 ppm NH_4^+-N was mixed with the soil. This indicated that under these conditions, ammonium was oxidized to nitrate with little or no ammonium or nitrite being present in the soil. It was also noted that with higher concentrations of ammonium (800 and 1600 ppm NH_4^+-N), not all the mineral nitrogen was present as nitrate. Only 53% of the mineral nitrogen was present as nitrate even after twelve weeks of incubation when 1600 ppm NH_4^+-N was added to the soil. Rate of nitrification appeared to decrease with concentration of added nitrogen. About two-thirds of the ammonium-nitrogen applied at 200 ppm had disappeared by the second week as compared to less than one-third of the applied ammonium at 400 ppm (table 7). Virtually all the mineral nitrogen added remained in the ammonium form when N-Serve was added. Application of straw did not affect the

relative appearance of nitrate-nitrogen or disappearance of ammonium-nitrogen (table 7).

Banding the nitrogen fertilizer reduced nitrification or the fraction of nitrogen present as nitrate. Application of straw reduced the fraction of nitrogen in the nitrate form when the nitrogen fertilizer was banded. The effect of fertilizer placement on the fraction of mineral nitrogen occurring as nitrate was consistent with the data in tables 5 and 6 which showed higher concentrations of KCl-extractable ammonium-nitrogen in banded as compared to the treatments in which the nitrogen fertilizer was mixed with the soil.

(E) Percent Recovery of Mineral Nitrogen

Except for minor variations between sampling periods, the percent recovery of mineral nitrogen was consistently high in all treatments varying from 82 to 103% except when straw was added where recovery was as low as 56% (tables 9 and 10). No trends in the percentage recoveries with incubation time were noted. Also, percent recovery was independent of the amount of fertilizer added. Addition of N-Serve did not affect percent recovery. Percent recoveries when nitrogen was banded were slightly less than when nitrogen was mixed with the soil .

(F) Percent Total (Kjeldahl) Nitrogen in the Soil After Extraction with KCl

Table 7. Nitrate as a percent of total extractable mineral nitrogen when fertilizer was mixed with the soil. Experiment 1.

Incubation Period (wk)	Amounts of $(NH_4)_2SO_4$ added (ppm N)					
	200	400	400 + Straw	400 + N-Serve	800	1600
0	0	0	0	0	0	0
2	67	29	36	0	19	6
4	98	75	90	0	42	18
8	101	101	101	0	87	40
12	101	100	92	0	98	53

Table 8. Nitrate as a percent of total extractable mineral nitrogen when fertilizer was banded in the soil. Experiment 1.

Incubation Period (wk)	Amount of $(NH_4)_2SO_4$ added (ppm N)		
	400	400 + Straw	400 + N-Serve
0	0	0	0
2	8	0	0
4	33	9	0
8	71	66	0
12	86	76	0

Table 9. Percent recovery of mineral nitrogen when fertilizer was mixed with the soil. Experiment 1.

Incubation Period (wk)	Amounts of $(NH_4)_2SO_4$ added (ppm N)					
	200	400	400 + Straw	400 + N-Serve	800	1600
0	94	90	98	93	93	101
2	90	96	63	91	92	86
4	102	84	56	96	86	91
8	91	97	67	104	90	103
12	83	78	56	68	91	80

Table 10. Percent recovery of mineral nitrogen when fertilizer was banded in the soil. Experiment 1.

Incubation Period (wk)	Amount of $(NH_4)_2SO_4$ added (ppm N)		
	400	400 + Straw	400 + N-Serve
0	90	90	89
2	88	69	78
4	80	63	95
8	88	63	72
12	80	49	61

Table 11. Percent total (Kjeldahl) nitrogen in soil after extraction with KCl when fertilizer was mixed with the soil. - Experiment 1.

Incubation Period (wk)	Amounts of $(NH_4)_2SO_4$ added (ppm N)						
	0	200	400	400 + Straw	400 + N-Serve	800	1600
0	0.309	0.314	0.310	0.318	0.312	0.316	0.322
2	0.326	0.329	0.327	0.338	0.328	0.323	0.327
4	0.321	0.325	0.334	0.338	0.323	0.329	0.322
8	0.368	0.355	0.352	0.360	0.353	0.346	0.354
12	0.325	0.342	0.318	0.334	0.325	0.364	0.318

Table 12. Percent total (Kjeldahl) nitrogen in soil after extraction with KCl when fertilizer was banded in the soil. - Experiment 1.

Incubation Period (wk)	Amount of $(NH_4)_2SO_4$ added (ppm N) and soil sampled					
	400		400 + Straw		400 + N-Serve	
	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	0.314	0.309	0.314	0.316	0.312	0.315
2	0.361	0.312	0.348	0.332	0.343	0.331
4	0.326	0.328	0.338	0.332	0.368	0.397
8	0.344	0.344	0.382	0.371	0.386	0.370
12	0.324	0.315	0.339	0.330	0.319	0.310

The percent total nitrogen in the soil after extraction of the mineral nitrogen with KCl, was not influenced by the treatments, time of incubation or method of fertilizer application (tables 11 and 12). This is to be expected as most of the nitrogen added was recovered as nitrate, nitrite or ammonium-nitrogen, which was extracted prior to soil analysis for total nitrogen. Also, the Kjeldahl technique would not be expected to accurately measure small amounts of immobilized or fixed nitrogen. The values tended to vary, the variance most likely due to errors of analysis.

(G) Percent N^{15} Excess

Percent N^{15} excess at zero incubation time was very low indicating nearly complete extraction of mineral nitrogen prior to incubation and therefore little or no fixation of nitrogen by clays. Since little or no fixation of nitrogen by clay was observed for samples not incubated, it is most likely that clay fixation was not a major process by which nitrogen was retained by the soil even after incubation. Thus most of the nitrogen retained by the soils when incubated probably was mainly due to immobilization.

Percent N^{15} excess did not vary greatly with treatments except where straw was added and when 1600 ppm NH_4^+-N was added and incubated for two weeks (table 13). Percent N^{15} excess in the straw-treated soil was much

Table 13. Percent N^{15} excess in soil after extraction with KCl when fertilizer was mixed with the soil. - Experiment 1.

Incubation Period (wk)	Amounts of $(NH_4)_2SO_4$ added (ppm N)						
	0	200 (21.70)*	400 (10.63)	400 + Straw (10.63)	400 + N- Serve (10.63)	800 (3.26)	1600 (3.26)
0	0.021	0.005	0.021	0.023	0.019	0.020	0.021
2	0.006	0.168	0.141	0.169	0.202	0.122	0.435
4	0.001	0.250	0.172	0.428	0.216	0.109	0.173
8	0.023	0.207	0.184	0.447	0.272	0.106	0.146
12	0.020	0.222	0.160	0.521	0.245	0.121	0.151

Table 14. Percent N^{15} excess in soil after extraction with KCl when fertilizer was banded in the soil. - Experiment 1.

Incubation Period (wk)	Amount of $(NH_4)_2SO_4$ added (ppm N) and soil sampled					
	400 (10.63)*		400 + Straw (10.63)		400 + N-Serve (10.63)	
	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	0.021	0.021	0.054	0.000	0.030	0.015
2	0.188	0.020	0.403	0.031	0.268	0.015
4	0.265	0.027	0.489	0.054	0.387	0.046
8	0.223	0.035	0.462	0.108	0.259	0.078
12	0.234	0.041	0.570	0.146	0.356	0.078

* Brackets denote % N^{15} excess in $(NH_4)_2SO_4$ added.

greater than for soil without straw indicating that addition of straw increased immobilization of added nitrogen. Also immobilization increased with incubation time when straw was added. The N^{15} excess in soil generally increased with time during the 0 to 4-week incubation period for all treatments except the 800 and 1600 ppm NH_4^+-N. N-Serve increased immobilization of added nitrogen slightly.

(H) Percent N^{15} Immobilized or Fixed

Percent nitrogen immobilized or fixed was independent of the amount of fertilizer added (table 15). In general, the percent nitrogen immobilized increased with incubation time during the first four weeks of incubation except for straw-treated soils in which immobilization of nitrogen increased with time during all 12 weeks of incubation. In general, about 16 to 18% of the added nitrogen was immobilized. Straw increased the percentage of nitrogen immobilized. About 42 percent of the added nitrogen mixed with the soil was immobilized during the 12 weeks of incubation when straw was added (table 15). Thus nearly one-half of the added nitrogen was immobilized by the soil when straw was added.

Table 16 shows the effect of banding the fertilizer on immobilization or fixation of the added nitrogen. Less nitrogen was immobilized or fixed when the nitrogen was banded than when it was mixed with the soil. About 16% of the added nitrogen was immobilized or fixed when nitrogen

Table 15. Percent N^{15} immobilized or fixed when fertilizer was mixed with the soil. - Experiment 1.

Incubation Period (wk)	Amounts of $(NH_4)_2SO_4$ added (ppm N)					
	200	400	400 + Straw	400 + N-Serve	800	1600
0	0.4	1.6	1.8	1.4	2.5	1.4
2	12.1	15.0	13.7	15.9	15.9	28.7
4	18.7	13.8	34.8	16.8	14.5	11.2
8	16.9	15.6	38.7	23.1	14.8	10.4
12	17.5	12.2	41.8	19.1	17.8	9.7

Table 16. Percent N^{15} immobilized or fixed when fertilizer was banded in the soil. - Experiment 1.

Incubation Period (wk)	Amount of $(NH_4)_2SO_4$ added (ppm N)		
	400	400 + Straw	400 + N-Serve
0	1.6	1.2	1.5
2	5.7	11.3	7.1
4	7.4	14.3	12.8
8	7.3	14.3	11.8
12	7.4	21.5	11.9

was mixed with the soil at 400 ppm NH_4^+-N (no straw or N-Serve) whereas only 7% of the added nitrogen was immobilized or fixed when the nitrogen was placed in a band. Thus for this particular set of data, banding the fertilizer in the soil reduced immobilization or fixation to about one-half of that obtained when the nitrogen was mixed with the soil. Straw increased immobilization of nitrogen regardless of fertilizer placement. Banding the nitrogen in straw-treated soil also reduced immobilization. In all treatments N-Serve increased immobilization of added nitrogen indicating that retaining the nitrogen in the ammonium form increased immobilization or fixation.

Both methods of calculations (N^{15} immobilized and percent recovery of mineral nitrogen) showed greater immobilization of added nitrogen with straw than without straw. However, calculations of amounts of nitrogen immobilized using N^{15} data did not agree with percent recoveries calculated on the basis of recovery of mineral nitrogen mixed with the soil. N^{15} data indicated less immobilization of added nitrogen for the nitrogen banded in the soil than for the nitrogen mixed with the soil. Percent recoveries based on recovery of mineral nitrogen were greater for nitrogen mixed with the soil than for nitrogen banded in the soil. Some of the possible reasons for this discrepancy are discussed in the next chapter.

Experiment 2

Effect of Placement of Nitrogen Fertilizer and Straw on Immobilization or Fixation of Added Nitrogen

(A) Nitrate-Nitrogen Content

Tables 17 and 18 show the concentration of nitrate in soil without straw and with straw, respectively. Nitrate concentrations in straw-treated soil were less than in soil not treated with straw when $(NH_4)_2SO_4$ was not applied (tables 17 and 18). However, placing the straw in a band reduced nitrate concentration only near the band when no fertilizer was applied. Straw did not reduce nitrate concentration, except after 12 weeks of incubation, when both the nitrogen fertilizer and straw were mixed with the soil. Nitrate concentration, although variable, appeared not to be affected by straw application when the nitrogen fertilizer was banded. Nitrate concentrations in soil mixed with straw and banded with straw were similar when the nitrogen fertilizer was banded.

In all cases nitrate concentration increased with time of incubation. The increase in nitrate concentration occurred mostly during the first four weeks of incubation. Nitrification slowed down probably as a result of decreasing concentration of ammonium.

(B) Nitrite-Nitrogen Content

Tables 19 and 20 show the concentration of nitrite-

Table 17. Nitrate concentration (ppm N) in soil without straw. Experiment 2.

Amount of $(NH_4)_2SO_4$ added and soil sampled

Incubation Period (wk)	No nitrogen	400 ppm N mixed	400 ppm N banded	
			0 to 3 cm from band	3 to 10 cm from band
0	7	7	7	7
2	70	76	78	60
4	102	347	227	178
8	128	423	290	337
12	116	452	450	376

Table 18. Nitrate concentration (ppm N) in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw and soil sampled

Incubation Period (wk)	1% straw mixed, no nitrogen	1% straw banded, no nitrogen		1% straw mixed, 400 ppm N mixed	1% straw mixed, 400 ppm N banded		1% straw banded, 400 ppm N banded	
		0 to 3 cm from band	3 to 10 cm from band		0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	7	8	7	7	7	7	7	7
2	8	53	88	100	89	18	59	54
4	10	53	113	354	328	133	420	246
8	27	54	130	414	336	349	470	374
12	37	79	127	348	417	352	425	392

Table 19. Nitrite concentration (ppm N) in soil without straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and soil sampled

Incubation Period (wk)	No nitrogen	400 ppm N mixed	400 ppm N banded	
			0 to 3 cm from band	3 to 10 cm from band
0	0.1	0.1	0.1	0.1
2	0.5	25.3	37.0	0.3
4	0.4	30.5	80.4	2.2
8	0.3	9.9	49.5	1.0
12	0.4	0.3	0.3	0.4

Table 20. Nitrite concentration (ppm N) in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw and soil sampled

Incubation Period (wk)	1% straw mixed, no nitrogen	1% straw banded, no nitrogen		1% straw mixed, 400 ppm N mixed	1% straw mixed, 400 ppm N banded		1% straw banded, 400 ppm N banded	
		0 to 3 cm from band	3 to 10 cm from band		0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	0.1	0.2	0.1	0.2	0.2	0.1	1.2	0.1
2	0.8	0.6	0.1	0.6	37.9	3.2	17.3	2.7
4	1.4	0.1	0.3	0.3	23.0	0.0	0.3	0.1
8	0.4	0.5	0.4	0.1	17.0	0.4	0.1	0.4
12	0.6	0.7	0.4	0.3	0.1	0.5	0.3	0.4

nitrogen in soil without and with straw, respectively. In contrast to the findings noted in Experiment 1, considerable quantities of nitrite were found in the soil, particularly when the ammonium sulphate was banded. Nitrite-nitrogen concentrations of about 80 ppm were found when ammonium sulphate was banded and about 30 ppm was found when the fertilizer was mixed with the soil without straw. About 38 ppm nitrite-nitrogen was present when the fertilizer alone was banded in the soil whereas 17 ppm nitrite-nitrogen was present when both straw and fertilizer were banded. Less than 1 ppm nitrite-nitrogen occurred in soil when both straw and fertilizer were mixed with the soil. Thus straw reduced the quantities of nitrite. High nitrite concentrations occurred in the portions of the soil adjacent to the fertilizer band or where the concentration of ammonium-nitrogen was high. Nitrite concentration increased with time of incubation, generally reaching a maximum concentration at about 2 to 4 weeks of incubation and then decreased with time. Very little or no nitrite was present in the soil after 12 weeks of incubation.

(C) Ammonium-Nitrogen Concentration

Ammonium concentration decreased with time for all treatments (tables 21 and 22). Ammonium concentration decreased more rapidly with time when the nitrogen fertilizer was mixed with the soil than when the fertilizer was banded

Table 21. Concentration of KCl-extractable ammonium (ppm N) in soil without straw. Experiment 2.

Incubation Period (wk)	No nitrogen	400 ppm N mixed	400 ppm N banded	
			0 to 3 cm from band	3 to 10 cm from band
0	16	332	1118	16
2	9	323	901	43
4	3	105	656	25
8	1	6	119	7
12	9	7	50	4

Table 22. Concentration of KCl-extractable ammonium (ppm N) in soil with straw. Experiment 2.

Incubation Period (wk)	1% straw mixed, no nitrogen	1% straw banded, no nitrogen		1% straw mixed, 400 ppm N mixed	1% straw mixed, 400 ppm N banded		1% straw banded, 400 ppm N banded	
		0 to 3 cm from band	3 to 10 cm from band		0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	25	26	24	306	1372	27	1370	38
2	11	9	1	183	880	35	1084	96
4	4	5	2	23	593	6	495	11
8	3	3	0.5	3	117	2	195	2
12	13	14	12	8	43	9	24	5

in the soil. The ammonium concentrations were very high in the soil adjacent to the fertilizer band. Ammonium concentration in straw-treated soil was lower than in soil not treated with straw when 400 ppm NH_4^+-N was mixed with the soil. Ammonium concentration, although variable, appeared not to be affected by straw application when the fertilizer was banded (table 22).

(D) Nitrate as a Percent of Total Mineral Nitrogen

During the first four weeks of incubation, the percentage of nitrogen present as nitrate in soil mixed with the nitrogen fertilizer, was greater than when the fertilizer was banded (tables 23 and 24). Straw application increased the fraction of nitrogen present as nitrate during the 2 to 8 weeks incubation period (tables 23 and 24). This was due to the nitrite concentrations in soil treated with straw being lower than in soil without straw (tables 19 and 20).

After 12 weeks of incubation, virtually all the mineral nitrogen extracted was present as nitrate. Nitrification in soil banded with straw and in soil mixed with straw appeared to be similar (table 24).

(E) Percent Recovery of Mineral Nitrogen

Results for Experiment 2 were similar to those obtained in Experiment 1. Percent recovery varied between

Table 23. Nitrate as a percent of total extractable mineral nitrogen in soil without straw. Experiment 2.

Amount of $(NH_4)_2SO_4$ added

Incubation Period (wk)	400 ppm N mixed	400 ppm N banded
0	0	0
2	3	0
4	65	29
8	95	79
12	100	97

Table 24. Nitrate as a percent of total extractable mineral nitrogen in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw

Incubation Period (wk)	1% straw mixed, 400 ppm N mixed	1% straw mixed, 400 ppm N banded	1% straw banded, 400 ppm N banded
0	0	0	0
2	45	9	0
4	95	51	58
8	100	89	83
12	102	98	101

Table 25. Percent recovery of mineral nitrogen in soil without straw. Experiment 2.

Amount of $(NH_4)_2SO_4$ added

Incubation Period (wk)	400 ppm N mixed	400 ppm N banded
0	79	78
2	86	70
4	94	79
8	77	62
12	84	73

Table 26. Percent recovery of mineral nitrogen in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw

Incubation Period (wk)	1% straw mixed, 400 ppm N mixed	1% straw mixed, 400 ppm N banded	1% straw banded, 400 ppm N banded
0	70	96	98
2	66	64	89
4	90	88	86
8	97	88	87
12	77	82	72

sampling periods but with no trend to an increase or a decrease in percent recovery as a function of incubation time. Percent recoveries in Experiment 2 were less than in Experiment 1, and ranged from 66 to 97 percent when the fertilizer was mixed with the soil and from 62 to 98 percent when the fertilizer was banded in the soil (tables 25 and 26). In general, percent recovery for nitrogen banded was less than when the nitrogen fertilizer was mixed with the soil. Percent recovery of nitrogen added in a band in straw-treated soil was greater than when no straw was added. Percent recovery of mineral nitrogen when the fertilizer was mixed with the soil was greater when no straw was added. Placement of straw did not affect recovery of mineral nitrogen. The effect of straw on percent recovery of mineral nitrogen was not consistent with results obtained in Experiment 1. Percent recovery of added nitrogen was decreased by straw application in Experiment 1.

(F) Percent Total (Kjeldahl) Nitrogen

As observed in the results obtained for the first experiment, percent total nitrogen was not influenced by treatment. The marked decrease in total nitrogen between the eighth and twelfth week of incubation (tables 27 and 28) was probably due to experimental error.

(G) Percent N^{15} Excess

Percent N^{15} excess increased with time and reached

Table 27. Percent total (Kjeldahl) nitrogen in the soil after extraction with KCl, in soil without straw. Experiment 2.

Amount of $(NH_4)_2SO_4$ added and soil sampled

Incubation Period (wk)	No nitrogen	400 ppm N mixed	400 ppm N banded	
			0 to 3 cm from band	3 to 10 cm from band
0	0.359	0.392	0.359	0.412
2	0.360	0.390	0.359	0.418
4	0.369	0.370	0.394	0.388
8	0.367	0.380	0.392	0.380
12	0.303	0.312	0.316	0.322

Table 28. Percent total (Kjeldahl) nitrogen in the soil after extraction with KCl, in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw and soil sampled

Incubation Period (wk)	1% straw mixed, no nitrogen	1% straw banded, no nitrogen		1% straw mixed, 400 ppm N nixed	1% straw mixed, 400 ppm N banded		1% straw banded, 400 ppm N banded	
		0 to 3 cm from band	3 to 10 cm from band		0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	0.379	0.369	0.365	0.375	0.403	0.372	0.416	0.388
2	0.380	0.367	0.364	0.382	0.400	0.372	0.420	0.378
4	0.385	0.388	0.370	0.385	0.415	0.370	0.389	0.369
8	0.385	0.387	0.369	0.385	0.410	0.370	0.390	0.370
12	0.324	0.321	0.314	0.332	0.338	0.328	0.330	0.322

Table 29. Percent N^{15} excess in soil after extraction with KCl in soil without straw. Experiment 2.

Amount of $(NH_4)_2SO_4$ added and soil sampled

Incubation Period (wk)	No nitrogen	400 ppm N mixed (10.63)*	400 ppm N banded	
			0 to 3 cm from band	3 to 10 cm from band
0	0.010	0.011	0.285	0.009
2	0.012	0.185	0.257	0.024
4	0.014	0.208	0.317	0.052
8	0.018	0.225	0.346	0.059
12	0.021	0.194	0.297	0.032

Table 30. Percent N^{15} excess in soil after extraction with KCl in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw and soil sampled

Incubation Period (wk)	1% straw mixed, no nitrogen	1 % straw banded, no nitrogen		1% straw mixed, 400 ppm N mixed (10.63)*	1% straw mixed, 400 ppm N banded (10.63)		1% straw banded 400 ppm N banded (10.63)	
		0 to 3 cm from band	3 to 10 cm from band		0 to 3 cm from band	3 to 10 cm from band	0 to 3 cm from band	3 to 10 cm from band
0	0.007	0.008	0.011	0.016	0.050	0.010	0.032	0.008
2	0.013	0.014	0.013	0.456	0.389	0.044	0.456	0.028
4	0.018	0.019	0.020	0.408	0.501	0.096	0.660	0.041
8	0.016	0.017	0.023	0.411	0.586	0.075	0.721	0.037
12	0.014	0.013	0.013	0.392	0.503	0.085	0.686	0.037

* Brackets denote $\%N^{15}$ excess in $(NH_4)_2SO_4$ added.

a maximum value at about 4 to 8 weeks of incubation (tables 29 and 30). Percent N^{15} excess in soil banded with the nitrogen fertilizer were usually greater than in soil mixed with the fertilizer, but only in the portion of soil adjacent to the fertilizer band. Percent N^{15} excess in soil 3 to 10 cm from the fertilizer band, was much less than in soil mixed with the fertilizer. Application of straw increased percent N^{15} excess in all instances.

(H) Percent N^{15} Immobilized or Fixed

Percent of nitrogen immobilized or fixed increased with incubation time and reached a maximum at about 4 to 8 weeks of incubation (tables 31 and 32). Percent N^{15} immobilized for samples obtained after 12 weeks of incubation were less than for samples obtained after 8 weeks of incubation. This reduction was probably due to mineralization of the immobilized nitrogen.

Straw application increased immobilization of fertilizer nitrogen in all instances. Application of straw at 1% of soil weight doubled the percentage of immobilized nitrogen (tables 31 and 32). Banding the fertilizer decreased immobilization of added nitrogen. The percent N^{15} immobilized after 8 weeks of incubation varied from 13 to 38% depending upon treatment. Without straw, percent N^{15} immobilized was 12 to 13% for nitrogen banded and 19 to 21% when the nitrogen was mixed with the soil (table 31).

Table 31. Percent N^{15} immobilized or fixed in soil without straw. Experiment 2.

Amount of $(NH_4)_2SO_4$ added

Incubation Period (wk)	400 ppm N mixed	400 ppm N banded
0	1.0	7.6
2	17.4	8.0
4	19.0	12.0
8	20.6	13.2
12	14.6	6.6

Table 32: Percent N^{15} immobilized or fixed in soil with straw. Experiment 2.

Amount and placement of $(NH_4)_2SO_4$ and straw

Incubation Period (wk)	1% straw mixed, 400 ppm N mixed	1% straw mixed, 400 ppm N banded	1% straw banded, 400 ppm N banded
0	1.4	1.9	1.4
2	41.1	13.0	14.8
4	37.8	20.3	20.1
8	38.0	21.3	21.9
12	31.3	16.4	17.5

With straw, percent N^{15} immobilized was 38 to 41% for nitrogen mixed with the soil and 20 to 21% when the nitrogen was banded in the soil. Thus, banding fertilizer nitrogen decreased immobilization or fixation to about one-half of that obtained when the nitrogen was mixed with the soil. Placement of straw did not affect percent N^{15} immobilized.

V. DISCUSSION

Nitrate concentrations were usually less in straw-treated than in soil not treated with straw in Experiment 1. Broadbent and Tyler (1962) also showed lower nitrate concentrations in soil treated with straw than in soil without straw when ammonium fertilizers were added. They suggested that heterotrophic microorganisms could compete better than nitrifiers for the available ammonium. Reduction in nitrate concentrations with straw addition in Experiment 2 was observed only when fertilizer nitrogen was not added. Addition of straw did not affect nitrate concentration in soil treated with 400 ppm NH_4^+-N in Experiment 2. Thus it would appear that immobilization of nitrate as a result of straw addition did not occur. However, nitrite concentrations in soil were much greater in Experiment 2 than in Experiment 1. Also nitrite concentrations were much greater in soil without straw than in soil with straw. If chemo-denitrification occurred, denitrification would be greater in soil without straw than in soil with straw due to the high nitrite concentrations in soil without straw. Thus nitrate may have been reduced to a greater extent by chemo-denitrification in soil without straw than in soil with straw. This difference in denitrification may have masked differences in nitrate concentrations due to immobilization. Placement of straw did not affect

the concentration of nitrate in soil. This is consistent with results of Cochran *et al.* (1975) who showed that straw and its mode of placement did not have any effect on nitrate concentration in soil for the same method of ammonia placement.

The concentration of nitrite-nitrogen in all soil samples obtained in Experiment 1 was low or negligible. However, considerable quantities of nitrite-nitrogen were formed in soil samples obtained from Experiment 2, particularly when the fertilizer was banded in the soil. Jones and Hedlin (1970) and Chapman and Liebig (1952) also observed a tendency for nitrite to accumulate in soils when high concentrations of ammonium fertilizers were added to soil. It is interesting to note, however, that in Experiment 1 where the soil and all experimental methods and incubation procedures were essentially the same as for Experiment 2, nitrite concentrations were very low (less than 3 ppm) even when 800 and 1600 ppm NH_4^+-N was added to the soil. The factors responsible for the accumulation of nitrite in Experiment 2 but not in Experiment 1 are unknown. The author did not observe any differences in incubation procedures which would suggest reasons for the discrepancy.

Nitrate expressed as a percent of total extractable mineral nitrogen usually decreased with increasing concentration of added ammonium sulphate. Also, percent of

mineral nitrogen present as nitrate was usually less for nitrogen fertilizer banded than for nitrogen mixed with the soil. This was probably due to a salt effect of the high concentration of ammonium which retarded the activity of nitrifiers. The effect of high salt concentrations on nitrification was observed by Pesek *et al.* (1971) and Cochran *et al.* (1975).

Percent recovery of added nitrogen was high for all treatments except when straw was added in Experiment 1. For soil without straw, percent recovery did not vary with incubation time. Pang *et al.* (1975) also found no variation in recovery with incubation time for an acid Keld soil and an alkaline Morton soil using various ammonium fertilizers. Percent recoveries of added nitrogen in Experiment 2 were usually less than in Experiment 1. The lower percent recoveries in Experiment 2 were most likely due to greater losses of applied nitrogen by chemo-denitrification. Chemo-denitrification probably occurred in Experiment 2 as a result of the high nitrite concentrations. Nitrite concentrations in Experiment 1 were negligible. Addition of straw to soil in Experiment 1 usually decreased percent recovery of added nitrogen. Alexander (1961) and Bartholomew (1965) also reported a decrease in recoveries of mineral nitrogen after straw addition to soil. Percent recoveries of added nitrogen were not affected by addition of straw in

Experiment 2. Cochran *et al.* (1975) also observed that the recovery of inorganic nitrogen was constant for soil without straw and for soil mixed with straw. The reason for constancy in the recovery of mineral nitrogen with and without straw may be due to some of the soil nitrogen being released (mineralized) from the native soil organic matter as the added inorganic nitrogen was immobilized by soil microflora. Such a biological interchange of mineral nitrogen was noted by Broadbent and Tyler (1962) and Overrein (1970). Also, a greater amount of mineral nitrogen may have been lost by chemo-denitrification from the soil without straw as the nitrite concentration in soil without straw were greater than in soil treated with straw.

It is interesting to note that percent recovery of mineral nitrogen was lower when the nitrogen was banded than when it was mixed with the soil. This finding was not consistent with results obtained for the percentage of N^{15} immobilized which showed nitrogen mixed with the soil to be immobilized to a greater extent than nitrogen banded in the soil. It would be expected that nitrogen banded in the soil would be less susceptible to immobilization or fixation than nitrogen mixed with the soil as banding the nitrogen reduces the physical contact of the fertilizer with clay minerals and soil organic matter. The data obtained for percent N^{15} immobilized show this to be a valid postulate. The data

obtained for percent recovery of added nitrogen, based on amounts of nitrate, nitrite and ammonium nitrogen extracted, however, show no advantage to banding of the nitrogen fertilizer. The discrepency between the two lots of data may be due to;

(1) Biological interchange: immobilization may have been balanced by mineralization of nitrogen from soil organic matter for each treatment. This postulate supposes that mineralization would increase with increases in immobilization and the nitrogen being mineralized would be nitrogen from the soil organic matter and not from fertilizer nitrogen. If this reaction was operative, percent recovery calculated on the basis of recovery of mineral nitrogen would be constant for all treatments and yet percent N^{15} immobilized would vary with treatment.

(2) If chemo-denitrification occurred as a result of nitrite-nitrogen accumulation, nitrogen losses would be greater for the fertilizer banded than when it was mixed with the soil. This would tend to reduce recovery of mineral nitrogen from the soil banded with nitrogen.

The percent recoveries based on amounts of nitrate, nitrite and ammonium, obtained for nitrogen banded and for nitrogen mixed with the soil were not consistent with field observations. The percent recoveries showed no difference between nitrogen banded and nitrogen mixed with the soil. However, results

obtained from field studies (unpublished data, Dept. of Soil Science, University of Manitoba) indicate greater yield and greater nitrogen uptake by crops when the nitrogen is banded. In the field, less immobilization and fixation of added nitrogen probably occurs when the nitrogen fertilizer is banded (as shown by the N^{15} data in this study) than when it is broadcast. This is probably due to a restriction in physical contact between the fertilizer and the soil heterotrophic microorganisms. In the soil between the fertilizer bands, both plants and heterotrophic microorganisms would compete for the mineral nitrogen. Since the concentration of mineral nitrogen between the bands would be low, only small amounts of mineral nitrogen would be fixed or immobilized. However, if the nitrogen was mixed with the soil, the nitrogen concentration through the surface soil would be relatively high and heterotrophic microorganisms and clay minerals would have access to the added nitrogen and the microorganisms would immobilize considerable quantities of mineral nitrogen prior to utilization by plants. It is also possible that due to the higher concentration of nitrogen throughout the soil system, when the nitrogen is mixed with the soil, more nitrogen would be immobilized per unit of carbonaceous residue decomposed than in instances in which nitrogen concentration in the soil would be low such as between nitrogen fertilizer bands.

Regardless of the reactions which may occur when nitrogen is added to the soil, agronomic data on yields and nitrogen uptake indicate that banding of nitrogen is superior to mixing with the soil when the effectiveness of the nitrogen fertilizer is measured on a one crop basis. The N^{15} data obtained in this study is consistent with the field data obtained by others (Nyborg 1975). N^{15} data in addition to indicating less immobilization of nitrogen banded than of nitrogen mixed with the soil also showed that immobilization was greater with N-Serve than without. Broadbent and Nakashima (1970) noted that immobilization or fixation of nitrogen was considerable when added nitrogen was retained in the ammonium form. The N^{15} data in this study also indicated that percent N^{15} immobilized did not depend on the amount of added ammonium when the fertilizer was mixed with the soil. Broadbent and Nakashima (1970) noted that percent immobilization was virtually identical when 30 ppm and 60 ppm of NH_4^+-N was added.

In both experiments, the percent N^{15} immobilized was about 42% of the added nitrogen when straw was mixed with the soil. For both methods of nitrogen application, mixing straw with the soil doubled the percentage of nitrogen immobilized . Banding the nitrogen reduced immobilization of N^{15} by one-half even in the presence of straw. N^{15} studies by Wojcik-Wojtowiak (1969) indicated that straw reduced fertilizer utilization to 14 to 42% of the added nitrogen.

VI. SUMMARY AND CONCLUSIONS

Two laboratory studies were conducted on a clay loam Newdale soil to determine the effect of placement of nitrogen fertilizer on immobilization or fixation of applied nitrogen enriched with N^{15}. Nitrogen fertilizer was either mixed with the soil or banded in the soil. Other treatments included: soil with and without straw, placement of straw (mixed with the soil or banded in the soil), soil with and without N-Serve and varying the amounts of nitrogen fertilizer mixed with the soil.

From the results of this study, the following conclusions could be drawn:

(1) Immobilization or fixation of nitrogen as measured by percent recovery of added mineral nitrogen (nitrate, nitrite and ammonium) usually increased when straw was added. Placement of nitrogen fertilizer, placement of straw, amount of nitrogen mixed with the soil and addition of N-Serve had little or no effect on percent recovery of added mineral nitrogen.

(2) Immobilization or fixation of N^{15} banded in the soil was about one-half that when the nitrogen was mixed with the soil. Immobilization was doubled by straw application at 1% of soil weight for both nitrogen mixed with the soil and for nitrogen banded in the soil although percent nitrogen

immobilized was greater in all instances where the nitrogen was mixed with the soil. Straw placement did not alter amounts of nitrogen immobilized. N-Serve increased immobilization of added nitrogen.

(3) Immobilization as measured by recovery of mineral nitrogen was not consistent with the results obtained for immobilization of added nitrogen using N^{15}. Due to this discrepancy, it is suggested that more experimentation be conducted to more clearly define the reactions occurring when nitrogen is banded and when it is mixed with the soil. The studies need to include plant growth experiments as well as complete nitrogen balance studies. Also the effects of banding versus mixing fertilizer in the soil need to be studied over a longer period of time to assess residual effects of nitrogen as affected by methods of placement.

BIBLIOGRAPHY

Agarwal, A.S., Singh, B.R. and Kanehiro, Y. 1972. Differential effect of carbon sources on the nitrogen transformations in Hawaiian soils. Plant and Soil 36: 529-737.

Alexander, M. 1961. Introduction to soil microbiology. John Wiley and Sons, Inc. N.Y. pp 248-270.

Allison, F.E. 1955. Does nitrogen applied to crop residues produce more humus. Soil Sci. Soc. Amer. Proc. 19: 210-211.

Allison, F.E. 1963. Lossess of gaseous nitrogen from soil by chemical mechanisms involving nitrous acid and and nitrite. Soil Sc. 96: 404-409.

Allison, F.E. 1966. The fate of nitrogen applied to soils. Adv. Agron. 18: 219-258.

Allison, F.E., Doetsch, J.H. and Roler,E.M. 1951. Ammonium fixation and availability to Harpster clay loam. Soil Sci. 72: 187-200.

Allison, F.E., Doetsch, J.H. and Roller, E.M. 1953. Availability of fixed ammonium in soils containing different clay minerals. Soil Sci. 75: 373-381.

Allison, F.E. and Klein, C.J. 1961. Comparative rates of decomposition in soil of wood and bark particles of several softwood species. Soil Sci. Soc. Amer. Proc. 25:194-196.

Allison, F.E. and Klein, C.J. 1962. Rates of immobilization and release of nitrogen following additions of carbonaceous materials and nitrogen to soils. Soil Sci. 93: 383-386.

Allison, F.E. and Roller, E.M. 1955. A comparison of leaching and distillation procedures for determining fixed ammonium in soils. Soil Sci. 80:349-362.

Aomine, S. and Higashi, T. 1953. Studies on the fixation of ammonium in soils: V. Availability of fixed ammonia by crops. J. Sci. Soil Man. Japan 23: 105-108.

Aomine, S. and Wada, K. 1952. Studies on the fixation of ammonium in soils. II. Manner of ammonium fixation. J. Sci. Soil Man. Japan, 22: 227-230.

Axley, J.H. and Legg, J.O. 1960. Ammonium fixation in soils and the influence of potassium on nitrogen availability from nitrate and ammonium sources. Soil Sci. 90: 151-156.

Barshad, I. 1954. Cation exchange in micaceous minerals: I. Replaceability of ammonium and potassium from vermiculite, biotite and montmorillonite. Soil Sci. 78: 57-76.

Bartholomew, R.P. amd Janssen, G. 1931. Rate of absorption of potassium by plants and its possible effect on the amount of potassium remaining in soils from application of potassium fertilizers. Arkansas Agr. Expt. Sta. Bul. 265.

Bartholomew, W.V. 1955. Fertilization of crop residues. Does it pay? Agr. Chem. 10: 38-40, 97-99.

Bartholomew, W.V. 1965. Mineralization and immobilization of nitrogen in the decomposition of plant and animal residues. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin. pp 287-302.

Bower, C.A. 1950. Fixation of ammonium in difficultly exchangeable form under moist conditions by some soils of semi-arid regions. Soil Sci. 70: 375-382.

Bower, C.A. 1951. Availability of ammonium fixed in difficultly exchangeable form by soils of semi-arid regions. Soil Sci. Soc. Amer. Proc. (1950) 15: 119-122.

Bremner, J.M. 1955. Nitrogen transformations during the biological decomposition of straw composted with inorganic nitrogen. J. Agr. Sci. 45: 469-475.

Bremner, J.M. 1965a. Total nitrogen. *In* Methods of Soil Analysis Part II. Monograph No. 9. Amer. Soc. Agron. C.A. Black (ed.). pp 1149-1176.

Bremner, J.N_{15}1965b. Isotope-ratio analysis of nitrogen in N^{15} tracer investigations. *In* Methods of Soil Analysis Part II. Monograph No. 9. Amer. Soc. Agron. C.A. Black (ed.). pp 1256-1283.

Bremner, J.M. and Shaw, K. 1957. The mineralization of some nitrogen materials in soil. J. Sci. Food Agr. 8: 341-347.

Bremner, J.M. and Shaw, K. 1958. Denitrification in soil II. Factors affecting denitrification. J. Agr. Sci. 51: 40-52.

Broadbent, F.E., Burge, W.D. and Nakashima, T. 1961. Factors influencing the reaction between ammonia and soil organic matter. Trans. 7th Int. Congr. Soil Sci. 2: 509-516.

Broadbent, F.E. and Clark, F. 1965. Denitrification. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin. pp 347-358.

Broadbent, F.E. and Nakashima, T. 1970. Nitrogen immobilization in flooded soils. Soil Sci. Soc. Amer. Proc. 34: 218-222.

Broadbent, F.E. and Norman, A.G. 1946. Some factors affecting the availability of organic nitrogen in soil: - a preliminary report. Soil Sci. Soc. Amer. Proc. 11: 264-267.

Broadbent, F.E. and Tyler, K.B. 1962. Laboratory and greenhouse investigations of nitrogen immobilization. Soil Sci. Soc. Amer. Proc. 26: 459-462.

Broadbent, F.E. and Tyler, K.B. 1965. Effect of pH on the nitrogen immobilization in two California soils. Plant and Soil 23: 314-322.

Burge, W.D. and Broadbent, F.E. 1961. Fixation of ammonia by organic soils. Soil Sci. Soc. Amer, Proc. 25: 199-204.

Burns, O.R. and Dean, L.A. 1964. *In* The fate of nitrogen applied to soils. Adv. Agron. 18: 219-258.

Cady, F.B. and Bartholomew, W.V. 1960. Greenhouse recovery of added tracer nitrogen. Soil Sci. Soc. N.C. Proc. 3: 44-54.

Carefoot, J.M. 1971. Effect of urea and urea-ammonium nitrate solution (28-0-0) on barley emergence and growth. M.Sc. Thesis, University of Manitoba, Winnipeg, Man.

Chalk, P.M., Keeney, D.R. and Walsh, L.M. 1975. Crop recovery and nitrification of fall and spring applied anhydrous ammonia. Agron. J. 67: 33-36.

Chapman, H.D. and Liebig, G.F. 1952. Field and laboratory studies on nitrite accumulation in soils. Soil Sci. Soc. Amer. Proc. 16: 276-282.

Chu, J. P-H and Knowles, R. 1966. Mineralization and immobilization of nitrogen in bacterial cells and in certain soil organic fractions. Soil Sci. Soc. Amer. Proc. 30: 210-213.

Clark, F.E. 1962. Losses of nitrogen accompanying nitrification. International Soil Conference Transactions, New Zealand, 1962. pp 173-176.

Clark, F.E. and Beard, N.E. 1960. Influence of organic matter on volatile loss of nitrogen from soil. Intern. Congr. Soil Sci. 7th Congr. Madison, Comm, Ill. 501-508.

Cochran, V.L., Koehler, F.E. and Papendick, R.I. 1975. Straw placement: Its effect on nitrification of anhydrous ammonia. Agron. J. 67: 537-540.

Craswel, E.T. and Martin, E.A. 1975. Isotopic studies of the nitrogen balance in crackling clay. I: Recovery of added nitrogen from soil and wheat. Aust. J. Soil Res. 13: 43-52.

Donald, L., Stangel, H. and Pesek, J. 1963. Advances in knowledge of nitrogen fertilization in the USA since 1950. *In* Fertilizer technology and usage. Published by Soil Sci. Soc. Amer. Madison, Wisconsin. M.H. McVickar (ed.): pp 75-125.

Doughty, J.F., Cook, F.D. and Warder, F.G. 1954. Effect of cultivation on the organic matter and nitrogen of brown soils. Can. J. Agr. Sci. 34: 406-411.

Drake, N., Vengris, J. and Colby, W.G. 1951. Cation exchange capacity of plant roots. Soil Sci. 72: 139-147.

Evans, C.E. and Attoe, O.J. 1948. Potassium supplying power of virgin and cropped soils. Soil Sci. 66: 323-334.

Fenn, L.B. 1975. Ammonia volatilization from surface application of ammonium compounds on calcareous soils. III. Effects of mixing low and high loss ammonium compounds. Soil Sci. Soc. Amer. Proc. 39: 366-368.

Field-Ridley, G. 1975. Nitrogen movement in two Manitoba soils. M.Sc. Thesis, University of Manitoba, Winnipeg, Man.

Forsyth, J.B. 1971. Comparison of source of nitrogen for peach trees. Agric. Gazette of NSW. 82: 227-229. Yamo Agric. College and Res. Station, N.S.W. Australia.

Gasser, J.K.R., Greenland, D.G. and Rawson, R.A.G. 1967. Measurement of losses from fertilizer nitrogen during incubation in acid sandy soils and during subsequent growth of rye grass using N^{15}-labelled fertilizers. J. Soil Sci. 18: 289-300.

Ghildyal, B.P. and Singh, P.N. 1961. Ammonium fixation in cultivated and afforested alluvial soils. Soil and Plant Food 6: 164-169.

Goring, C.A.I. and Clark, F.E. 1948. Influence of crop growth on mineralization of nitrogen in the soil. Soil Sci. Soc. Amer. Proc. 13: 261-266.

Goring, C.A.I. and Hamaker, J.W. 1972. Organic chemicals in the soil environment Vol. 2. Marcel Dekker Inc. N.Y. pp 633-670.

Greenland, D.J. 1962. Denitrification in some tropical soils. Agr. Sci. 58: 227-233.

Hallam, M.J. and Bartholomew, W.V. 1953. Influence of rate of plant residue addition in accelerating the decomposition of soil organic matter. Soil Sci. Soc. Amer. Proc. 17: 365-368.

Harada, T. and Katsuna, K. 1954. Ammonium fixation by residual soil from crystalline schistat. Yahatahama Bull. Nat. Inst. Agr. Sci. Japan Ser. B No. 3: 17-41.

Harmsen, G. W. and Kolenbrander, G.J. 1965. Soil inorganic nitrogen. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin. pp 43-71.

Harmsen, G.W. and Lindenbergh, D.J. 1949. Investigation on the nitrogen nutrition of plants. Plant and Soil. 2: 1-29.

Hauck, R.D. and Koshino, M. 1971. Slow release and ammended fertilizers. *In* Fertilizer Technology and Use 2nd edition. R.A. Olson, editor-in-chief. Soil Sci. Soc. Amer. Inc. Madison, Wisconsin. pp 455-487.

Hiltbold, A.E., Bartholomew, W.V. and Werkman, C.H. 1951. The use of tracer technique in simultaneous measurements of mineralization and immobilization of nitrogen in the soil. Soil Sci. Soc. Amer. Proc. 15: 166-173.

Huber, D.M., Murray, G.A. and Crane, J.M. 1969. Inhibition of nitrification as a deterent to nitrogen losses. Proc. Soil Sci. Amer. 33: 975-976.

Iritani, W.M. and Arnold, C.Y. 1960. Nitrogen release of vegetable crop residues during incubation as related to their chemical composition. Soil Sci. 89: 74-82.

Ivonov, P. 1962. Ammonium fixation in soils. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison Wisconsin. pp 198-250.

Jaiswal, S.P., Verma, A.K. and Tripathi, R.L. 1972. Effects of some nitrification suppressants in nitrification of urea and its implications on growth and nitrogen nutrition of cane sugar. Plant and Soil. 36: 185-189.

Jansson, S.L. 1958. Tracer studies on the nitrogen transformations in soil with special attention to mineralization-immobilization relationships. Kuagl. Lanbrukshogskolans Ann. 24: 101-361. *In* Soil Nitrogen. Monograph No.10. Amer. Soc. Agron. Madison, Wisconsin. pp 198-250.

Jansson, S.L. 1963. A balance sheet and residual effects of fertilizer nitrogen in a 6 year study. Soil Sci. 95: 31-37.

Jansson, S.L. and Ericsson, J. 1962. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin. pp 198-250.

Jansson, S.L., Hallam, M.J. and Bartholomew, W.V. 1955. Preferential utilization of ammonium over nitrate by microorganisms in the decomposition of oat straw. Plant and Soil. 6: 382-390.

Jasson, W.A. and Volk, R.J. 1966. Physiological aspects of ammonium nutrition of selected higher plants. Isotopes in Plant Nutrition and Physiology. Proc. of a Symp. IAEA/FAO Vienna, Austria, 1966.

Jones, R.W. and Hedlin, R.A. 1970. Ammonium, nitrite and nitrate accumulation in three Manitoba soils as influenced by added ammonium sulphate and urea. Can. J. Soil Sci. 50:331-338.

Karlsson, N. 1952. Kalium marken. Kungl. Lanthbnsksakad. Tidskr. 91: 297-329. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin, pp 198-250.

Kamphake, L.J. Hannah, S.A. and Cohen, J.M. 1966. Automated analysis for nitrate by hydrazine reduction. Water Research Vol. 1. pp 205-216. Pergaman Press, 1967.

Kuo, M.H. 1955. Factors influencing the immobilization of nitrogen during the decomposition of plant residues. M.Sc. Thesis, Iowa State College Library, Ames, Iowa.

Legg, J.O. and Allison, F.E. 1959. Recovery of N^{15}-tagged nitrogen from ammonium fixing soils. Soil Sci. Soc. Amer. Proc. 23: 131-134.

Leggett, G.E. 1958. Ammonium fixation in soils and minerals. State College of Washington Project 1253. Dept. of Agronomy.

Leggett, G.E. and Moodie, C.D. 1962. The aeration-recovery method for determining ammonium fixation by soils under moist conditions. Soil Sci. Soc. Amer. Proc. 26: 160-163.

Lewis, D.C. and Stefanson, R.C. 1973. Effect of N-Serve on nitrogen transformations and wheat yields in some Australian soils. J. Agr. Sci. 119: 273-279.

Malquori, A. and Radaelli, L. 1960. Fosfatolisis and ammonio fissato nel terveno. Agrochimia. 4: 288-298.

Mattson, S. and Koutler-Anderson, E. 1942. The acid-base condition in vegetation litter and humus: V. Products of partial oxidation and ammonia fixation. Lantbruskshogsk. Ann. 10: 284-332.

McDonnell, P.M., Stevensen, F.J. and Bremner, J.M. 1959. Release of fixed ammonium from soil by ball milling. Nature 183: 1414-1415.

McGill, K.S. 1971. Uptake of nitrogen by barley from spring and fall applied urea and ammonium nitrate. M.Sc. Thesis, University of Manitoba, Winnipeg, Man.

Mertensens, J., Winkel, P.V. and Massart, F.L. 1975. Determination of nitrate in water with an ammonia probe. Analytical Chem. 47: 522-526.

Nielsen, J.D. 1972. Fixation and release of potassium and ammonium ions in Danish soils. Plant and Soil 36: 71-88.

Nightingale, G.F. 1948. The nitrogen nutrition of green plants. Botan. Rev. 14: 185-221.

Nommik, H. 1957. Fixation and defixation of ammonium ions in soils. Acta Scand. 7: 395-436.

Nommik, H. 1965. Ammonium fixation and other reactions involving a nonenzymic immobilization of mineral nitrogen in soil. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin. pp 198-251.

Norman, A.G. 1931. The biological decomposition of plant materials. IV. The effect of hydrogen ion concentration on the rates of immobilization of nitrogen in straw. Biochem. J. 25: 1779-1787.

Nyborg, M. 1975. Effect of nitrogen fertilizer and time and method of application on barley grain yield in Alberta. (Unpublished data, Dept. of Soil Science, University of Alberta, Edmonton, Alberta).

Overrein, L.N. 1970. Immobilization and mineralization of tracer nitrogen in forest raw humus: II. Effect of temperature and incubation time on the interchange of urea, ammonium and nitrate-N^{15} under waterlogged conditions. Plant and Soil. 32: 207-220.

Pang, P.C., Cho, C.M. and Hedlin, R.A. 1975. Effect of pH and nitrifier population on nitrification of band-applied and homogenously mixed urea in soils. Can. J. Soil Sci. 55: 15-21.

Parker, D.T. 1962. Decomposition in the field of buried and surface-applied corn stalk residues. Soil Sci. Soc. Amer. Proc. 26: 559-562.

Parker, D.T., Larson, W.E. and Bartholomew, W.B. 1957. Studies on nitrogen tie up as influenced by location of plant residues in soils. Soil Sci. Soc. Amer. Proc. 21: 608-612.

Pesek, J., Stanford, G. and Case, N.L. 1971. Nitrogen production and use. *In* Fertilizer Technology and Use. 2nd edition, R.A. Olson (editor) Soil Sci. Soc. Amer. Inc. Madison, Wisconsin, pp 217-269.

Pinck, L.A., Allison, F.E. and Gaddy, V.L. 1946. The nitrogen requirement in the utilization of residue in soil. J. Amer. Soc. Agron. 38: 410-420.

Pinck, L.A., Allison, F.E. and Gaddy, V.L. 1948. Utilization of nitrogen in cropping systems without green manure in the greenhouse. Soil. 66: 39-52.

Plhak, F. and Vicherkova, M. 1970. The influence of previous plant cultivation on soil nitrification. Plant and soil 32: 50-55.

Porter, L.K. and Strewart, B.A. 1970. Organic interferences in fixation of ammonium by soils and clay minerals. Soil Sci. 109: 229-223.

Reiteimer, R.F. 1951. Soil potassium. Adv. in Agron. 3: 113-164.

Rhoads, F.M. 1972. A comparison of ammonium and nitrate nitrogen for cigar wrapper tobacco. Agron. J. 64: 209-210.

Rich, C.I. 1960. Ammonium fixation by two red-yellow podzolic soils as influenced by interlayer-Al in clay minerals. Trans. 7th Int. Congr. Soil Sci. 4: 468-475.

Russell, E.W. 1961. Soil conditions and plant growth. 9th edition, pp 311-317. Longmans, N.Y.

Scarsbrook, C.E. 1965. Nitrogen availability. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin. pp 456-501.

Stanford, G. 1948. Fixation of potassium in soils under moist conditions and on drying in relation to type of clay mineral. Soil Sci. Soc. Amer. Proc. (1947) 12: 167-171.

Stanford, G. and Pierre, W.H. 1947. The relation of fixed potassium to ammonium fixation. Soil Sci. Soc. Amer. Proc. (1946) 11:155-160.

Stojanovic, B.J. and Broadbent, F.E. 1956. Immobilization and mineralization rates of nitrogen during decomposition of plant residues in soil. Soil Sci. Soc. Amer. Proc. 20:213-218.

Stojanovic, B.J. and Broadbent, F.E. 1960. Recovery of ammonium nitrogen from soils. Soil Sci. 90: 93-97.

Stotzky, G. and Mortensen, J.L. 1957. Effect of crop residues and nitrogen addition on the decomposition of Ohio muck. Soil Sci. 83: 165-174.

Swezey, A.W. and Turner, G.O. 1962. Crop experiments on the effects of 2-chloro-6-(trichloromethyl) pyridine for the control of nitrification of ammonium and urea fertilizers. Agron. J. 54: 532-535.

Tamini, Y.N., Kanehiro, Y. and Sherman, G.D. 1963. Ammonium fixation in amorphous Hawaiian soils. Soil Sci. 95: 426-430.

Toews, W.H. 1971. Comparison of urea and ammonium nitrate as determined by yield data, nitrogen uptake and ammonia volatilization in field, greenhouse and laboratory experiments. M.Sc. Thesis, University of Manitoba, Winnipeg, Man.

Tyler, K.B. and Broadbent, F.E. 1958. Nitrogen uptake by ryegrass from three tagged ammonium fertilizers. Soil Sci. Soc. Amer. Proc. 22: 231-234.

Van Uyen, N. 1971. Effect of time and depth of nitrogen application on growth and yield of rice. Acta Agronomica Academial Scientarum Hungaricae. 20: 311-317.

Walsh, L.M. and Murdock, J.T. 1960. Native fixed ammonium and fixation of applied ammonium in several Wisconsin soils. Soil Sci. 89: 183-193.

Watkins, S.H., Strand, R.F., DeBell, D.S. and Esch, J. Jr. 1972. Factors influencing ammonium losses from urea applied to North-western forest soil. Soil Sci. Soc. Amer. Proc. 36: 354-357.

Welch, L.F. and Scott, A.D. 1959. Nitrification in nutrient solution with low levels of potassium. Can. J. Bact. 5: 425-430.

Winsor, J.W. and Pollard, A.G. 1956. Carbon-nitrogen relationships in soil. I: The immobilization of nitrogen in presence of carbon compounds. J. Sci. Food Agr. 7: 134-141.

Wittich, W. 1961. Die grundlagen der Stickstoffernahrung des Waldes und Moglichkeiten fur ihre Verbesserung. *In* Soil Nitrogen. Monograph No. 10. Amer. Soc. Agron. Madison, Wisconsin, pp 198-251.

Wojcik-Wojtowiak, D. 1969. Application of N^{15} to study transformation of nitrogen fertilizer in soil. Agrokem. Talajt. 18: 93-101.

Wullstein, L.H., Gilmour, C.M. and Bollen, W.B. 1963. Gaseous losses of soil nitrogen by chemical and microbial pathways. Agron. Abstr. 196: p 34.

Zamyatina, V.B. 1969. Nitrogen balance studies using N^{15} in soil-plant studies. Proc. of Res. Coord. Meeting. FAO/IAEA, Sofia. December, 1969.