

ISOTOPE STUDIES ON CROP UTILIZATION AND SOIL FIXATION OF NITROGEN FROM
UREA, CALCIUM NITRATE AND AMMONIUM SULPHATE IN SEVERAL MANITOBA SOILS

by

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A thesis
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ABSTRACT

Crop utilization and soil fixation of nitrogen from three ^{15}N -labelled N-carriers were studied on several Manitoba soils. In a growth chamber study, more nitrogen from $\text{Ca}(\text{NO}_3)_2$ was utilized by wheat than from $(\text{NH}_2)_2\text{CO}$ in the slightly acid soils. The 'A' value indicates that $\text{Ca}(\text{NO}_3)_2$ is more available to wheat than $(\text{NH}_2)_2\text{CO}$ on the slightly acid soils. Dry matter yield of wheat was significantly greater with $\text{Ca}(\text{NO}_3)_2$ treatment than with $(\text{NH}_2)_2\text{CO}$ in Pine Ridge, Wellwood and Granville soils. A much greater part of NH_4^+ -N from $(\text{NH}_2)_2\text{CO}$ than NO_3^- -N from $\text{Ca}(\text{NO}_3)_2$ remained in all soils at the end of the experiment.

The oxidation of NH_4^+ -N from urea was slower in the slightly acid soils. Persistence of NH_4^+ -N might lead to fixation of this form of N in slightly acid soils. Accumulation of NO_2^- -N occurred in Pine Ridge and Wellwood soils. These two soils demonstrated a substantial production of molecular N following treatment with ^{15}N -labelled NaNO_2 . Nitrite accumulation also occurred in alkaline Almasippi soil but only for a transient period, since this was rapidly oxidized to nitrate.

An incubation study showed that more of the N added as urea or ammonium sulphate was fixed than of the N added as $\text{Ca}(\text{NO}_3)_2$ in all soils used. Rapid fixation of N from NH_4^+ -yielding carriers occurred especially in the slightly acid soils. About 10% of added N from NH_4^+ -yielding carriers was fixed in Granville soil during the 1st day of incubation. Fixation of N in all the soils was more of a problem with NH_4^+ -carriers than with the NO_3^- source. This provides a partial expla-

nation of the greater amount of N from $(\text{NH}_2)_2\text{CO}$ than from $\text{Ca}(\text{NO}_3)_2$ remaining in the soils at the end of the growth chamber experiment.

Most of the added N fixed in the soils was organically bound. The soil organic matter fixed about 5 to 10 times as much N per unit weight as clay. The capacity of both the soil organic matter and clay to fix added N increased with decrease in soil pH. More added N from both $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ was fixed when Newdale soil was acidified.

Liming Pine Ridge and Wellwood soils decreased the amount of added N fixed from NH_4^+ -yielding carriers, but did not significantly increase the dry matter yield of wheat on these soils. Utilization of added N by wheat from NH_4^+ -yielding carriers was brought closer to that of $\text{Ca}(\text{NO}_3)_2$ when Pine Ridge and Wellwood soils were limed. In acidified Newdale soil, more N from $\text{Ca}(\text{NO}_3)_2$ was utilized by wheat than N from NH_4^+ -yielding carriers. Acidifying Newdale soil increased the added N fixed and consequently decreased the utilization of N from both ammonium carriers.

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Chapter I

INTRODUCTION

One means of increasing crop production to meet the rapidly growing world population is through the use of chemical fertilizers. Among these, nitrogenous fertilizers are the most widely used. Increased use of nitrogen has made a tremendous contribution towards successful crop production throughout the world. Although nitrogen fertilizer is important as a means of increasing crop yields, its utilization by crops is only about 50 percent of that applied (Allison, 1966; Soper et al. 1971; Toews and Soper 1978). Failure of the crop to use a greater percentage of the added nitrogen has been attributed to reactions in the soil which cause nitrogen to become temporarily or permanently unavailable. The most important of these are fixation of nitrogen by both organic and inorganic soil fractions, immobilization, ammonia volatilization, leaching and denitrification.

The extent to which the above factors result in a low uptake of added nitrogen is influenced by such things as soil properties, the form of added nitrogen and the time and method of nitrogen application. The study reported in this thesis is concerned in particular with the relationship of soil properties and form of nitrogen used on the efficiency of utilization of added nitrogen. It involves eight soils differing in texture and pH, and three nitrogen carriers, namely urea, calcium nitrate and ammonium sulphate. The studies included laboratory incubation

and growth chamber experiments with wheat. In order to accurately trace the transformation and uptake of nitrogen most of the experiments involved the use of carriers labelled with N-15, a stable nitrogen isotope.

Chapter II

LITERATURE REVIEW

2.1 FORMS OF NITROGEN IN THE SOIL

2.1.1 Organic Nitrogen

Well over 90% of the total nitrogen (N) in the surface horizons of most soils is organically combined. In certain subsoils, however, about 30-40% of the total N may be present as fixed ammonium (NH_4^+) (Bremner 1965). About half of the organically combined N is known to be in the form of amino compounds. The form of the remainder is not clearly understood. Information concerning the nature of the organic nitrogen in soil is based solely on studies involving identification and estimation of the forms of nitrogen released by treatment with hot acids (Bremner, 1965; Stevenson, 1957; Cheng and Kurtz, 1963). Bremner (1965) concluded that the organic forms isolated generally include amino acids, amino sugars (hexosamines), purine and pyrimidine derivatives, urea and many others. The organic nitrogen is well protected from rapid microbial attack and hence very slowly converted to inorganic forms.

2.1.2 Inorganic Nitrogen

Inorganic forms of nitrogen constitute only a very small fraction of the total soil nitrogen. In most soils it is present mainly in the form of ammonium and nitrate nitrogen. Nitrite (NO_2^-) nitrogen is sometimes present in some soils, and usually, but not always, in a relatively small amount. It is the inorganic forms of N which are available for direct uptake by plants. These forms of N are mainly derived from one or more of the following processes: (i) Mineralization of organic nitrogen; (ii) Nitrification of ammonium and ammonium containing compounds; and (iii) Addition of nitrogen fertilizers.

2.2 MINERALIZATION OF ORGANIC NITROGEN

Nitrogen undergoes complex transformation between its various forms by means of chemical, physical and biological processes operating in the soil. The process of mineralization denotes the microbial transformation of the organic nitrogen to inorganic forms (usually ammonium). Ammonia (NH_3) is typically produced from organic compounds, when the soil microflora set free more nitrogen from the organic matter than they can assimilate into their own protoplasm. Organic carbon is the major source of energy for the non-specific heterotrophs. Nitrogen is assimilated as protein, nucleic acid, and other nitrogenous constituents in the microbial tissue as a function of the growth of the organisms. The amount of inorganic nitrogen released and in turn metabolized by the microorganisms is a function of the carbon to nitrogen (C:N) ratio of the

organic material and the metabolizing microorganisms (Bartholomew, 1965). When the C:N ratio of the residue is less than 20:1, net mineralization of nitrogen results from microbial degradation of the residue. With residues having a C:N ratio between 20:1 and 30:1, nitrogen mineralization may or may not occur. When C:N ratio of the residue is greater than 30:1, microbial attack on the residue results in immobilization of nitrogen (Ferguson, 1957; Alexander, 1965; Bartholomew, 1965; Clark, 1966).

2.2.1 Nitrification

Nitrification is the biological conversion of the inorganic nitrogen from a reduced to a more oxidized state. The inorganic nitrogen resulting from net mineralization, or from the addition of ammonium fertilizers undergoes nitrification. This is brought about in nature by two highly specialized groups of obligate aerobic autotrophs. Nitrification occurs in two steps: first, the ammonium is oxidized to nitrite by Nitrosomonas sp. Then, nitrite is oxidized to nitrate by Nitrobacter sp. Five other genera of nitrogen autotrophs have been identified. These are the ammonium-oxidizing Nitrosococcus, Nitrospira, Nitrosogloea, and Nitrosocystis and the nitrite-oxidizing Nitrocystis (Breed et al., 1957). All these bacteria are strict autotrophs. They cannot use sugars or other compounds for their energy supply. These autotrophs obtain most of their energy by oxidation of inorganic nitrogenous compounds. They utilize carbon dioxide as their main source of carbon.

Under ideal conditions, nitrification occurs very rapidly. Daily rates of up to 22 lbs per acre of nitrogen were found to be oxidized to nitrate when 100 lbs of N in the ammonium form was added (Broadbent and Tyler, 1957). The nitrifying bacteria are extremely sensitive to their environment. Soil conditions that influence the intensity of nitrification are: aeration, temperature, moisture, fertilizer salts and C:N ratio.

A heavy application of anhydrous ammonia or ammonium yielding fertilizer to neutral or alkaline soil inhibits nitrification. Ammonia is toxic to Nitrobacter sp. but does not adversely affect Nitrosomonas sp. Consequently, nitrite accumulation occurs. Numerous researchers have reported nitrite accumulation in acid soils whose pH has risen as a result of the addition of ammonium or ammonium yielding fertilizers (Chapman and Leibig, 1952; Stojanovic and Alexander, 1958; Broadbent et al., 1958; Jones and Hedlin, 1970a; Colliver and Welch, 1970). Accumulation of nitrite near fertilizer granules (Hauck and Stephenson, 1965; Bezdicek et al., 1971) and band applied fertilizer (Isensee and Walsh, 1971; Wetselaar et al., 1972; Pang, et al., 1974) have been reported. Nitrite accumulation usually leads to a loss of nitrogen through denitrification and volatilization. These gaseous losses of nitrogen have been found to be related to nitrite accumulation (Clark et al., 1960; Hauck and Stephenson, 1965; Meek and Mackenzie, 1965).

When soil conditions are favourable, nitrite is readily oxidized to nitrate. Nitrate is the principal plant available nitrogenous material

in soil and hence the one mostly utilized by plants. Nitrate, being mobile, is easily leached from the soil. Under anaerobic conditions it is subject to loss as gaseous N through denitrification.

2.3 CROP UTILIZATION OF ADDED NITROGEN (N)

Plant uptake of added nitrogen is of prime concern in agriculture. Adequate knowledge of the initial and subsequent distribution of inorganic forms of N in soil is of vital importance in determining the effectiveness of the added nitrogen. Due to various physical, chemical and biological processes taking place in the soil, added fertilizer N is subject to numerous changes. These include immobilization, ammonia volatilization, fixation by clay minerals, formation of stable organic complexes by non-biological means, leaching and denitrification. Because of transformations and losses by these processes, crop recovery of fertilizer N seldom amounts to more than half of that added.

Plants usually take up nitrogen from the soil either in the ammonium or nitrate form. These forms of N occur as a result of mineralization of organic compounds, and through the addition of N-fertilizers. The efficiency of utilization of added N is a function of several factors, among which are: crop species, soil type, rate of N application, type of fertilizer N added, time and method of application and moisture status of the soil.

There are two methods that can be used in determining crop recovery of added N. The first one is the difference method which involves cal-

culating the difference in total uptake between control and N treated crops. The use of tracer technique is a more recent method of determining crop recovery of added N. This new method involves using labelled nitrogen which permits adequate monitoring of added N in soil-plant systems.

The difference method overestimates utilization of fertilizer added (Andreeva and Shcheglova, 1968). Zamyatina et al. (1963) reported that fertilizer N utilization by oats was 32.54% according to isotope method, and 44-70% according to difference method. This overestimation is due in part to the stimulation in root activity and greater root proliferation in the soil with N treatment (Legg and Stanford, 1967). This facilitates N uptake and intensifies mineralization of the native soil organic N.

The tracer technique provides the only available means of accurately measuring actual fertilizer uptake by a crop (Fried et al., 1975). A potential source of error is isotopic exchange. This is a process by which a tagged atom may end up in another molecule without net chemical reaction occurring. Olson (1978) reported that no measurable exchange occurs between ^{14}N and ^{15}N that isotopic exchange of N is insignificant in the soil-plant system in virtually all situations.

One of the first field experiments studying crop recovery of added N with the aid of ^{15}N labelled fertilizer was reported by Bartholomew et al. (1950). They treated oats with different rates of labelled ammonium sulphate and measured recoveries in the range of 11-29% of added N.

They encountered a high degree of variability in their results as a consequence of their plot size (53 by 91cm).

Tyler and Broadbent (1958) observed low recovery of tagged N-fertilizer in several greenhouse experiments and one field trial. Hence, they concluded that a substantial part of nitrogen fertilizer applied became at least temporarily (if not permanently) unavailable to crops. In various field experiments, a number of workers have reported values not greater than 50% crop utilization of added N (Martin and Skyring, 1962; Allison, 1965; 1966; Chalk et al., 1974; Hedlin and Cho, 1974; Patrick and Reddy, 1976; Sachdeva, et al., 1977; Ardakani, et al., 1977; Pirozhenko et al. 1980).

Fertilizer-N uptake was greater on clay soil than on sandy loam, probably owing to more favourable moisture conditions (Myer and Paul, 1971). In their studies with ¹⁵N labelled ammonium nitrate, they noted that plant recovery was about 25% of added N for the coarse textured and about 50% for clay soil. Field experiments on sandy loam and loamy-podzolic soils of the Moscow province showed that on a loamy soil 30-42% of added N was recovered by crops and on a sandy loam 43-49% was recovered (Blyum et al. 1978).

Some workers have studied the effect of moisture status of the soil on crop utilization of added N. Takahashi (1967) in his studies with ¹⁵N labelled ammonium sulphate reported crop recovery of 21.34% by a crop planted early in the summer and grown under drought conditions and 35.33% in a crop planted in autumn and grown under favourable moisture conditions. Pesche et al. (1979) observed no difference in grain and

straw yield between the nitrogen forms, but moisture levels did affect nitrogen utilization by the crops. In their studies nitrogen utilization was 34-38% at low water supply and 45-65% at high water supply. Broadbent and Carlton (1978) employing different rates of ^{15}N labelled fertilizer and different irrigation regimes found N utilization efficiencies by maize to range from 30-68%. The highest level of N utilization occurred at fertilizer rates that afforded maximum grain yield.

Method of fertilizer application has a considerable effect on the degree of utilization of added N. Cho et al. (1967) observed that in the early stages of growth, more applied N was taken up by maize when the fertilizer was placed near the plant. Surface application of ammonium form of fertilizer, and of urea, especially on calcareous soils, leads to inefficient utilization of the added N (Martin and Chapman, 1951; Volk, 1959; Meyer et al. 1961). MacLeod et al. (1975) reported higher grain yield of barley when nitrogen fertilizer was placed 5cm to the side of, and 5cm below the seed, than when broadcast on the surface.

Considerable attention has been given to timely application of N fertilizer for effective crop utilization. Fall application of N-fertilizer has been shown to be inferior to spring application in terms of crop utilization. Pearson et al. (1961) noted that crop recovery of fall added N was only 62% as large as that obtained from a spring application. In similar studies Ridley (1975) reported that crop recovery of fall added urea was 77.3% of spring added urea.

Crop recovery of added N varies with application rate. Grove et al. (1980) obtained 60% crop recovery of added N at 60 kg N/ha application and 35% at 220 kg N/ha with maize as the test crop. Gashaw et al. (1977) also found that efficiency of nitrogen utilization decreased with increasing N levels. The results of the studies carried out by Alessi and Power (1978) showed that fertilizer efficiency is greatest when N rate is adequate for maximum crop production.

Studies have been conducted on the influence of forms of fertilizer N on crop recovery of added N. Such studies are usually affected by other factors like soil texture, soil reaction, moisture status of the soil, and type of crop grown. A field experiment, utilizing ^{15}N labelled fertilizers was conducted by Koyama et al. (1979). Their result showed that rice plant recovered almost 50% of N added in ammonium form; 45% of that added as urea and 20% of that added as nitrate. Low crop recovery of nitrate might have been due to N loss through denitrification since they worked with waterlogged soil. Rennie and Rennie (1973) observed that uptake of fertilizer N by the crops clearly indicated the superiority of NO_3^- -N source in terms of plant availability. Sodium nitrate was followed by ammonium sulphate, with urea the least effective. These results were confirmed in the studies conducted by Dev and Rennie (1979). Mate and Varga (1963) concluded that the efficiency of labelled calcium nitrate was greatly increased by liming. This was especially true when calcium carbonate and fertilizer were applied simultaneously. They observed that liming promoted Ca and N uptake from the fertilizer and also increased the utilization of both soil N and fertilizer N.

Crop recovery of added N is also influenced by losses and immobilization of added N. All factors favouring these reactions contribute to a low recovery of added N. Excess moisture content, that results in oxygen deficiency in the soil, will decrease crop utilization of N added as nitrate. A very low recovery of added N was obtained with rice crop in a waterlogged soil (Sanchez and de Calderon, 1971).

2.4 FATE OF ADDED NITROGEN IN THE SOIL

A considerable portion of added N is not utilized by crops. This unutilized N may remain in the soil and be slowly released to crops, or it may be lost from the soil system. Added N can become temporarily or permanently unavailable to crops through one or more of the following processes: (i) immobilization; (ii) fixation; (iii) leaching; (iv) ammonia volatilization; and (v) denitrification.

2.4.1 Immobilization

Immobilization is the conversion of inorganic nitrogen into organic nitrogen by microorganisms. Both inorganic soil N and fertilizer N may be immobilized during the microbial decomposition of carbonaceous residue with a wide C:N ratio. Numerous workers have reported N immobilization in various incubation experiments with added organic matter such as straw (Allison and Klein, 1962; Broadbent and Tyler, 1964), and sawdust (Bollen and Lu, 1957; Allison and Cover, 1960). Immobilization accounted for over 50% of the added N in the studies conducted by Kissel et al.

(1979). They concluded that immobilization of fertilizer N on coastal Bermuda grass would be substantial for a large number of years. Other workers have noted that a significant quantity of added N was immobilized (Ferguson, 1957; Myer and Paul, 1970; Power, 1980). Okereke et al. (1980) have reported rapid immobilization of added N. After 12 hours of incubation, they observed that 10% of added ammonium sulphate was immobilized. After the same length of time 9% of urea N added was immobilized. Olson et al. (1979), found that most of the fertilizer N in the 0-10cm layer of soil after harvest was immobilized. They concluded that N immobilization was the principal reason for differences in plant utilization of spring and fall applied N fertilizer.

Immobilization of N varied directly with the amount of organic matter present and the ease of decomposition of the organic matter (Walunjkar et al. 1959). Addition of sucrose increases immobilization of added nitrogen (Agarwal et al. 1972). They also found that without added sucrose, nitrogen was immobilized particularly if the soil organic matter had a wide C:N ratio. Maximum immobilization of added N occurs when large quantities of readily decomposable crop residue of wide C:N ratio are added to soils (Myer and Paul, 1970). It has been shown (Jansson et al. 1965; Winsor and Pollard, 1956a) that both ammonium and nitrate nitrogen can be immobilized. Immobilization of N is however greater with NH_4^+ -N. Preferential utilization of NH_4^+ -N by soil microorganisms and of nitrate N by crops has been reported by a number of workers (Broadbent and Tyler, 1962; Turchin et al. 1964; Fack, 1965; Andreeva and Scheglova, 1966). This often results in increased immobilization and

decreased utilization of added NH_4^+ -N, especially where crop residues are added (Legg and Allison, 1959; Jansson, 1963). Studies with ^{15}N labelled fertilizers indicate that a considerably higher percentage of the labelled NH_4^+ -N than of the NO_3^- -N remained in the soil after cropping (Barlett and Simpson, 1967; Hauck, 1971; Hargrove and Kissel, 1977; Crasswell, 1979; Dev and Rennie, 1979).

Myer and Paul (1971) found that immobilization was greater in coarse textured than in fine textured soil in the presence of straw and at a higher rate of N application. Many other factors such as temperature, aeration, soil pH and moisture content affect the amount of nitrogen immobilized. This is a consequence of the effect of these factors on microbial population and activity. Overrein (1967) noted a positive correlation between temperature and immobilization of N added as ^{15}N urea at temperatures of 4, 12, and 20°C. Agarwal et al. (1972) showed that N immobilization was fastest in alkaline soil in the presence of sucrose.

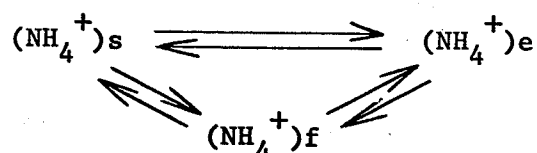
Immobilized N is not permanently unavailable to plants. When the microorganisms die, decomposition and mineralization of the organic substrate occur. Thus, the inorganic N immobilized is returned to the soil (Winsor and Pollard, 1956b; Allison and Klein, 1962; Agarwal et al. 1972).

2.4.2 Ammonia Fixation

Both the organic and inorganic soil fractions have the capacity of fixing ammonia in forms relatively unavailable to higher plants or microorganisms. Nommik (1965) noted that fixation of ammonium by clay minerals and fixation of ammonia by organic matter is quite extensive in some soils.

2.4.2.1 Fixation by Clay Minerals

It is well known that clay minerals with expanding lattices, such as montmorillonite and vermiculite have the ability to fix ammonium. Fixed ammonium is held in such a way that it is not readily available to higher plants or microorganisms. There is a dynamic equilibrium between soluble ammonium, $(\text{NH}_4^+)s$, exchangeable ammonium $(\text{NH}_4^+)e$ and fixed ammonium $(\text{NH}_4^+)f$ in the soil. The equilibrium can be represented by the following equation:



According to this equation, a change in any of the above forms of NH_4^+ will affect the other forms. An increase in the concentration of $(\text{NH}_4^+)s$, resulting from addition of NH_4^+ -containing fertilizers disturbs the equilibrium and some added NH_4^+ -N will be fixed. When the $(\text{NH}_4^+)e$ falls below the equilibrium value, the fixed ammonium $(\text{NH}_4^+)f$ will be slowly released. Shirlova and Smirnov (1968) reported that uti-

lization of fixed ammonium began only when almost all the exchangeable ammonium had been utilized.

Fixation usually occurs to a much greater extent in the subsoil than in the surface soil. This may be due to increased clay content in the subsoil. Sowden (1975) noted that 40% of NH_4^+ -N of manure and fertilizer was fixed by a Brunisolic soil containing 20% clay which was largely vermiculite. The fixed NH_4^+ was protected against rapid nitrification and leaching, and only slowly released to crops.

The amount of NH_4^+ -N being fixed can be decreased and exchangeable K increased by adding KCl to soil (Nommik, 1957; Walsh and Murdock, 1960; Hinman, 1966). The decrease in NH_4^+ fixing capacity is proportional to the amount of KCl added, thus proving that K^+ inhibited fixation of NH_4^+ by clay mineral.

2.4.2.2 Fixation by Organic Matter

The organic fraction of the soil has the capacity to fix a considerable amount of ammonia, (NH_3). The ammonia-organic matter complex thus formed, is extraordinarily resistant to decomposition. Hence this fixed N is very slowly available to plants and microflora. Fixed ammonia is defined as that fraction of added NH_3 which is retained by soil organic matter after intensive extraction and leaching with acid (Broadbent et al. 1961; Burge and Broadbent, 1961; Nommik and Nilsson, 1963) or neutral salt solution (Nommik and Nilsson, 1963a). Some workers (Bunyakina, 1976; Lavrova, 1977; Pirozhenko and Petrushina, 1979) have shown

that a substantial amount of added N was fixed in the soil organic fraction. It has been observed that this organic matter-fixed ammonia is only released in mineral forms with difficulty (Filimonov and Rudelev, 1977; Sachdev et al. 1976).

Broadbent et al. (1961) and Nommik and Nilsson (1963) indicated that ammonia fixation occurs to a large extent only on soils with pH above neutrality. In addition Broadbent et al. (1967) demonstrated a linear relationship between pH and ammonia fixation at a pH greater than 7. Shoji and Matsumi (1961) and Nommik and Nilsson (1963b) in independent studies found that the capacity of the soil to fix ammonia is highly dependent on H-ion concentration in the treated sample. They concluded that at pH less than 7 fixation was insignificant and, in general, not measurable analytically.

Sohn and Peech (1958) presented a contrary view. They indicated that acid soil containing a large amount of organic matter had the greatest ammonia fixing capacity. Ammonia fixed by soil increases with increased organic carbon or organic matter content of the soil (Sohn and Peech, 1958; Burge and Broadbent, 1961; Nommik and Nilsson, 1963). It has been observed (Sohn and Peech, 1958; Mortland, 1963), that oxidation of organic matter by hydrogen peroxide, reduced by half, the capacity of the soil to fix ammonia. Burge and Broadbent (1961) treated soil with dimethyl sulphate, thereby blocking the hydroxyl groups in organic matter. This caused a decrease in the ammonia fixing capacity of the soil. They concluded that hydroxyl groups are involved in the ammonia fixation re-

action. On the other hand, Hinman (1966) demonstrated that destruction of organic matter increases the fixing capacity of the soil. He speculated that the organic matter blocked the entry of NH_4^+ to the clay minerals.

2.4.3 Nitrite and Organic Matter

Studies carried out by Bremner and others (Bremner and Shaw, 1957; Bremner and Furr, 1963; Furr and Bremner, 1964) has directed attention to a possible reaction between the nitrite form of N and soil organic matter. In their work they found that a considerable part of applied NO_2^- -N was fixed by the soil. Other workers studied decomposition of nitrite in the soil and confirmed that part of the N becomes organically fixed, while some N is simultaneously evolved as N_2 , N_2O , and $\text{NO} + \text{NO}_2$ (Reuss and Smith, 1965; Bremner and Furr, 1966; Nelson and Bremner, 1969, 1970; Steen and Stojanovic, 1971; Cawse and Cornfield, 1972; Christianson et al 1979).

Organic matter fixation of nitrite N has been shown to be directly related to soil organic matter content and inversely related to soil pH (Bremner and Furr, 1966; Nelson and Bremner, 1969). Smith and Chalk (1980) demonstrated the effect of pH and organic matter content of the soil on NO_2^- -N fixation. They used two soils of similar pH but different organic carbon contents (5.29 and 2.42% respectively). They found that NO_2^- -N fixation in the former was about twice that of the latter soil. Comparison between soils of similar organic carbon but different pH showed the marked effect of soil pH. Fixation in alluvial soil (pH

5.8) was about ten times greater than fixation in Terra Rosa soil (pH 7.5) after 96 hours of incubation. The rate of fixation decreases with time and is usually most rapid during the initial 24 hours in the acid soils (Smith and Chalk, 1980).

Bremner (1968) proposed that phenolic constituents of soil organic matter react with NO_2^- to form nitrosophenols which eventually partly decompose to yield N_2 and N_2O . This suggestion is based on reactions of NO_2^- with model compounds. Smith and Chalk (1980) suggested that nitrite fixed by soil organic matter may occur in heterocyclic compounds. The premise for their contention was that Smith and Chalk (1979c) have shown that fixed N is resistant to mineralization.

2.4.4 Leaching

Next to crop uptake loss of added nitrogen by leaching constitutes one of the most important mechanisms of inorganic nitrogen removal from field soils. The most oxidized form of nitrogen, NO_3^- , is particularly mobile and moves with the percolating water to the watertable. Nitrate moves readily with the wetting front, following irrigation (Barker, 1962; Cassel, 1970; Liao and Bartholomew, 1974). Nitrogen fertilizers, regardless of form added, are ultimately converted to mobile NO_3^- by natural processes (Edward et al., 1972; Olson, 1972). Nitrite (NO_2^-) is an intermediate product of nitrification, which also is very mobile but unstable. Nitrite is converted to NO_3^- under aerobic conditions. In anaerobic conditions NO_2^- is reduced to gaseous forms and lost to the atmosphere.

The amount of water moving through the soil profile will determine rate and extent of NO_3^- movement. Wetselaar (1961; 1962) found a high correlation between NO_3^- movement and amount of rainfall in tropical soils of Australia. Downward movement of NO_3^- does depend on the water holding capacity of the soil. Soils with higher water holding capacity will have less nitrogen lost to deeper layers by the same rainfall than soils with lower water holding capacity (Cooke and Cunningham, 1957). Nitrate nitrogen thus moved either accumulates at depth, is lost in the drainage water, or is subject to denitrification. Accumulation of leached NO_3^- -N has been detected below the 90 cm depth (Campbell et al. 1975; Cleemput et al., 1977; Alessi and Power, 1978). Alessi and Power (1978) reported that leaching of N beyond the 90 cm depth accounted for 4 to 37% of the nitrogen added.

Irrigation methods and form of nitrogen added affect the total amount and depth of NO_3^- leached from the soil. Bauder and Montgomery (1980) indicated that high volume-low frequency irrigation leached solutes to a greater depth than did low volume-high frequency irrigation. Minimum leaching of added urea-N occurred with optimum irrigation and a split application (Bauder and Schneider, 1979). Some workers concluded that leaching of N was mainly of that added in the NO_3^- form and least with urea (Crasswell, 1979; Bauder and Montgomery, 1980; El Wali, 1980).

Leaching loss of N is much less of a problem under a continuous cropping system than when no crop is growing (Allison, 1955; Nelson and Uhlend, 1955). This is due to nitrate assimilation by the growing crop

and also high evapotranspiration, which reduces the amount of water in the soil. This prevents accumulation and downward movement of nitrate in the soil (Wetselaar, 1961). Michalyna and Hedlin (1971) indicated that inclusion of summerfallow in crop rotation may result in a large amount of NO_3^- being located below the rooting zone. Even under continuous cropping, leaching of N can be very important in the tropics, especially in areas with high rainfall. Gamboa et al. (1971) reported leaching of N and potassium (K) of 65% and 50% of the amount added, respectively. In this study, conducted in Costa Rica, Gamboa et al. (1971) grew five crops of maize over a period of three years.

It is important to minimize loss of nitrogen through leaching, if maximum utilization of added N is to be obtained. Timely applications of NH_3 -based fertilizers and low volume irrigation minimize leaching below the crop root zone (Bauder and Montgomery, 1980). Since leaching loss of N occurs mainly in the NO_3^- form, retardation of nitrification may reduce leaching loss. To this end, nitrification inhibitors and slow release fertilizers were developed (Gasser, 1970; Prasad et al., 1971). "N-Serve", the trade name for 2-chloro-6-(trichloromethyl) pyridine, has been found to inhibit nitrification of ammonium and ammonium yielding fertilizers (Goring, 1962a; Gasser and Penny, 1964; Vlassak, 1964; Prasad and Rajale, 1972; Bundy and Bremner, 1973).

2.4.5 Ammonia Volatilization

Surface application of urea or ammonium yielding fertilizers on neutral or alkaline soil, results in escape of ammonia (Martin and Chapman, 1951; Volk, 1959; 1961; Gasser, 1961; Morrison and Foster, 1977). When ammonia is not chemically sorbed by soil, it is free to diffuse slowly through the soil to the atmosphere. Ammonia volatilization from N fertilizer is due to the reaction: $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$.

Ammonia volatilization usually does not occur when soil pH is below neutral (Martin and Chapman, 1951; More and Varade, 1978). Losses of urea ranging from 20 - 70% of added N in brown calcareous Mediterranean soil was reported by Gama (1977). Conversely, Ernst and Massey (1960) and Wahab et al. (1961) have shown that volatilization of ammonia can occur in slightly acid soils, especially after a heavy application of urea. Hydrolysis of urea to form ammonium carbonate leads to a rise in soil pH to near or above neutrality. Such a condition is favourable for ammonia volatilization. Matocha (1976) reported volatilization loss of N of as much as 18.5% of added N, when urea was applied to a fallowed acid fine sand. In a laboratory study, Panossian and Anderson (1980) noted that ammonia volatilization loss from urea ranged from 14 - 48% of the added N. On the other hand, addition of acidic ammonium salts to acid soils is less likely to result in ammonia volatilization (Martin and Chapman, 1951; Volk, 1961).

Nitrogen loss through ammonia volatilization is inversely related to the cation exchange capacity (C.E.C.) of the soil (Gasser, 1964; Chai and Hou, 1977; Lyster et al., 1980). Lyster and others reported that

volatilization loss of NH_3 from urea is negligible in soils with C.E.C. values greater than 25 meq/100g. Losses however increased dramatically at lower C.E.C. values. The magnitude of NH_3 volatilization depends on the type of fertilizer added. Ammonia volatilization is greater with urea than ammonium sulfate (Prasad, 1976; Ventura and Yoshida, 1977; More and Verade, 1978; Panossian and Anderson, 1980). The following ranges of N loss through ammonia volatilization were observed by Hargrave et al. (1977): 3 - 10% of N added as NH_4NO_3 ; 36 - 45% for pelletted $(\text{NH}_4)_2\text{SO}_4$ and 25 - 55% for liquid ammonia. The initial soil condition prior to N addition also determines the intensity of ammonia volatilization. Volatilization losses are greater when soil is wet at the time of application than when the soil is initially dry (Fenn and Escarzaga, 1976). When there are a number of factors favouring N loss at the time of N-application, considerable loss can occur through ammonia volatilization. The quantity of ammonia volatilized is reduced when fertilizers are incorporated into the soil (Ernst and Massey, 1960; Volk, 1961; Connell et al., 1979).

2.4.6 Denitrification

Denitrification is the production of molecular nitrogen or gaseous nitrogen oxides through the reduction of nitrate or nitrite (Wijler and Delwiche, 1954). Denitrification is the most important source of N loss as gaseous products, and may be a major cause of inefficient utilization of added nitrogen. Various workers have reported a substantial amount

of N loss through denitrification (Gerretsen and de Hoop, 1957; Soulides and Clark, 1958; Broadbent and Clark, 1965; Cleemput et al., 1977; Christianson et al., 1979; Kowalenko, 1980). Two pathways have been found to operate in the process of denitrification. One is the biological reduction of nitrate or nitrite to volatile nitrogenous gases. Biological denitrification is an enzymatic process accomplished mainly under anaerobic condition. The second pathway is non-biological, and takes place under aerobic condition by chemical processes. This is referred to as chemodenitrification (Clark, 1962).

2.4.6.1 Biological Denitrification

Biological denitrification is carried out by facultative anaerobic bacteria. These bacteria are capable of utilizing nitrate in place of oxygen as an electron acceptor. The complete reduction of nitrate to elemental nitrogen, coupled with the complete oxidation of organic matter (represented by glucose) is written as: $C_6H_{12}O_6 + 4NO_3^- \rightarrow 6CO_2 + 6H_2O + 2N_2 + 4e^-$. Nitrate is first reduced to nitrite and then simultaneously converted to gaseous products - nitrous oxide and/or molecular nitrogen (Wijler and Delwiche, 1954; Nommik, 1956; Schwarzbeck et al., 1961; Bollag et al., 1973).

The denitrifier population is very abundant in most soils. The most numerous denitrifiers are Pseudomonas sp., Achromobacter sp., and Bacillus sp. (Alexander, 1977). Different denitrifying species have different rates of gas production under similar environmental conditions (Valera and Alexander, 1961).

Many factors that affect denitrification loss of N have been reported. Reviews on these factors have been prepared by Delwiche (1956); Nommik (1956); Broadbent and Clark (1965); Payne (1973) and Westerman and Tucker (1978a). Among factors discussed were: partial pressure of oxygen in the soil atmosphere, a readily available energy source, nitrate content, moisture content, pH, and temperature in the soil. McGarity and Meyer (1968) reported that denitrification activity was highest in the upper soil horizons and declined with depth. The observed activity was significantly correlated with organic carbon and total N content of the soil. Organic matter content affects denitrification in three ways: (i) organic matter serves as a reductant and donates electrons in both aerobic and anaerobic microbial respiration; (ii) organic matter is used in cell synthesis during growth and maintenance of microorganisms; (iii) a microbial population undertaking rapid decomposition of organic matter has a high biological oxygen demand (BOD). This creates anaerobic conditions which are conducive to denitrification. Bremner and Shaw (1958a); (1958b); Myers and McGarity (1972); Stefansson (1972) reported an increase in microbial activity and subsequent oxygen stress as a result of organic matter addition. Such a condition favours denitrification. Maximum denitrification occurred in fully saturated or flooded conditions (Bailey and Beauchamp, 1973b; Bremner and Shaw, 1958; Cho and Sakdinan, 1978). This could occur in soil after a heavy rain, irrigation or during a spring thaw.

Loss of N through denitrification may be pronounced in neutral and alkaline soil, with poor aeration and an active microbial population present. Broadbent and Clark (1965) observed reduced biological denitrification when soil pH is below 7.0. Acid conditions reduce the metabolic activity and growth of most microorganisms (Bollag et al., 1970; Paul and Victoria, 1978). Raising the pH of an acid soil by liming (Atkinson, 1964) increases denitrification rate (Bremner and Shaw, 1958b; Cady and Bartholomew, 1960; Bollag et al., 1973; Cho and Sakdinan, 1978).

Some workers (Allison et al., 1960; Carter and Allison, 1960; Cady and Bartholomew, 1960; 1961; Myers and McGarity, 1972) have reported denitrification in apparently well aerated soils, especially when supplied with readily decomposable organic matter. Two hypotheses are commonly advanced to explain this phenomena:

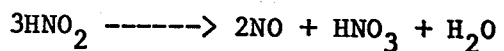
1. Many moist soils may possess a range of microhabitats containing varying levels of oxygen supply (Russell, 1973). Such soils may contain clods that have no free air at field capacity, and the soil within the clod is anaerobic.
2. In the presence of easily decomposable organic material, rapid decomposition of this material by the microbial population results in high biological oxygen demand (BOD). Thus anaerobic conditions favourable to denitrification are created (Bremner and Shaw, 1958a; Myers and McGarity, 1972; Stefansson, 1972).

2.4.6.2 Chemical Denitrification

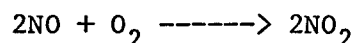
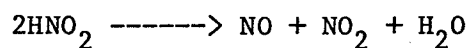
Loss of added-N can occur through chemical reactions involving nitrite formed by nitrification of ammonium and ammonium yielding fertilizers in the soil (Broadbent and Clark, 1965; Allison, 1966). In their studies, Smith and Chalk (1980) concluded that gaseous N-losses can occur via chemical transformation of nitrite, when the competitive biological oxidation of NO_2^- by nitrobacter is inhibited. Nitrite may accumulate in soil as a result of a heavy application of urea or ammonium yielding fertilizers (Jones and Hedlin, 1970; Pang et al., 1973). Various workers have reported chemical decomposition of nitrite when nitrite is added to, or when it accumulates in soils of acidic or slightly acidic nature (Tyler and Broadbent, 1960; Reuss and Smith, 1965; Jones and Hedlin, 1970b; Nelson and Bremner, 1970; Bollag et al., 1973; Pang et al., 1974; Shankhyan and Shukla, 1980; Smith and Chalk, 1980). In the absence of oxygen and at low soil moisture content, Cady and Bartholomew (1960) and Bollag et al. (1973) reported evolution of NO when NaNO_2 was added to soils of pH 4.5 - 5.0.

A review by Broadbent and Clark (1965) summarized the likely pathways for chemical denitrification:

1. Since nitrous acid is unstable under acid conditions (pH 5 or less), it decomposes according to the reaction:

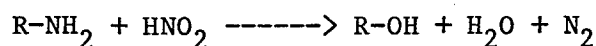


Nitrogen dioxide thus formed may react with water to form nitrous acid and nitric acid. Nelson and Bremner (1969), in their studies indicated that self decomposition of nitrous acid may be represented by:

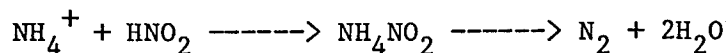


Nitrogen dioxide produced from the reaction can be converted to nitrate. Nitric oxide (NO) and NO_2 are the gaseous products of denitrification when oxygen is present.

2. Reaction of nitrous acid with α -amino acids (a van Slyke reaction). Under acid conditions, nitrous acid reacts with α -amino acids to yield molecular nitrogen according to the reaction:



3. In a similar reaction to the above, ammonia reacts with nitrous acid to yield molecular nitrogen.



4. Reactions of nitrous acid with other soil constituents such as organic matter, organic reducing compounds and soil minerals. It has been reported (Nelson and Bremner, 1969, 1970a) that a gaseous loss of N in nitrite-treated soil was related to the organic matter content of the soil. They also noted that the role of soil mineral in nitrite decomposition was insignificant. Some other workers have confirmed the evolution of N_2 , N_2O , and NO +

NO_2 from nitrite treated soils (Reuss and Smith, 1965; Stevenson et al., 1970; Steen and Stojanovic, 1971; Cawse and Cornfield, 1972). Bremner (1968) indicated that phenolic substances react readily with nitrite to form nitrosophenols that are decomposed by nitrous acid to yield N_2 and N_2O .

2.5 RESIDUAL EFFECTS OF NITROGEN

Evaluation of the residual effects of N-fertilizer involves yield measurement or N uptake by a crop grown on unfertilized plots in the year following a known fertilizer application. It is possible to measure the residual effect of labelled material even when a subsequent application of unlabelled materials is made (Broadbent, 1980). Recent studies of nitrogen transformation in soils has shown that all forms of nitrogen fertilizers have some residual effects (Jansson, 1963; Filimonov and Rudelev, 1977). McGill (1980) reported a gradual increase in the nitrogen soil test values of farm samples from previously cropped fields. This suggests that where farmers add nitrogen on a regular basis some of the nitrogen not used by the crop is present as nitrate nitrogen and hence available to the next crop.

Various studies have indicated that only a small fraction of the residual fertilizer N is utilized by crop in the following year (Sachdev et al., 1976; Makarov, 1977; Koyama et al., 1977; Reddy and Patrick, 1978; Tomar, 1981). Mikkelsen and DeDatta (1980) reported that recovery of residual fertilizer N in the second rice crop varied from 0.8 to 1.2% of added N over the entire range of N fertilizer treatments. Korenkov et

al. (1976) suggested that the insignificant residual effect of N was due to incorporation of fertilizer N into various organic matter fractions.

2.6 NITROGEN BALANCE

An accurate accounting of the nitrogen balance in the total biosphere requires an evaluation of the individual nitrogen balance components for the entire soil-plant system (Hauck, 1978). The components of this system are: nitrogen added, crop removal, leaching, volatilization, immobilization, fixation and denitrification. The amount of added N and crop recoveries can be easily measured, but other components of N balance are not easily determined. Leaching loss of N is an important factor in determining the N balance. The difficulty of accurately measuring the leaching component has been demonstrated (Biggar and Nielsen, 1976). Incorporation of urea or ammonium yielding fertilizers into the soil may prevent ammonia volatilization (Ernst and Massey, 1960; Connell et al. 1979). Residual soil N is also difficult to measure, due to the size of the organic N pool and the variability of the pool (Rolston, 1978). Presumptive evidence of denitrification has always been obtained by indirect means (Hauck, 1971). This is done by measuring other components of the system and assuming that the nitrogen unaccounted for was lost by denitrification. In growth chamber studies, such measurements have shown that between 18 and 40% of added N could be lost by denitrification (Dilz and Woldendorp, 1961; Dinchev, 1964; Zamyatina, 1968; Hauck, 1978). In two long term field experiments, Jolley and Pierre (1977) re-

ported N deficits of 37 and 46% for 2 soils at the highest rate of N application (168 and 134 Kg/ha, respectively). Values of denitrification thus obtained are affected by the uncertainties associated with sampling each of the other parameters involved in N balance.

It is only through the use of ^{15}N labelled fertilizer that direct measurement of added nitrogen in the soil-plant system can be made accurately (Olson, 1978). The isotopic method gives a satisfactory account of added N and thus permits an acceptable determination of N balance. It is recognized that the tracer technique is based on certain assumptions: (i) that the isotope composition of the tracer is constant, (ii) that living organisms can distinguish one isotope from another of the same element only with difficulty, (iii) that the chemical identity of isotopes is maintained in biochemical systems (Fried et al. 1975; Pomares-Garcia and Pratt, 1978). Although these assumptions are not entirely valid for all experimental conditions, they may be considered valid in most studies in which ^{15}N compounds are used as tracers (Hauck and Bremner, 1976; Olson, 1978).

A number of growth chamber experiments and some field studies have been undertaken to prepare a nitrogen balance with ^{15}N labelled fertilizers. In most of the results, imbalance in N budgets has been used to estimate gaseous loss of N via denitrification (Jansson, 1962; Zamyatina, 1971; Alessi and Power, 1978; Dev and Rennie, 1979; Crasswell, 1979). Rolston et al (1976) demonstrated that N_2 and N_2O from denitrification of fertilizer can be measured in a field profile using a high enrichment of ^{15}N labelled fertilizer. It has also been shown that a

complete nitrogen balance by direct, quantitative measurement of all components involved can be obtained through use of a gas lysimeter (Ross et al. 1968). The gas lysimeter is a closed system in which plants can be grown for several weeks. This permits measurement of gaseous exchange, soil transformation and crop use of added N. It is claimed that this apparatus is the best closed-system approximation of nitrogen balance in a productive ecosystem (Hauck, 1971).

Chapter III
MATERIALS AND METHODS

3.1 SOIL SAMPLES

Eight soils: Pine Ridge, Wellwood, Granville, Waitville, Holland, Newdale, Red River, and Almasippi were used in these studies. These soils were collected early in the fall of 1978 from 0 - 15 cm depths of cultivated fields. The soil samples were air-dried, ground to pass through a 2mm sieve, and stored at 5°C. The locations, subgroup designations and some physical and chemical properties of the soils are shown in Tables 1 and 2.

3.1.1 Experiment I: Utilization of Nitrogen from ¹⁵N-labelled Urea and Calcium Nitrate by Wheat Grown on Various Soils.

Two kilograms of air-dried soil were weighed into each pot and loosely packed. The top 5 cm of soil was removed from each pot. The remaining soil was moistened to field capacity.

The soils had different amounts of native macronutrients. Yield comparisons of wheat grown on various soils was not the primary objective of this study. Therefore the basal applications of macronutrients applied as described below did not take into consideration the initial nutrient levels. All pots received 50 ppm P₂O₅ and 33 ppm K₂O as 10 ml

TABLE 1

Subgroup designation, legal location and some physical and
chemical properties of the soils studied.

Soil Name	Pine Ridge	Wellwood	Granville	Waitville
Subgroup	Eluviated Eutric Brunisol	Orthic Black Chernozem	Orthic Gray Luvisol	Orthic Gray Luvisol
Legal location	SE 26-4-7E	NE 19-11-14	SW 8-17-16	SW 32-16-16
Texture	FS	FSL	CL	L
pH	5.8	6.0	6.3	6.9
C.E.C. (meq/100g)	8.2	21.7	25.3	28.4
Conductivity (mmho/cm)	0.1	0.2	0.3	0.3
Organic matter (%)	2.4	4.1	3.0	5.3
CaCO ₃ (%)	0.4	2.2	0.8	1.4
NaHCO ₃ extract P (ppm)	7.9	11.4	9.1	8.5
H ₂ O at field capacity (%)	17.0	27.0	26.0	29.0
Total N by Kjeldahl (%)	0.10	0.19	0.15	0.23
Exchangeable K (ppm)	37.4	307	139	167

TABLE 2

Subgroup designation, legal location and some physical and chemical properties of the soils studied.

Soil Name	Holland	Newdale	Red River	Almasippi
Subgroup	Orthic Black Chernozem	Orthic Black Chernozem	Gleyed Rego Black	Gleyed Rego Black carbonated phase
Legal location	NE 32-7-10	NE 22-11-17	Lot6-8-3E	SW 28-11-10
Texture	L	CL	C	VFSL
pH	7.3	7.4	7.3	7.7
C.E.C. (meq/100g)	39.2	41.2	54.1	20.8
Conductivity (mmho/cm)	1.6	0.5	1.4	1.6
Organic Matter (%)	8.1	9.1	5.9	4.6
CaCO ₃ (%)	0.6	2.4	1.5	6.6
NaHCO ₃ extract P (ppm)	6.7	14.8	16.5	14.7
H ₂ O at field capacity (%)	34.6	34.0	36.2	27.0
Total N by Kjeldahl (%)	0.36	0.48	0.27	0.24
Exchangeable K (ppm)	398	227	498	168

of KH_2PO_4 which was part of H_2O required to bring the soil to field capacity. The soils were fertilized with ^{15}N -labelled urea and calcium nitrate to supply 100 ppm N on a weight basis of air dry soil. The labelling in these N-sources were 19.1 and 21.8% ^{15}N excess for urea and $\text{Ca}(\text{NO}_3)_2$ respectively. Exact amounts of N-fertilizer added were 428 mg urea per 2 kg soil and 1172 mg $\text{Ca}(\text{NO}_3)_2$ per 2 kg soil. These fertilizers were spread uniformly on the surface of the soil in the pots. This corresponds to the application at 5 cm depth from soil surface. A three cm column of soil was replaced and the soil moistened to field capacity. Ten wheat seeds (c.v. Neepawa) were sown in each pot and the final 2 cm depth of soil was replaced. More water was added to bring the soil to field capacity. There were three replications for each treatment. The pots were arranged in a completely randomized design in the growth chamber. The temperature of the growth chamber was 20°C during the day and 16°C at night. Humidity of the chamber was 50% in the day and 80% at night. The plants were grown under a light intensity of $450 \text{ u Einstein/m}^2/\text{sec}$ at 50 cm from the bottom of the growth chamber.

After germination, wheat seedlings were thinned to seven plants per pot. During the experiment, water was added as required to keep the soils at field capacity. Routine maintenance included removal of weeds, rearranging the pots to compensate for the draft effects on pots close to the chamber doors. The plants were harvested after 52 days of growth. The soil was removed from each pot, sieved and roots were separated and washed. Soil from each pot was placed in plastic bags, thor-

oughly mixed and sampled for analysis. The above ground and below ground portions of the plant were dried to a constant weight at 70°C. The plant samples were ground in a mill fitted with a sieve of 1 mm screen size.

The plant parts and soil samples were analyzed for total nitrogen by Kjeldahl digestion and for ^{15}N as described below. The distillate was placed on a hot plate and concentrated to about 5 ml for ^{15}N analysis. Isotope ratio analysis was carried out with mass spectrometer as described later.

3.1.2 Experiment II: Forms and Distribution of Inorganic N in Urea [(NH₂)₂CO] Treated Soils.

Duplicate samples of the air-dried soil were weighed into 250-ml beakers to provide a 3 cm depth of soil. Ten ml of a solution containing non-labelled urea were added. This gave a concentration of 500 ppm N on an air dry soil weight basis. Soil and fertilizer were thoroughly mixed, moistened to field capacity and the beakers were covered with a polythene sheet to minimize loss of water. Duplicate check treatments for each soil were included. The containers were placed in a humidified desiccator and incubated at 20°C for 33 days. A 10 gm sample was taken from each container every three days, and the remaining soil was kept at field capacity. The soils were analyzed for $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{NO}_2^-\text{-N}$. Moisture content of the soil at the time of sampling was determined.

3.1.3 Experiment III: Chemical Denitrification in Some Manitoba Soils Treated with Labelled Nitrite.

A previous incubation study indicated that addition of urea resulted in accumulation of nitrite (NO_2^-) in the acidic Pine Ridge and Wellwood soils and in the alkaline Almasippi soil. This nitrite persisted in the Pine Ridge and Wellwood soils but in the Almasippi soil it was soon oxidized to nitrate. In all the eight soils used the possible loss of N by chemical denitrification was investigated. Twenty-five gram samples of each of these soils were treated with ^{15}N -labelled sodium nitrite (% $^{15}\text{N} = 50.0$) to provide 100 ppm NO_2^- -N. The soil and NaNO_2 were thoroughly mixed to obtain a uniform concentration of nitrogen. The incubation vessel (Figure 1) was connected to a vacuum line. The pressure of the incubation atmosphere was reduced to 650 mm Hg while the Hg manometer was also connected to the vacuum line. The samples were then incubated for 4 days in a closed vessel at 20°C . Two gas sample tubes (Figure 2) were used to collect the evolved gases from each incubation vessel. One gas sample tube contained about 5 g of potassium hydroxide as a water and carbon dioxide absorbent. The other contained 5 ml of concentrated sulphuric acid to absorb water only. Gas samples were taken at 1, 2, 3 and 4 days after incubation. Gas collected from the incubation vessels was analyzed with a mass spectrometer by scanning for mass to charge (m/e) ratios of 28 through 46. An air sample was also analyzed to estimate the m/e of 28 through 46 present in the atmosphere.

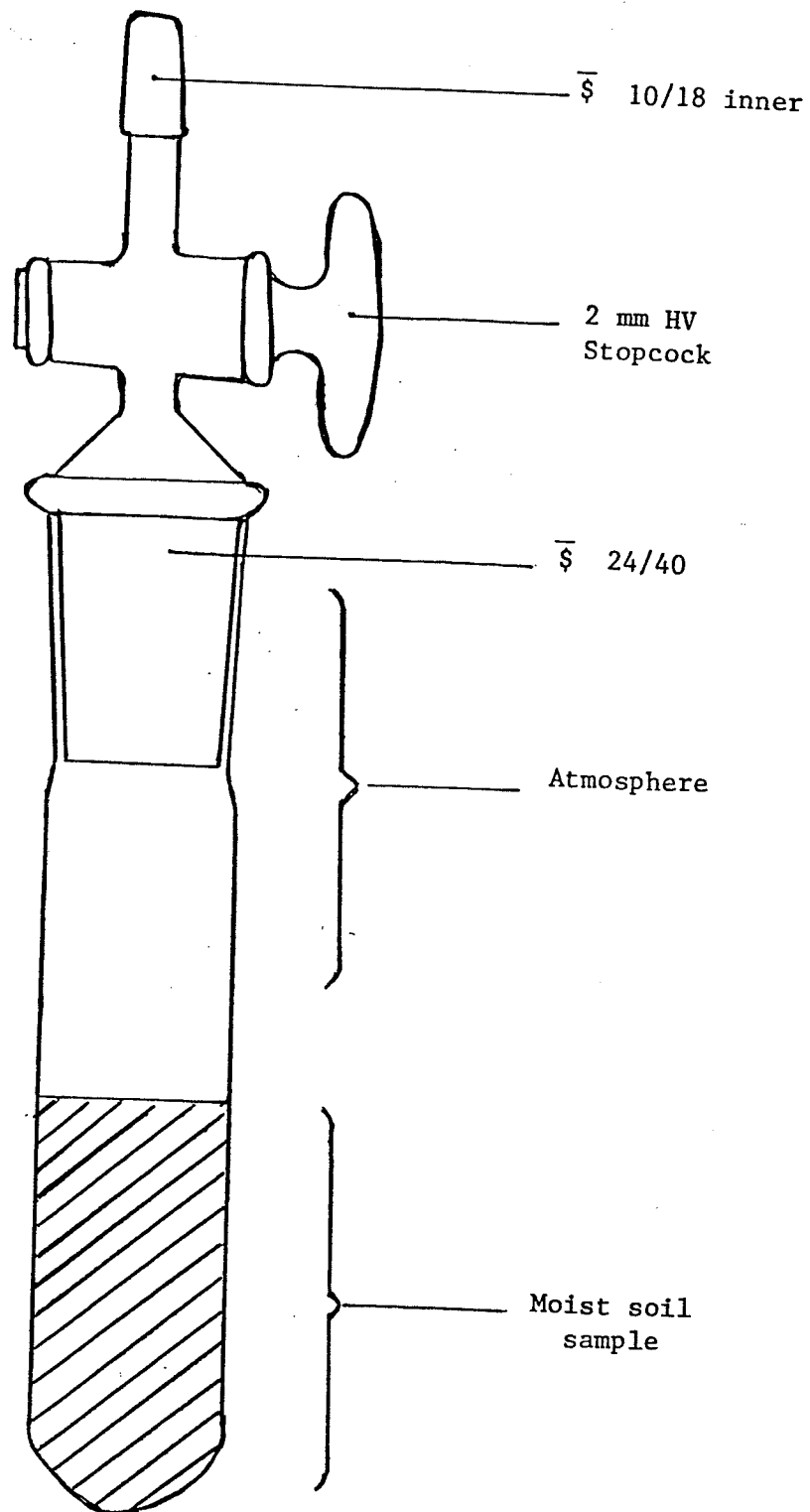


Figure 1: Incubation tube

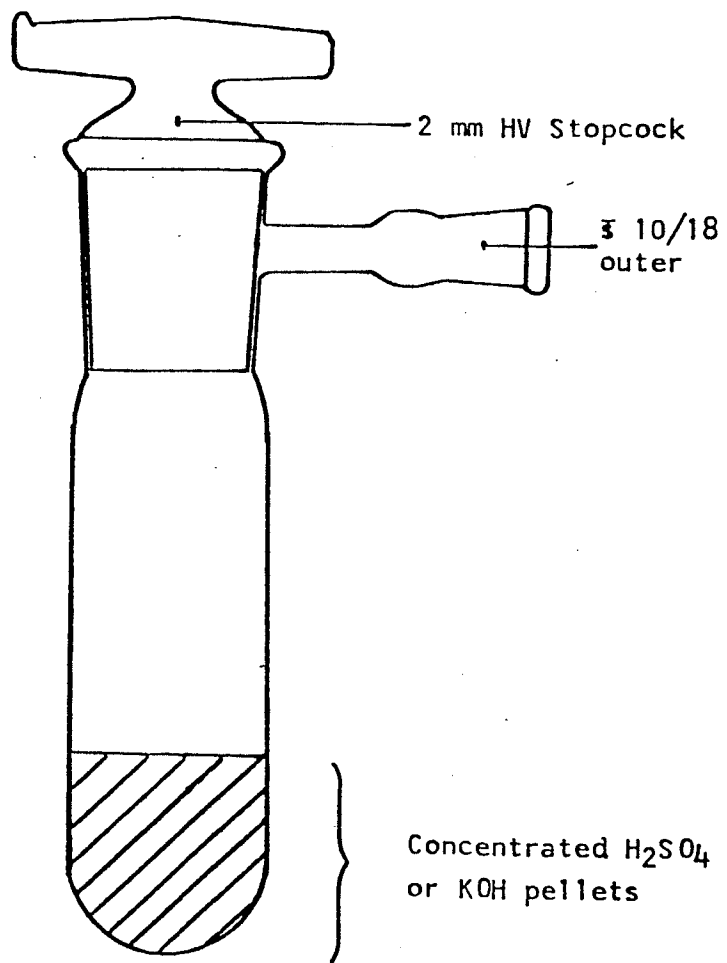


Figure 2: Gas sample tube

3.1.4 Experiment IV(i): Nitrogen Fertilizer and Soil Interactions.

All the eight soils mentioned earlier were used for this investigation. Urea, $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ labelled with ^{15}N were the nitrogen sources added. The labelling in these N-sources were 52.67, 52.3 and 54.4% excess for urea, calcium nitrate and ammonium sulphate, respectively.

Duplicate samples of 50 g of air-dried soil were weighed into 100 ml beakers. To each beaker nitrogen was added in solution as urea, $\text{Ca}(\text{NO}_3)_2$ or $(\text{NH}_4)_2\text{SO}_4$. In each case the solutions were of such concentration that adding enough solution to bring the soil to field capacity gave a concentration of 500 ppm N on a dry soil weight basis. Exact weight of N sources added were: 53.6 mg urea per 50 g soil; 146.5 mg $\text{Ca}(\text{NO}_3)_2$ per 50 g soil and 117.9 mg $(\text{NH}_4)_2\text{SO}_4$ per 50 g soil. The soil and fertilizer were mixed thoroughly, and the beaker was covered with a perforated polythene sheet. The soil samples were placed in humidified desiccators and incubated at 20°C for 2, 4 and 8 weeks. The desiccators were opened each day to permit air exchange. At every sampling date, the soils were analyzed for total inorganic N and organic N. Moisture contents of the soils were also determined.

3.1.5 Experiment IV(ii): Rapid Reactions of N-Fertilizers in Four Slightly Acid to Neutral Soils.

Four soils; Pine Ridge, Wellwood, Granville and Waitville were chosen for this study. Previous investigation showed that these soils fixed more nitrogen than the slightly alkaline soils. Calcium nitrate was ex-

cluded from the N-treatments since this N-source was not appreciably fixed in any of the eight soils. Procedures for incubation and the amount of N added were the same as in Experiment IV(i). Soil samples were taken at 1, 2, 4, 6 and 10 days after incubation. The soils were analyzed for the same parameters as in Experiment IV(i).

3.1.6 Experiment V: Determination of Organically Fixed N in Four Manitoba Soils.

This study was undertaken to ascertain the amount of N fixed in previous incubation studies that was organically bound. The same four soils as in the last two experiments were used without adjusting the pH. Labelled $(\text{NH}_2)_2\text{CO}$ was the source of N (% $^{15}\text{N} = 52.96$) and it was added at a rate which provided 500 ppm N on the basis of dry soil weights. Fifty gram soil samples were treated with urea-N, and soil and fertilizer were thoroughly mixed. Each treatment was replicated four times. The soils were moistened to field capacity and incubated at 20°C for 4 weeks. At the end of the incubation period, the inorganic N was extracted with 2N KCl from all four samples of all soils. From two samples of each soil the soil residue was analyzed for total N by the Kjeldahl procedures. The other two samples were treated with 1N H_2SO_4 and 30% hydrogen peroxide to destroy the organic matter. The H_2O_2 digestion was intended to destroy organic matter only without affecting the release of inorganically fixed NH_4^+ . The soil was then analyzed for total N bound organically.

3.1.7 Experiment VI: Interactions of Ammonium Yielding Fertilizers in pH Ammended Soils.

Two slightly acid soils, Pine Ridge and Wellwood, and two slightly alkaline soils, Newdale and Almasippi, were used for this study. Sources of labelled N used were $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ for reasons given in experiment IV(i). The study was set out to ascertain if the amount of N fixed in Pine Ridge and Wellwood soils could be reduced by liming these soils and if Newdale and Almasippi soils would fix more N when acidified.

Pine Ridge soil (pH 5.8) was limed with 0.628 g (6.28 mmole) CaCO_3 per 50 g soil to increase the pH to 7.5. Wellwood soil (pH 6.0) was limed with 2.634 g (26.34 mmole) CaCO_3 per 50 g soil to increase the pH to 7.5. Newdale soil (pH 7.4) was acidified to pH 5.5 with 1.96 ml of 2M H_2SO_4 (3.92 mmole) per 50 g soil. Almasippi soil (pH 7.7) was also acidified to pH 5.5 with 3.23 ml of 2M H_2SO_4 (6.46 mmole) per 50 g soil. Water was added to bring the soils to field capacity. The soils were preincubated for 1 week at 20°C before N additions were made. Amount of N added and procedures for incubation were as explained for experiment IV. Soil samples were taken at 1, 2, 4, 6, 10, 14, 28 and 56 days after incubation. The soils were analyzed for total inorganic N and organic N. Soil moisture contents at the time of sampling were also determined.

3.1.8 Experiment VII: Utilization of Nitrogen from ^{15}N -labelled Fertilizers by Wheat Grown on pH Ammended Soils.

Four soils, Pine Ridge, Wellwood, Newdale and Almasippi were used for this investigation. The pH of these soils were adjusted as explained in experiment VI. Pine Ridge and Wellwood soils were limed to pH 7.5 with 27.28 g and 105.36 g CaCO_3 per 2 kg soil, respectively. Newdale soil was acidified with 78.4 ml 2M H_2SO_4 , and Almasippi soil with 129.2 ml 2M H_2SO_4 per 2 kg soil to bring both soils to pH 5.5. Sources of labelled N used were $(\text{NH}_2)_2\text{CO}$; $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$. The labelling in the N sources were 20.8; 17.7 and 21.1% excess for urea, calcium nitrate and ammonium sulphate, respectively. The soils were preincubated at 20°C for 1 week before adding N-fertilizers and seeding. Wheat (c.v. Neepawa) was grown for 52 days in the growth chamber, under the same condition as stated for the first experiment. Each treatment was replicated four times. Added N-sources provided 100 ppm N. All subsequent experimental and analytical procedures were as obtained for experiment I. Soil pH at harvest time was also determined.

3.2 ANALYTICAL PROCEDURES

3.2.1 Soil pH

Soil pH was determined according to the procedures outlined by Schofield and Taylor (1955). A 1:2 ratio (w/v) of soil to 0.01 M CaCl_2 solution was prepared. Samples were shaken and allowed to equilibrate for 30 minutes. Soil pH measurement was made with a digital pH meter equipped with glass and calomel electrode (Model 801, Ionalyzer Orion Research).

3.2.2 Organic Matter

The potassium dichromate-conc. H_2SO_4 oxidation method described by Peech et al. (1947) was used to determine the soil organic matter. After oxidizing the sample, the excess chromic acid in the solution was back-titrated with 0.5N $FeSO_4$, using an automatic titrator which measured the oxidation-reduction potential electrometrically.

3.2.3 Calcium Carbonate

A one-gram soil sample was digested in 10% HCl for 10 minutes. Carbon dioxide evolved was drawn through a drying absorption train. The CO_2 was absorbed by ascarite in a Nesbitt tube. The weight of CO_2 absorbed was determined. The carbonate content of the soil was then calculated.

3.2.4 Cation Exchange Capacity

The cation exchange capacity was determined by the ammonium saturation method described by Chapman (1965). A 25 g soil sample was shaken for 1 hour with 50 ml 1N NH_4OAc (pH 7.0). After filtering, the excess NH_4OAc was washed from the soil with 200 ml 99% isopropyl alcohol. The NH_4^+ -saturated soil was leached with 10% acidified NaCl to remove ammonium from the exchange sites. The leachate was distilled into 50 ml boric acid (2%) solution. The ammonium in the distillate was determined by titration with 0.1N H_2SO_4 .

3.2.5 Electrical Conductivity

The conductivity of a soil-water saturated paste extract was measured with a Radiometer direct reading conductivity metre (Type CDM 2, Bach-Simpson Ltd.).

3.2.6 Available Phosphorus (NaHCO₃ Method)

Sodium bicarbonate extractable P was determined as outlined by Olsen et al. (1954). Five grams of soil were shaken for 30 minutes with 100 ml of 0.5N NaHCO₃ extracting solution (pH 8.5). The sample was filtered and 25 ml of filtrate was treated with 5 ml of mixed reagent (7.5 g ammonium paramolybdate, 0.14 g antimony potassium tartrate and 88 ml sulphuric acid). After allowing this to stand for five minutes, the absorbance was read on Cecil Spectrophotometer.

3.2.7 Moisture Content at Field Capacity

An air dried soil sample was placed in a graduated cylinder. Sufficient water was added to wet the upper half of the soil column. The cylinder was covered with plastic film fastened with a rubber band. The soil was allowed to equilibrate for 4 days. A sample of the soil was taken from above the wetting front in the cylinder. The soil sample was dried in the oven at 105°C and moisture content was calculated.

3.2.8 Total Nitrogen to include Nitrite plus Nitrate

Total nitrogen of the soil was determined as described by Bremner (1965). A five-gram moist soil sample was treated with 5% potassium permanganate to oxidize nitrite to nitrate. This was followed by the addition of 20 ml of 50% H_2SO_4 solution. Reduction of nitrate to ammonium was accomplished by adding 2 g iron powder and predigesting at low heat for 40-45 minutes. One Kelpak (0.3 g $CuSO_4$ plus 10 g K_2SO_4) and 20 ml conc. H_2SO_4 were added. This was followed by the conversion of organic N to ammonium N by digesting at full heat for 1 hour. The ammonium in solution was converted to ammonia by the addition of 75 ml 50% NaOH solution. The liberated ammonia was collected in 50 ml 0.1N H_2SO_4 containing mixed indicator, the excess H_2SO_4 was back titrated with 0.1N NaOH and N content of the sample was calculated. This method results in overestimation of ammonium in solution from soils having high amine content. In such case, use of MgO will be more appropriate. In surface soils, a high amount of amine does not normally occur since the soil is aerobic. Hence the 50% NaOH method which has been routinely adopted in this department was used.

Following titration the solution was acidified with 1 drop of conc. H_2SO_4 . This solution was concentrated to 5 ml on a hot plate. The concentrated solution was converted to nitrogen gas by treatment with sodium hypobromite ($NaOBr$). The nitrogen gas was analyzed for mass to charge (m/e) ratio of 28 and 29 on Mass Spectrometer as described by Cho and Sakdinan (1978).

3.2.9 Total Inorganic Nitrogen by Distillation

Ten grams of moist soil was shaken for 1 hour in 50 ml 2N KCl solution to extract inorganic nitrogen. The soil suspension was filtered and the residue leached with 100 ml 2N KCl. The soil extract was placed in a Kjeldahl flask and 1.5 g Devarda's alloy was added to reduce NO_3^- to NH_4^+ . The extract was treated with 20 ml 50% NaOH and distilled into 50 ml 0.1N H_2SO_4 containing a mixed indicator. The distillate was back-titrated with 0.1N NaOH. Further procedures for determination of N and measurement of ^{15}N were as described for total N determination.

3.2.10 Soil Organic Nitrogen

A portion of the soil residue from the preceding determination was placed in a Kjeldahl flask. One Kelpak and 30 ml conc. H_2SO_4 were added. This was digested at full heat for 1 hour to convert the organic N to ammonium N. Also to release organically fixed N, a second portion of the soil residue was digested with 30% H_2O_2 - H_2SO_4 (dil.) as described by McKenzie and Wallace (1953) to determine organic nitrogen only. Subsequent procedures for nitrogen and ^{15}N determinations were as earlier described for total N.

3.2.11 Ammonium Nitrogen

The inorganic nitrogen was extracted by shaking 10 g of moist soil in 100 ml 2N KCl solution for one hour. The suspension was filtered through a Whatman No. 42 filter paper. To a 50 ml aliquot of the filtrate 0.5 ml of 10M NaOH was added. The solution was thoroughly mixed

and direct reading was taken on the ammonium electrode - Orion Model 801 digital pH/mv meter. A calibration curve was constructed each time a new set of samples was analyzed. The standard solutions consisted of 1.0, 2.5, 5.0, 8.0, 10.0 and 100 ppm of NH_4Cl .

3.2.12 Nitrite and Nitrate Nitrogen

Nitrite and nitrate nitrogen were determined using an aliquot of soil extract obtained for the ammonium determination. Nitrite and the sum of nitrate and nitrite were determined colorimetrically using a Technicon autoanalyzer as outlined by Kamphake et al. (1967). A reagent blank and standard soil sample were included with each set of 48 samples analyzed. Standard solutions and calibration curves were prepared in order to obtain nitrite and nitrate concentration in ppm.

3.2.13 Total Nitrogen (Plant)

A two-gram samples of plant material with 1 Kelpak added was treated with 25 ml conc. H_2SO_4 . This was digested until the contents of the flask became clear. The digested plant material was treated with 250 ml water and 50 ml of 50% NaOH. This was followed by distillation into 50 ml 0.1N H_2SO_4 . Subsequent procedures for N determination are the same as explained for total nitrogen in soil.

3.2.14 ¹⁵N Analysis

Determination of ¹⁵N abundance in soil or plant material involved Kjeldahl digestion of soil or plant material as described earlier. The concentrated ammonium from the distillate was converted to molecular nitrogen by treatment with sodium hypobromite (NaOBr) in a vacuum system as described by Cho (1980) (personal communication).

The nitrogen gas was analyzed by the mass spectrometer for m/e 28 and 29. The ¹⁵N abundance was expressed as atom percent ¹⁵N excess. This was calculated by using the following equations:

$$\text{Atom \% } ^{15}\text{N Excess} = 100/(2R + 1) - B.$$

where R is the ratio of the relative peak heights of mass to charge (m/e) ratio of 28 and 29. The value B represents atom percent ¹⁵N in the atmosphere.

The ammonium solution from the soil inorganic nitrogen extraction usually contains a relatively small amount of N. Thus, the nitrogen gas generated after treatment with NaOBr is also very small. It was, therefore, necessary to have an increased pressure in the reaction vessel to transfer N₂ from the reaction vessel to the gas container and from gas container to the mass spectrometer (micromass 602C). Argon gas at a pressure of 40 mm Hg was introduced into the reaction vessel before NH₃ oxidation so that the total pressure in the gas container becomes higher than that due to produced N₂ alone. Such an elevated pressure was found necessary to have appreciable peak heights of m/e 28 and 29.

Chapter IV

RESULTS AND DISCUSSIONS

4.1 EXPERIMENT 1: UTILIZATION OF NITROGEN FROM ^{15}N -LABELLED UREA AND CALCIUM NITRATE BY WHEAT GROWN ON VARIOUS SOILS.

The purpose of this investigation was to evaluate, under a controlled environment, the efficiency of $(\text{NH}_2)_2\text{CO}$ and $\text{Ca}(\text{NO}_3)_2$ as nitrogen sources for wheat on various Manitoba soils. A second objective was to ascertain the extent to which added N from these sources could be recovered in the plant and the soil using ^{15}N -labelled carriers. The experiment was carried out in clay pots each containing 2 kg of air-dried soil. The soils were treated with ^{15}N -labelled $(\text{NH}_2)_2\text{CO}$ and $\text{Ca}(\text{NO}_3)_2$ at rates sufficient to supply 100 ppm N based on an air dry soil weight. Wheat was grown in the growth chamber at 20°C for 52 days. Dry matter yields of shoots and roots were measured. Both the plant parts and soil samples were analyzed for total nitrogen. Performance of the nitrogen sources were assessed by using (a) uptake of N by plant in the above ground portion and in roots (b) residual N in soil at the end of the experiment (c) standard isotope criteria, i.e., percent N derived from fertilizer (%N.d.f.f.); nitrogen 'A' values and % utilization of added N were carried out on a comparative basis.

4.1.1 Dry Matter and Total N-yields of Wheat

The dry matter yield of shoot in $(\text{NH}_2)_2\text{CO}$ -treated soils ranged from a low of 5.32g per pot in Granville soil to a high of 23.9g per pot in the Red River soil (Table 3). With $\text{Ca}(\text{NO}_3)_2$ -treated soils corresponding values ranged from 7.94 to 23.3g per pot. Here again the highest yield was obtained from the Red River soil. The lowest yield was obtained from the Pine Ridge soil. There were significant differences in dry matter yield of wheat between soils with both N-sources. These yield differences were greater with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$. In terms of dry matter yield, the soils were nearly in the same order for both N-carriers. There were three soils (Pine Ridge, Wellwood and Granville) in which the yield was significantly greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$. The average difference in favour of $\text{Ca}(\text{NO}_3)_2$ for these soils was 35.5 percent. The yield on two of these soils (Pine Ridge and Granville) was significantly lower than yield on the other soils with both N carriers. With the other five soils the yield difference between carriers was considerably smaller and in one of these (Almasippi soil) the yield was significantly greater with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$. The yield data suggest that $\text{Ca}(\text{NO}_3)_2$ is the more available nitrogen carrier, especially on the slightly acid soils (Pine Ridge, Wellwood and Granville).

Total N yield is a yield-dependent parameter and it ranged from 94.13 mg per pot with $(\text{NH}_2)_2\text{CO}$ in Granville to 329.47mg per pot with $\text{Ca}(\text{NO}_3)_2$ in Red River. There appears to be an inverse relationship between yields and N percentage of the plant tissue. The lower the yield the

TABLE 3

Dry matter and total N-yields in the above ground portion
of wheat grown on various soils treated with $(\text{NH}_2)_2\text{CO}$
and $\text{Ca}(\text{NO}_3)_2$ at 100 ppm N (200 mg/pot)

Soil Name	Yield (g/pot)		N-Yield (mg/pot)	
	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$
Pine Ridge	5.89h	7.94g	138.30	145.80
Wellwood	12.57ef	14.31cd	143.27	157.04
Granville	5.32h	8.39g	94.13	105.38
Waitville	11.62f	12.84def	136.80	145.07
Holland	14.73c	14.08cde	151.54	159.75
Red River	23.90a	23.33a	327.75	329.47
Newdale	13.79cde	14.07cde	199.93	208.55
Almasippi	16.11b	14.69c	157.88	160.11

*Means not followed by the same letter differ at a 0.05 probability level according to Duncan's multiple range test.

higher the N percentage thus reducing the gap in total N-yield between low and high dry-matter yield samples. In all the soils, the total N-yield was greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$. This showed that plant uptake of N from $\text{Ca}(\text{NO}_3)_2$ source was better than N uptake from $(\text{NH}_2)_2\text{CO}$.

4.1.2 Nitrogen Derived from N-carriers and Percent Utilization of Added N

The isotope derived criteria commonly used to evaluate the comparative availability of different N-sources include: Percent nitrogen derived from fertilizer (percent N.d.f.f), 'A' values and percent utilization of added N. The first two values are yield independent parameters that is their calculation does not require the assessment of plant yield. Percent N.d.f.f. was significantly different between the soils with both N-carriers (Table 4). Nitrogen derived from $\text{Ca}(\text{NO}_3)_2$ source was significantly greater than N derived from $(\text{NH}_2)_2\text{CO}$ in Granville and Waitville soils. In Red River soil %N.d.f.f. was greater with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$. Differences in percent N.d.f.f. between the N-carriers were not significant in the other five soils.

Percent utilization of added-N is a yield-dependent criterion, and it ranged from 30.61% with $(\text{NH}_2)_2\text{CO}$ in Granville to 55.26% with $(\text{NH}_2)_2\text{CO}$ in Red River. In seven of the eight soils used, utilization of added-N as $\text{Ca}(\text{NO}_3)_2$ was greater than that of $(\text{NH}_2)_2\text{CO}$. It was only significantly greater in Wellwood, Granville and Waitville soils. With Red River soil utilization of nitrogen from urea was significantly greater than from

TABLE 4

Nitrogen derived from N-carriers in wheat
tops and utilization of added N

Soil Name	N D F F (%)		Utilization (%)	
	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$
Pine Ridge	54.21c	55.30c	37.44efg	40.32cde
Wellwood	48.91ef	49.68ef	35.03gh	39.01def
Granville	65.00b	68.59a	30.61i	36.13fg
Waitville	48.63f	50.24e	33.25hi	36.45fg
Holland	52.47d	51.89d	39.76de	41.45bcd
Red River	33.72h	32.50i	55.26a	53.55a
Newdale	41.36g	41.60g	41.35bcd	43.40b
Almasippi	54.29c	54.59c	42.86bc	43.72b

*Means within the same parameters, not followed by the same letter differ at 0.05 probability level according to Duncan's multiple range test.

calcium nitrate. Percent utilization of added N varied considerably between the soils. The lowest percent utilization was obtained from Granville soil with both carriers. On the other hand, Red River soil showed the highest utilization with both sources of added N. The four slightly acid soils showed greater differences in percent utilization of N between the two carriers than the slightly alkaline soils. More of the nitrogen added as $\text{Ca}(\text{NO}_3)_2$ was utilized by wheat than N added as $(\text{NH}_2)_2\text{CO}$, especially in the slightly acid soils. Thus the uptake of N from NH_4^+ source, urea, was slower and less than that from NO_3^- source. This could be partially due to the adsorption and fixation of the ammonium ions to the soil particles.

4.1.3 Yield and Percent Utilization of Added N by Wheat Roots

As with the tops, there were significant differences in root yield between the soils (Table 5). The yield of roots ranged from 1.69g per pot in Granville soil treated with $(\text{NH}_2)_2\text{CO}$ to 7.24g per pot in $\text{Ca}(\text{NO}_3)_2$ treated Wellwood soil. Root yield on Pine Ridge and Wellwood soils was significantly greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$. There was no significant difference in root yield between the N-sources in the remaining six soils. In Pine Ridge, Wellwood and Granville soils a significantly greater percentage of nitrogen added as $\text{Ca}(\text{NO}_3)_2$ than as $(\text{NH}_2)_2\text{CO}$ was utilized by roots. There was no significant difference in utilization of added N between the two carriers in the other five soils. Nitrogen from $\text{Ca}(\text{NO}_3)_2$ was utilized to a significantly greater degree than N from $(\text{NH}_2)_2\text{CO}$ in three of the four slightly acid soils.

TABLE 5

Dry matter yield and percent utilization
of added-N of wheat roots

Soil Name	Yield (g/pot)		Utilization (%)	
	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$
Pine Ridge	4.65ef	5.98bc	12.14b	14.56a
Wellwood	5.52bcde	7.24a	12.40b	14.37a
Granville	1.69h	2.43h	4.66g	6.62ef
Waitville	3.81g	3.50g	8.16de	7.42ef
Holland	3.91fg	3.39g	6.92ef	6.15fg
Red River	6.25b	6.23b	8.11de	7.52ef
Newdale	5.27cde	5.04de	9.83cd	9.59cd
Almasippi	5.55bcd	4.89de	10.22c	9.66cd

*Means within the same parameters, not followed by the same letter differ at 0.05 probability level according to Duncan's multiple range test.

4.1.4 The "A" Values of the Experimental Soils

The 'A' value is a yield-independent criterion and it is defined as the amount of available nutrient in a particular source, for example soil, measured in terms of a fertilizer standard. This is based on the concept that if a plant is confronted by two sources of a nutrient, it will take up nutrient from each source in direct proportion to the amount available. The 'A' value was calculated using the following equation:

$$A = B \frac{(\%^{15}\text{N excess standard})}{(\%^{15}\text{N excess sample})} - 1$$

where A = available soil nitrogen in ppm of dry soil weight.
B = the amount of labelled N-fertilizer added in ppm.

The 'A' value data, based on above ground portion (Table 6) provides a measure of the availability of the soil nitrogen in the eight soils during the 52-day growth period. The 'A' values of the experimental soils, as calculated from $\text{Ca}(\text{NO}_3)_2$ ranged from 46 ppm (Granville soil) to 207 ppm (Red River soil). Thus the soil (Granville) which produced the least dry matter yield had the least available N while Red River soil with highest yield production had the highest 'A' value. As the yield is not related to 'A' value alone, there is no clear cut relation between 'A' value and yield among the remaining six soils. The 'A' values obtained with urea are in nearly the same order of magnitude as those obtained with NO_3^- . It was, however, noticed that the values obtained with urea were generally higher than those with NO_3^- on all acid soils.

The two values are nearly equal, for neutral to alkaline soils, with the exception of those obtained with Red River soil. It was speculated that a difference in 'A' value measured using different N-sources may be due to N-source itself rather than to soil N. Thus, the relative efficiency of one carrier as compared to the other was estimated by assuming that the 'A' value of the soil obtained from NO_3^- source remained constant. Such a calculation using 'A' value obtained from NO_3^- as standard is listed in the last column of Table 6. Relative efficiency of urea as compared to $\text{Ca}(\text{NO}_3)_2$ ranged from 85.1 percent that of $\text{Ca}(\text{NO}_3)_2$ (Granville soil) to 105.6% that of $\text{Ca}(\text{NO}_3)_2$ (Red River soil). The data suggest that N from $\text{Ca}(\text{NO}_3)_2$ is more available than N from $(\text{NH}_2)_2\text{CO}$ especially on slightly acid Pine Ridge, Wellwood, Granville and Waitville soils. However, NO_3^- did not seem to be as available as urea on Red River soil. This could probably be due to possible loss of N from NO_3^- source as the soil was very heavy in texture.

4.1.5 Total Nitrogen Balance

The distribution of the two nitrogen carriers in plant and soil at the end of the experiment together with the estimated loss from the soil-plant system (unrecovered N) is given in Table 7. In most of the soils, the total nitrogen in the plant was greater from $\text{Ca}(\text{NO}_3)_2$ than from $(\text{NH}_2)_2\text{CO}$. The average values of N recovered by plants were 48.5 and 51.3% for urea and $\text{Ca}(\text{NO}_3)_2$, respectively. This confirms the relative inefficiency of $(\text{NH}_2)_2\text{CO}$ as a source of N for wheat under the con-

TABLE 6 "A" Values of the experimental soils measured using $\text{Ca}(\text{NO}_3)_2$ and urea and relative efficiency of the urea as compared to $\text{Ca}(\text{NO}_3)_2$

Soil Name	"A" Value (ppm)		Urea efficiency (%) (100 ppm = $\text{Ca}(\text{NO}_3)_2$)
	(NO_3^-)	Urea	
Pine Ridge	81	84	95.7
Wellwood	101	104	96.9
Granville	46	54	85.1
Waitville	99	106	93.8
Holland	93	91	102.4
Red River	207	197	105.6
Newdale	140	142	99.0
Almasippi	83	84	98.8

ditions in which the experiment was conducted. The amount of labelled ^{15}N remaining in the soil was greater with $(\text{NH}_2)_2\text{CO}$, than with $\text{Ca}(\text{NO}_3)_2$. The average value of N remaining in the soils after the removal of plant top and roots were 34.9 and 25.7% for urea and $\text{Ca}(\text{NO}_3)_2$, respectively. Thus, recovery of total nitrogen from both plant and soil was greater from $(\text{NH}_2)_2\text{CO}$ than from $\text{Ca}(\text{NO}_3)_2$. Hence, the calculated nitrogen loss from the two N-carriers was greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$ in most of the soils (23.1 and 16.6% respectively). The inefficient utilization of urea by plant was the result of immobilization or fixation of N from urea by soil constituents. The higher value of unaccounted for N from $\text{Ca}(\text{NO}_3)_2$ may possibly be due to denitrification.

4.1.6 Summary

This investigation showed better utilization of added-N from $\text{Ca}(\text{NO}_3)_2$, by wheat than from $(\text{NH}_2)_2\text{CO}$ in the Pine Ridge, Wellwood, Granville and Waitville soils. The yield-independent isotope criterion, the 'A' value, suggests that $\text{Ca}(\text{NO}_3)_2$ is the more available nitrogen on these slightly acid soils. The 'A' value data support the conclusion that, for the above mentioned soils, $(\text{NH}_2)_2\text{CO}$ was less efficient as a nitrogen source for wheat. Dry matter yield of wheat from Pine Ridge, Wellwood and Granville soils was significantly greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$. Total nitrogen balance indicates that labelled ^{15}N remaining in the soil at the end of the experiment was consistently greater with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$. Since this residual N was not

TABLE 7 Total nitrogen balance (percent of added N-fertilizer)

Soil Name	Urea			Ca(NO ₃) ₂		
	Plant	Soil	Unrec. N.	Plant	Soil	Unrec. N
Pine Ridge	49.6	27.3	23.1	54.9	13.4	31.7
Wellwood	47.4	31.1	21.5	53.4	24.2	22.4
Granville	35.3	48.2	16.5	42.7	41.6	15.7
Waitville	41.5	43.2	15.3	43.9	32.0	24.1
Holland	46.7	41.4	11.9	47.7	33.6	18.7
Red River	63.4	29.7	6.9	61.1	21.4	17.5
Newdale	51.2	28.9	19.9	53.0	17.2	29.8
Almasippi	53.1	29.0	17.9	53.4	22.3	24.3
Average	48.5	34.9	16.6	51.3	25.7	23.1

Unrec N = Unrecovered N

readily available for plant uptake, it might have been adsorbed, fixed or otherwise immobilized in the soil system. As a result, total recovery of added N from $(\text{NH}_2)_2\text{CO}$ was equal to, and in most cases greater than N recovery from $\text{Ca}(\text{NO}_3)_2$. The unrecovered N was somewhat greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$ in most of the soils. This may be due to a greater loss of N by denitrification in soils treated with $\text{Ca}(\text{NO}_3)_2$ than in soils treated with $(\text{NH}_2)_2\text{CO}$.

4.2 EXPERIMENT II: FORMS AND DISTRIBUTION OF INORGANIC N IN UREA $[(\text{NH}_2)_2\text{CO}]$ TREATED SOILS INCUBATED AT 20°C

The growth chamber experiment indicated that nitrogen remaining in the soil at harvest in $(\text{NH}_2)_2\text{CO}$ -treated soil was greater than N in $\text{Ca}(\text{NO}_3)_2$ -treated soil. The purpose of this study was to ascertain the forms and distribution of inorganic N from $(\text{NH}_2)_2\text{CO}$ in the eight soils used. Urea was added to each soil in the amount of 500 ppm N on an air dry soil weight basis. Soil and fertilizer were thoroughly mixed, kept at field moisture capacity and incubated at 20°C for 33 days.

4.2.1 Distribution of Inorganic N in Pine Ridge Soil

Ammonium-N concentration in Pine Ridge soil decreased with increase in time of incubation (Figure 3). This was due to transformation of NH_4^+ -N to other inorganic forms and probably also to adsorption and fixation of NH_4^+ -N to soil particles. The presence of NH_4^+ -N throughout the incubation period indicates a slow oxidation of NH_4^+ -N in acid Pine Ridge soil. Accumulation of NO_2^- -N started slowly but did occur early

in the incubation period. Nitrite accumulation reached a maximum of 145 ppm N (29% of added N) after 12 days incubation. Concentration of NO_2^- -N remained constant at 90 ppm N between the 15th and 21st days, after which it slowly declined. A trace of NO_2^- -N persisted till the end of the incubation period. Nitrite accumulation in this soil was probably due to inhibition of biological oxidation of nitrite by Nitrobacter sp. Production of NO_3^- -N was slow up to the 24th day of incubation, during which time the concentration was below 35 ppm N. From 24th day onward, NO_3^- concentration increased with time until the end of the incubation period. The total inorganic N did not reach 500 ppm N at any time. This might be due to slow enzymatic hydrolysis of urea at the initial period and to loss of N at the later stage of incubation. Ammonium-N constituted the bulk of the total inorganic N throughout the incubation period. About 75% of added urea-N was recovered, mainly as NH_4^+ -N and NO_3^- -N at the end of the incubation period. Nitrogen deficit in this soil might be due to NH_4^+ -N fixation and denitrification of accumulated NO_2^- -N.

4.2.2 Distribution of Inorganic N in Wellwood Soil

The concentration of NH_4^+ -N in Wellwood soil followed a similar pattern to that obtained for Pine Ridge soil (Figure 4). Ammonium-N in Wellwood soil was more rapidly oxidized than in Pine Ridge soil, probably because Wellwood soil is less acidic than Pine Ridge. Presence of NH_4^+ -N was still observed at the end of the incubation period indicating a slow rate of oxidation of NH_4^+ -N in the slightly acid Wellwood soil.

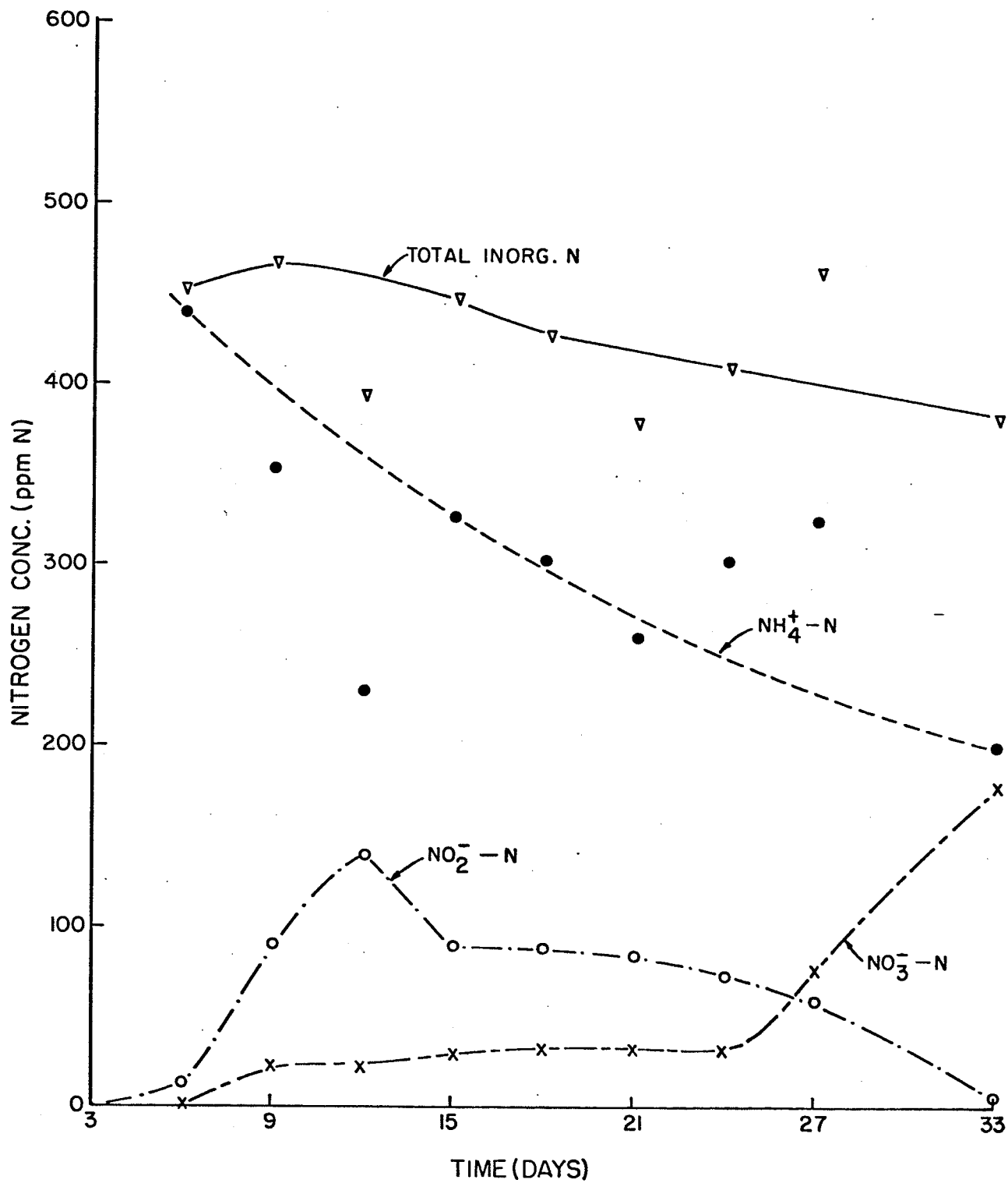


Figure 3: Ammonium, nitrite, nitrate and total inorganic nitrogen in Pine Ridge soil treated with urea-N at 500 ppm.

Nitrite accumulation occurred in Wellwood soil, but to a lesser degree than in Pine Ridge soil. The maximum concentration of NO_2^- -N was obtained on the 12th day of incubation. A small quantity of nitrite-N persisted until the end of the incubation period. Accumulation of NO_3^- started between three days and six days of incubation and continued until the end of the incubation period. Total inorganic N reached a maximum of 575 ppm N after 9 days of incubation. This is probably due to increased mineralization occurring in this soil. About 320 ppm N was recovered as total inorganic N at the end of the incubation period. Unrecovered N was presumably fixed or lost to the system through denitrification.

4.2.3 Distribution of Inorganic N in Granville Soil

Unlike the two previous soils, oxidation of ammonium-N in Granville soil was fast enough that no NH_4^+ -N was found after 21 days of incubation (Figure 5). Very little NO_2^- -N was measured. The highest concentration of 15 ppm NO_2^- -N was observed at 12 days of incubation. By the 18th day, all of the NO_2^- -N had disappeared. Production of nitrate-N was very rapid until the 27th day after which it levelled off. Total inorganic N at 6 days of incubation was 600 ppm N and decreased to 350 ppm N at the end of incubation. By the end of the experiment inorganic N was mainly in NO_3^- -N form. Since no substantial nitrite accumulated in Granville soil, N-loss in Granville might be mainly due to NH_4^+ -N fixation or immobilization, and not via chemical denitrification, the

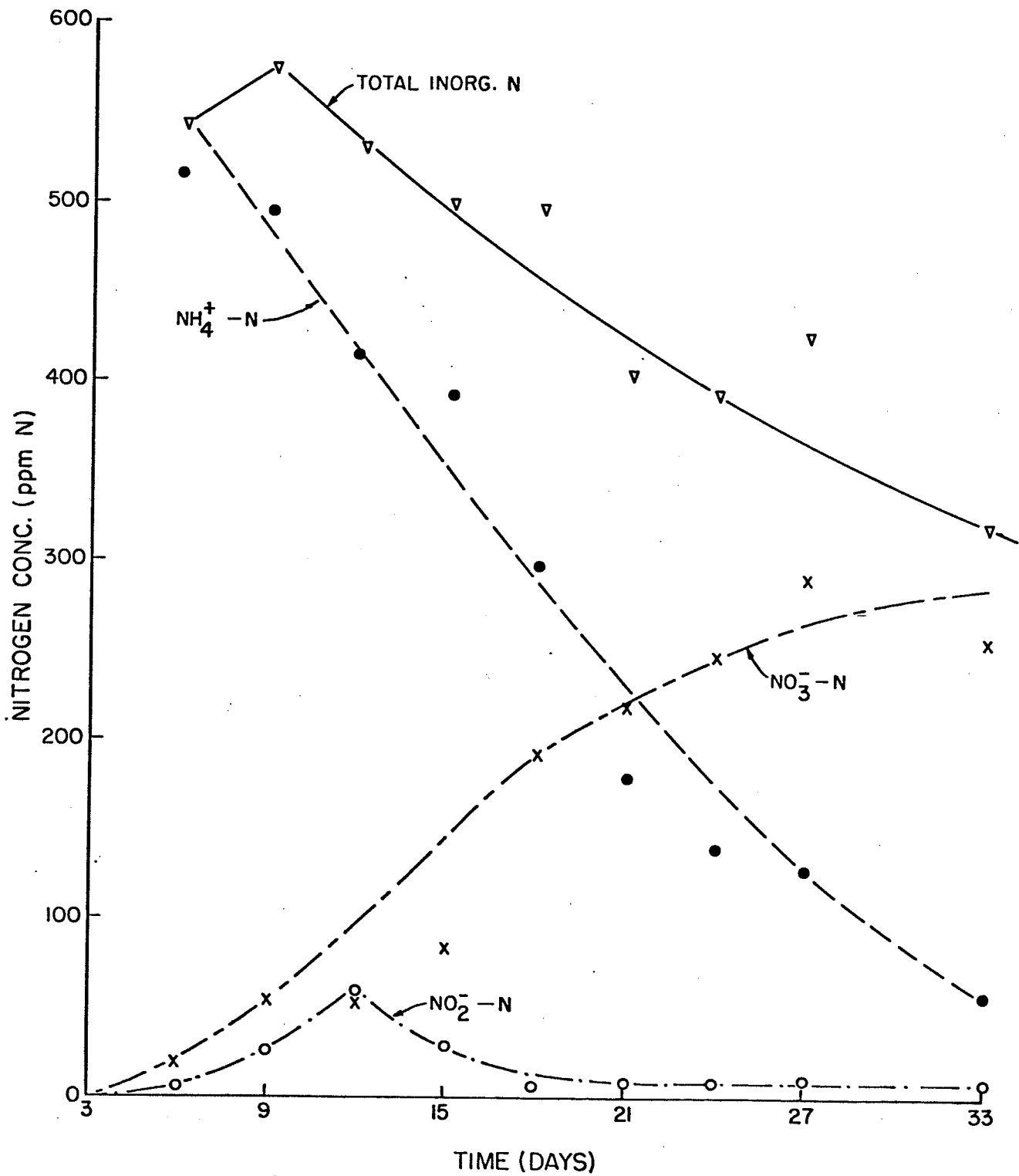


Figure 4: Ammonium, nitrite, nitrate and total inorganic nitrogen in Wellwood soil treated with urea-N at 500 ppm.

pathway of which includes NO_2^- . However biological denitrification could also have occurred.

4.2.4 Distribution of Inorganic N in Waitville Soil

In the Waitville soil the pattern of inorganic N distribution was similar to that in the Granville soil (Figure 6). There was no ammonium-N present after 18 days of incubation. The trace amount of NO_2^- -N formed in this soil was completely transformed by the 12th day of incubation. Nitrate-N production was rapid and it continued accumulating until the end of the incubation period. Mineralization of both soil-N and added urea was rapid in Waitville soil. The total inorganic N at 6 days was over 750 ppm N. This had decreased to 500 ppm N at the end of incubation. Total inorganic N towards the end of incubation was mainly in the form of nitrate-N.

4.2.5 Distribution of Inorganic N in Holland Soil

The concentration of NH_4^+ -N in Holland soil was 700 ppm N after 6 days of incubation (Figure 7). This high concentration of NH_4^+ -N may be due to increased microbial activity and rapid mineralization in Holland soil. By the 15th day of incubation, all the ammonium-N had been completely oxidized. Nitrite production was small and no trace of this was left by 15th day of incubation. Nitrate accumulation reached a maximum of 400 ppm N at 15 days of incubation. After this, NO_3^- -N concentration declined to about 250 ppm N at the end of the incubation period. This

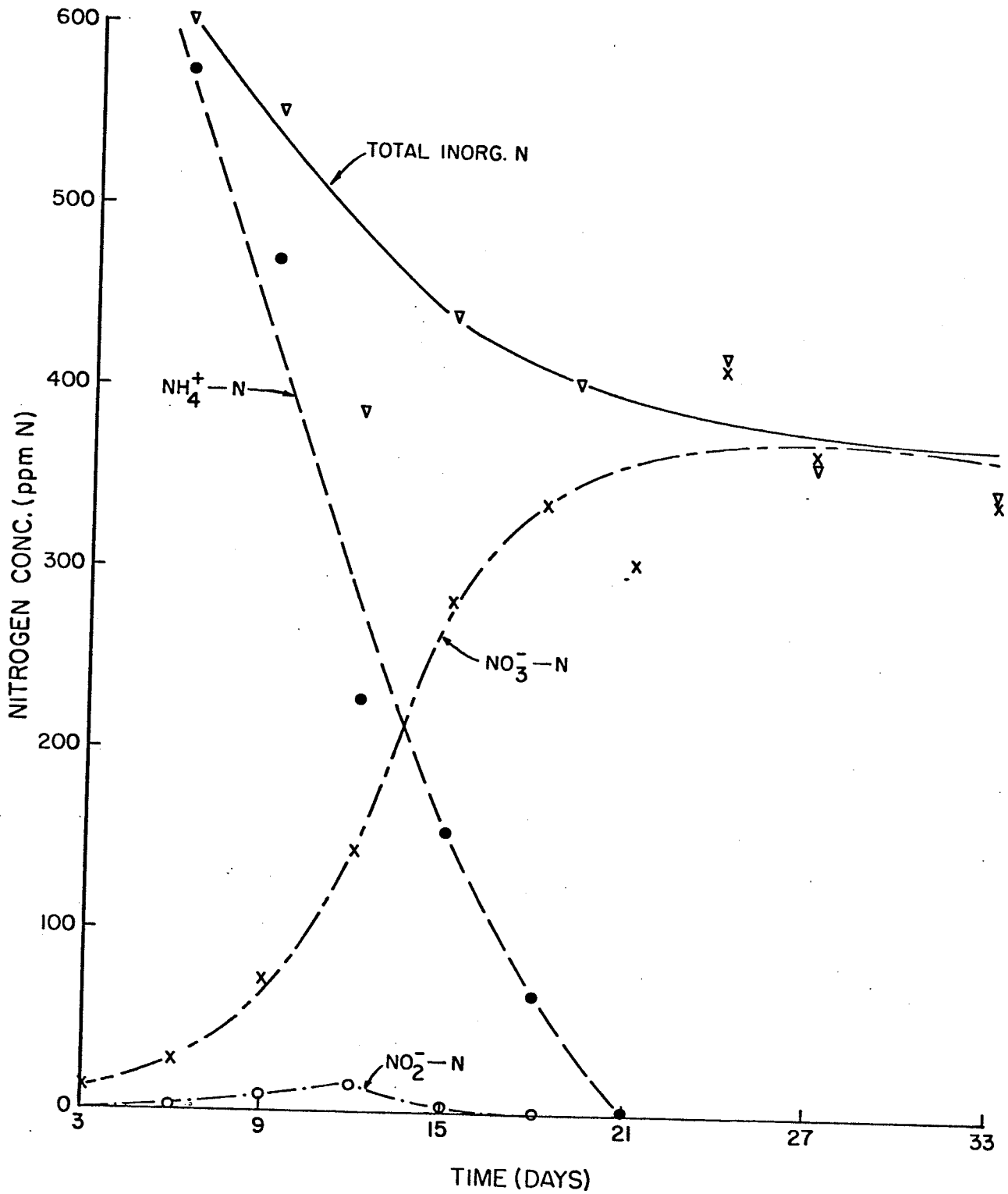


Figure 5: Ammonium, nitrite, nitrate and total inorganic nitrogen in Granville soil treated with urea-N at 500 ppm.

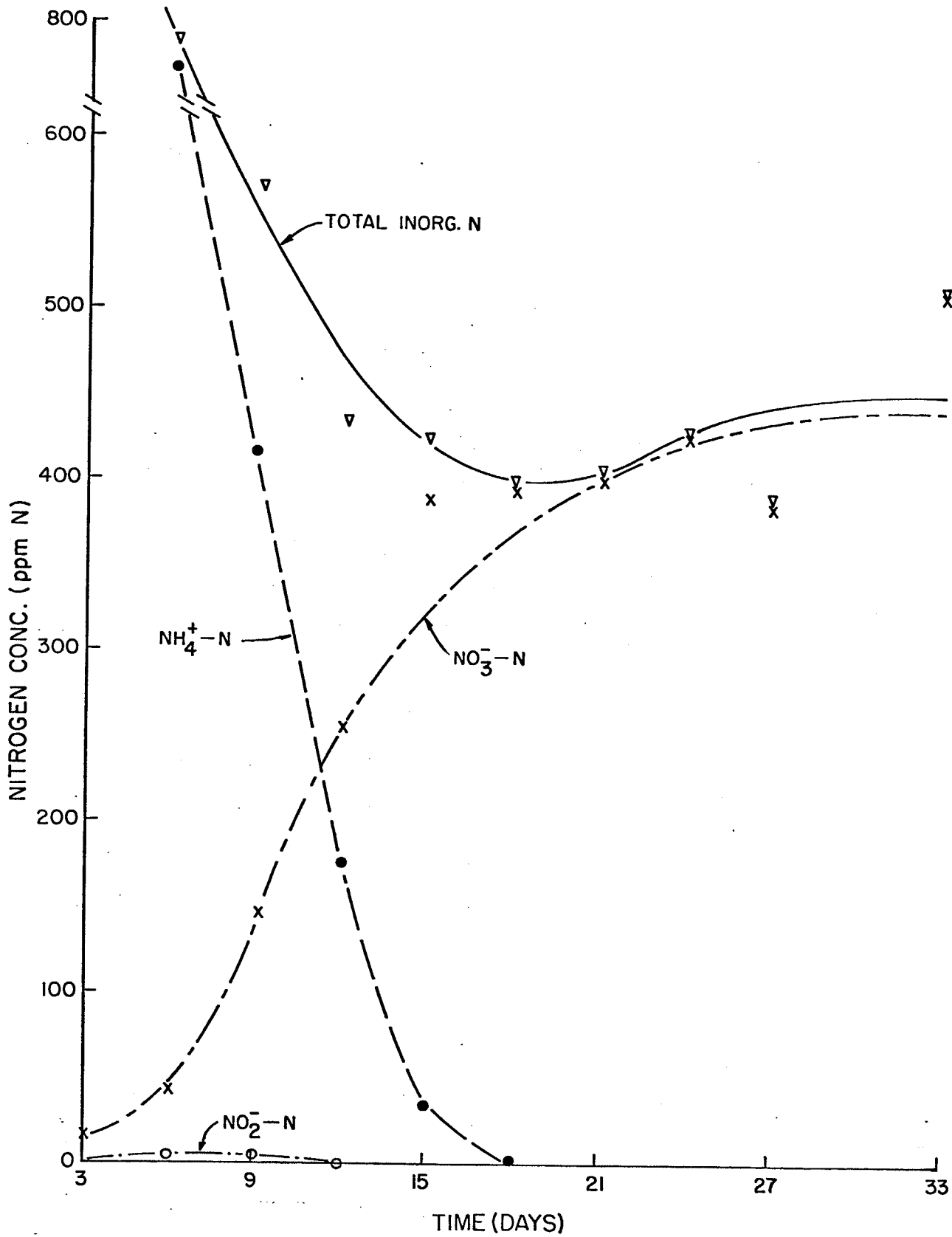


Figure 6: Ammonium, nitrite, nitrate and total inorganic nitrogen in Waitville soil treated with urea-N at 500 ppm.

decline may be due to immobilization of N in Holland soil. Total inorganic N at 6 days was about 800 ppm N and this was mainly in NH_4^+ -N form. From 15 days onward, total inorganic N was solely in the NO_3^- -N form. Transformation of NH_4^+ -N did not match the production of nitrate-N and NO_2^- -N formation was minimal.

4.2.6 Distribution of Inorganic N in Newdale Soil

Both hydrolysis of urea and oxidation of NH_4^+ -N were rapid in Newdale soil (Figure 8). All the NH_4^+ -N had disappeared by the 12th day of incubation. No substantial nitrite build up was observed. Production of NO_3^- -N started early in the incubation period and NO_3^- -N continued to accumulate during the first 18 days of incubation. The decline in nitrate-N concentration after 18 days may be due to immobilization of added-N. The total inorganic N decreased with time, and in the later period of incubation followed the same pattern as nitrate-N distribution. Over 80% of added-N was recovered in form of nitrate-N at the end of the incubation period.

4.2.7 Distribution of Inorganic N in Red River Soil

As was observed for Newdale soil, mineralization of both soil and added N was rapid in Red River soil (Figure 9). Concentration of NH_4^+ -N was 680 ppm N after 6 days of incubation. By the 18th day of incubation all the NH_4^+ -N had been completely nitrified. There was virtually no nitrite accumulation in Red River soil. Nitrate-N increased very rapid-

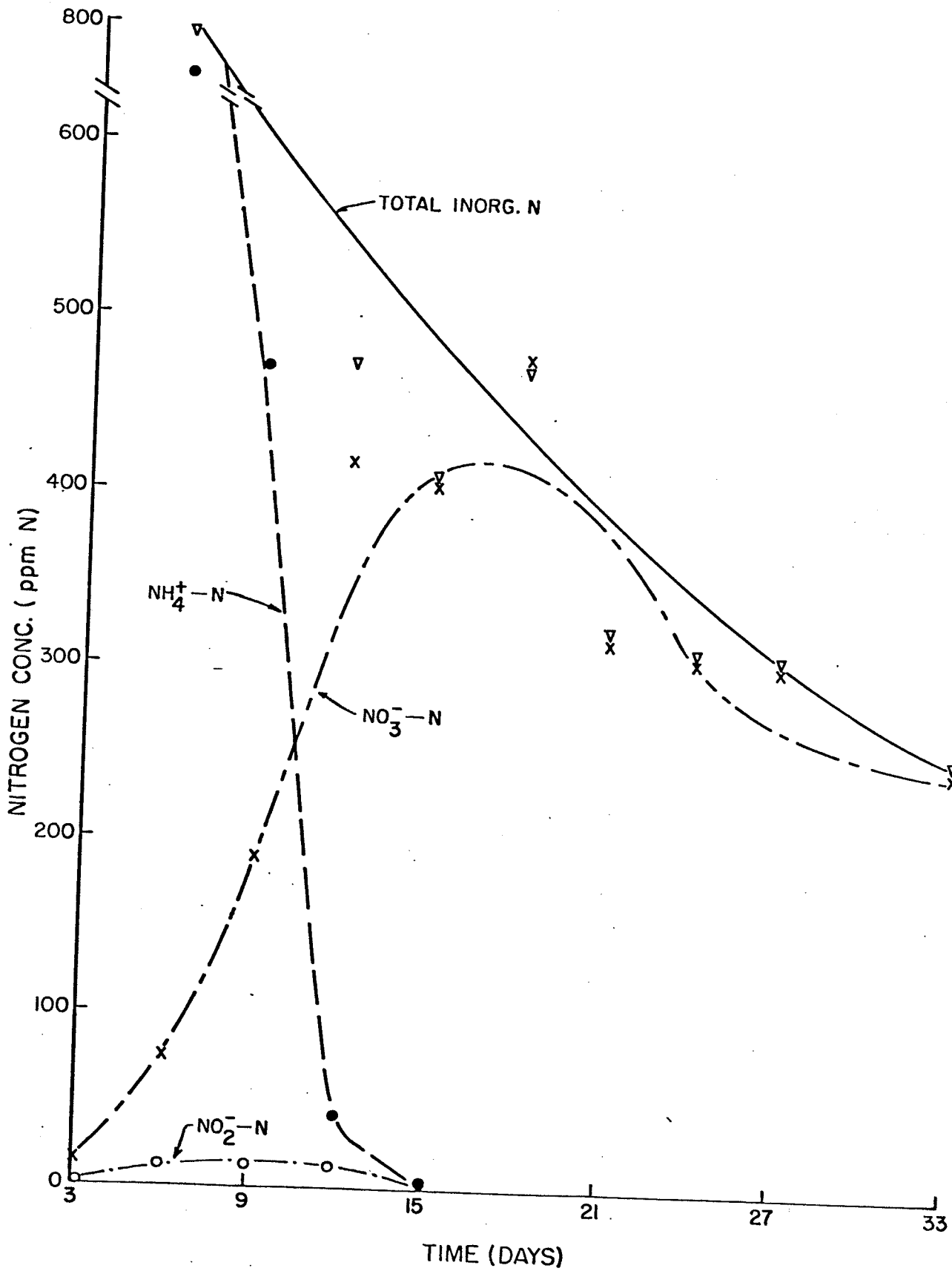


Figure 7: Ammonium, nitrite, nitrate and total inorganic nitrogen in Holland soil treated with urea-N at 500 ppm.

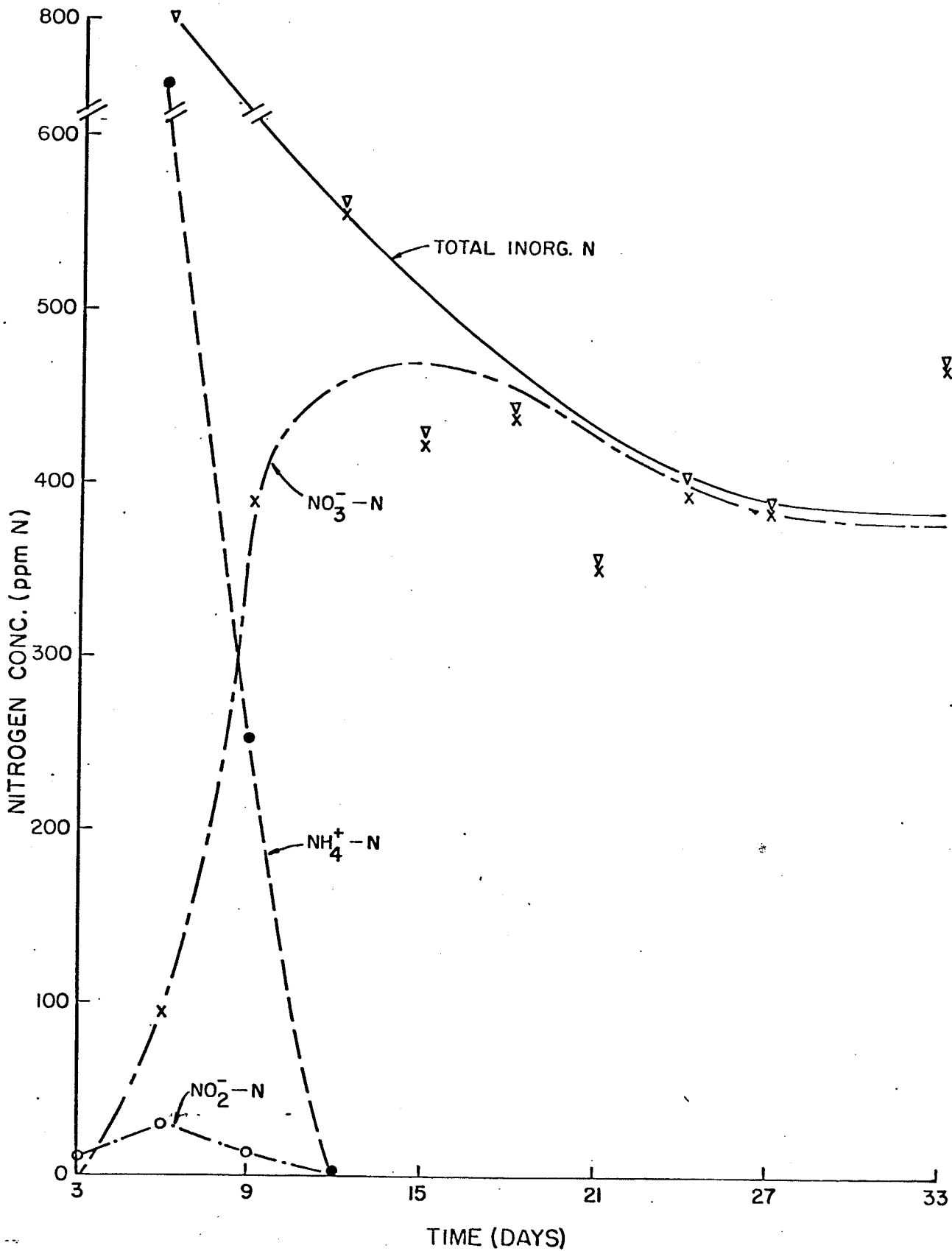


Figure 8: Ammonium, nitrite, nitrate and total inorganic nitrogen in Newdale soil treated with urea-N at 500 ppm.

ly and reached a maximum of 425 ppm N after 15 days of incubation. By the 21st day the nitrate-N content had started to decrease. Total inorganic N decreased from 770 ppm N at 6 days to 285 ppm N at the end of the incubation. This considerable N-loss might probably be due to denitrification of NO_3^- -N in this soil, as this soil had very high clay content.

4.2.8 Distribution of Inorganic N in Almasippi Soil

Nitrification of NH_4^+ -N was rapid in the alkaline Almasippi soil, such that no NH_4^+ -N remained in the soil at 15th day of incubation (Figure 10). A considerable amount of nitrite accumulated early in the period of incubation. Nitrite-N attained its maximum concentration of 270 ppm N by 12th day of incubation. Accumulation of nitrite-N in Almasippi soil may be due to inhibition of nitrite oxidizing bacteria. All the accumulated nitrite was completely transformed by the 21st day of incubation. Formation of NO_3^- -N started very early and kept increasing until the end of the incubation period. The total inorganic N was high initially, and then decreased to 460 ppm N at 15th day, but kept increasing thereafter. This decrease in total inorganic N followed by an increase may have been due to immobilization process taking place in the soil with the immobilized nitrogen subsequently being mineralized. Recovery of N in the mineral form at the end of the experiment was 658 ppm and hence exceeded that added as urea.

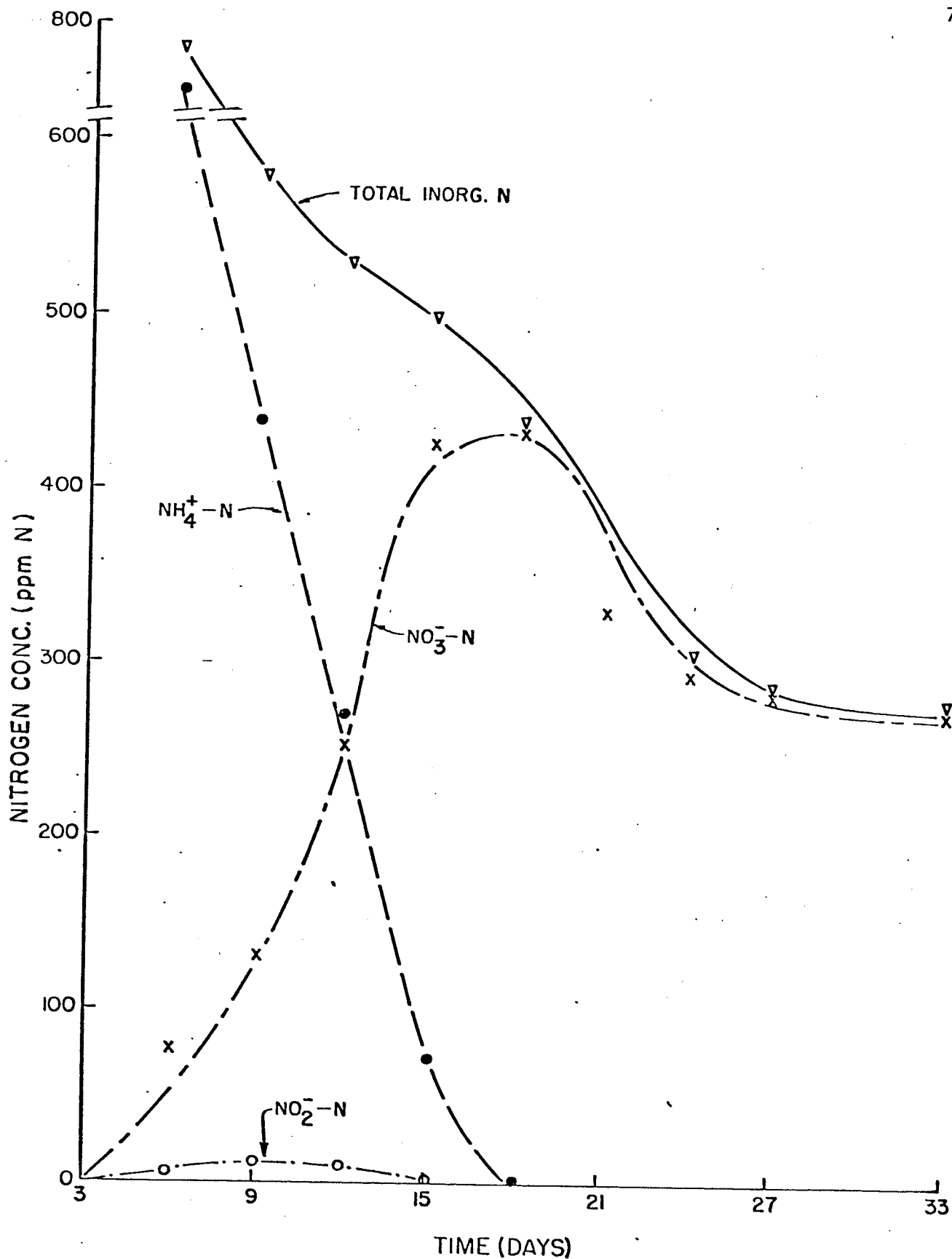


Figure 9: Ammonium, nitrite, nitrate and total inorganic nitrogen in Red River soil treated with urea-N at 500 ppm.

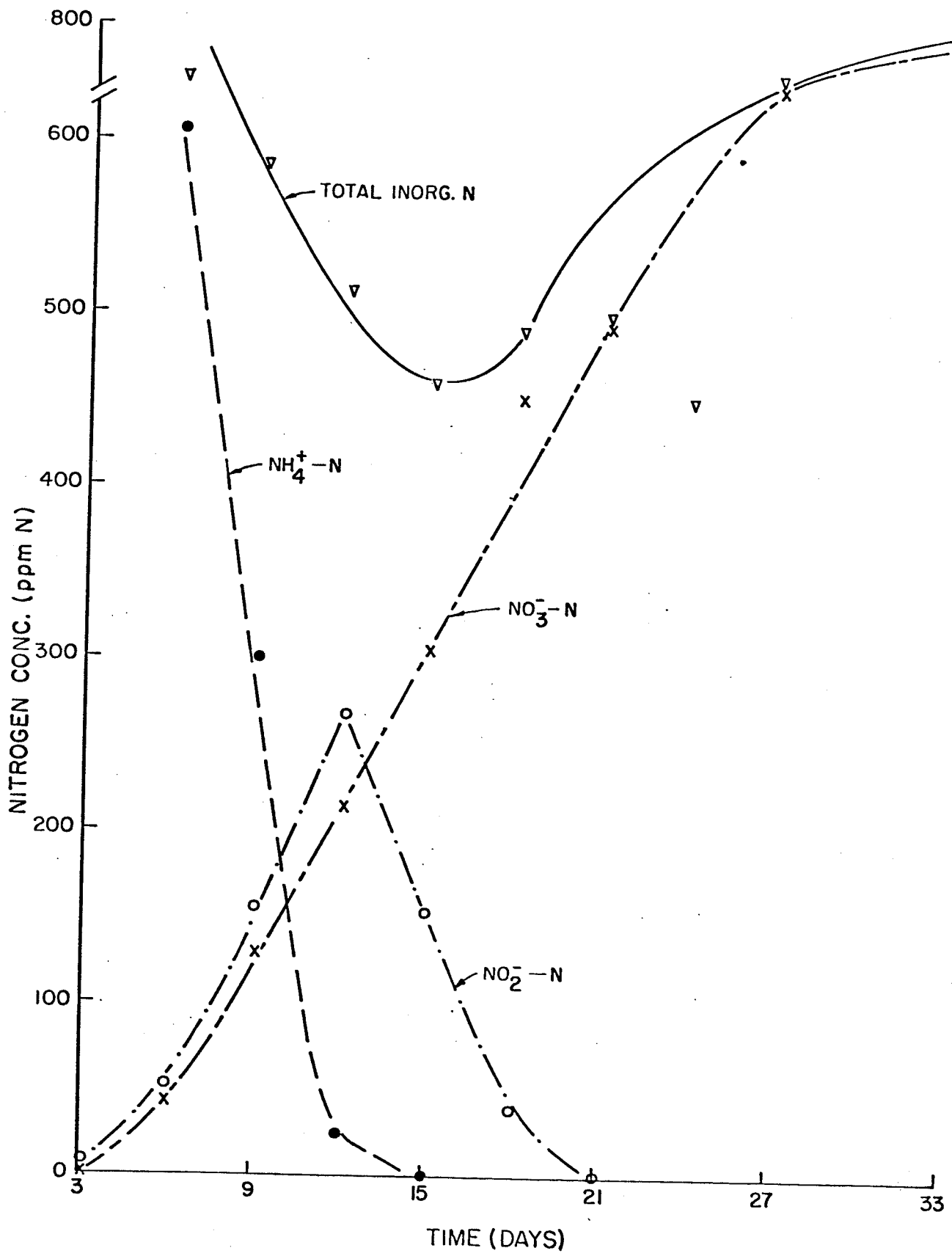


Figure 10: Ammonium, nitrite, nitrate and total inorganic nitrogen in Almasippi soil treated with urea-N at 500 ppm.

4.2.9 Effect of Added Urea-N on Soil pH

Addition of urea-N caused an immediate increase in pH of the soils, due to hydrolysis of this N-source (Table 8). The soil pH reached its maximum in all the soils after 6 days of incubation, indicating the completion of urea hydrolysis. The soil pH started to decrease after 6 days reaching its lowest point at the end of the incubation period. The difference in the pH values between 6 days and the end of incubation was more in the slightly acid soils than in the alkaline soils. A pH decrease of 2.21 units occurred in slightly acid Wellwood soil, while a similar value for slightly alkaline Newdale soil was 0.60 units. This decline in soil pH might have intensified the inhibition of both ammonium and nitrite oxidizing bacteria especially in soils that are originally slightly acid. This in turn could result in nitrite accumulation and persistence of NH_4^+ -N in soils with low pH.

4.2.10 Effect of Soil pH on Oxidation of Ammonium-N

Figure 11 summarizes the trend in NH_4^+ -N transformation. It was abstracted from Figures 3, 4, 5 and 10. The purpose of including Figure 11 is to emphasize the effect of difference in soil pH on the oxidation of ammonium-N. Initial pH values of the soils before N addition are indicated on the figure. The transformation of NH_4^+ -N was so rapid in Al-missippi soil that all the NH_4^+ -N was completely nitrified by the 15th day of incubation. Granville soil with a lower pH had completely nitrified the NH_4^+ -N by the 21st day. Wellwood soil, more acid than Gran-

TABLE 8

Effects of urea-N addition on soil pH
during incubation at 20°C

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Soil Name	Soil pH		
	After 6 days incubation	At the end of incubation	Difference between the 2
Pine Ridge	7.45	5.91	1.54
Wellwood	6.83	4.62	2.21
Granville	7.73	5.66	2.07
Waitville	7.83	6.73	1.10
Holland	7.82	6.57	1.25
Newdale	7.94	7.34	0.60
Red River	7.64	6.32	1.32
Almasippi	8.43	7.58	0.85

ville soil, and less so than Pine Ridge still had 60 ppm NH_4^+ -N at the end of the incubation. This confirms the fact that oxidation of NH_4^+ -N is considerably reduced in acid soil. This may be attributed to inhibition of the microbial population responsible for NH_4^+ -N transformation in soils as earlier observed.

4.2.11 Summary

This investigation showed that nitrite-N accumulated in slightly acid Pine Ridge and Wellwood soils. The accumulated NO_2^- -N persisted in these soils until the end of the incubation period, even though at a very low concentration. Nitrite accumulation especially in slightly acid soils may lead to loss of N through denitrification. Accumulation of NO_2^- -N also occurred in alkaline Almasippi soil (pH 7.7), but for a relatively short period. This NO_2^- -N was subsequently oxidized to nitrate-N. No substantial accumulation of nitrite-N occurred in the remaining soils under investigation. Oxidation of ammonium-N was considerably slower in slightly acid soils. A fair amount of NH_4^+ -N remained in Pine Ridge soil after 33 days of incubation. Conversely, rapid nitrification of ammonium-N occurred in alkaline Almasippi soil. Persistence of NH_4^+ -N and accumulation of NO_2^- -N in slightly acid soil might have been accelerated by the reduction in soil pH. Addition of urea caused an immediate increase in soil pH, but subsequent oxidation of NH_4^+ -N produced, resulted in pH reduction. Slow oxidation of NH_4^+ -N in these soils might be due to inhibition of the nitrifying bacteria by the slightly acid environment.

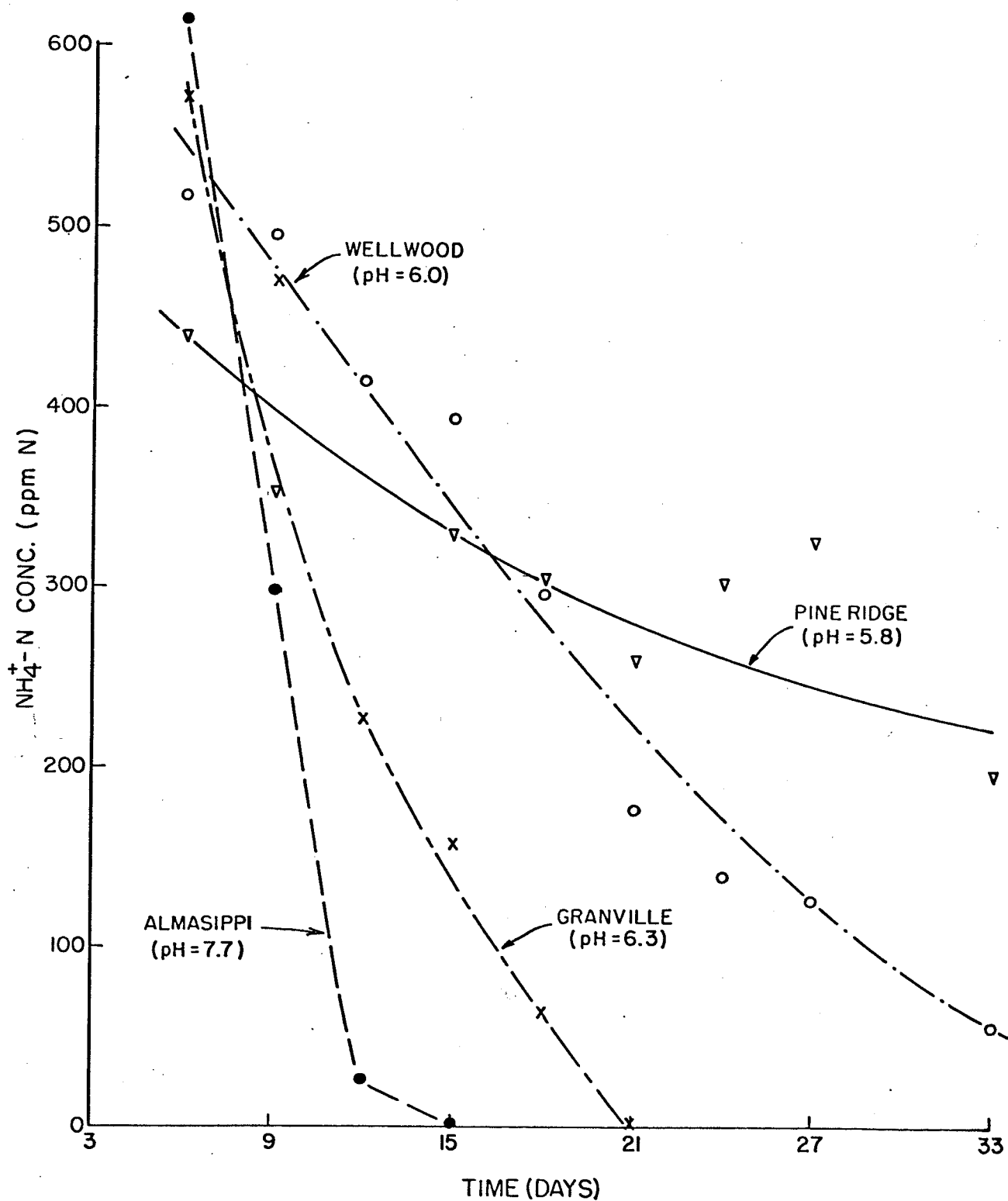


Figure 11: Changes in $\text{NH}_4^+\text{-N}$ concentration in soils with different pH treated with 500 ppm urea-N.

4.3 EXPERIMENT III, CHEMICAL DENITRIFICATION IN SOME MANITOBA SOILS TREATED WITH ¹⁵N-LABELLED NITRITE

The growth chamber experiment showed that recovery of added nitrogen was incomplete. A subsequent incubation study indicated that an accumulation of nitrite occurred in some of the soils when treated with urea. Hence incomplete recovery of added N in the growth chamber study could have been due to denitrification. An experiment was conducted on eight Manitoba soils to determine whether unaccounted for nitrogen could be recovered as N-containing gases. These soils were treated with ¹⁵N-labelled NaNO₂ to supply 100 ppm N, kept at the desired moisture content and incubated at 20°C for four days. Gas samples from the incubation vessels were transferred to 2 gas containers, one containing 5 gm solid KOH and the other with 5 ml conc. H₂SO₄. The KOH removed CO₂ and H₂O while H₂SO₄ removed H₂O from the sample gas. The possible gaseous products having mass to charge ratio (m/e) of 28 through 46 are given in Table 9.

The gas sample analyzed by the mass spectrometer contained a mixture of the original atmosphere and probable products of chemical or biological processes taking place in the soil. In order to estimate the relative magnitude of produced or consumed gases the following procedures were taken. Argon (m/e 40) in the sample was chosen as a standard. Therefore, normalized peak heights of m/e 40 were used as a basis for comparing the intensities of other m/e's. A sample of air was scanned.

TABLE 9
Possible gaseous products having mass to
charge (m/e) ratio 28 through 46 and
their probable components

m/e	Gases	Probable Components
28	N_2	$^{14}_N\ ^{14}_N$
29	N_2	$^{14}_N\ ^{15}_N$
30	$N_2; NO$	$^{15}_N\ ^{15}_N; ^{14}_N\ ^{16}_O$
31	NO	$^{15}_N\ ^{16}_O$
32	O_2	O_2
40	Ar	Ar
44	$CO_2; N_2O$	$CO_2; ^{14}_N\ ^{14}_N\ ^{16}_O$
45	N_2O	$^{14}_N\ ^{15}_N\ ^{16}_O$
46	$N_2O; NO_2$	$^{15}_N\ ^{15}_N\ ^{16}_O; ^{14}_N\ ^{16}_O\ ^{16}_O$

The contribution of air to each m/e in the sample was deducted in order to establish the actual peak heights of produced or consumed gases (Table 10). The difference in the production of m/e 44 between H₂SO₄ and KOH containers was used to calculate peak heights due to CO₂.

Probability of fragmentation of N₂O to NO and to N₂ was determined and found to be 0.177 and 0.053 respectively. Individual values were corrected after %¹⁵N of N₂O was measured. Determination of the peak heights of produced gases and %¹⁵N in the gases were calculated as follows: The peak heights of m/e 45 and 46 from sample contained with KOH were found to be due to N₂O while m/e 44 was always contaminated with CO₂. This may have been due to formation of CO₂ within mass spectrometer since the sample contained O₂. Designating measured peak heights of m/e 45 and 46 as (45)N₂O and (46)N₂O respectively, the %¹⁵N in N₂O was calculated using equation 1.

$$\%^{15}\text{N}(\text{N}_2\text{O}) = 200 / (\text{R} + 2) \quad (1)$$

$$\text{where } \text{R} = (45)\text{N}_2\text{O} / (46)\text{N}_2\text{O}$$

The peak heights of m/e 44 due to N₂O, (44)N₂O, was calculated with equation 2.

$$(44)\text{N}_2\text{O} = \text{R}^2(46)\text{N}_2\text{O} / 4 \quad (2)$$

The total peak height due to N₂O, i.e., (N₂O)_T, was the sum of peak heights of (44)N₂O, (45)N₂O and (46)N₂O.

$$(\text{N}_2\text{O})_{\text{T}} = (44)\text{N}_2\text{O} + (45)\text{N}_2\text{O} + (46)\text{N}_2\text{O} \quad (3)$$

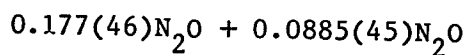
The peak height of m/e 31 due to fragmentation of N₂O corresponds to:

TABLE 10

Mass spectrometric analyses of incubation atmosphere after 2 days

m/e	Normalized Peak Height				
	NO ₂ ⁻ - Pine Ridge			NO ₂ ⁻ - Wellwood	
	Air (KOH)	(KOH)	Difference	(KOH)	Difference
28	3419.35	3473.10	53.75	3466.70	47.35
29	25.47	34.19	8.72	42.29	16.82
30		1.40	1.40	1.75	1.75
31		0.95	0.95	1.05	1.05
32	825.43	6650.00	(-)175.43	740.95	(-)84.48
40	100.00	100.00		100.00	
44	5.79	6.90	1.11	8.11	2.32
45		4.90	4.90	7.60	7.60
46		2.48	2.48	3.07	3.07
(44)*CO ₂			336.05		349.68

* Difference in amu 44 between H₂SO₄ and KOH containers.



In order to obtain the net production of m/e 31, the peak height m/e 31 due to fragmentation was subtracted from the measured peak height of m/e 31. The peak height of m/e 30 due to NO was calculated using the equation:

$$(30)\text{NO} = R/2 (31)\text{NO} \quad (4)$$

where (30)NO is the net production of m/e 30 due to NO
and (31)NO is the net m/e 31 due to production of NO other than
by fragmentation

The net production of $^{15}\text{N}^{15}\text{N}$, i.e. (30) N_2 was calculated by subtracting the fragmentation products, N_2 and NO formed from N_2O and the net production of NO, i.e., (30)NO from the intensity of m/e 30. By subtracting the fragmentation contribution from the measured intensity of m/e 29, the net production of $^{14}\text{N}^{15}\text{N}$, i.e., (29) N_2 was calculated. It has been reported (Cho et al., 1978; Cho and Sakidinan 1978) that the production of m/e 28 as calculated by deducting the intensity of m/e 28 of air from the measured intensity of m/e 28 of the sample was not reliable. The reason is that $^{14}\text{N}^{14}\text{N}$ is a major component in the air while the production of $^{14}\text{N}^{14}\text{N}$ by denitrification is relatively small, thus there is a great error in the calculation of $^{14}\text{N}^{14}\text{N}$ production. For this reason (29) N_2 and (30) N_2 were used to calculate (28) N_2 . There are two ways by which N_2 can be derived from added NO_2^- . Two nitrogen atoms in N_2 can be derived from added NO_2^- by regular denitrification pathway or from a "van Slyke type reaction" in which one atom of N originates from a soil source and the other atom from a labelled source.

These atoms are designated as N_2^1 and N_2^2 indicating that they are derived from 1 source or 2 sources respectively. In order to obtain individual intensities, $(29)N_2^1$, $(29)N_2^2$, $(30)N_2^1$, and $(30)N_2^2$ four equations are required, two of which are already known. Thus in addition to equations:

$$(29)N_2 = (29)N_2^1 + (29)N_2^2$$

$$(30)N_2 = (30)N_2^1 + (30)N_2^2$$

two additional relationships were chosen. The relationship between $(29)N_2^1$ and $(30)N_2^1$ was chosen to be

$$(29)N_2^1 / (30)N_2^1 = R \quad (5)$$

where R is as defined in equation (1). The relation between $(29)N_2^2$ and $(30)N_2^2$ was chosen to be

$$(29)N_2^2 / (30)N_2^2 = 269.27 + R/2 \quad (6)$$

An equation similar to equation (2) with $(28)N_2^1$ replacing $(44)N_2O$ was used to calculate $(28)N_2^2$. The intensity of m/e 28 due to van Slyke type nitrogen, i.e., $(28)N_2^2$ was calculated using equation 7:

$$(28)N_2^2 / (29)N_2^2 = R/2 + 0.0037R \quad (7)$$

The partial pressures of N_2^1 and N_2^2 were calculated by using the total peak heights of these components. The total production of N_2 from the labelled source $(N_2^2)_T$ is obtained using equation (8):

$$(N_2^2)_T = (28)N_2^2 + (29)N_2^2 \quad (8)$$

Total mg N_2^2 -N produced is given by the relationship

$$N_2^{-N} = 0.00725(N_2^2)_T$$

where 0.00725 is the factor of conversion from peak height to weight in mg.

Therefore production from $NO_2^{-N} = 0.00725(N_2^2)_T/2$.

An example of the method of calculation with the result of an MS scan is shown in Table 11.

Of all the eight soils studied, only Pine Ridge and Wellwood soils demonstrated substantial production of molecular nitrogen, hence tendencies for chemical denitrification. The initial rate of production of molecular N from added nitrite in Wellwood soil was 3.2% of added N per day (Figure 12). Corresponding value for Pine Ridge soil was 1.4% of added N per day. The difference in the rate of chemically produced N between the two soils may be due to higher organic matter (4.1%) in Wellwood than in Pine Ridge soil (2.4%). It was noted that these two soils demonstrated persistent accumulation of NO_2^{-N} in the previous incubation study. Almasippi soil which accumulated NO_2^{-N} over a short period of time in the previous study did not show any measurable production of molecular N in this investigation. This may be due to rapid oxidation of NO_2^{-N} to NO_3^{-N} in Almasippi soil.

with the results of MS scan after

2 days of incubation

	NO_2^- - Pine Ridge Soil
R	1.98
% ¹⁵ N (N_2)	50.30
(44) N_2O	2.42
(N_2O)T	9.81
(30) N_2	0.33
(29) N_2	7.93
(30) N_2^1	0.30
(30) N_2^2	0.03
(29) N_2^1	0.60
(29) N_2^2	7.33
(28) N_2^1	0.30
(28) N_2^2	7.24
(N_2^1)T	1.20
(N_2^2)T	14.60

* Values are measured heights normalized at ⁴⁰Ar.

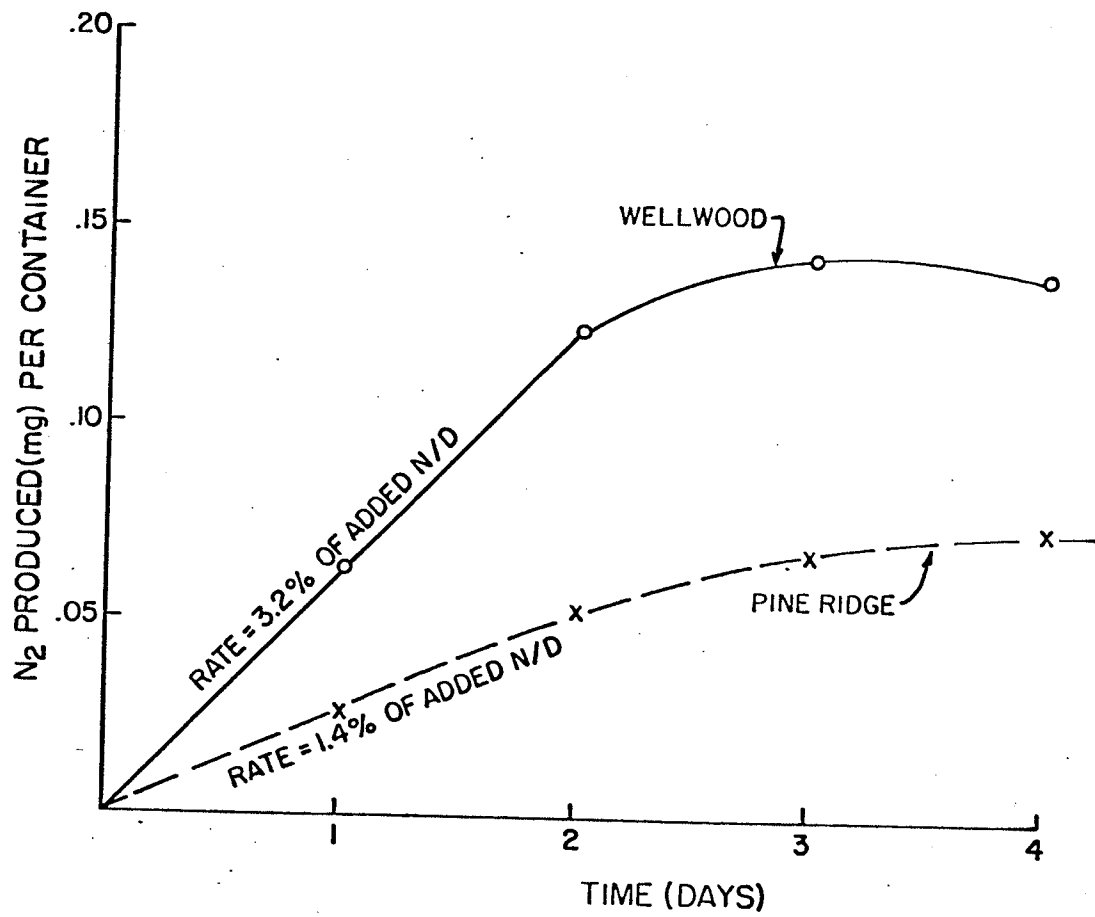


Figure 12: Chemical denitrification in Wellwood and Pine Ridge soils following addition of 2 mg N as $NaNO_2$ to 20 g soil.

4.4 EXPERIMENT IV (I). NITROGEN CARRIERS AND SOIL INTERACTIONS.

The growth chamber experiment showed that much of the added N remained in the soil after harvesting. In addition, the incubation study showed that not all the added urea could be recovered as mineral nitrogen after 33 days. The objective of this study was to investigate the interactions between N-carriers and soil that prevented the applied N from being fully utilized by wheat or recovered as mineral N. All the eight soils were used in this study. Nitrogen carriers used were labelled urea, ammonium sulphate and calcium nitrate. The soils were kept at field capacity and incubated at 20°C for 8 weeks. Labelled nitrogen remaining in the soils, after extractions with 2N KCl, was determined. Nitrogen not removed by 2N KCl was designated as fixed N. Soil-fixed nitrogen can be defined as N remaining in the soil after prolonged extraction with 2NKCl. This may include N fixed chemically by both organic matter and the clay fraction, and also biologically immobilized N. Since biologically immobilized N cannot be distinguished by chemical means, it is here defined as fixed N. However the N fixed from added $\text{Ca}(\text{NO}_3)_2$ was negligible. This indicates that the amount of nitrogen immobilized by micro organisms was small.

4.4.1 Nitrogen Fixed in Pine Ridge Soil

After 2 weeks of incubation, 9.5% of added urea-N (500 ppm) was fixed in Pine Ridge soil (Fig. 13). The amount of fixed N, which was not extractable with 2N KCl, increased with time to 16.8% by the 8th week of incubation. The amount of N fixed from $(\text{NH}_4)_2\text{SO}_4$ also increased with time, but less of the N from $(\text{NH}_4)_2\text{SO}_4$ was fixed than urea. At the end of incubation about 9% of N as $(\text{NH}_4)_2\text{SO}_4$ was fixed. Thus only 54% as much of the $(\text{NH}_4)_2\text{SO}_4$ nitrogen was fixed as was the case with $(\text{NH}_2)_2\text{CO}$ nitrogen. In contrast to the above, the amount of N fixed from added $\text{Ca}(\text{NO}_3)_2$ was very small amounting to less than 1% of that added. The greater fixation of $(\text{NH}_2)_2\text{CO}$ nitrogen than $\text{Ca}(\text{NO}_3)_2$ nitrogen no doubt accounts for the greater amounts of the former remaining in the soil after harvesting wheat in the growth chamber experiment.

4.4.2 Nitrogen Fixed in Wellwood Soil

The amount of N fixed from $(\text{NH}_2)_2\text{CO}$ added to Wellwood soil increased with time until the 6th week of incubation and remained nearly constant until the incubation was terminated at eight weeks (Fig. 14). After eight weeks about 14% of added $(\text{NH}_2)_2\text{CO}$ was fixed. Nitrogen fixed from added $(\text{NH}_4)_2\text{SO}_4$ also increased with time amounting to 11.2% of added N after eight weeks incubation. As was observed for Pine Ridge soil, less than one percent of the N added as $\text{Ca}(\text{NO}_3)_2$ to Wellwood soil was fixed. Throughout the incubation period, the greatest amount of N fixation occurred with $(\text{NH}_2)_2\text{CO}$ while added $\text{Ca}(\text{NO}_3)_2$ was the least fixed.

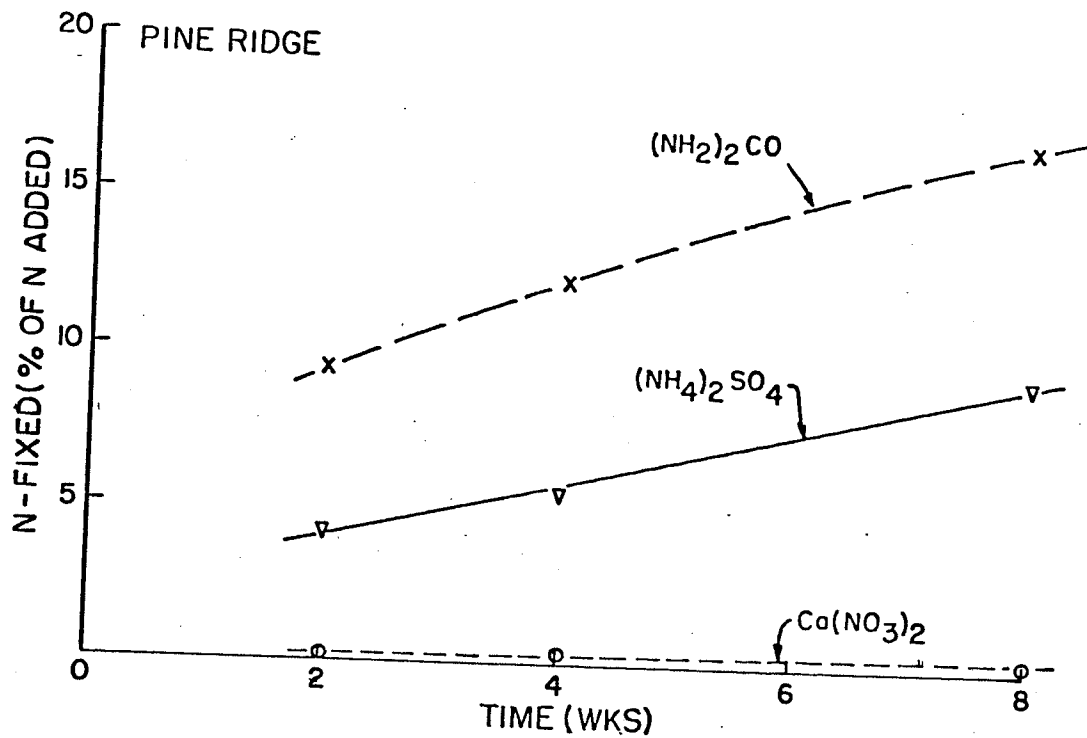


Figure 13: Nitrogen remaining in soil treated with ¹⁵N-labelled carriers (500 ppm N) after extraction with 2NKCl.

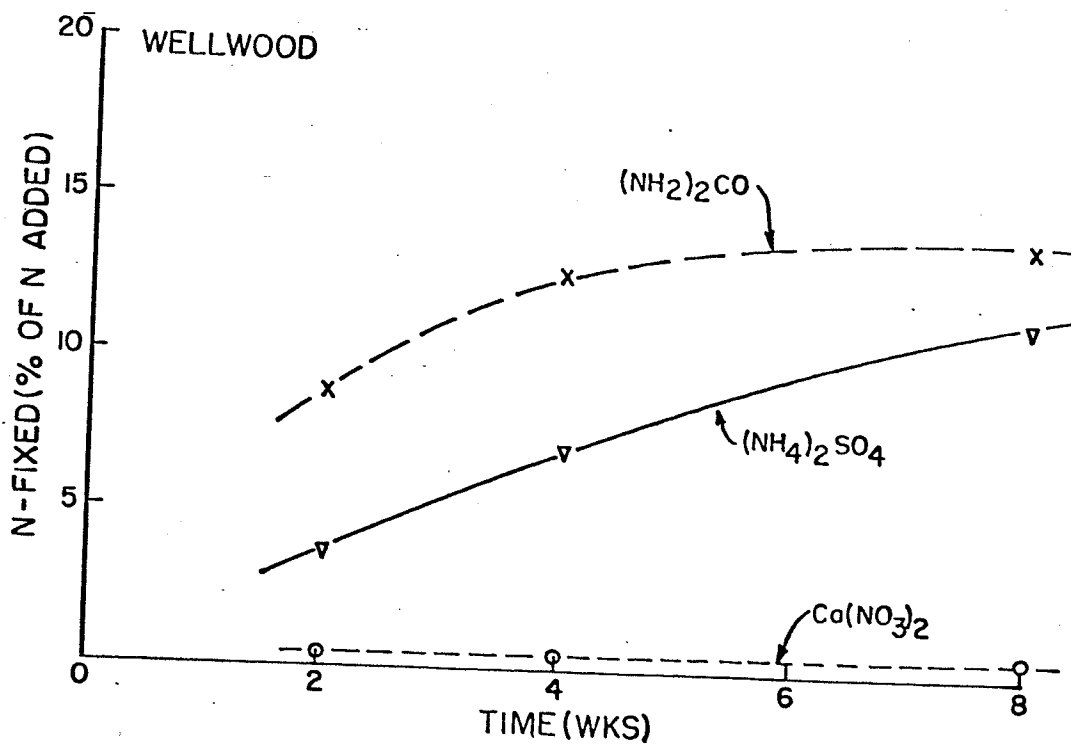


Figure 14: Nitrogen remaining in soil treated with ¹⁵N-labelled carriers (500ppm N) after extraction with 2NKCl.

4.4.3 Nitrogen Fixed in Granville Soil

After two weeks incubation 16.8% of the N added as $(\text{NH}_4)_2\text{SO}_4$ was fixed in Granville soil (Fig. 15). The amount fixed increased gradually to 18.2% by the end of the incubation period. Nitrogen fixed from added $(\text{NH}_2)_2\text{CO}$ remained constant at about 15% from 4th to 8th week of incubation. Unlike Pine Ridge and Wellwood soils, in Granville soil more N was fixed from $(\text{NH}_4)_2\text{SO}_4$ than from $(\text{NH}_2)_2\text{CO}$. As previously observed, very little of the N from added $\text{Ca}(\text{NO}_3)_2$ was fixed in this soil.

4.4.4 Nitrogen Fixed in Waitville Soil

In Waitville soil after 2 weeks about equal amounts (14%) of N were fixed from $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ (Fig. 16). This increased to a maximum of 16.8% after 4 weeks of incubation and then remained nearly constant until the end of incubation period. There was an increase of 1% in the amount of added $(\text{NH}_2)_2\text{CO}$ fixed between the 2nd and 8th weeks of incubation. Only one percent of N added as $\text{Ca}(\text{NO}_3)_2$ was fixed after eight weeks incubation.

4.4.5 Nitrogen Fixed in Holland Soil

Throughout the incubation period, slightly more of the added N from $(\text{NH}_2)_2\text{CO}$ than from $(\text{NH}_4)_2\text{SO}_4$ was fixed in Holland soil (Fig. 17). The amount of urea-N fixed reached a maximum of 13% of added N at 4 weeks of incubation. This amount decreased to about 11% by the 8th week of incubation. Fixation of added N from $(\text{NH}_4)_2\text{SO}_4$ remained nearly constant at

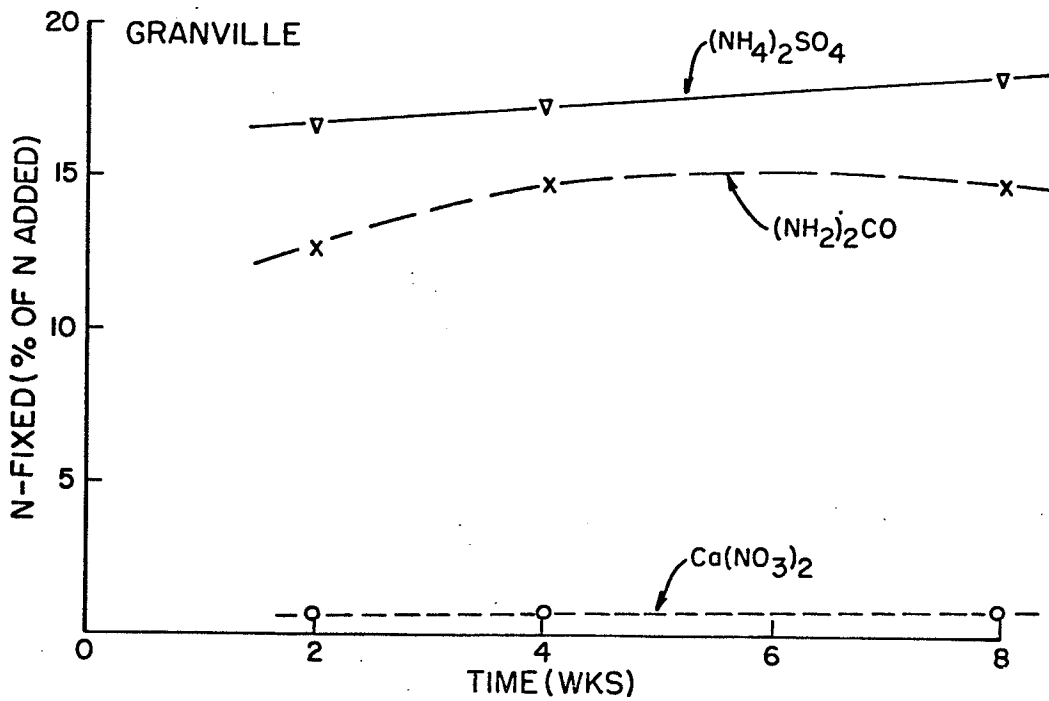


Figure 13: Nitrogen remaining in soil treated with ^{15}N -labelled carriers (500 ppm N) after extraction with 2NKCl.

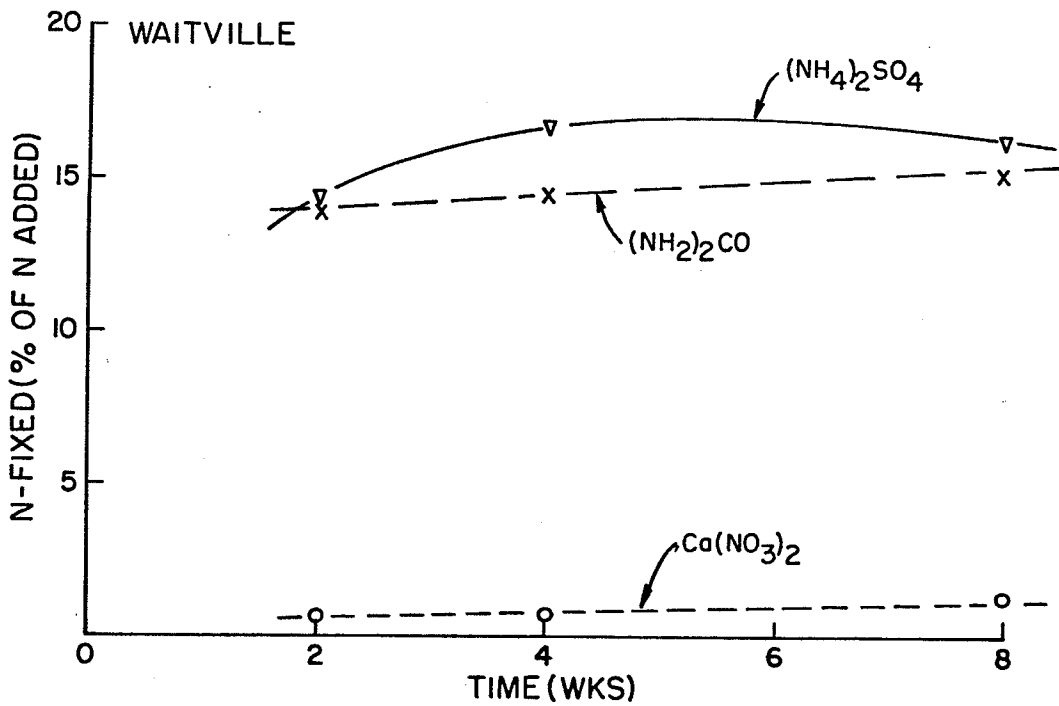


Figure 16: Nitrogen remaining in soil treated with ^{15}N -labelled carriers (500ppm N) after extraction with 2NKCl.

about 10% from 4th week until the end of incubation. As previously noted with other soils, very little N added as $\text{Ca}(\text{NO}_3)_2$ was fixed in Holland soil.

4.4.6 Nitrogen Fixed in Newdale Soil

With Newdale soil, the amount of added N fixed from both $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ remained nearly constant throughout the incubation period (Fig. 18). About 9% of added $(\text{NH}_2)_2\text{CO}$ and 7.5% of added $(\text{NH}_4)_2\text{SO}_4$ was fixed in Newdale soil at each sampling date during the incubation. Thus considerably less N-fixation of these carriers occurred in this soil than in the soils previously described. Nitrogen fixed from added $\text{Ca}(\text{NO}_3)_2$ was less than 1% throughout the incubation period.

4.4.7 Nitrogen Fixed in Red River Soil

The amount of fixed N from added $(\text{NH}_4)_2\text{SO}_4$ decreased from 9% at 2nd week to 5.5% by the 8th week of incubation (Fig. 19). Nitrogen fixed from added $(\text{NH}_2)_2\text{CO}$ decreased from 8% at 2 weeks to a constant value of 7% at 4th and 8th week of incubation. There was a very slight difference between the amount of added N fixed from $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ throughout the incubation period. Even though the soil has a relatively high amount of organic matter, the magnitude of N fixation was not as great as was observed with Granville or Waitville soil. Here again very little N added as $\text{Ca}(\text{NO}_3)_2$ was fixed.

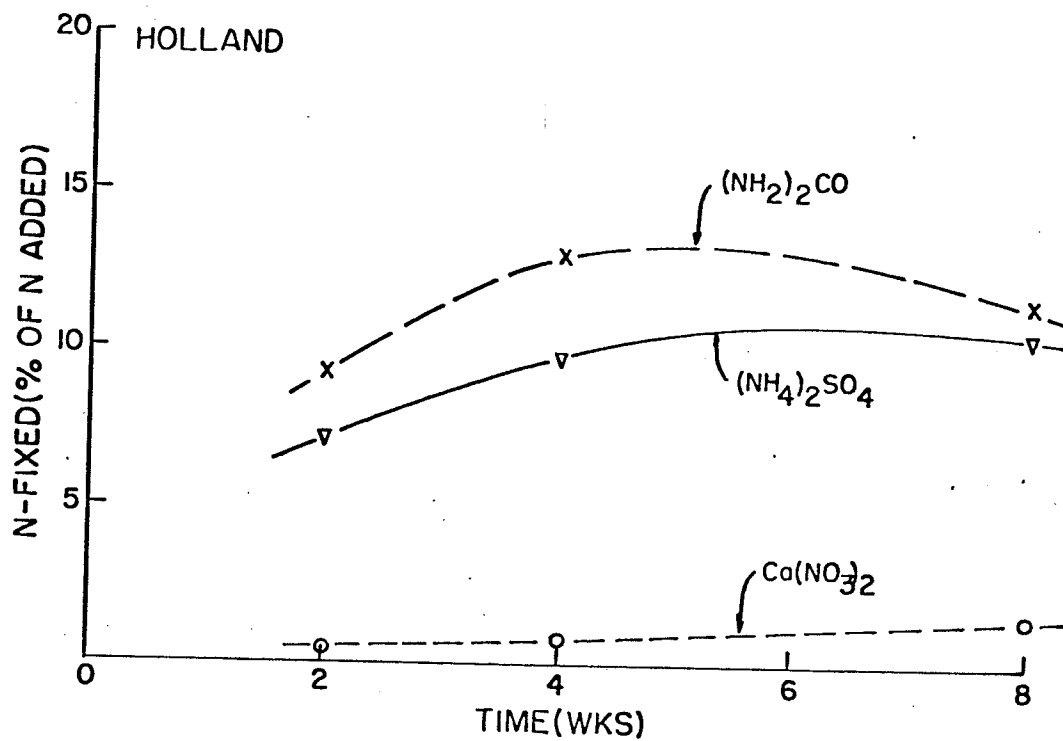


Figure 17: Nitrogen remaining in soil treated with ^{15}N -labelled carriers (500ppm N) after extraction with 2NKCl.

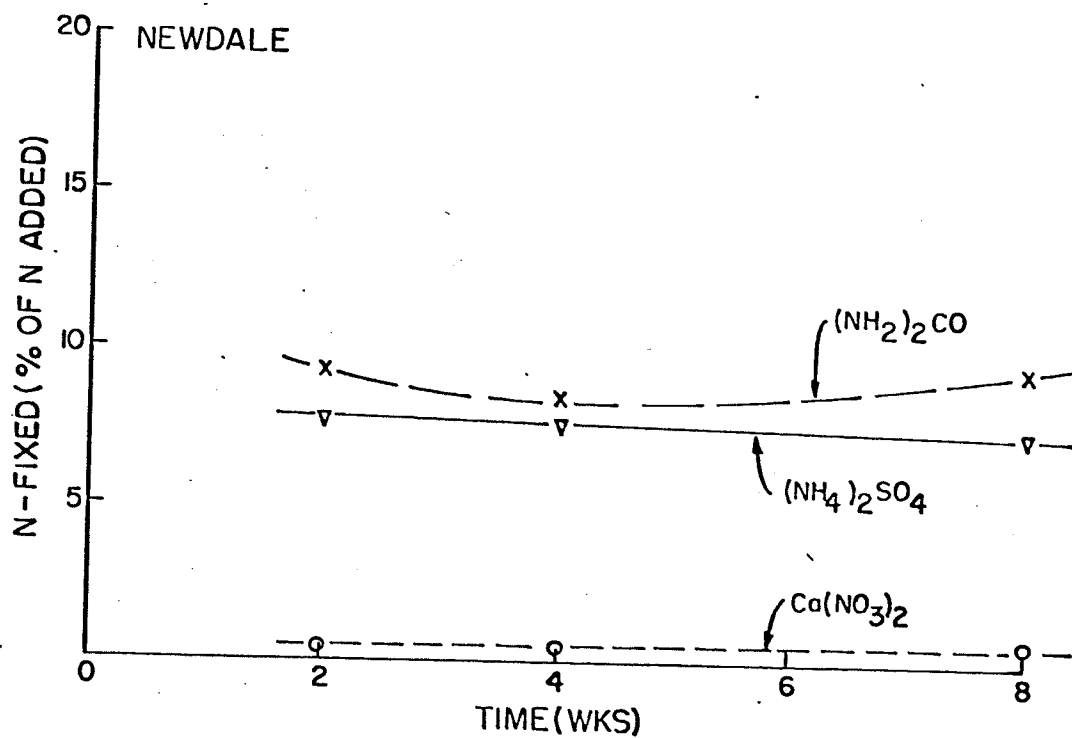


Figure 18: Nitrogen remaining in soil treated with ^{15}N -labelled carriers (500ppm N) after extraction with 2NKCl.

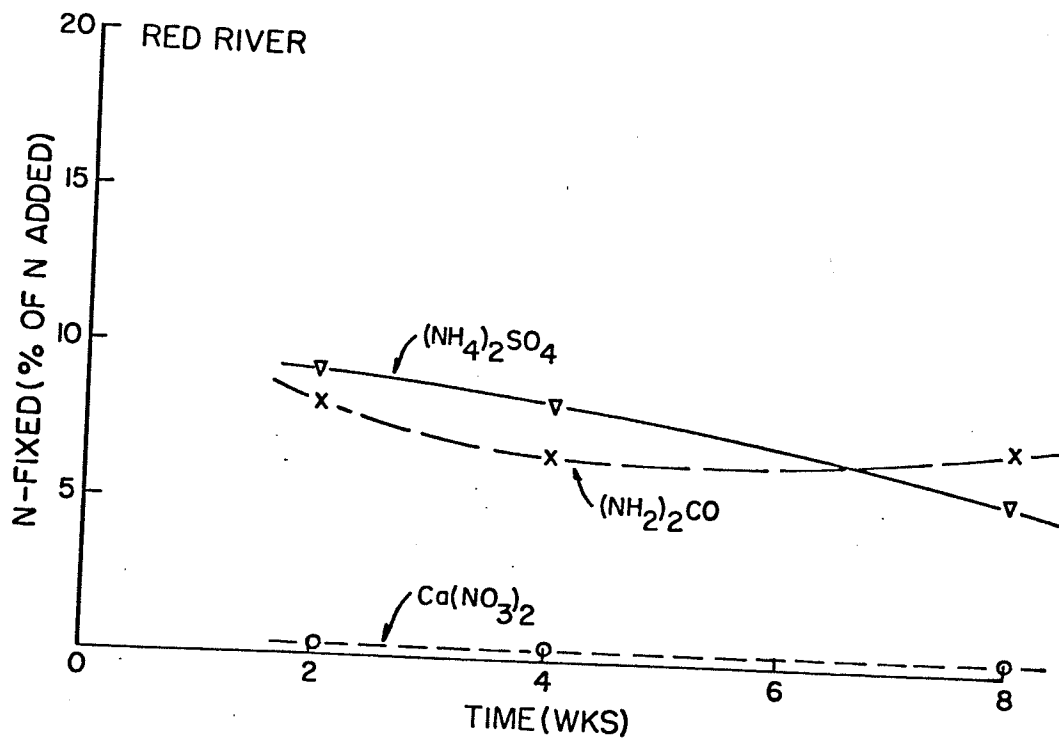


Figure 19: Nitrogen remaining in soil treated with ^{15}N -labelled carriers (500ppm N) after extraction with 2NKCl.

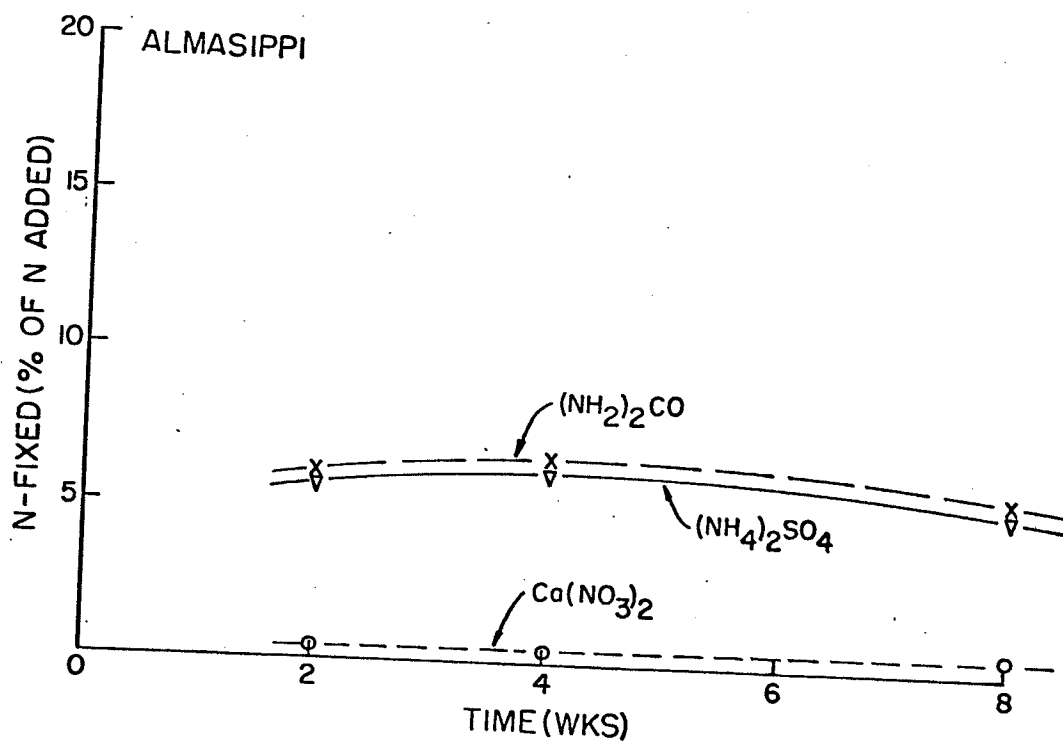


Figure 20: Nitrogen remaining in soil treated with ^{15}N -labelled carriers (500ppm N) after extraction with 2NKCl.

4.4.8 Nitrogen Fixed in Almasippi Soil

With Almasippi soil, there was virtually no difference between $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ in the amount of added N fixed throughout the 8 weeks of incubation (Fig. 20). Nitrogen fixed remained nearly constant at about 6% of added N. Less than 1% of added N from $\text{Ca}(\text{NO}_3)_2$ was fixed in Almasippi soil throughout the period of incubation. Of the eight soils studied, amount of added N fixed from $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ was least in Almasippi soil. It was observed from experiment II that ammonium-N was rapidly nitrified in Almasippi soil. This lack of persistence of NH_4^+-N in Almasippi soil was responsible for the small amount of fixation.

4.4.9 Summary

This study showed that the amount of added N fixed by experimental soils from $\text{Ca}(\text{NO}_3)_2$ was small. More of the nitrogen added as $(\text{NH}_2)_2\text{CO}$ was fixed than of N added as $\text{Ca}(\text{NO}_3)_2$ in all the eight soils. This provides an explanation of the greater amount of added N from $(\text{NH}_2)_2\text{CO}$ than from $\text{Ca}(\text{NO}_3)_2$ remaining in the soil at the end of the growth chamber experiment. More $(\text{NH}_2)_2\text{CO}$ than $(\text{NH}_4)_2\text{SO}_4$ nitrogen was fixed in Pine Ridge and Wellwood soils, while the reverse was true in Granville and Waitville soils. There was not much difference in the amount of N fixed between $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ in slightly alkaline soil, namely, Holland, Newdale, Red River and Almasippi.

The interaction between N-carrier species and soil characteristics, especially soil pH, could be described as follows: Two acid soils, Pine Ridge and Wellwood seemed to fix more N from urea, an alkaline N-source than from $(\text{NH}_4)_2\text{SO}_4$, an acid N-carrier. In soils with a higher pH but still slightly acid, Waitville and Granville soils, there was little difference in the amount of N fixed from the two sources. As the soil pH increased further, the magnitude of the fixation decreased and there was little difference between N-carriers. Fixation of added N in all the soils was more of a problem with the NH_4^+ -yielding carriers rather than NO_3^- -source. It is probable that the slightly alkaline soils provided a better environment than the slightly acid soils, for microbial activity. Thus oxidation of NH_4^+ -N was faster in the slightly alkaline soils. This was substantiated by results obtained in experiment II where NH_4^+ -N was nitrified more rapidly in Almasippi than Pine Ridge soil. However, there was a reversal of the order of N fixation from urea to $(\text{NH}_4)_2\text{SO}_4$ due to increase in soil pH on slightly acid Granville and Waitville soils. This could be due to longer life of NH_4^+ from $(\text{NH}_4)_2\text{SO}_4$, than from $(\text{NH}_2)_2\text{CO}$ on these acid soils because of the acid-forming characteristics of $(\text{NH}_4)_2\text{SO}_4$ as compared to $(\text{NH}_2)_2\text{CO}$.

4.5 EXPERIMENT IV (II): FIXATION OF AMMONIUM YIELDING CARRIERS IN SLIGHTLY ACID SOILS

Fixation of added N was mostly from ammonium yielding carriers and occurred more on slightly acid soil. A study was undertaken to ascertain the extent of N fixation that occurs in the first few days after N addition. Four slightly acid soils were chosen for this investigation. The sources of N were $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$. The soils were incubated at 20°C for 10 days.

4.5.1 Fixed N in Pine Ridge Soil Within Few Days of N-addition

Added nitrogen fixed from $(\text{NH}_2)_2\text{CO}$ increased from 2.5% at 1 day to 9% after 10 days of incubation (Fig. 21). Corresponding amounts from added $(\text{NH}_4)_2\text{SO}_4$ were 1.5% at 1 day and 3.6% by the 10th day of incubation. Thus fixation of N added as $(\text{NH}_2)_2\text{CO}$ by the end of the incubation period was two and one half times as much as the amount of N fixed from added $(\text{NH}_4)_2\text{SO}_4$. Amount of N fixed from the two carriers conformed with N fixed after 2 weeks of incubation by the same soil in a previous study (Fig. 13).

4.5.2 Fixed N in Wellwood Soil Within Few Days of N-addition

Fixation of added N in Wellwood soil followed a similar pattern as was observed for Pine Ridge soil. Added N fixed from $(\text{NH}_2)_2\text{CO}$ increased from 3.5% at one day to 8.5% by the 10th day of incubation (Fig. 22). Two percent of added $(\text{NH}_4)_2\text{SO}_4$ was fixed on the first day and by the end of incubation period 5% was fixed. Thus more nitrogen from $(\text{NH}_2)_2\text{CO}$ than from $(\text{NH}_4)_2\text{SO}_4$ was fixed in Wellwood soil. The trend of increase

in the amount of added N fixed in this soil was in agreement with N fixed at 2 week period in the previous investigation.

4.5.3 Fixed N in Granville Soil Within Few Days of N-addition

There was a rapid fixation of added N from both carriers in the Granville soil. About 10% of the added N (irrespective of source) was fixed after incubating the soil for one day (Fig. 23). Fixation of urea nitrogen kept increasing and it was over 18% by the 10th day of incubation. Fixation of added N as $(\text{NH}_4)_2\text{SO}_4$ remained nearly constant at about 11% from 2nd to the 6th day of incubation, after which it increased to 15% at the end of incubation. From 2nd day to the end of incubation period, more N from $(\text{NH}_2)_2\text{CO}$ than from $(\text{NH}_4)_2\text{SO}_4$ was fixed in Granville soil. Added N fixed from both carriers in Granville soil was greater than added N fixed at the same time in Pine Ridge or Wellwood soil.

4.5.4 Fixed N in Waitville Soil Within Few Days of N-addition

The pattern of fixation of added N in Waitville soil was similar to that observed for Granville soil. About 9.8% of added $(\text{NH}_2)_2\text{CO}$ and 9% of $(\text{NH}_4)_2\text{SO}_4$ was fixed after one day of incubation (Fig. 24). Fixation of $(\text{NH}_2)_2\text{CO}$ nitrogen increased to about 18% by the 10th day of incubation. The corresponding value for fixed N from $(\text{NH}_4)_2\text{SO}_4$ was 14% of added N.

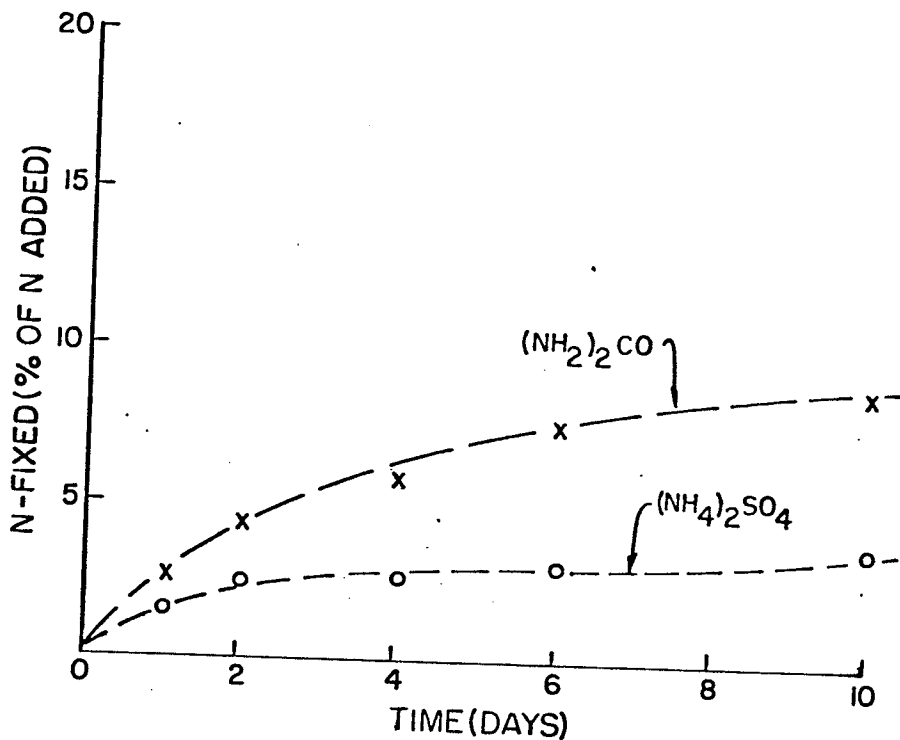


Figure 21: Ammonium fixation from two carriers (500 ppm N) by Pine Ridge soil during incubation at 20°C.

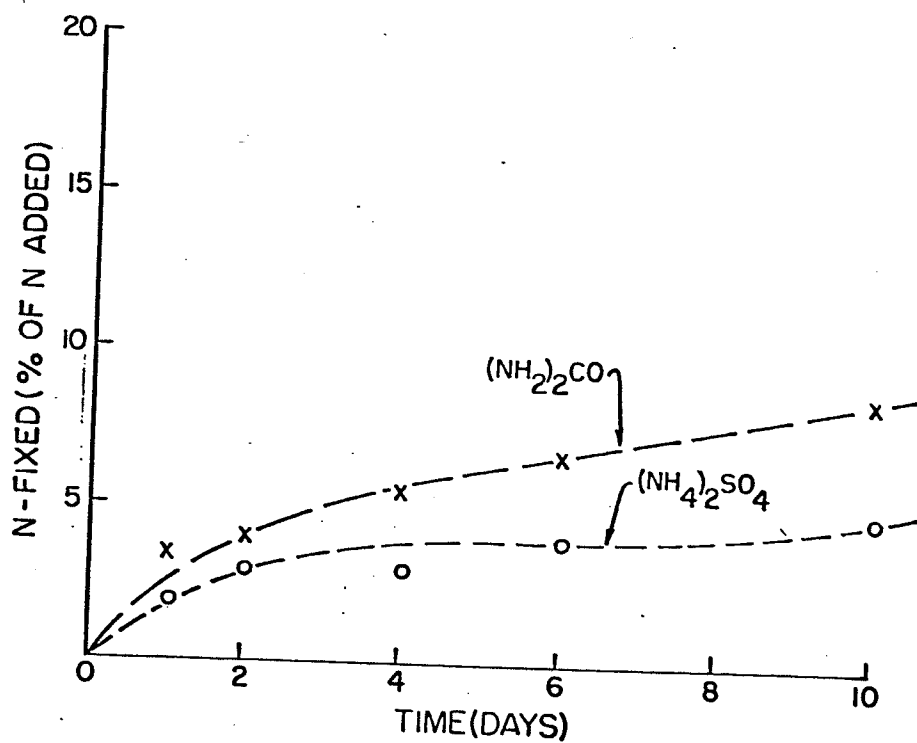


Figure 22: Ammonium fixation from two carriers (500 ppm N) by Wellwood soil during incubation at 20°C.

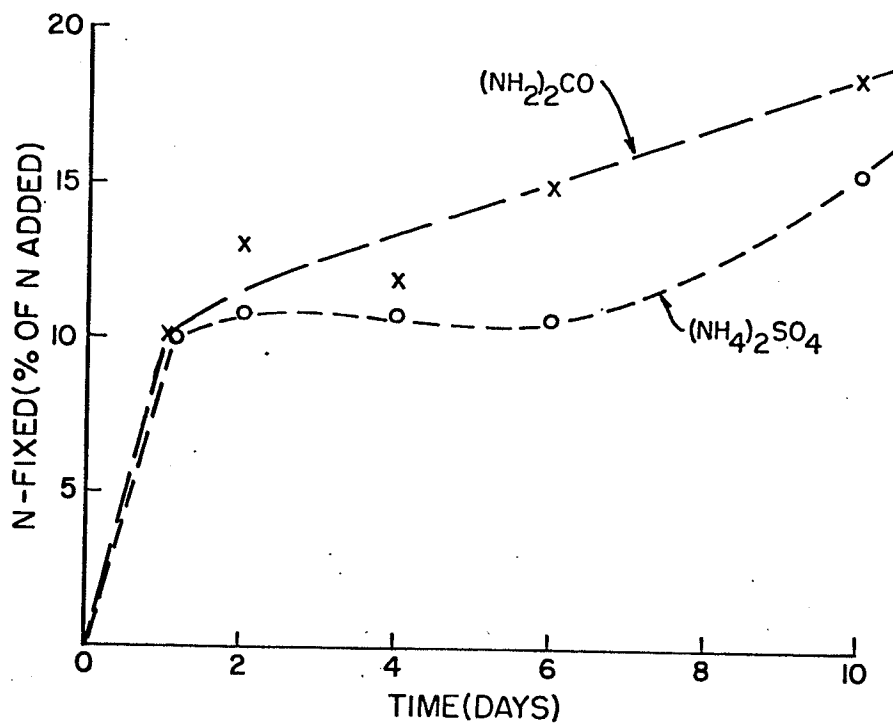


Figure 23: Ammonium fixation from two carriers (500 ppm N) by Granville soil during incubation at 20°C.

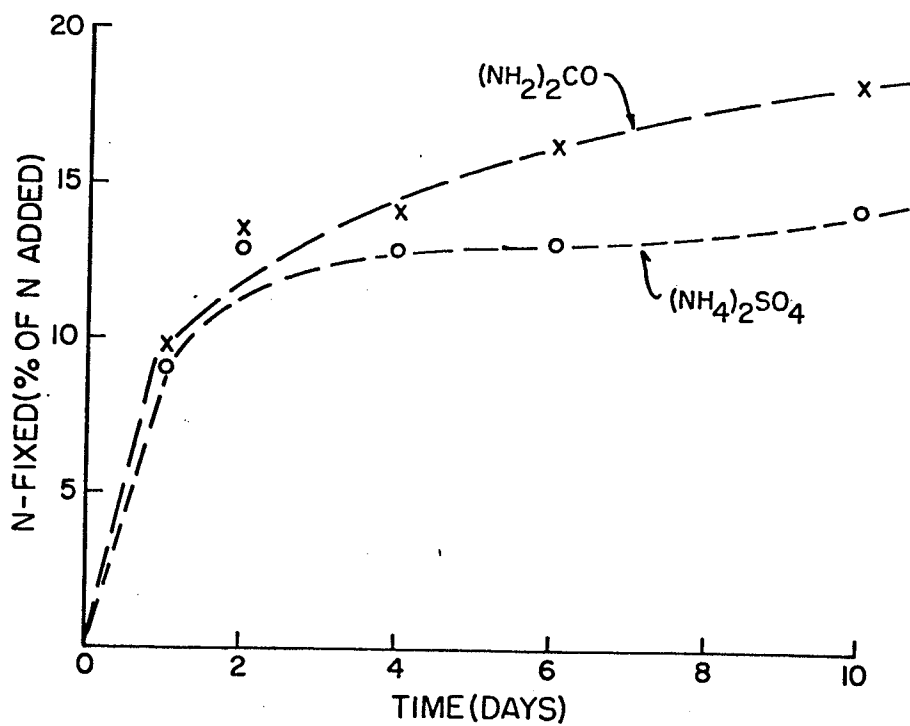


Figure 24: Ammonium fixation from two carriers (500 ppm N) by Waitville soil during incubation at 20°C.

After the first day of incubation slightly more added N from $(\text{NH}_2)_2\text{CO}$ than from $(\text{NH}_4)_2\text{SO}_4$ was fixed in Waitville soil. These results are in quite good agreement with those presented earlier (Fig. 16) where it was found that added N fixed from both $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ in Waitville soil was about 15% after 2 weeks of incubation. Added N fixed in this soil was nearly equal to that of Granville and greater than that of Pine Ridge or Wellwood soil.

4.5.5 Summary

This study indicated the occurrence of a rapid fixation of added NH_4^+ -yielding carriers in slightly acid soils. More nitrogen from added $(\text{NH}_2)_2\text{CO}$ than from $(\text{NH}_4)_2\text{SO}_4$ was fixed in Pine Ridge and Wellwood soils. This was only true for Granville and Waitville soils from 2nd day of incubation onward. There was greater fixation of added N in Granville and Waitville soils than in Pine Ridge and Wellwood soils. By the 10th day of incubation, about 18% of added $(\text{NH}_2)_2\text{CO}$ was fixed in Granville and Waitville soils, while about 9% was fixed in Pine Ridge and Wellwood soils. Thus a considerable amount of added N was fixed in all the soils within few days of N addition.

4.6 EXPERIMENT V: DETERMINATION OF ORGANICALLY AND INORGANICALLY FIXED N IN FOUR MANITOBA SOILS

A substantial amount of added N from ammonium yielding carriers was fixed in slightly acid soils. Both the organic and inorganic soil fractions are capable of fixing ammonia in relatively unavailable forms. Nitrite-N can also be fixed by the organic fraction of the soil (Bremner et al 1957). In both the growth chamber and incubation studies surface soils, which are higher in organic matter and, more often than not, lower in clay content than sub-soils, were used. It was the purpose of this investigation to determine the amount of N fixed by the soils that was bound in the organic and the inorganic soil fractions. After extracting the inorganic N with 2N KCl, the soil residue was analyzed for total and organic N. The determination by Kjeldahl digestion method was designated as total N, while N determined by 30% $H_2O_2-H_2SO_4$ (dil.) digestion method was designated as organic N. The difference between the two was termed inorganically fixed N.

4.6.1 Total Nitrogen in Soil

Nitrogen remaining in soil after 2N KCl extraction ranged from 0.11% in Pine Ridge to 0.42% in Newdale soil (Table 12). The fixation of N ranged between 6.94% of that added in Almasippi soil and 12.59% in the Wellwood soil. Percent of ^{15}N of N obtained by Kjeldahl method was between 0.71% in Almasippi and 2.96% in Pine Ridge soil.

TABLE 12

Nitrogen contents remaining after 2N KCl extraction
and urea-N fixed in four soils after 4 weeks
of incubation (N rate = 500 ppm)

Soil Name	% Nitrogen (Kjeldahl)	% ¹⁵ N excess	% of added N fixed
Pine Ridge	0.11	2.96	12.56
Wellwood	0.20	1.70	12.59
Newdale	0.42	0.72	11.46
Almasippi	0.26	0.71	6.94

%¹⁵ N excess (standard) = 52.96

4.6.2 Organic Nitrogen

The organic nitrogen in the four soils ranged between 0.09% in Pine Ridge and 0.36% in Newdale soil (Table 13). The organic N constituted between 80 and 87% of the total soil N. Nitrogen that was organically fixed was 5.39 and 9.06% of that added for Almasippi and Pine Ridge soils respectively. The amount of organically fixed N was expressed per unit weight of soil organic matter (OM) in order to compare the intensity of fixation of N by organic matter. The following calculations were undertaken:

Example:

Pine Ridge soil, pH = 5.8; % OM = 2.4; % clay = 5.0

Added N = 500 ppm N = 500 micrograms/gram soil

$$\text{mg of added N fixed per g of OM} = \frac{0.0906 \times 500}{24} \text{ mg}$$

$$= 1.89 \text{ mg}$$

The Pine Ridge soil fixed 1.89 mg of added N per g of soil organic matter. This value decreased to 0.92 for Wellwood and further decreased to about 0.5 mg/g for the two alkaline soils. The capacity of soil organic matter to fix added N was greater at a lower soil pH than higher pH.

TABLE 13

Organic nitrogen and fixation of added urea-N by organic matter in four Manitoba soils (N rate = 500 ppm)

Soil Name	% organic N	% ¹⁵ N excess in organic N	% of added N fixed	added N fixed (mg/g OM)
Pine Ridge	0.09	2.58	9.06	1.89
Wellwood	0.16	1.28	7.54	0.92
Newdale	0.36	0.62	8.37	0.46
Almasippi	0.23	0.63	5.39	0.58

%¹⁵ N excess (standard) = 52.96

4.6.3 Inorganic Nitrogen

The calculated difference between total soil N (Kjeldahl) and organic N was the inorganic N and this ranged from 0.02% in Pine Ridge to 0.06% of added N in Newdale soil (Table 14). Similarly the difference between total fixed N and organically fixed N constituted the inorganically fixed N and was designated as 'clay fixed' N. The 'clay fixed' N ranged from 1.55% in very fine sandy loam Almasippi to 5.05% of added N in fine sandy loam Wellwood soil. Since % ^{15}N of N obtained by Kjeldahl method was higher than that of $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ method, the 'clay fixed' N must have a higher % ^{15}N than organically fixed N. The percent ^{15}N of the 'clay fixed' N was calculated as follows: According to ^{15}N balance: The calculated percent ^{15}N excess in 'clay fixed' N ranged from 1.32% in Almasippi to 4.67% in Pine Ridge soil (Table 14) corresponding value of % ^{15}N excess in total N were 0.71% and 2.96% (Table 12). In all the soils tested the % ^{15}N excess in 'clay fixed' N was 1.5 to 2 times greater than the % ^{15}N excess in total N.

Calculation similar to those carried out for organic nitrogen were undertaken for 'clay fixed' N to express the amount of N fixed per unit weight of clay. The value obtained for Pine Ridge soil was 0.35mg/g clay. This value decreased to 0.05mg/g for the two alkaline soils. The capacity of clay to fix added N was approximately one fifth (in acid soil) to one tenth (in alkaline soil) of that of organic matter. It was thus observed that both organic matter and clay fixed more of the added N in NH_4^+ form under acid rather than alkaline conditions.

TABLE 14

Inorganic N contents remaining after 2N KCl extraction and
fixation of added urea N by 'clay' in four Manitoba soils

Soil Name	% Nitrogen	% ¹⁵ N excess	% of added N fixed	Added N fixed (mg/g clay)
Pine Ridge fs	0.02	4.67	3.50	0.35
Wellwood fsl	0.04	3.38	5.05	0.15
Newdale cl	0.06	1.32	3.09	0.05
Almasippi vfl	0.03	1.32	1.55	0.05

%¹⁵ N excess (standard) = 52.96

4.6.4 Summary

It was found, from this experiment, that a substantial amount of added urea N was fixed by soil and unextracted by 2NKCl. The fixed N was separated into organically and 'clay fixed' N by separate digestion methods. Approximately 7 to 12.5% of added urea N was fixed by the soils, of which about 80 to 87% was found to be organically bound and the remaining was 'clay fixed'.

The capacity of organic matter and clay to fix N were compared. Organic matter was found to fix approximately 5 to 10 times as much nitrogen per unit weight as clay. Both organic matter and clay had a greater capacity to fix added N at low pH. The N fixation capacity gradually decreased with increasing soil pH.

4.7 EXPERIMENT VI: INTERACTION OF AMMONIUM YIELDING CARRIERS IN PH AMENDED SOILS

Previous incubation studies indicated that added N from ammonium-yielding carriers was fixed more in slightly acid than in alkaline soils. The purpose of the present investigation was to determine if liming reduces the amount of N fixed in slightly acid soils and if acidifying alkaline soils increases the amount of added N fixed. Two slightly acid and two alkaline soils were used. The slightly acid soil, Pine Ridge (pH 5.8) and Wellwood (pH 6.0), were limed with the amount of CaCO_3 required to bring their pH to 7.5. The alkaline soils, Newdale (pH 7.4) and Almasippi (pH 7.7) were acidified to pH 5.5 by the addition of 2M H_2SO_4 . Nitrogen was added as $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ and the soils were incubated for 56 days.

4.7.1 Nitrogen Fixed in pH Amended Pine Ridge Soil

Nitrogen fixed from added $(\text{NH}_2)_2\text{CO}$ in limed Pine Ridge soil increased from about 2.3% at one day to 9% by the end of incubation (Fig. 25). With $(\text{NH}_4)_2\text{SO}_4$, N fixed increased from 2.2% at 1 day to 5% at the 10th day and remained nearly constant until the end of incubation period. Fixation of added N in limed Pine Ridge soil was greater with $(\text{NH}_2)_2\text{CO}$ than with $(\text{NH}_4)_2\text{SO}_4$. Liming Pine Ridge soil decreased the amount of N fixed from added $(\text{NH}_2)_2\text{CO}$. By the 10th day of incubation about 7% of added $(\text{NH}_2)_2\text{CO}$ was fixed. The corresponding value in unlimed Pine Ridge soil was 9% of added N (Fig. 21). The difference in N-fixed between limed and unlimed Pine Ridge soils was substantial at 56 days (8 weeks) incubation period. At this time, limed Pine Ridge soil fixed 9% while unlimed fixed 16.8% of added N (Fig. 13). There was also a difference in the amount of N fixed from $(\text{NH}_4)_2\text{SO}_4$ between limed and unlimed Pine Ridge soil. After 10 days of incubation fixed N in limed soil was 5% of that added and it remained constant at this value until the end of incubation. The corresponding value in unlimed soil was 9% (Fig. 13).

4.7.2 Nitrogen Fixed in pH Amended Wellwood Soil

In limed Wellwood soil, N fixed from added $(\text{NH}_2)_2\text{CO}$ increased from 2.5% at the 1st day to about 6.5% by the 10th day of incubation (Fig. 26). Nitrogen fixed remained constant at this value until the end of incubation. There was very little difference between the N sources, $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_2)_2\text{CO}$, in the amount of N fixed from 1st to 4th day of

incubation. There was, however, slightly more $(\text{NH}_2)_2\text{CO}$ nitrogen fixed from the 6th day to the end of incubation. From 10th day to the end of the incubation period, added N fixed from $(\text{NH}_4)_2\text{SO}_4$ remained constant at about 5%.

Liming Wellwood soil reduced the amount of added N fixed from $(\text{NH}_2)_2\text{CO}$. Ten days after incubation 6.5% of added N was fixed in limed Wellwood soil. When the soil was not limed, 8.5% (Fig. 22) was fixed. By the end of the incubation period, 13.4% of added N from $(\text{NH}_2)_2\text{CO}$ (Fig. 14) was fixed in unlimed, while 6.5% was fixed in limed Wellwood soil. With added $(\text{NH}_4)_2\text{SO}_4$, liming Wellwood soil decreased N fixed from 28th day (4th week) to the end of incubation. Nitrogen fixed from $(\text{NH}_4)_2\text{SO}_4$ in limed soil was 5% at the end of incubation, while N-fixed in unlimed soil at the same period was about 11% (Fig. 14) and had a tendency to increase. As was observed for Pine Ridge soil, liming decreased the amount of N fixed from both carriers in Wellwood soil.

4.7.3 Nitrogen Fixed in pH Amended Newdale Soil

There was very little difference between N sources in the amount of N fixed in pH amended Newdale soil (Fig. 27). Nitrogen fixed from each of the carriers increased from 3.5% at first day to 11% and 11.5% with $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$, respectively at the end of incubation. The trend of N-fixed kept increasing under reduced soil pH with both carriers as opposed to its constancy when the pH was not amended (Fig. 18). Acidifying Newdale soil increased the amount of added N fixed by this

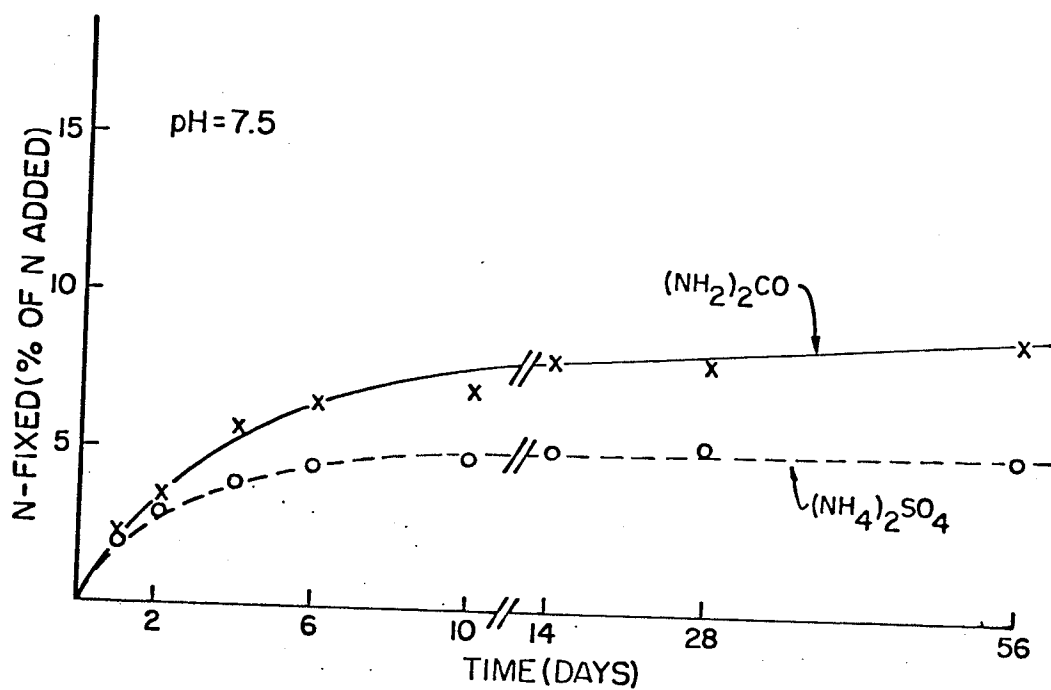


Figure 25: Ammonium fixation from two carriers (500 ppm N) by pH amended Pine Ridge soil during incubation at 20°C.

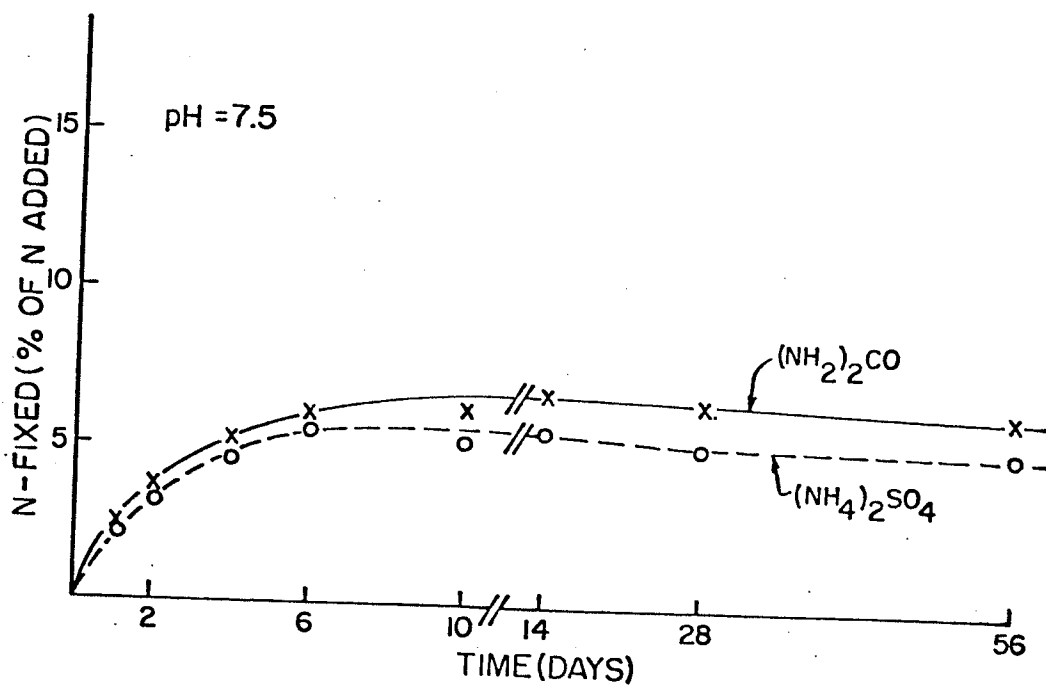


Figure 26: Ammonium fixation from two carriers (500 ppm N) by pH amended Wellwood soil during incubation at 20°C.

soil. By the end of incubation, 11% and 11.5% of added N was fixed from $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$, respectively. When the soil pH was not reduced, corresponding values were 9% and 7% (Fig. 18).

4.7.4 Nitrogen Fixed in pH Amended Almasippi Soil

In the pH amended Almasippi soil, the amount of N fixed from $(\text{NH}_2)_2\text{CO}$ increased from 3% at 1 day to a maximum of 6.5% of added N by the 6th day of incubation (Fig. 28). Nitrogen fixed remained constant at this value until 28th day of incubation. By the end of incubation, N fixed from $(\text{NH}_2)_2\text{CO}$ decreased to 5.7% of added N. With $(\text{NH}_4)_2\text{SO}_4$ N fixed increased from 2.5% at 1st day to about 6% after 14 days of incubation. As with $(\text{NH}_2)_2\text{CO}$, amount of N fixed from $(\text{NH}_4)_2\text{SO}_4$ decreased to 5.7% at the end of incubation. There was no real difference in the amount of N fixed from the two N sources. From 14 to 28 days (2-4 weeks) of incubation, 6.5% of added $(\text{NH}_2)_2\text{CO}$ was fixed, while 6% was fixed at the same time when the soil pH was not reduced (Fig. 20). With $(\text{NH}_4)_2\text{SO}_4$, the amount of N fixed from this source was not appreciably affected by reducing the soil pH (Figs. 20 and 28). Thus acidifying Almasippi soil did not cause any apparent increase in the amount of N fixed from either carrier. In a subsequent investigation, the pH of acidified Almasippi soil was found to increase during incubation. This might also have occurred here although the pH was not measured at the end of the incubation period.

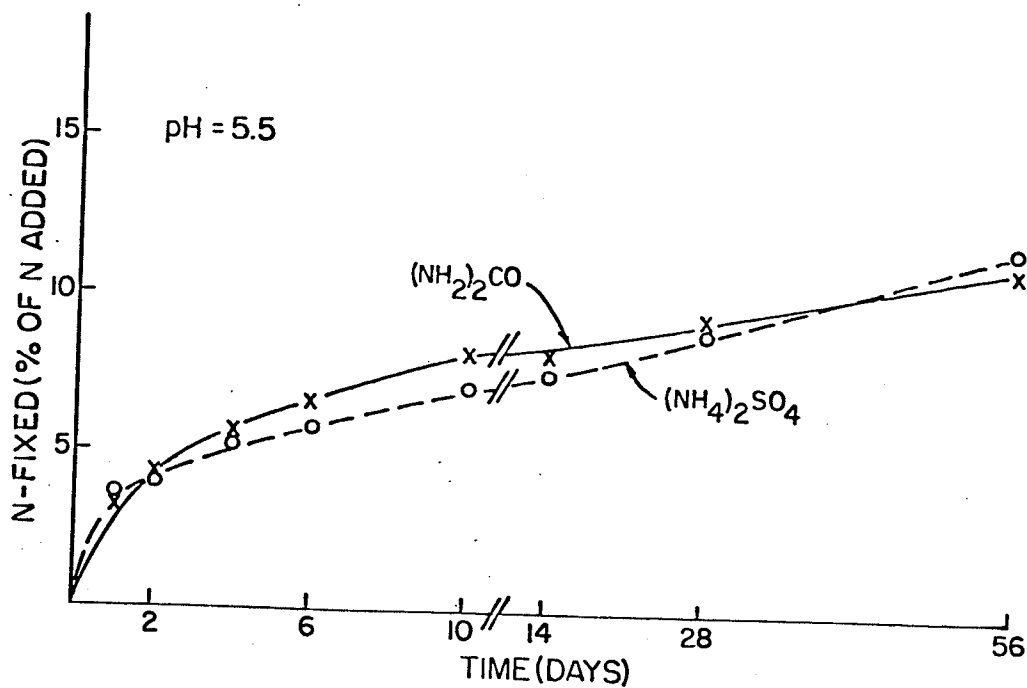


Figure 27: Ammonium fixation from two carriers (500 ppm N) by pH amended Newdale soil during incubation at 20°C.

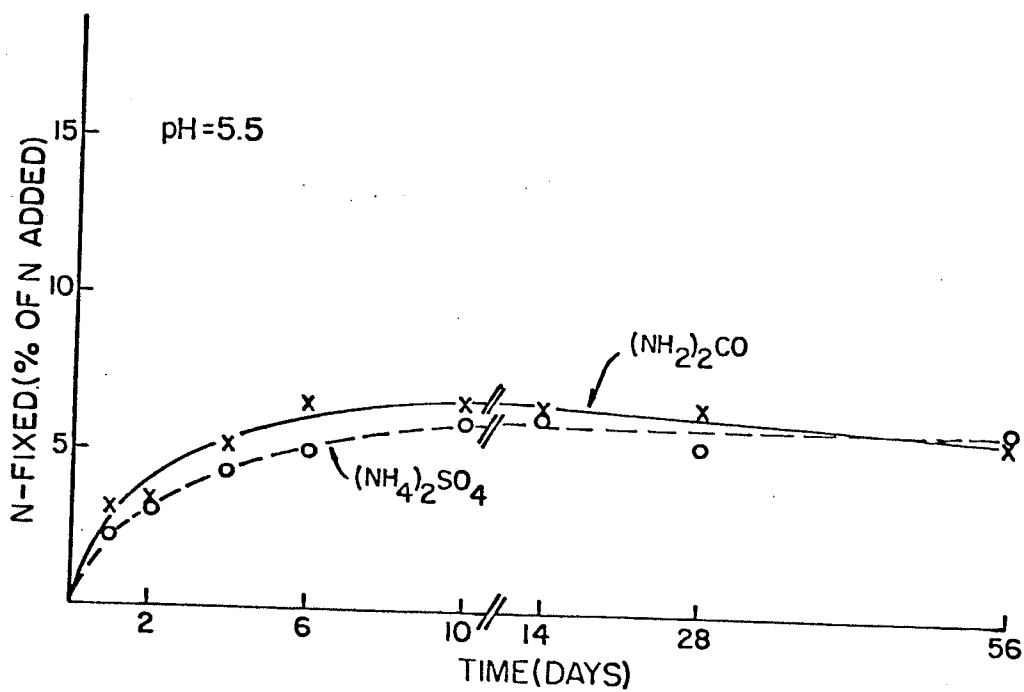


Figure 28: Ammonium fixation from two carriers (500 ppm N) by pH amended Almasippi soil during incubation at 20°C.

4.7.5 Recovery of Added Nitrogen From Limed and Unlimed Soils.

The total recovery of nitrogen (Figures 29 to 32) represent the sum of ammonium, nitrite, nitrate and fixed nitrogen in the treated soils. These figures were included to show the effect of liming on recovery of added N. Also to evaluate the magnitude of N that was unaccounted for under limed and unlimed soil conditions.

4.7.6 Pine Ridge Soil

Throughout the incubation period recovery of added N was greater in limed than unlimed Pine Ridge soil. Recovery of added N from $(\text{NH}_2)_2\text{CO}$ in Pine Ridge soil after one day of incubation was 60% and 27% for limed and unlimed soils, respectively (Fig. 29). Corresponding values at the end of the incubation period were 68% and 56% of added N.

There was virtually no difference between limed and unlimed soil in the amount of N recovered from $(\text{NH}_4)_2\text{SO}_4$ between 6 and 28 days of incubation (Fig. 30). However after 56 days of incubation, added $(\text{NH}_4)_2\text{SO}_4$ recovered was 90% and 81% from limed and unlimed soils, respectively. Nitrogen that was unaccounted for was greater with $(\text{NH}_2)_2\text{CO}$ than with $(\text{NH}_4)_2\text{SO}_4$ in both limed and unlimed Pine Ridge soils. By 56th day of incubation, 10% of added $(\text{NH}_4)_2\text{SO}_4$ and 32% of added $(\text{NH}_2)_2\text{CO}$, was unaccounted for in limed soil (Fig. 29 and 30). Earlier study showed a considerable accumulation of NO_2^- -N during the incubation of Pine Ridge soil with $(\text{NH}_2)_2\text{CO}$ added. This might result in chemical denitrification, thus contributing to the magnitude of unaccounted for N from added $(\text{NH}_2)_2\text{CO}$ in Pine Ridge soil.

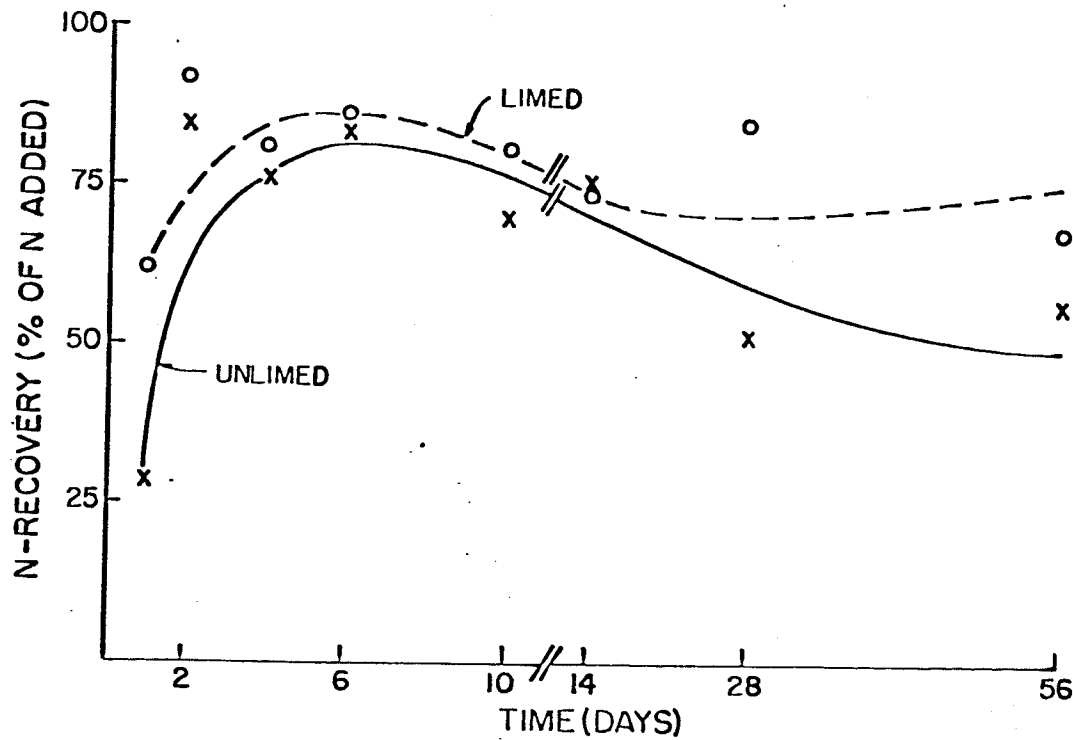


Figure 29: Nitrogen recovery from added urea in limed and unlimed Pine Ridge soil incubated at 20°C.

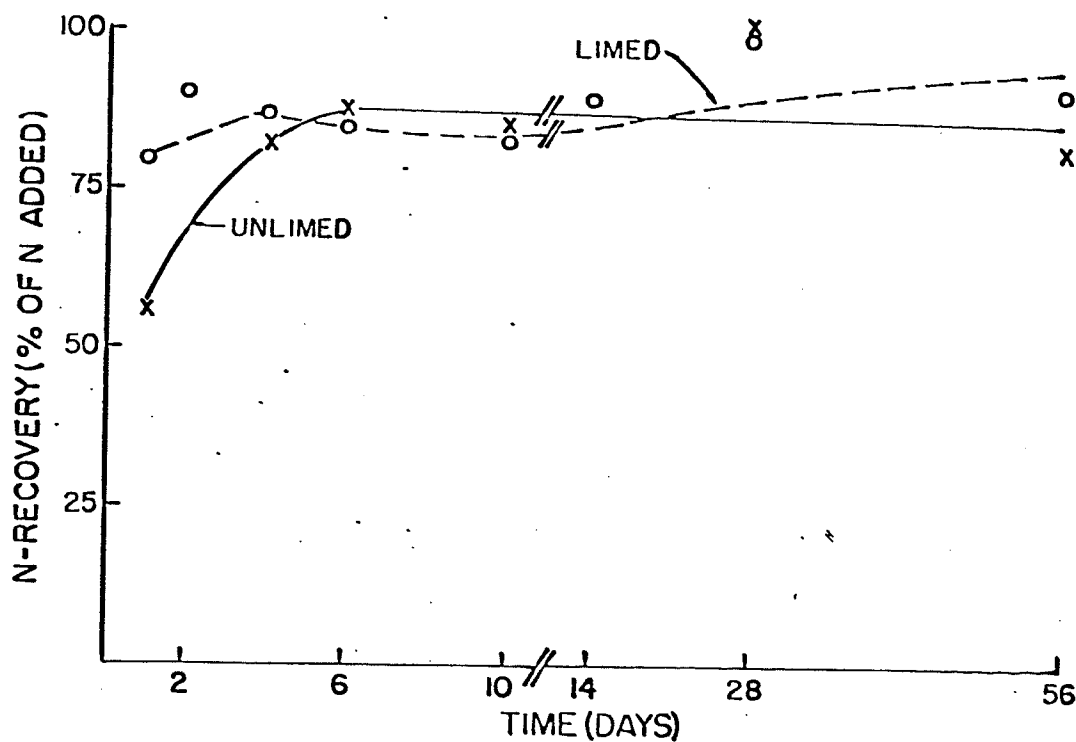


Figure 30: Nitrogen recovery from added ammonium sulphate in limed and unlimed Pine Ridge soil incubated at 20°C.

4.7.7 Wellwood Soil

In both limed and unlimed Wellwood soil, N recovery from added $(\text{NH}_2)_2\text{CO}$ took a similar pattern up to 2 days of incubation (Fig. 31). Liming Wellwood soil did not increase N recovery until 14 days of incubation. From this date onward, the slight difference in N recovery that occurred was in favour of limed soil. At 56 days of incubation 95% and 90% of added $(\text{NH}_2)_2\text{CO}$ were recovered from both limed and unlimed soils, respectively.

There was substantial difference in N recovered from $(\text{NH}_4)_2\text{SO}_4$ between limed and unlimed soil by the end of incubation period (Fig. 32). By this date 90% of added $(\text{NH}_4)_2\text{SO}_4$ was recovered in unlimed soil.

4.7.8 Summary

This study showed that liming Pine Ridge and Wellwood soils decreased the amount of N fixed from both added $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$. More of added $(\text{NH}_2)_2\text{CO}$ than $(\text{NH}_4)_2\text{SO}_4$ was fixed in the two soils when the pH was amended. Liming Pine Ridge soil increased the amount of N recovered from both carriers. There was a slight increase in N recovered from added $(\text{NH}_2)_2\text{CO}$ in limed Wellwood soil. Recovery of added $(\text{NH}_4)_2\text{SO}_4$ was not substantially increased by liming Wellwood soil.

When the pH of Newdale soil was reduced, more added N was fixed from both carriers. There was not much difference between the carriers in the amount of N fixed, but a tendency towards increased fixation of added N. In Almasippi soil, pH reduction did not increase the amount of N

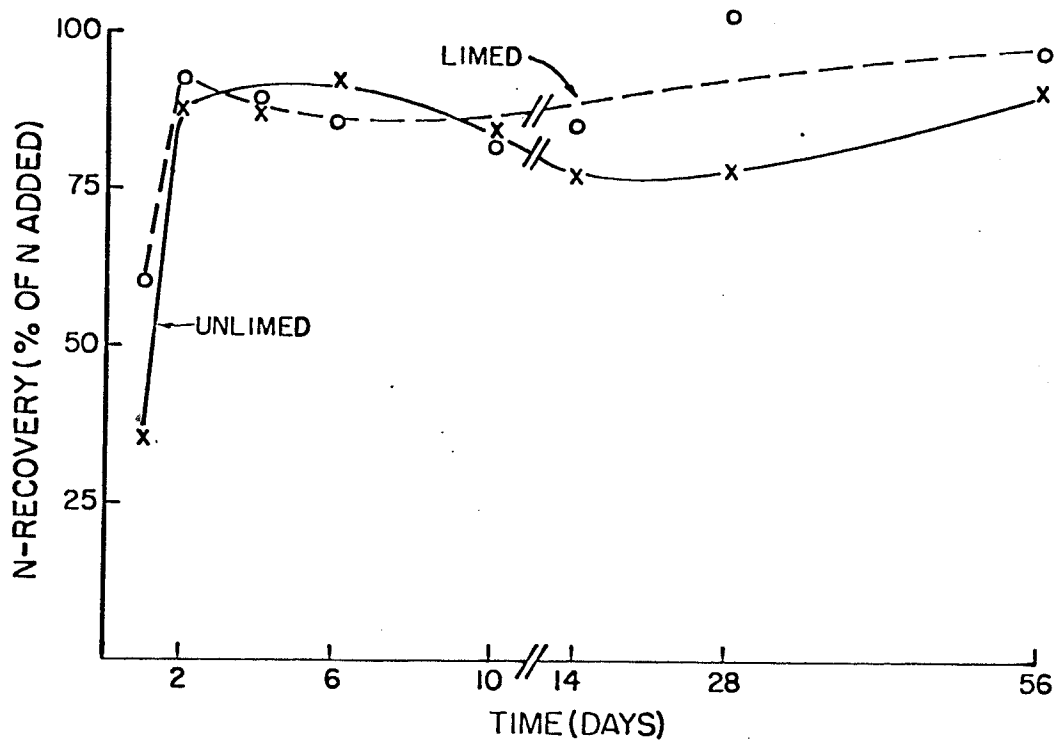


Figure 31: Nitrogen recovery from added urea in limed and unlimed Wellwood soil incubated at 20°C.

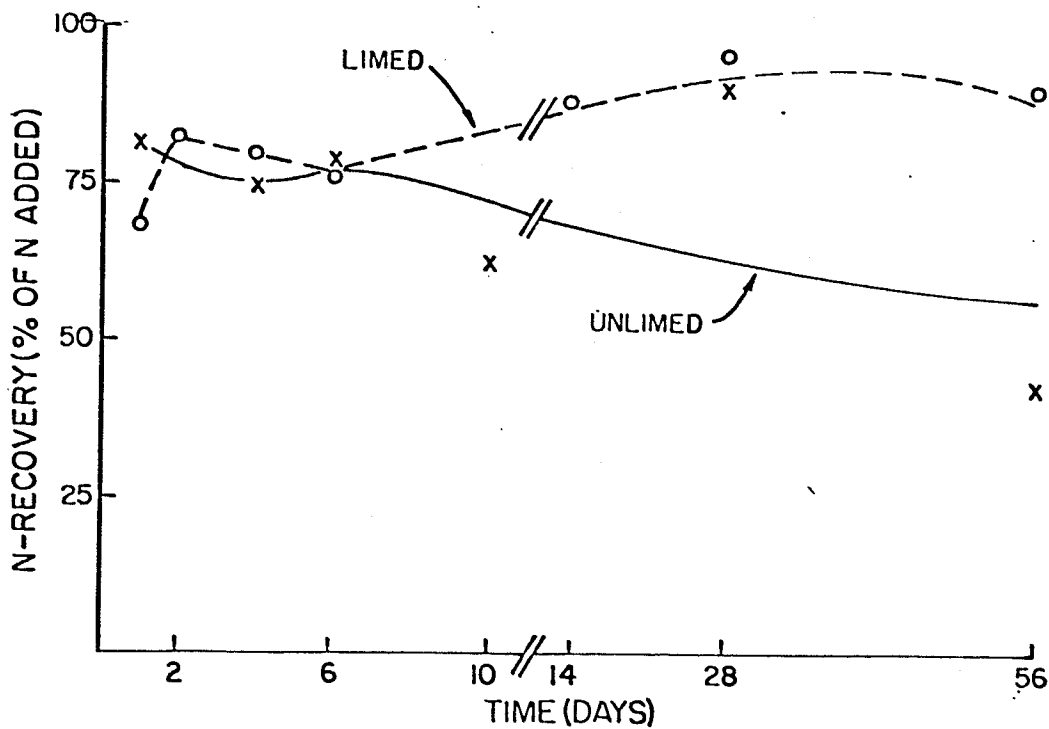


Figure 32: Nitrogen recovery from added ammonium sulphate in limed and unlimed Wellwood soil incubated at 20°C.

fixed. This might be due to increase in pH that probably occurred during the incubation. This speculation was confirmed in subsequent study.

4.8 EXPERIMENT VII: UTILIZATION OF NITROGEN FROM ^{15}N -LABELLED CARRIERS BY WHEAT GROWN ON PH AMENDED SOILS.

The results of the incubation study in experiment VI indicated that liming Pine Ridge and Wellwood soils decreased the amount of added N fixed by these soils. Conversely, reducing the soil pH increased the amount of N Fixed in Newdale but not in Almasippi soil. The objective of this study was to evaluate the efficiency of three nitrogen sources for wheat grown on pH amended soils and to ascertain the extent of recovery of added N by plant and soil.

The pH of the soils was amended as explained in experiment VI. Pine Ridge and Wellwood soils were limed to pH 7.5, while Newdale and Almasippi soils were acidified to pH 5.5. The soils were preincubated at 20°C for one week before adding N carriers and planting wheat seeds. Subsequent procedures and analysis were as explained for the first growth chamber experiment. The soil pH at harvest time was measured.

4.8.1 Dry Matter and Total N Yields of Wheat

In urea treated soils, the dry matter yield of shoots ranged from 6.66 g per pot in limed Pine Ridge soil to 11.58 g per pot in acidified Almasippi soil (Table 15). There was a significant difference in dry matter yield between the soils treated with $(\text{NH}_2)_2\text{CO}$. With $\text{Ca}(\text{NO}_3)_2$ treatment, the dry matter yield ranged from 6.63 g per pot in Pine Ridge

to 11.40 g per pot in Newdale soil. The yields from Newdale and Almasippi soils were significantly greater than yields from the other two soils. Dry matter yield in Wellwood soil was significantly greater than yield from Pine Ridge soil. With $(\text{NH}_4)_2\text{SO}_4$ treatment dry matter yield of wheat shoots in Almasippi soil was significantly greater than yields from the remaining soils. There was no significant difference in yields from Wellwood and Newdale soils, but both had significantly greater yield than that of Pine Ridge soil. In three of the soils (Pine Ridge, Wellwood and Almasippi) there was no significant difference in dry matter yield between the N-sources. The yield from $\text{Ca}(\text{NO}_3)_2$ treated Newdale soil was significantly greater than yields from the other two N-carriers, which were not significantly different from each other. Of the four soils used, dry matter yield from Pine Ridge soils was the least. Dry matter yield of wheat tops in this study was lower in almost all soils than those obtained in the first growth chamber experiment. This was probably due to high sulphate concentration especially when the soil was acidified by the addition of sulphuric acid. In the two limed soils, the cause of the decreased yields due to liming is unknown.

The total N-yield ranged from 101.2 mg per pot with $\text{Ca}(\text{NO}_3)_2$ treated Pine Ridge soil to 218.2 mg per pot with $\text{Ca}(\text{NO}_3)_2$ -treated Newdale soil. In Newdale soil, total N-yield was considerably greater with $\text{Ca}(\text{NO}_3)_2$ treatment than N-yield from the other two N-sources. In the remaining three soils, total N-yield from $(\text{NH}_4)_2\text{SO}_4$ treatment was slightly greater than N-yield from $(\text{NH}_2)_2\text{CO}$ and $\text{Ca}(\text{NO}_3)_2$.

TABLE 15

Dry matter and total N-yields in the above ground portion
of wheat grown on pH amended soils treated with
three different N-carriers

Soil Name	Yield (g/pot)			N-Yield (mg)		
	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_4)_2\text{SO}_4$
Pine Ridge	6.66f	6.63f	6.98ef	106.1	101.2	110.0
Wellwood	8.11de	7.96.de	8.87cd	129.8	123.9	145.8
Newdale	9.77bc	11.40a	9.23cd	168.6	218.2	168.3
Almasippi	11.59a	10.85ab	11.10a	180.3	177.4	190.3

* Means not followed by the same letter differ at a 0.05 probability level according to Duncan's multiple range test.

4.8.2 Nitrogen Derived from N-Carriers and Percent Utilization of Added N

Nitrogen derived from $\text{Ca}(\text{NO}_3)_2$ source was significantly greater than N derived from either $(\text{NH}_2)_2\text{CO}$ or $(\text{NH}_4)_2\text{SO}_4$ in all the soils (Table 16). There was no significant difference in percent N.d.f.f. between the two NH_4^+ -yielding carriers. The lowest % N.d.f.f. of 34.8 was obtained with urea-treated Newdale soil while the highest of 62.4% was from $\text{Ca}(\text{NO}_3)_2$ -treated Pine Ridge soil.

Percent utilization of added N ranged from 28.7% with urea in Pine Ridge soil to 50.9% with $\text{Ca}(\text{NO}_3)_2$ in Almasippi soil (Table 16). A greater percentage of the nitrogen from $\text{Ca}(\text{NO}_3)_2$ was utilized by wheat than of the N from $(\text{NH}_2)_2\text{CO}$. The difference was significant only in Newdale and Almasippi soils. Except for Newdale soil, there was no significant difference between the utilization of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$. Utilization of added N was not significantly different between the N-sources in limed Pine Ridge and Wellwood soils. There was a reduction in the yield of wheat in this experiment as compared to experiment I. Thus, in order to compare the effect of acidification or liming upon the efficiency of N-carriers, a yield-independent parameter was chosen. Nitrogen derived from fertilizer (N.d.f.f.) is a yield-independent parameter and can be used to compare the N-carriers only if native soil N was unaffected by pH change. The values of N.d.f.f. (urea) was generally not affected when two acid soils were limed (Tables 4 and 16). On the other hand, the values of N.d.f.f. (urea) decreased when alkaline soil was acidified. Such a trend was not observed with $\text{Ca}(\text{NO}_3)_2$ treatment.

TABLE 16

Nitrogen derived from N-carriers in wheat tops
and percent utilization of Added-N

Soil Name	N D F F (%)			Utilization (%)		
	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_4)_2\text{SO}_4$
Pine Ridge	54.1bc	62.4a	55.2b	28.7c	31.5c	30.3c
Wellwood	45.9e	50.6cd	43.5e	29.6c	31.2c	31.5c
Newdale	34.8f	42.4e	36.4f	29.3c	46.2b	30.6c
Almasippi	49.6d	57.4b	49.8d	44.7b	50.9a	47.3ab

* Means within the same parameter not followed by the same letter differ at 0.05 probability level according to Duncan's multiple range test.

Thus acidifying alkaline soil decreased the availability of NH_4^+ -yielding carriers as compared to native soil N.

4.8.3 Yield and Percent Utilization of Added N by Wheat Roots

Dry matter yield of wheat roots ranged from 2.86 g/pot in $(\text{NH}_4)_2\text{SO}_4$ -treated Newdale soil to 4.67 g/pot in $(\text{NH}_2)_2\text{CO}$ -treated Almasippi soil (Table 17). There was no significant difference in root yield between the N-carriers in any of the soils. However, there were significant differences in root yield between the soils. Dry matter yield of roots in urea-treated Almasippi soil was significantly greater than yield from the same N-source in Wellwood and Newdale soils. With $\text{Ca}(\text{NO}_3)_2$ treatment there was no significant difference in root yield between Pine Ridge, Wellwood and Almasippi soils. Yield from Almasippi soil, however, was significantly greater than yield from Newdale soil. Dry matter yield of roots from $(\text{NH}_4)_2\text{SO}_4$ treated Newdale soil was significantly lower than yield from Pine Ridge and Almasippi soils with the same N-source.

Utilization of added N by wheat roots was not significantly different between N-sources. Percent utilization of added N from $\text{Ca}(\text{NO}_3)_2$ was slightly greater (though not significantly so) in all the soils than utilization from the other N-sources.

TABLE 17

Dry matter yield and percent utilization of added-N
by wheat roots in pH amended soils

Soil Name	Yield (g/pot)			Utilization (%)		
	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_2)_2\text{CO}$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NH}_4)_2\text{SO}_4$
Pine Ridge	4.27abc	3.53bcd	4.20abc	10.4de	11.2bcd	10.9cde
Wellwood	3.16cd	3.43bcd	3.37bcd	10.4de	11.4bcd	10.1de
Newdale	3.8cd	2.91d	2.86d	8.9ef	9.1ef	8.0f
Almasippi	4.67a	4.36ab	4.43ab	12.6abc	13.5a	13.1ab

* Means within the same parameters not followed by the same letter differ at a 0.05 probability level according to Duncan's multiple range test.

4.8.4 Total Nitrogen Balance

The recovery of added N by plant and soil at the end of the experiment and calculated unrecovered N are shown in Table 18. The total nitrogen recovery in plant was nearly equal for all the N-sources in limed Pine Ridge and Wellwood soils. An attempt was made to compare the change in the efficiency of either NH_4^+ -yielding carrier or $\text{Ca}(\text{NO}_3)_2$ due to change in soil pH. Difference in percent N recovery by plant between two different types of N carriers was used for this purpose. Liming the acid soils brought utilization of added N from NH_4^+ -carriers closer to that of $\text{Ca}(\text{NO}_3)_2$ (Tables 7 and 18). For Newdale soil, total nitrogen in the plant was greater from $\text{Ca}(\text{NO}_3)_2$ -treatment than from the other two N-carriers, which were nearly equal. Without liming (Table 7), total nitrogen recovery of urea and $\text{Ca}(\text{NO}_3)_2$ -N by wheat grown on Newdale soil were nearly equal (51 and 53% respectively). Lowering the pH of Newdale soil reduced total N in plant from NH_4^+ -yielding carriers to approximately 38% while the value for total N in plant from $\text{Ca}(\text{NO}_3)_2$ was 55% which was similar to that of unamended Newdale soil. In Almasippi soil, nitrogen in plant from $\text{Ca}(\text{NO}_3)_2$ -treated soil was slightly greater than N in plant from the other two N-carriers. Absence of significant difference between N-sources in total N in plant may be due to the increase in soil pH that occurred in Almasippi soil during the experiment. This increase might have led to increased utilization of added N from NH_4^+ -yielding carriers.

TABLE 18

Nitrogen balance on pH amended soils (% of added N)

Soil Name	$(\text{NH}_2)_2\text{CO}$			$\text{Ca}(\text{NO}_3)_2$			$(\text{NH}_4)_2\text{SO}_4$		
	Plant	Soil	Unrec.N	Plant	Soil	Unrec.N	Plant	Soil	Unrec.N
Pine Ridge	39.1	47.4	13.5	42.7	45.3	12.0	41.3	40.4	18.3
Wellwood	40.0	50.4	9.6	42.6	46.7	10.7	41.6	39.7	18.7
Newdale	38.2	57.9	3.9	55.3	39.6	5.1	38.6	50.9	10.5
Almasippi	57.3	30.2	12.5	64.3	26.8	8.9	60.4	24.2	15.4
Average	43.7	46.5	9.9	51.2	39.6	9.2	45.5	38.8	15.7

Unrec N = Unrecovered N

The amount of labelled ^{15}N remaining in limed Pine Ridge, Wellwood and Almasippi soils was greatest with $(\text{NH}_2)_2\text{CO}$ and least with $(\text{NH}_4)_2\text{SO}_4$. In acidified Newdale soil ^{15}N remaining in the soil was greatest with $(\text{NH}_2)_2\text{CO}$ and least with $\text{Ca}(\text{NO}_3)_2$. This could account for the inefficient utilization of NH_4^+ -yielding carriers in Newdale soil. Total recovery of added N was greater in this experiment than the first growth chamber study. This was because more N remained in the pH amended soils.

The amount of N unaccounted for was greatest with $(\text{NH}_4)_2\text{SO}_4$ in all soils. There was virtually no difference between $(\text{NH}_2)_2\text{CO}$ and $\text{Ca}(\text{NO}_3)_2$ in unrecovered N in limed Pine Ridge and Wellwood soils. For acidified Newdale soil, unrecovered N was slightly greater with $\text{Ca}(\text{NO}_3)_2$ than $(\text{NH}_2)_2\text{CO}$ whereas the reverse was true with Almasippi soil.

4.8.5 Soil Reaction

In limed Pine Ridge and Wellwood soils, there was no substantial change in soil pH throughout the growth period with $(\text{NH}_2)_2\text{CO}$ and $\text{Ca}(\text{NO}_3)_2$ treatments (Table 19). A pH drop of about 0.2 units occurred in these soils with $(\text{NH}_4)_2\text{SO}_4$. An increase of about 0.4 pH units occurred with all the N-sources in Newdale soil. In acidified Almasippi soil, a considerable increase in soil pH occurred during the growth period. The increase ranged from 2.33 pH units with $(\text{NH}_2)_2\text{CO}$ treatment to 2.41 with $(\text{NH}_4)_2\text{SO}_4$ treatment. This increase in soil pH may be due to gradual dissolution of some CaCO_3 particles remaining in the soil af-

ter the H_2SO_4 treatment. This subsequently neutralized the acid added to the highly calcareous Almasippi soil. Similar pH change could have occurred in the incubation study in experiment VI which may explain why Almasippi soil did not fix more N when the soil was acidified.

4.8.6 Summary

There was no significant difference in dry matter yield of wheat between the N-carriers in limed Pine Ridge and Wellwood soils, and also in acidified Almasippi soil. Conversely, in Newdale soil, dry matter yield was significantly greater with $\text{Ca}(\text{NO}_3)_2$ treatment than with the other two N-carriers. In this study, a lower dry matter yield was obtained than in the first growth chamber experiment. Liming Pine Ridge and Wellwood soils brought utilization of added N from NH_4^+ -yielding carriers closer to that of N from $\text{Ca}(\text{NO}_3)_2$. More nitrogen from added $\text{Ca}(\text{NO}_3)_2$ was utilized in Newdale soil than from the other nitrogen sources. Acidifying this soil probably reduced the utilization of N from NH_4^+ -carriers. This was reflected in the amount of N remaining in Newdale soil at the end of the study. In acidified Almasippi soil, the soil pH changed considerably during the experiment and this probably led to increased utilization of added N from NH_4^+ -carriers. More of added N from $(\text{NH}_2)_2\text{CO}$ than from $\text{Ca}(\text{NO}_3)_2$ remained in all the soils at the end of the experiment. This was in agreement with the first growth chamber experiment. Nitrogen unaccounted for was greatest with $(\text{NH}_4)_2\text{SO}_4$ in all the soils. Total recovery of added N in this study was greater than that obtained in experiment I with the same soil and N-source. This was

TABLE 19

Soil reaction before and after the growth of wheat
following addition of different N-carriers

Soil Name	Urea		Ca(NO ₃) ₂		(NH ₄) ₂ SO ₄	
	pH ₁ *	pH ₂ **	pH ₁ *	pH ₂ **	pH ₁ *	pH ₂ **
Pine Ridge	7.50	7.40	7.50	7.40	7.50	7.24
Wellwood	7.50	7.47	7.50	7.43	7.50	7.35
Newdale	5.50	5.91	5.50	5.84	5.50	5.81
Almasippi	5.50	7.83	5.50	7.86	5.50	7.91

* Soil pH as amended before cropping.

**Soil pH as determined after cropping.

due to the fact that a relatively greater amount of N remained in the soil at the end of the experiment in this study.

Chapter V

GENERAL DISCUSSION

In a growth chamber study, the dry matter yield of wheat was significantly greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$ in acid Pine Ridge, Wellwood and Granville soils. There was no difference between N-sources in terms of dry matter yield in neutral and alkaline soils, except for Almasippi. In Almasippi soil, dry matter yield of wheat was significantly better with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$. In this study percent utilization of added N, which is a yield dependent criterion was greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$ in seven of the eight soils studied. It was only significantly so in Wellwood, Granville and Waitville soils. Thus a better utilization of added N from $\text{Ca}(\text{NO}_3)_2$ than $(\text{NH}_2)_2\text{CO}$ was obtained in the acid soils.

Percent of N derived from fertilizer is a yield-independent parameter used to evaluate the relative efficiencies of different N-sources. Percent N.d.f.f was significantly greater with $\text{Ca}(\text{NO}_3)_2$ than with $(\text{NH}_2)_2\text{CO}$ in acid Granville and Waitville soils. This is further evidence that $\text{Ca}(\text{NO}_3)_2$ is a more available N-source for wheat in these acid soils. Similarly the 'A' value data indicates that $\text{Ca}(\text{NO}_3)_2$ is a better source of N for wheat than is $(\text{NH}_2)_2\text{CO}$ especially in acid soils.

Incubation studies indicated that the lower efficiency of $(\text{NH}_2)_2\text{CO}$ as a nitrogen source in acid soils may be due to its fixation in such soils. An incubation study showed that fixation of added N from $(\text{NH}_2)_2\text{CO}$ was considerable, particularly in acid soils, and that it took place rapidly. Within one day 10 percent of added $(\text{NH}_2)_2\text{CO}$ was fixed in Granville and Waitville soils. Substantial fixation also took place in Pine Ridge and Wellwood soils, although in these soils it took place more slowly. Removal of added N in this form appears to have been due largely to chemical fixation as NH_4^+ by clay and organic matter rather than as immobilization by microorganisms since $\text{Ca}(\text{NO}_3)_2$ was not similarly affected.

There appears to be some inconsistency in results obtained with $(\text{NH}_2)_2\text{CO}$ in that, although Granville and Waitville soils fixed about 20 percent of added $(\text{NH}_2)_2\text{CO-N}$, it was found from incubation studies that the remaining 80 percent could be recovered as nitrate in less than three weeks. This was comparable to recoveries obtained in the alkaline Holland, Newdale and Red River soils.

Added N fixed was mainly organically bound. Assessment of the amount fixed per unit weight of organic matter indicated that soil fixation of added N was inversely related to soil pH. This is in agreement with the findings of Smith and Chalk (1980). Also the incubation study showed that organic matter fixes more added N at low pH values. Sohn and Peech (1958) indicated that acid soil containing a large amount of organic matter had the greatest ammonia-fixing capacity. In this study more

$(\text{NH}_2)_2\text{CO}$ -N may have been fixed by Pine Ridge and Wellwood soils because the half life of NH_4^+ -N was greater in these soils than in alkaline soils. This was a consequence of the low rate of nitrification resulting from low microbial activity. However in Granville and Waitville soils nitrification was relatively fast, but this was not reflected in the yield or N.d.f.f. The loss of N in Granville and Waitville soils could be attributed to increased rate of soil fixation and immobilization of added N. Liming an acid soil decreased fixation of added N by reducing the residence time of NH_4^+ -N and probably increasing microbial activity.

Nitrogen balance studies showed that some of the added N was not taken up by the plant or recovered in the soil. This unaccounted-for N could have been lost through chemical denitrification particularly in the acid Pine Ridge and Wellwood soils. These two soils and alkaline Almasippi soil demonstrated a substantial accumulation of nitrite from added urea during an incubation study.

A subsequent study with ^{15}N -labelled nitrite-N showed that acid Pine Ridge and Wellwood soils are capable of producing elemental N from nitrite. Therefore chemical denitrification might have been responsible for unaccounted-for N in these soils during the growth chamber study. The alkaline Almasippi soil accumulated nitrite following urea application, but did not show any capacity for chemical denitrification of nitrite. This may be due to rapid oxidation of nitrite to nitrate by the Almasippi soil. None of the other five soils showed a tendency for chemical denitrification.

These studies showed a greater uptake of nitrogen from $\text{Ca}(\text{NO}_3)_2$ than from urea in acid soils. It is significant that recovery of added nitrogen in plant plus that remaining in soil was equal to or greater with urea than with $\text{Ca}(\text{NO}_3)_2$ in all cases. This indicates that whereas urea nitrogen is more subject to fixation than nitrogen from $\text{Ca}(\text{NO}_3)_2$ the latter was more subject to loss from the soil-plant system, presumably by denitrification.

Chapter VI

SUMMARY AND CONCLUSION

Growth chamber experiments and incubation studies were conducted to determine crop utilization and soil fixation of three nitrogen carriers in several Manitoba soils with varying physical and chemical properties. In a growth chamber study, eight soils were treated with ^{15}N -labelled urea and calcium nitrate and wheat was grown for 52 days at 20°C .

More nitrogen from $\text{Ca}(\text{NO}_3)_2$ was utilized by wheat than from $(\text{NH}_2)_2\text{CO}$ in the Pine Ridge, Wellwood, Granville and Waitville soils. The yield-independent isotope criterion, the 'A' value, suggests that $\text{Ca}(\text{NO}_3)_2$ is the more available N carrier and $(\text{NH}_2)_2\text{CO}$ the less efficient N-source for wheat on these slightly acid soils. The dry matter yield of wheat from Pine Ridge, Wellwood, and Granville soils was significantly greater with the $\text{Ca}(\text{NO}_3)_2$ treatment than where $(\text{NH}_2)_2\text{CO}$ was used. A total nitrogen balance showed that ^{15}N remaining in the soil at the end of the experiment was consistently greater with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$ in all the soils used. The total recovery of added N (including soil fixed N) from $(\text{NH}_2)_2\text{CO}$ was at least equal to and in most cases greater than that of $\text{Ca}(\text{NO}_3)_2$. This may have been due to a greater loss of N by denitrification in $\text{Ca}(\text{NO}_3)_2$ -treated than $(\text{NH}_2)_2\text{CO}$ -treated soils.

An incubation study indicated that oxidation of NH_4^+ -N was considerably slower in slightly acid soils. Some of the NH_4^+ -N remained in urea-treated Pine Ridge soil after 33 days of incubation at 20°C. Persistence of NH_4^+ -N in slightly acid soil might lead to fixation of NH_4^+ -N. In the same study, nitrite-N accumulated and persisted in Pine Ridge and Wellwood soil following treatment with $(\text{NH}_2)_2\text{CO}$. Accumulation of nitrite-N also occurred in alkaline Almasippi soil, but only for a short time since it was rapidly oxidized to nitrate.

A subsequent investigation using ^{15}N -labelled NaNO_2 demonstrated a tendency for chemical denitrification with the production of molecular nitrogen from Pine Ridge and Wellwood soils. The initial rate of production of molecular N in Wellwood soil was 3.2% of added N per day, and 1.4% per day for Pine Ridge soil. None of the remaining six soils used showed a substantial production of molecular N throughout the period of incubation.

In studying the interaction between soil and N-carriers in the laboratory, it was observed that more of the N added as $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ was fixed than N added as $\text{Ca}(\text{NO}_3)_2$ in all the eight soils used. This provides a partial explanation of the greater amount of added N from $(\text{NH}_2)_2\text{CO}$ than from $\text{Ca}(\text{NO}_3)_2$ remaining in the soil at the end of the growth chamber experiment. Fixation of added N from NH_4^+ -yielding carriers occurred very rapidly especially in slightly acid soils. About 18% of added N from $(\text{NH}_2)_2\text{CO}$ was fixed in Granville soil by the 10th day of incubation.

In a subsequent incubation study, it was found that most of the fixed N was organically bound. The soil organic matter fixed approximately 5 to 10 times as much N per unit weight as clay. Both organic matter and clay had a greater capacity to fix added N at low pH. Added N fixed from both $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$ was increased when Newdale soil was acidified. This was not true with acidified Almasippi soil. It was subsequently found that the pH of Almasippi soil increased during the incubation period. Liming Pine Ridge and Wellwood soils decreased the amount of added N fixed from NH_4^+ -yielding carriers. Even after amendment of the soil pH by liming more $(\text{NH}_2)_2\text{CO}$ than $(\text{NH}_4)_2\text{SO}_4$ was fixed.

The second growth chamber experiment was designed to study the effect of pH amendments on crop utilization of added N. There was no significant difference in dry matter yield of wheat between N-carriers in limed Pine Ridge and Wellwood soils and also in acidified Almasippi soil. Liming Pine Ridge and Wellwood soils, however, brought the utilization of added N from NH_4^+ -yielding carriers closer to that of N from $\text{Ca}(\text{NO}_3)_2$. Dry matter yield of wheat in acidified Newdale soil was significantly greater with $\text{Ca}(\text{NO}_3)_2$ treatment than either of the NH_4^+ -yielding sources. In pH amended Newdale soil, wheat utilized more N from $\text{Ca}(\text{NO}_3)_2$ than from ammonium carriers. Thus acidifying the alkaline Newdale soil decreased the utilization of N from both $(\text{NH}_2)_2\text{CO}$ and $(\text{NH}_4)_2\text{SO}_4$. In acidified Almasippi soil, the pH changed considerably during the experiment and this probably led to increased utilization of added N from NH_4^+ -carriers. Such increase in pH explains the lack of an

increase in the amount of N fixed in acidified Almasippi soil during the incubation experiment. Nitrogen remaining in soil at the end of the second growth chamber experiment was greater with $(\text{NH}_2)_2\text{CO}$ than with $\text{Ca}(\text{NO}_3)_2$. Unrecovered N by plants and in the soil was greatest with $(\text{NH}_4)_2\text{SO}_4$ in all the soils used. In this investigation total recovery of added N was generally greater than that obtained in experiment I with the same N-source. This was due to the fact that a greater amount of N remained in the soil at the end of the study with pH amended soils probably due to lower crop utilization of added N.

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