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
presented to the University of Manitoba
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
Department of Soil Science

Winnipeg, Manitoba, 1981

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr. Robert A. Hedlin for his guidance and constructive criticisms during the course of this investigation and the preparation of the manuscript.

I also wish to express my deep appreciation to Dr. Chai M. Cho for his valuable advice and helpful suggestions throughout the course of this study.

The assistance received from my colleagues and from members of staff of Soil Science, Soil Survey and Soil Testing Laboratories is gratefully acknowledged.

A special word of thanks is due to the University of Ife, Nigeria for financial assistance and to the University of Manitoba for supporting me in the last 2 months.

Gratitude is due to all members of Obi´s family particularly ´Funke, ´Tayo, ´Kemi and ´Bukola for their patience and co-operation.

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 $Ca(NO_3)_2$ was utilized by wheat than from $(NH_2)_2CO$ in the slightly acid soils. The ′A′ value indicates that $Ca(NO_3)_2$ is more available to wheat than $(NH_2)_2CO$ on the slightly acid soils. Dry matter yield of wheat was significantly greater with $Ca(NO_3)_2$ treatment than with $(NH_2)_2CO$ in Pine Ridge, Wellwood and Granville soils. A much greater part of NH_4^+-N from $(NH_2)_2CO$ than NO_3^--N from $Ca(NO_3)_2$ 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. Accummulation 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 accummulation 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 $Ca(NO_3)_2$ 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 explanation of the greater amount of N from $(NH_2)_2CO$ than from $Ca(NO_3)_2$ 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 $(NH_2)_2CO$ and $(NH_4)_2SO_4$ 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 $Ca(NO_3)_2$ when Pine Ridge and Wellwood soils were limed. In acidified Newdale soil, more N from $Ca(NO_3)_2$ 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.

CONTENTS

ACKNOWLEDGEMENTS ii

ABSTRACT iii

Chapter

page

I. INTRODUCTION 1

II. LITERATURE REVIEW 3

- Forms Of Nitrogen In the Soil 3
  - Organic Nitrogen 3
  - Inorganic Nitrogen 4
- Mineralization of Organic Nitrogen 4
  - Nitrification 5
- Crop Utilization of Added Nitrogen (N) 7
- Fate of Added Nitrogen in the Soil 12
  - Immobilization 12
  - Ammonia Fixation 15
    - Fixation by Clay Minerals 15
    - Fixation by Organic Matter 16
  - Nitrite and Organic Matter 18
  - Leaching 19
  - Ammonia Volatilization 22
  - Denitrification 23
    - Biological Denitrification 24
    - Chemical Denitrification 27
- Residual Effects of Nitrogen 29
- Nitrogen Balance 30

III. MATERIALS AND METHODS 33

- Soil Samples 33
  - Experiment I: Utilization of Nitrogen from ^{15}N-labelled Urea and Calcium Nitrate by Wheat Grown on Various Soils. 33
  - Experiment II: Forms and Distribution of Inorganic N in Urea [$(NH_2)_2CO$] Treated Soils. 37
  - Experiment III: Chemical Denitrification in Some Manitoba Soils Treated with Labelled Nitrite. 38
  - Experiment IV(i): Nitrogen Fertilizer and Soil Interactions. 41

Experiment IV(ii): Rapid Reactions of N-Fertilizers in Four Slightly Acid to Neutral Soils. 41
Experiment V: Determination of Organically Fixed N in Four Manitoba Soils. 42
Experiment VI: Interactions of Ammonium Yielding Fertilizers in pH Ammended Soils. 43
Experiment VII: Utilization of Nitrogen from ^{15}N-labelled Fertilizers by Wheat Grown on pH Ammended Soils. . 44
Analytical Procedures 44
Soil pH 44
Organic Matter 45
Calcium Carbonate 45
Cation Exchange Capacity 45
Electrical Conductivity 46
Available Phosphorus ($NaHCO_3$ Method) 46
Moisture Content at Field Capacity 46
Total Nitrogen to include Nitrite plus Nitrate 47
Total Inorganic Nitrogen by Distillation 48
Soil Organic Nitrogen 48
Ammonium Nitrogen 48
Nitrite and Nitrate Nitrogen 49
Total Nitrogen (Plant) 49
^{15}N Analysis 50

IV. RESULTS AND DISCUSSIONS 51

Experiment 1: Utilization of Nitrogen from ^{15}N-labelled Urea and Calcium Nitrate by Wheat Grown on Various Soils. 51
Dry Matter and Total N-yields of Wheat 52
Nitrogen Derived from N-carriers and Percent Utilization of Added N 54
Yield and Percent Utilization of Added N by Wheat Roots . 56
The "A" Values of the Experimental Soils 58
Total Nitrogen Balance 59
Summary 61
Experiment II: Forms and Distribution of Inorganic N in Urea $[(NH_2)_2CO]$ Treated Soils Incubated at 20°C . . . 63
Distribution of Inorganic N in Pine Ridge Soil 63
Distribution of Inorganic N in Wellwood Soil 64
Distribution of Inorganic N in Granville Soil 66
Distribution of Inorganic N in Waitville Soil 68
Distribution of Inorganic N in Holland Soil 68
Distribution of Inorganic N in Newdale Soil 71
Distribution of Inorganic N in Red River Soil 71
Distribution of Inorganic N in Almasippi Soil 74
Effect of Added Urea-N on Soil pH 77
Effect of Soil pH on Oxidation of Ammonium-N 77
Summary 79
Experiment III. Chemical Denitrification in Some Manitoba Soils Treated with ^{15}N-labelled Nitrite 81
Experiment IV (i). Nitrogen Carriers and Soil Interactions. 90

Nitrogen Fixed in Pine Ridge Soil 91
Nitrogen Fixed in Wellwood Soil 91
Nitrogen Fixed in Granville Soil 93
Nitrogen Fixed in Waitville Soil 93
Nitrogen Fixed in Holland Soil 93
Nitrogen Fixed in Newdale Soil 95
Nitrogen Fixed in Red River Soil 95
Nitrogen Fixed in Almasippi Soil 98
Summary 98
Experiment IV (ii): Fixation of Ammonium Yielding Carriers in Slightly Acid Soils 100
Fixed N in Pine Ridge Soil Within Few Days of N-addition. 100
Fixed N in Wellwood Soil Within Few Days of N-addition 100
Fixed N in Granville Soil Within Few Days of N-addition 101
Fixed N in Waitville Soil Within Few Days of N-addition 101
Summary 104
Experiment V: Determination of Organically and Inorganically Fixed N in Four Manitoba Soils 105
Total Nitrogen in Soil 105
Organic Nitrogen 107
Inorganic Nitrogen 109
Summary 111
Experiment VI: Interaction of Ammonium Yielding Carriers in pH Amended Soils 111
Nitrogen Fixed in pH Amended Pine Ridge Soil 112
Nitrogen Fixed in pH Amended Wellwood Soil 112
Nitrogen Fixed in pH Amended Newdale Soil 113
Nitrogen Fixed in pH Amended Almasippi Soil 115
Recovery of Added Nitrogen From Limed and Unlimed Soils..117
Pine Ridge Soil 117
Wellwood Soil 119
Summary 119
Experiment VII: Utilization of Nitrogen from ^{15}N-Labelled Carriers by Wheat Grown on pH Amended Soils. 121
Dry Matter and Total N Yeilds of Wheat 121
Nitrogen Derived from N-Carriers and Percent Utilization of Added N 124
Yield and Percent Utilization of Added N by Wheat Roots 126
Total Nitrogen Balance 128
Soil Reaction 130
Summary 131

V. GENERAL DISCUSSION 134

VI. SUMMARY AND CONCLUSION 138

BIBLIOGRAPHY 142

LIST OF FIGURES

Figure

page

1. Incubation tube 39
2. Gas sample tube 40
3. Ammonium, nitrite, nitrate and total inorganic nitrogen in Pine Ridge soil treated with urea-N at 500 ppm. 65
4. Ammonium, nitrite, nitrate and total inorganic nitrogen in Wellwood soil treated with urea-N at 500 ppm. 67
5. Ammonium, nitrite, nitrate and total inorganic nitrogen in Granville soil treated with urea-N at 500 ppm. 69
6. Ammonium, nitrite, nitrate and total inorganic nitrogen in Waitville soil treated with urea-N at 500 ppm. 70
7. Ammonium, nitrite, nitrate and total inorganic nitrogen in Holland soil treated with urea-N at 500 ppm. 72
8. Ammonium, nitrite, nitrate and total inorganic nitrogen in Newdale soil treated with urea-N at 500 ppm. 73
9. Ammonium, nitrite, nitrate and total inorganic nitrogen in Red River soil treated with urea-N at 500 ppm. 75
10. Ammonium, nitrite, nitrate and total inorganic nitrogen in Almasippi soil treated with urea-N at 500 ppm. 76
11. Changes in NH_4^+-N concentration in soils with different pH treated with 500 ppm urea-N. 80
12. Chemical denitrification in Wellwood and Pine Ridge soils following addition of 2 mg N as $NaNO_2$ to 20 g soil. 89
13. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500 ppm N) after extraction with 2NKCl. 92
14. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500ppm N) after extraction with 2NKCl. 92

15. Nitrogen remaining in soil treated with ^{15}-labelled carriers (500 ppm N) after extraction with 2NKCl. 94

16. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500ppm N) after extraction with 2NKCl. 94

17. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500ppm N) after extraction with 2NKCl. 96

18. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500ppm N) after extraction with 2NKCl. 96

19. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500ppm N) after extraction with 2NKCl. 97

20. Nitrogen remaining in soil treated with ^{15}N-labelled carriers (500ppm N) after extraction with 2NKCl. 97

21. Ammonium fixation from two carriers (500 ppm N) by Pine Ridge soil during incubation at 20°C. 102

22. Ammonium fixation from two carriers (500 ppm N) by Wellwood soil during incubation at 20°C. 102

23. Ammonium fixation from two carriers (500 ppm N) by Granville soil during incubation at 20°C. 103

24. Ammonium fixation from two carriers (500 ppm N) by Waitville soil during incubation at 20°C. 103

25. Ammonium fixation from two carriers (500 ppm N) by pH amended Pine Ridge soil during incubation at 20°C. 114

26. Ammonium fixation from two carriers (500 ppm N) by pH amended Wellwood soil during incubation at 20°C. 114

27. Ammonium fixation from two carriers (500 ppm N) by pH amended Newdale soil during incubation at 20°C. 116

28. Ammonium fixation from two carriers (500 ppm N) by pH amended Almasippi soil during incubation at 20°C. 116

29. Nitrogen recovery from added urea in limed and unlimed Pine Ridge soil incubated at 20°C. 118

30. Nitrogen recovery from added ammonium sulphate in limed and unlimed Pine Ridge soil incubated at 20°C. 118

31. Nitrogen recovery from added urea in limed and unlimed Wellwood soil incubated at 20°C. 120

32. Nitrogen recovery from added ammonium sulphate in limed and unlimed Wellwood soil incubated at 20°C. 120

LIST OF TABLES

Table page

1. Subgroup designation, legal location and some physical and chemical properties of the soils studied. 34

2. Subgroup designation, legal location and some physical and chemical properties of the soils studied. 35

3. Dry matter and total N-yields in the above ground portion of wheat grown on various soils treated with $(NH_2)_2CO$ and $Ca(NO_3)_2$ at 100 ppm N (200 mg/pot). 53

4. Nitrogen derived from N-carriers in wheat tops and utilization of added N. 55

5. Dry matter yield and percent utilization of added N of wheat roots. 57

6. "A" values of the experimental soils measured using $Ca(NO_3)_2$ and urea, and relative efficiency of urea as compared to $Ca(NO_3)_2$. 60

7. Total nitrogen balance (percent of added N-fertilizer). 62

8. Effects of urea-N addition on soil pH during incubation at 20°C. . 78

9. Possible gaseous products having mass to charge ratio (m/e) 28 through 46 and their probable components. 82

10. Mass spectrometric analyses of incubation atmosphere after 2 days. 84

11. Illustration of the method of calculation with the results of MS scan after 2 days of incubation. 88

12. Nitrogen contents remaining after 2N KCl extraction and urea-N fixed in four soils after 4 weeks of incubation (N rate = 500 ppm). 106

13. Organic nitrogen and fixation of added urea-N by organic matter in four Manitoba soils (N rate = 500 ppm). 108

14. Inorganic N contents remaining after 2N KCl extraction and fixation of added urea-N by "clay" in four Manitoba soils. 110

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. 123

16. Nitrogen derived from N-carriers in wheat tops and percent utilization of added N. 125

17. Dry matter yield and percent utilization of added N by wheat roots in pH amended soils. 127

18. Nitrogen balance on pH amended soils (% of added N). 129

19. Soil reaction before and after the growth of wheat following addition of different N carriers. 132

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*, *Nitrosospira*, *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 calculating 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 acivity 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 exeperiments, 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; Sachdeve, 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 ^{15}N 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 ^{15}N 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).