

TRANSFORMATION AND MOVEMENT
OF BAND-APPLIED NITROGEN FERTILIZERS IN
SEVERAL MANITOBA SOILS

A Thesis
Submitted to
the Faculty of Graduate Studies and Research
The University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Patrick Chi-Kee Pang
December , 1973



TRANSFORMATION AND MOVEMENT
OF BAND-APPLIED NITROGEN FERTILIZERS IN
SEVERAL MANITOBA SOILS

BY

PATRICK CHI-KEE PANG

A dissertation submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
of the degree of

DOCTOR OF PHILOSOPHY

© 1973

Permission has been granted to the LIBRARY OF THE UNIVERSITY OF MANITOBA to lend or sell copies of this dissertation, to the NATIONAL LIBRARY OF CANADA to microfilm this dissertation and to lend or sell copies of the film, and UNIVERSITY MICROFILMS to publish an abstract of this dissertation.

The author reserves other publication rights, and neither the dissertation nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.	1
II. LITERATURE REVIEW	4
Forms of nitrogen	4
Sources of mineral nitrogen	5
Fates of mineral nitrogen	9
Nitrogen fertilizers.	27
III. MATERIALS AND METHODS	32
IV. RESULTS AND DISCUSSIONS	48
Experiment I. Transformation and movement of band-applied $(\text{NH}_2)_2\text{CO}$, NH_4OH and $(\text{NH}_4)_2\text{SO}_4$ during incubation in three soils.	48
Experiment II. Effect of rate of nitrogen application on transformation of band-applied N fertilizers in neutral Wellwood II soil.	69
Experiment III. Effect of temperature on the transformation and movement of band-applied nitrogenous fertilizer in neutral Wellwood II soil.	84
Experiment IV. Effect of pH on the transformation of band-applied urea in Keld and Wellwood II soils	97
Experiment V. The recovery of banded KNO_3 and KNO_2 in presence of added urea in Wellwood I soil.	106
Experiment VI. A mass spectrometric investigation on denitrification from nitrite treated soil	110
Experiment VII. Recovery of band-applied $(^{15}\text{NH}_2)\text{CO}$, $^{15}\text{NH}_4\text{OH}$ and $(^{15}\text{NH}_4)_2\text{SO}_4$ from Wellwood II soil as measured by the nitrogen-15 tracer technique.	120
Experiment VIII. Nitrification of urea in soil suspension and the nitrifier populations.	126
V. SUMMARY AND CONCLUSIONS	135
VI. BIBLIOGRAPHY.	140

LIST OF TABLES

<u>Tables</u>	<u>Page</u>
1. Subgroup designation, legal location and physical and chemical characteristics of the soils.	33
2. Nitrogen treatments in acid Wellwood I soil.	37
3. Percent recovery of applied N as total inorganic nitrogen from soils incubated for various times at 20C.	64
4. Calculated diffusion coefficient of NH_4^+ -N from three nitrogen carriers in three soils at 20C.	65
5. Calculated diffusion coefficient of NH_4^+ -N from three nitrogen carriers banded at two rates of N in neutral Wellwood II soil at 20C.	81
6. Calculated diffusion coefficient of NH_4^+ -N from three nitrogen carriers banded in Wellwood II soil at 10 and 20C	89
7. Percent recovery of applied N as total inorganic nitrogen from Wellwood II soil incubated at various temperatures and times.	90
8. Concentration of ionic species of nitrogen and percent recovery as total inorganic nitrogen of band-applied KNO_3 and KNO_2 in the presence of urea.	107
9. Mass to charge ratio (m/e) of some gases.	110
10. Possible gaseous products having m/e 28 through 48 obtained during incubation of Wellwood I soil to which nitrogen-15 labelled NaNO_2 was applied.	113
11. Possible gaseous products having m/e 28 through 48 obtained during incubation of Wellwood I soil to which non-labelled NaNO_2 was applied.	114
12. Percent recovery of total nitrogen (inorganic + organic fractions) from N-15 labelled nitrogen carriers banded in Wellwood II soil (rate = 200 kg N/ha)	121
13. Percent recovery of total inorganic nitrogen from N-15 labelled nitrogen carriers banded in Wellwood II soil (rate = 200 kg N/ha).	123
14. Percent N loss by immobilization and volatilization from three nitrogenous materials banded in Wellwood II soil (rate = 200 kg N/ha).	124

Tables

Page

15. pH of soil suspension treated with urea after one to four weeks incubation at 20C. 127
16. Nitrifier numbers in Keld, Wellwood II and Morton soils . 132

LIST OF FIGURES

<u>Figures</u>	<u>Page</u>
1. Diagrammatic scheme of soil nitrogen sources and transformations and fate of the end products.	20
2. Incubation column.	34
3. Incubation apparatus for mass spectrometric analysis of gaseous products due to denitrification.	38
4. Apparatus for preparation of $^{15}\text{NH}_4\text{OH}$ (52.20 atom % ^{15}N)	41
5. Incubation vessel for the study of nitrification in soil suspension	42
6. Changes in pH due to 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$, $(\text{NH}_4)_2\text{SO}_4$ and NH_4OH in acid Keld (A), neutral Wellwood II (B) and alkaline Morton (C) soils at 20C.	49
7. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the acid Keld soil (pH 5.4) from 92 mg N band-applied urea at 20C.	51
8. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the acid Keld soil (pH 5.4) from 92 mg N band-applied NH_4OH at 20C.	52
9. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the acid Keld soil (pH 5.4) from 92 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 20C.	53
10. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil (pH 6.6) from 92 mg N band-applied $(\text{NH}_2)_2\text{SO}$ at 20C.	55
11. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil (pH 6.6) from 92 mg N band-applied NH_4OH at 20C.	56
12. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil (pH 6.6) from 92 mg ^{15}N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 20C.	57
13. Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the alkaline Morton soil (pH 8.2) from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C	59
14. Distrubition of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the alkaline Morton soil (pH 8.2) from 92 mg ^{15}N band-applied NH_4OH at 20C.	60

15.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the alkaline Morton soil (pH 8.2) from 92 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 20C.	61
16.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the Wellwood II soil from 11.5 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C.	70
17.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the Wellwood II soil from 11.5 mg N band-applied NH_4OH at 20C	71
18.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the Wellwood II soil from 11.5 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 20C	72
19.	Change in soil pH due to 11.5 mg N band-applied nitrogenous substances in neutral Wellwood II soil at 20C	73
20.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil from 23 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C.	75
21.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil from 23 mg N band-applied NH_4OH at 20C.	76
22.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil from 23 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 20C	77
23.	Recovery of total mineral nitrogen from band-applied $(\text{NH}_2)_2\text{CO}$, NH_4OH and $(\text{NH}_4)_2\text{SO}_4$ at three rates of N	80
24.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in neutral Wellwood II soil from band-applied N in presence of 100 ppm N-serve at 20C after 2 weeks incubation (rate = 800 kg N/ha).	82
25.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 10C.	85
26.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 15C.	86
27.	Change in pH due to 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ in neutral Wellwood II soil at three temperatures	88
28.	Distribution of total inorganic N, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the neutral Wellwood II soil from 92 mg N band-applied NH_4OH at 10C.	91

Figures

Page

29.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in the neutral Wellwood II soil from 92 mg N band-applied NH_4OH at 15C.	92
30.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in the neutral Wellwood II soil from 92 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 10C.	93
31.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in the neutral Wellwood II soil from 92 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ at 15C.	94
32.	Change in pH due to 92 mg N band-applied $(\text{NH}_4)_2\text{SO}_4$ in neutral Wellwood II soil at three temperatures	95
33.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in acidified Wellwood II soil (pH 5.5) from band-applied $(\text{NH}_2)_2\text{CO}$ at 20C	98
34.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in limed acid Keld soil (pH 6.5) from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C	100
35.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in limed Keld soil (pH 7.3) from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C.	102
36.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in limed Keld soil (pH 7.3) inoculated with 1% Wellwood II soil from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C.	103
37.	Distribution of total inorganic N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in limed Keld soil (pH 7.3) inoculated with <u>Nitrosomonas europaea</u> culture from 92 mg N band-applied $(\text{NH}_2)_2\text{CO}$ at 20C	105
38.	The mass spectrometric scan of air and gas samples from $\text{Na}^{15}\text{NO}_2$ treated soil.	111
39.	Concentration of total mineral N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in Keld soil suspension treated with urea after one to four weeks incubation at 20C	128
40.	Concentration of total mineral N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in Wellwood II soil suspension treated with urea after one to four weeks incubation at 20C	130
41.	Concentration of total mineral N, NH_4^+ -N, NO_2^- -N and NO_3^- -N in alkaline Morton soil suspension treated with urea after one to four weeks incubation at 20C.	131

ACKNOWLEDGEMENT

I would like to express my gratitude to Dr. Robert A. Hedlin and Dr. Chai Moo Cho for their valuable advice and constructive criticism during the course of this investigation and the preparation of the manuscript.

I also wish to thank Mrs. Marlene Goodwin and Mr. Chi Chang for the computer programming.

ABSTRACT

The transformation, effect on soil pH and movement of nitrogen from banded nitrogen materials (urea, ammonium sulfate and ammonium hydroxide) were studied in three Manitoba soils of different initial soil pH values. The greatest effect on soil pH took place near the fertilizer zone, but the magnitude of the change varied greatly depending on soil characteristics. Irrespective of the fertilizer materials, the oxidation of ammonium form of nitrogen was the slowest with acid Keld soil (pH 5.4). Nitrification with neutral Wellwood II soil (pH 6.6) was rapid, with a high accumulation of nitrite taking place, when band-applied with 800 kg N/ha of urea and NH_4OH . With alkaline Morton soil (pH 8.2), oxidation of the ammonium form of nitrogen to nitrate was rapid without any accumulation of nitrite. The oxidation of band-applied $(\text{NH}_4)_2\text{SO}_4$ was slow in these three soils. The difference in nitrifying capacity among the three soils was related to the initial nitrifier numbers whose activities were affected by the initial soil pH.

The concentration of nitrite accumulated near the zone of urea and NH_4OH application in the Wellwood II soil was high enough to be phytotoxic. Further investigations indicated that temperature, soil pH and rate of nitrogen application affected the transformation of band-applied nitrogen and thus resulted in nitrite accumulation. Large quantities of nitrite accumulated at temperatures of 10, 15 and 20C, when band-applied with urea and NH_4OH . Accumulation of nitrite was slow at 10C, but greater than 15% of the banded urea was present at 10C after 12 weeks incubation. Acidifying Wellwood II temporarily

decreased the rate of nitrogen transformation. Liming Keld soil did not increase the rate of nitrification. Nitrite accumulation was observed in limed Keld soil (pH 7.3) only when it was inoculated with Nitrosomonas culture. This further showed that the initial nitrifier numbers are very important if rapid nitrification is to take place. Higher rates of nitrogen banded in the soil resulted in a higher amount of nitrite being accumulated. At the rate of 100 kg N/ha, the conversion of ammonium form of nitrogen to nitrate was quite rapid without accumulation of nitrite in Wellwood II soil.

Nitrogen-15 tracer studies showed that incomplete recovery of added nitrogen in the inorganic form was due to immobilization and volatilization. The amount of N loss depended on the type of nitrogen materials. Substantial amounts of N_2 and small amounts of NO and N_2O were evolved when nitrite was added to Wellwood I (pH 6.0). The N_2 gas formed was the result of Van Slyke type reaction of nitrite with organic constituents containing nitrogen in the soils.

Diffusion coefficients of ammonium in the soils were dependent upon the types of soil, nitrogen material, temperature and rate of application. Generally, the smaller diffusion coefficient restricted movement of ammonium away from the zone of application and therefore retarded the transformation to nitrite and nitrate.

INTRODUCTION

Successful crop production often requires the addition of large quantities of nitrogen since the amount of nitrogen mineralized during the growing season is not usually adequate to produce a high yield of crops. Nitrogenous fertilizers, ammonium sulfate, urea, ammonium nitrate and anhydrous ammonia, are widely used for this purpose. Recovery of nitrogen in the crop is usually approximately 50% of that applied. Only a portion of the remainder is recovered in the soil as mineral and organic nitrogen.

The importance of nitrogen as a fertilizer and its relatively low recovery has led to numerous studies to determine the most efficient source, rate and method of N application. In such studies, urea has often been found to be less effective than other ammonium sources particularly when applied with the seed. Field studies conducted in Manitoba showed that urea, when applied in excess of 20 lbs N/acre, reduced seedling emergence and yield of barley (Toews, 1971). This was found to be the result of ammonia toxicity within the seed (Carefoot, 1971). He also showed that ammonium sulfate, and ammonium nitrate have a toxic effect on seedling emergence and yield when applied at high rates. Other effects might also have been involved. Nitrite accumulation had been observed in Manitoba soils when urea was applied at a high rate (Jones and Hedlin, 1970a). Nitrite is toxic to crops.

The importance of nitrogen fertilizers has led to studies of the nitrification of ammonium and ammonium-yielding fertilizers in soils. Most of these studies have been conducted in the laboratory

using a system in which the nitrogen is mixed uniformly with the soil. Hence the concentration of nitrogen has usually been quite low as compared to that which commonly occurs when the same amount of nitrogen is applied in the field. Under field conditions, nitrogen fertilizer is very seldom uniformly distributed throughout the surface soil since fertilizers are generally broadcast, placed in band or drilled in with the seed.

A nitrogenous fertilizer applied at the rate of 50 lbs N per acre in the field results in an average concentration of about 25 ppm in the Ap layer based on the assumption that a 6-inch acre contains two million pounds of soil. Since the fertilizer is not uniformly mixed, there are locations near the fertilizer pellets and granules where the concentration of nitrogen is far in excess of 25 ppm. This is particularly true of band applications or those drilled in with the seed. Because of this high concentration of nitrogen, many processes such as the transport phenomena, transformation of nitrogen and local interaction of ions during the transport may take place. As a result, non-uniformly applied nitrogen fertilizer results in a different environment for nitrogen transformation as compared to that of uniformly applied nitrogen. Besides, the high concentration of nitrogen may have adverse effects on plant growth. It is known, however, that these effects vary considerably depending upon the nitrogen fertilizer used and the properties of the soil to which it is applied.

With this in mind, laboratory experiments were conducted to study the effects of temperature, pH and rate of application of nitrogen on the transformation of band-applied urea, ammonium hydro-

xide and ammonium sulfate with time and distance from the fertilizer zone. The recovery of banded nitrogen was also studied. Subsequently a series of experiments using nitrogen-15 tracer to allow for detailed study of N-loss, whether by immobilization and/or volatilization, were conducted.

LITERATURE REVIEW

FORMS OF NITROGEN IN SOIL

Organic nitrogen

Over 90% of the total nitrogen in the surface horizon of most soils is organically combined. However, in certain subsoils about 30-40% of the total nitrogen may be present as fixed ammonium (Bremner,1965). The nature of the organically combined nitrogen occurring in soils is not well understood. Information concerning these compounds is based largely on studies involving identification and estimation of the forms of nitrogen released by treatments with hot acids (Kojima,1947; Bremner,1965; Stevenson,1957; Cheng and Kurtz,1963). The organic forms isolated generally include amino acids, amino sugars (hexosamines), purine and pyrimidine derivatives, urea and many others (Bremner,1965). About 20-40% of the total soil nitrogen in most surface soils is represented by amino acid-N (Kojima,1947; Bremner, 1949; Stevenson,1954; Keeney and Bremner,1964), and about 5-10% of surface soil nitrogen is in the form of hexosamines (Bremner and Shaw, 1954).

The soil organic nitrogen is highly resistant to microbial attack and is converted to inorganic forms very slowly. The stability of the organic nitrogen may be related to its chemical, physical and physicochemical nature. One theory, which has been discussed by Swaby and Ladd (1962) states that polyphenols, amino acids and other nitrogenous substances are condensed into large molecules which resist decomposition by confining the actions of enzymes only to the outer surface of the three dimensional organic structure. Other

workers (Ensminger and Giesecking, 1942; Lynch and Contnoir, 1956; Pinck and Allison, 1951) postulated that clay minerals are involved in stabilizing the nitrogen by either adsorbing the enzymes or adsorbing proteins in a way that makes them inaccessible to enzymatic attack. They found that the degree of inhibition varied directly with the base exchange capacity of clay. Another group of investigators (Harmsen and van Schreven, 1953; Bartholomew and Clark, 1950) theorized that a low microbial population leads to stability of organic nitrogen. They reported that cropped land with its dense microbial population around the roots exhibits a more rapid breakdown of stable humus than uncropped soil.

Probably there is no single theory that adequately accounts for the stability of organic nitrogen in soil, and the stability is the result of a combination of several factors acting simultaneously.

Inorganic nitrogen

Only a small fraction of the total nitrogen in soil appears as inorganic forms. It is represented chiefly by ammonium (exchangeable ammonium and ammonium in solution), nitrite and nitrate. The amount of nitrite is generally negligible in normal soils. Conditions under which nitrite accumulates will be discussed later. Ammonium and nitrate are the immediate sources of nitrogen for plants. Nitrite can be utilized by crops. However, relatively low concentrations, for example, greater than 15 ppm NO_2^- -N may result in phytotoxic effects (Paul and Polle, 1965).

SOURCES OF SOIL INORGANIC NITROGEN

Inorganic forms of nitrogen are mainly derived from,

- 1) mineralization of organic nitrogen
- 2) nitrification of ammonium and ammonium containing compounds
- 3) addition of nitrogen fertilizers
- 4) addition of minute quantity of ammonium and/or ammonia and nitrate from rainwater.

1) Mineralization

The mineralization process results in the transformation of organic nitrogen to inorganic nitrogen, ammonium and/or ammonia, by non-specific heterotrophs as they decompose the organic matter. The organic carbon supplies the major energy source for the heterotrophs and nitrogen is assimilated as protein, nucleic acid and other nitrogenous constituents in the microbial tissues as a function of the growth of the organisms. The excess nitrogen is thus released as ammonia and/or ammonium into the soil. The amount of inorganic nitrogen released and in turn metabolised by the microorganisms depends on the C:N ratio of the organic material and the metabolizing microorganisms (Bartholomew,1965). Plant residues have a gross C:N ratio of approximately 30:1 as compared with 6:1 characteristic of protein or 5:1 characteristic of most microbial populations (Campbell and Lees,1967). Net nitrogen mineralization generally results from the microbial degradation of residues with C:N ratio of less than 20:1. Between C:N ratio of 20:1 and 30:1, nitrogen mineralization may or may not occur depending on the environmental conditions and type of substrate. Residues with C:N ratio greater than 30:1 are generally considered to induce immobilization of nitrogen (Harmsen and van Schreven,1955; Alexander,1965; Bartholomew, 1965; Clark,1966). Ferguson and Gorby (1964) showed that incorporation

of straw into Southern Manitoba soils did not generally induce a nitrogen deficiency in the succeeding crops. However, there was marked reduction in mineralization when soil samples with straw was incubated in laboratory. The reason why there was no nitrogen deficiency in the succeeding crop when straw was applied was explained by the authors (Ferguson and Gorby, 1964) that a low microbial activity was induced by cold temperature and lack of moisture in fall and spring thereby reducing the immobilization of native inorganic nitrogen.

2) Nitrification

The inorganic nitrogen resulting from net mineralization or from applied ammonium fertilizers undergoes nitrification. Nitrification is a biological process in which ammonium is oxidized to nitrate. The oxidation process consists of two steps and is carried out most commonly by two specific obligate aerobic autotrophs. The ammonium is first oxidized to nitrite by Nitrosomonas spp., then nitrite is subsequently oxidized to nitrate by Nitrobacter spp.. The two steps of nitrification are exothermic reactions. Several other forms of inorganic nitrogen such as hydroxylamine (NH_2OH), hyponitrous acid ($\text{HON}=\text{NOH}$), and nitroxyl ($\text{HN}=\text{O}$) may occur as intermediates of autotrophic nitrification, but these compounds are chemically unstable and therefore are not easily detected (Alexander, 1965). Five other genera of autotrophic nitrifiers have been recognized. These are the ammonium-oxidizing Nitrosococcus, Nitrosospira, Nitrosogloea and Nitrosocystis, and the nitrite oxidizer, Nitrocystis (Breed et al., 1957). These autotrophs are less common than Nitrosomonas spp. and Nitrobacter spp.. These autotrophic

nitrifiers do not metabolize organic compounds, but derive all their energy from the oxidation of inorganic nitrogenous compounds and utilize CO_2 as the main source of carbon.

Nitrite accumulation is generally negligible but it may accumulate in neutral and alkaline soils fertilized with a high rate of aqua or anhydrous ammonia or an ammonium-yielding compound, such as urea. Nitrite accumulation can also occur in acid soils whose pH has risen as result of the addition of ammonium and ammonium-yielding compounds (Chapman and Liebig, 1952; Colliver and Welch, 1970; Stojanovic and Alexander, 1958; Broadbent et al., 1958; Stephen and Waid, 1963; Jones and Hedlin, 1970a) when soil and fertilizer are uniformly mixed. Nitrite accumulation was observed near fertilizer granules (Hauck and Stephenson, 1965; Bezdicek et al., 1971) and band-applied fertilizer (Isensee and Walsh, 1971; Wetselaar et al., 1972; Passioura and Wetselaar, 1972). Accumulation of nitrite and the loss of nitrogen due probably to denitrification or volatilization was found to be related (Clark et al., 1960; Hauck and Stephenson, 1965; Meek and MacKenzie, 1965).

Under favorable conditions, nitrite is readily oxidized to nitrate. Nitrate, an end product of nitrification, is the form of nitrogen most readily utilized by plants and microorganisms. On the other hand, nitrate, being very mobile, is subject to loss by leaching. It is also subject to gaseous loss by denitrification when aeration is limited.

Heterotrophs, including bacteria, actinomycetes and fungi, are able to oxidize mineral nitrogen. The intermediate products of the nitrification and the biochemical processes due to the above

microbes differ from those of the autotrophs (Alexander, 1965). The heterotrophs need organic carbon compounds for both energy and carbon supply. They oxidize not only inorganic nitrogenous compounds but also a variety of organic nitrogenous substances including amides, amines, oximes, hydroxamates, and nitrocompounds. Although heterotrophic nitrification occurs, the contribution to inorganic nitrogen economy in soil is of doubtful significance. A list of the heterotrophic nitrifiers and their possible intermediates and products has been summarized by Alexander (1965).

FATE OF INORGANIC SOIL NITROGEN

The available soil nitrogen can become unavailable to plants, at least for a period of time, through the following processes:

- 1) immobilization
- 2) ammonium fixation
- 3) ammonia volatilization
- 4) denitrification by biological or chemical processes
- 5) leaching.

1) Immobilization

Inorganic soil nitrogen and fertilizer nitrogen may be immobilized during the decomposition of carbonaceous residues with a wide C:N ratio. This has been reported by numerous workers who incubated soil with added organic matter, such as straw (Allison and Klein, 1962; Broadbent and Tyler, 1964), sawdust (Bollen and Lu, 1957; Allison and Cover, 1960) and other readily available energy sources, such as sucrose (Windsor and Pollard, 1956; Agarwal et al., 1972). The immobilization of inorganic nitrogen proceeds very rapidly

during the early stages of incubation and is related to the C:N ratio of material added. The rate of nitrogen immobilization is directly proportional to the rate of carbon dioxide evolution. Jansson et al. (1955) demonstrated that immobilization of NH_4^+ -N is greater than NO_3^- -N at the same nitrogen concentration. This was confirmed by Winsor and Pollard (1956a). Agarwal et al. (1972) showed that the addition of sucrose increases immobilization of added nitrogen. However, in absence of added sucrose the immobilization of added N was related to the C:N ratio. These data showed that the rate of decomposition of a carbonaceous material is important in determining the maximum immobilization and also the rate at which it occurs. If only a portion of the added material is readily attacked by microorganisms, for example, straw and sawdust, the immobilization of nitrogen is much less than where a readily available carbon source, for example, sucrose has been added. The microflora is also a factor in N immobilization since fungi, which are more tolerant of acidity than are bacteria, usually contain less nitrogen and liberate a smaller percentage of the added carbon as carbon dioxide.

Allison and Klein (1962) reported that maximum immobilization of N occurs in 20 days and averaged 1.7% of the original weight of straw, while Winsor and Pollard (1956abc) showed that sucrose addition brought about an immobilization of approximately 3.7% of nitrogen based on the weight of added sugar in the presence of abundant mineral nitrogen. Other than the carbon source and C:N ratio, soil environment is also an important factor. Agarwal et al. (1972) showed that N immobilization varies with different soils, being the fastest in alkaline soil in presence of sucrose. The alkaline soil pH favors

the increase of microbial activity which in turn induces N immobilization in soil. Irrespective of the soil, nitrogen immobilization occurs more rapidly with addition of sucrose than finely ground sugar cane bagasse.

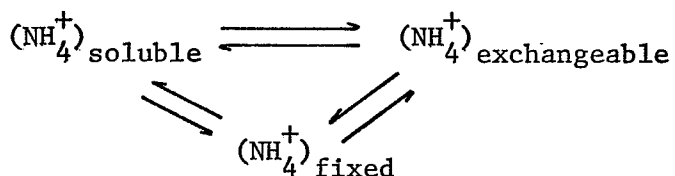
The inorganic nitrogen which becomes immobilized is temporarily unavailable to plants. After the microorganisms die, decomposition and mineralization of the organic substance takes place providing inorganic nitrogen (Winsor and Pollard, 1956c; Allison and Klein, 1962; Agarwal et al., 1972). In general, immobilization is always accompanied by mineralization, and vice versa.

2) Ammonium fixation

Nommik (1965) reported that fixation of ammonium by clay minerals and fixation of ammonia by organic matter is quite extensive. The ammonium and/or ammonia fixed is only very slowly available to plants and other organisms.

Fixation of ammonium by soils

There is an equilibrium between the different forms of ammonium in soils:



According to this equation, a change in one form of ammonium will affect the other forms. When the concentration of soluble NH_4^+ is increased, for example, after addition of NH_4^+ -containing fertilizers, the equilibrium is disturbed and fixation of some of the added NH_4^+ -N results. However, the fixed NH_4^+ will be released at an extremely

slow rate when exchangeable ammonium is removed.

Nommik (1957), Walsh and Murdock (1960) and Hinman (1966) showed that addition of KCl to soil increases the exchangeable K^+ and decreases the amount of NH_4^+ being fixed. The decrease in ammonium fixing capacity is proportional to the amount of KCl added, indicating that K^+ inhibited fixation of NH_4^+ . Potassium and ammonium ions have approximately the same ionic size which can be fixed snugly into the latticeholes of 2:1 type minerals, especially that of micaeous type, and thus become non-exchangeable with other cations (Nommik,1965).

Fixation of NH_3 by organic matter

Fixed ammonia was defined as that fraction of added ammonia which is retained by soil organic matter after intensive leaching with acid (Broadbent et al.,1961; Nommik and Nilsson,1963) and neutral salt solution (Nommik and Nilsson,1963). The organic matter reacts with ammonia and binds it in a difficultly hydrolyzable form which is only very slowly available to plants and soil microflora.

There are two different explanations concerning ammonia fixation by soil organic matter. One theory assumes that the uncharged ammonia is bound by the organic matter while the other feels that charged ammonium ion is bound to soil organic matter.

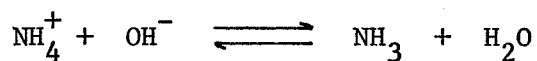
Since the formation of uncharged ammonia is controlled by soil acidity, it is evident that the pH of the soil may significantly affect ammonia fixation. This effect has been studied by Broadbent et al. (1961) and Nommik and Nilsson (1963). Their investigations demonstrated that ammonia fixation occurs to a large extent only

above neutrality. In addition, Broadbent et al. (1961) showed that there is a linear relationship between pH and ammonia fixation above pH 7.0.

On the other hand Sohn and Peech (1958) demonstrated that the greatest ammonia fixing capacity in soils occurs in acid soils containing a large amount of organic matter. The higher the carbon content or organic matter, the more ammonia fixed by the soil (Sohn and Peech, 1958; Burge and Broadbent, 1961; Nommik and Nilsson, 1963). Sohn and Peech (1958) and Mortland (1963) showed that ammonia fixing capacity of soils is reduced to approximately one half when organic matter is oxidized by hydrogen peroxide. In contrast to the above findings, Hinman (1966) demonstrated that destruction of organic matter increases the fixing capacity of soil, and the increase was greater when the organic matter content of the sample was higher. He suggested that the organic matter had either blocked the entry of NH_4^+ to the clay minerals. He speculated that although organic matter itself may have fixed some ammonium, its dominant effect was to prevent fixation of ammonium by clay.

3) Ammonia volatilization

Ammonia can be volatilized from surface-applied urea, ammonium salts and aqua and anhydrous ammonia, especially if the soil is neutral or alkaline in reaction (Volk, 1959; Volk, 1961; Simpson and Melsted, 1962; Gasser, 1964). The loss of N by ammonia volatilization is due to the reaction:



Ammonia volatilization usually does not occur when pH is below