

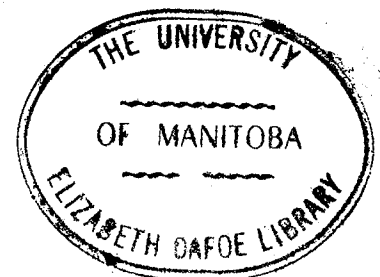
UPTAKE OF NITROGEN BY BARLEY FROM SPRING AND
FALL APPLIED UREA AND AMMONIUM NITRATE

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ABSTRACT

Field experiments were conducted in which nitrogen as $^{15}\text{NH}_4\text{NO}_3$, $\text{NH}_4^{15}\text{NO}_3$, and $\text{CO}(\text{NH}_2)_2$ was applied in the fall and spring to a Manitou clay loam (pH 5.9) and a calcareous Almasippi loamy fine sand (pH 7.9). Laboratory experiments to determine the extent of nitrogen loss by ammonia volatilization and leaching were also conducted.

Yields and total nitrogen uptake by barley and recovery of all forms of added nitrogen were greatest with spring applied nitrogen. Recovery of nitrogen was in the order: nitrate > urea > ammonium. By comparison, recovery by barley of ammonium and urea nitrogen applied in the fall was similar on the Manitou soil, and was markedly greater than for nitrate-nitrogen. All forms of nitrogen applied in the fall to the Almasippi soil were poorly recovered.

Ammonia volatilization was found to occur from broadcast application of urea and ammonium sources to the Almasippi soil when incubated at 22°C. Incomplete recoveries encountered from all forms of nitrogen applied in broadcast and incorporated treatments to both the Almasippi and Manitou soil may have been due to ammonium fixation by clay, denitrification, and/or immobilization. Ammonia volatilization was negligible when fertilized soils were subjected to alternate freezing and thawing. Nitrogen losses encountered in leaching experiments were apparently more attributable to such factors as denitrification than to leaching per se.

TABLE OF CONTENTS

CHAPTER	PAGE
I INTRODUCTION	1
II REVIEW OF LITERATURE	3
A. Forms and Reactions of Soil Nitrogen	3
B. Fertilizer Nitrogen Reactions in Soil	6
1. Hydrolysis of Urea	7
2. Nitrification of Ammonium.	8
C. Isotopic ¹⁵ N in Soil Nitrogen Research	10
D. Nitrogen Fertilization	12
1. Nitrogen Fertilizer Sources	13
2. Methods of Application of Nitrogen Fertilizers	15
3. Time of Application of Nitrogen Fertilizers	16
E. Loss of Fertilizer Nitrogen through Ammonia Volatilization	17
F. Loss of Fertilizer Nitrogen through Leaching	21
III FIELD EXPERIMENT	24
A. Introduction	24
B. Methods and Materials	24
1. Soils	24
2. Experimental Design and Procedure	24
3. Analytical Procedures	27
4. Calculations Involving ¹⁵ N Data	30
C. Results and Discussion	31
1. Effect of Nitrogen on Barley Yields	32
2. Plant Nitrogen	35
3. Recovery of Applied Nitrogen	42
D. Summary and Conclusions	50

TABLE OF CONTENTS (Continued)

CHAPTER	PAGE
IV LABORATORY EXPERIMENT I	52
A. Introduction	52
B. Methods and Materials	52
1. Soils	52
2. Apparatus for Incubation and Collection of Evolved Ammonia	52
3. Experimental Design and Procedures	55
4. Analytical Procedures	56
C. Results and Discussion	59
1. Ammonia Volatilization	59
2. Recovery of Applied Nitrogen	63
D. Summary and Conclusions	65
V LABORATORY EXPERIMENTS II	66
A. Introduction	66
B. Methods and Materials	66
1. Soils	66
2. Experimental Design and Procedure	66
C. Results and Discussion	67
1. Ammonia Volatilization	67
2. Recovery of Applied Nitrogen	67
D. Summary and Conclusions	72
VI LABORATORY EXPERIMENT III	73
A. Introduction	73
B. Methods and Materials	73
1. Soils	73

TABLE OF CONTENTS (Continued)

CHAPTER		PAGE
VI	2. Apparatus for Study of Nitrogen Movement	73
	3. Experimental Design and Procedure	74
	C. Results and Discussion	75
	1. Nitrogen Distribution	75
	2. Leached Nitrogen	84
	3. Recovery of Applied Nitrogen	86
	D. Summary and Conclusions	89
VII	SUMMARY AND CONCLUSIONS	90
VIII	BIBLIOGRAPHY	92
IX	APPENDIX	102

LIST OF TABLES

TABLE	PAGE
I CHARACTERISTICS OF SOILS IN FIELD EXPERIMENT	25
II YIELD OF BARLEY AS AFFECTED BY FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE ON MANITOU AND ALMASIPPI SOILS	33
III NITROGEN CONTENT OF BARLEY AT TWO GROWTH STAGES AND HARVEST AS AFFECTED BY FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE ON MANITOU AND ALMASIPPI SOILS	36
IV PERCENT NITROGEN IN BARLEY DERIVED FROM VARIOUS FORMS OF NITROGEN APPLIED IN UREA AND AMMONIUM NITRATE AS MEASURED BY ¹⁵ N UPTAKE	39
V NITROGEN UPTAKE BY BARLEY AS AFFECTED BY FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE ON MANITOU AND ALMASIPPI SOILS	41
VI EFFICIENCY OF UPTAKE OF FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE-NITROGEN AS MEASURED BY NITROGEN CONTENT OF BARLEY ON MANITOU AND ALMASIPPI SOILS	44
VII EFFICIENCY OF UPTAKE OF FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE-NITROGEN AS MEASURED BY ¹⁵ N CONTENT OF BARLEY ON MANITOU AND ALMASIPPI SOILS	45
VIII RECOVERY OF VARIOUS FORMS OF NITROGEN FROM FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE MEASURED BY ¹⁵ N CONTENT OF BARLEY ON MANITOU AND ALMASIPPI SOILS	47
IX CHARACTERISTICS OF SOILS IN LABORATORY EXPERIMENTS	53
X RATE OF RELEASE OF AMMONIA FROM BROADCAST APPLICATION OF NITROGEN SOURCES ON ALMASIPPI SOIL AND INCUBATED AT 22°C	60
XI RECOVERY OF NITROGEN ON MANITOU SOIL AFTER ONE WEEK INCUBATION AT 22°C	61

LIST OF TABLES (Continued)

TABLE	PAGE
XII	RECOVERY OF NITROGEN ON ALMASIPPI SOIL AFTER ONE WEEK INCUBATION AT 22°C 62
XIII	RATE OF RELEASE OF AMMONIA FROM BROADCAST APPLICATION OF NITROGEN SOURCES ON ALMASIPPI SOIL SUBJECTED TO ALTERNATE FREEZING AND THAWING 68
XIV	RECOVERY OF NITROGEN ON MANITOU SOIL AFTER ONE WEEK INCUBATION WITH ALTERNATE FREEZING AND THAWING 69
XV	RECOVERY OF NITROGEN ON ALMASIPPI SOIL AFTER ONE WEEK INCUBATION WITH ALTERNATE FREEZING AND THAWING 70
XVI	AMOUNT OF NITROGEN COLLECTED IN LEACHEATE AFTER ADDITIONS OF WATER TO COLUMNS OF SOIL TREATED WITH NITROGEN FERTILIZERS 85
XVII	RECOVERY OF NITROGEN APPLIED TO COLUMNS OF SOIL AND LEACHED WITH TEN INCHES OF WATER 87

LIST OF FIGURES

FIGURE		PAGE
I	Schematic Representation of the Nitrogen Cycle	4
II	Apparatus Used for Incubation and Collection of Evolved Ammonia	54
III	Distribution of Ammonium Nitrogen in Columns of Manitou Soil after Leaching with 10 Inches of Water	76
IV	Distribution of Nitrate-Nitrogen in Columns of Manitou Soil after Leaching with 10 Inches of Water	77
V	Distribution of Total Inorganic Nitrogen in Columns of Manitou Soil after Leaching with 10 Inches of Water	78
VI	Distribution of Ammonium Nitrogen in Columns of Almasippi Soil after Leaching with 10 Inches of Water	79
VII	Distribution of Nitrate-Nitrogen in Columns of Almasippi Soil after Leaching with 10 Inches of Water	80
VIII	Distribution of Total Inorganic Nitrogen in Columns of Almasippi Soil after Leaching with 10 Inches of Water	81

I. INTRODUCTION

Successful crop production in Manitoba often requires the addition of large quantities of fertilizer nitrogen since the amounts supplied by natural processes are generally inadequate for continuous high yields. Recovery of applied nitrogen in harvested crops is often very low, with efficiencies of utilization of the nitrogen varying around 50 percent. Numerous studies have been conducted to determine the most efficient source, rate, method, and time of application of nitrogen fertilizer, and varied results have been obtained. Often urea has been found to be less effective than inorganic nitrogen fertilizers while results with ammonium and nitrate sources have been inconsistent.

Several mechanisms are known to reduce the efficiency of the various forms of fertilizer nitrogen. A loss from the soil of gaseous ammonia has been credited with up to 30 percent or more of the inefficiency incurred from the application of ammonium fertilizers and urea. Gaseous ammonia losses have been found to be of major importance on alkaline and especially calcareous soils when fertilizers are broadcast and may be of less significance on soils of low pH or if the fertilizers have been incorporated. Other factors such as soil texture, cation exchange capacity, temperature, moisture status and evaporation rate have been found to influence this loss mechanism.

Leaching has often been credited with reduced availability or complete loss of fertilizer nitrogen especially of the more mobile nitrate form. Although growing season precipitation in Manitoba may be insufficient to cause leaching, fall applied fertilizer may be subject to some movement from late fall or early spring rains and melting snow.

A field experiment was conducted on a calcareous and a noncalcareous

soil in which barley was grown on plots fertilized in the fall and spring with urea and ammonium nitrate. The various nitrogen sources applied, ammonium, nitrate and urea nitrogen, were tagged with ^{15}N to allow for detailed study of the responses and recovery of the nitrogen species. Subsequently a series of laboratory experiments were conducted to study factors affecting the losses of various forms of fertilizer nitrogen. Two experiments were designed to measure the extent of ammonia volatilization and the recovery of broadcast and incorporated nitrogen. In one experiment incubation was conducted at room temperature (22°C) while in the second, the fertilized soils were subjected to alternate freezing and thawing to simulate late fall and early spring conditions. A third experiment was conducted to determine the effect which leaching had on the movement and recovery of fertilizer nitrogen.

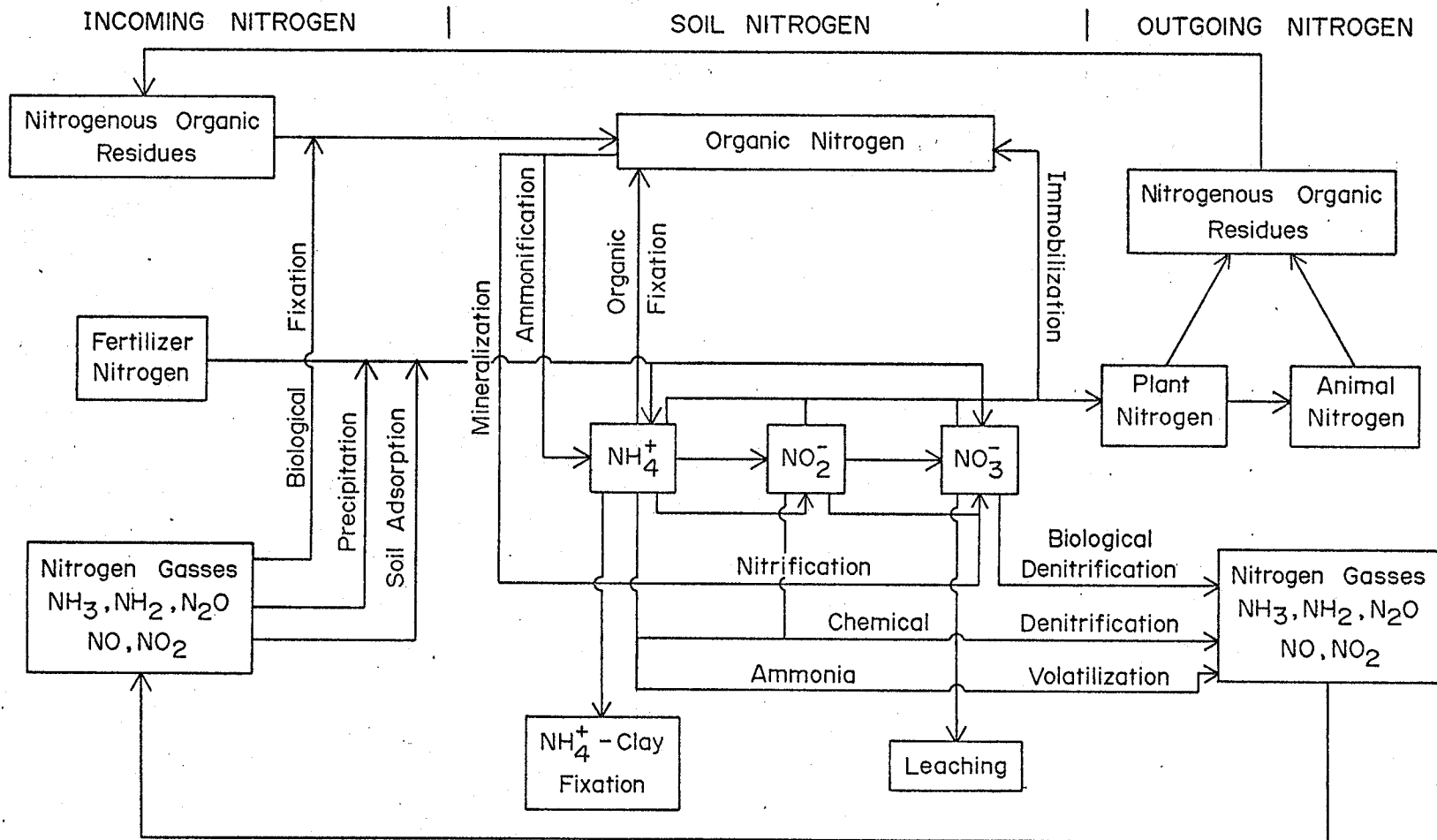
II. REVIEW OF LITERATURE

Soil nitrogen is an integral part of the nitrogen cycle in nature. Allison (2) and Stevenson (103) visualized the soil as an immense reservoir of nitrogen with several incoming and outgoing processes. Within the soil, nitrogen is present in several forms, interrelated by a vast complex of reactions and transformations (Figure 1). Each part of the cycle has been the subject of innumerable studies. This review considers some of those aspects which have a direct relationship to nitrogen fertilization and plant growth.

A. Forms and Reactions of Soil Nitrogen

Nitrogen in the soil can be divided into two major fractions: (a) organic fraction which, with few exceptions, comprises about 98 per cent of the total soil nitrogen (11, 52) and contains the greatest range in forms, and (b) inorganic fraction which comprises the remainder, and consists mainly of ammonium, nitrite and nitrate. Inorganic nitrogen represents the most important fraction to practical agriculture since it contains the forms upon which plant growth is dependent (96, 110), and which are most subject to loss from the soil. These two fractions are highly related through the processes of mineralization and immobilization which are continuously and simultaneously converting forms from one fraction to another. In a review of these processes, Bartholomew (7) states that immobilization is the assimilation of inorganic nitrogen by microbial activity and subsequent conversion into organic compounds within the living organism. A reverse of this occurs in mineralization where inorganic nitrogen is released from organic forms as a result of bacterial decay of organic residues. These conversions appear cyclic in nature, and an internal nitrogen cycle has been proposed whereby mineral nitrogen

Figure I. Schematic Representation of the Nitrogen Cycle⁽¹⁾



(1) Derived From Allison(2) and Stevenson (103)

is assimilated into organic forms in living organisms and subsequently released as mineral nitrogen upon death and decay of the organism (52).

Mineralization describes two overall reactions, ammonification and nitrification (7). Ammonification is the initial process where inorganic nitrogen is released from the organic constituents as ammonium. The second step is the microbial oxidation reactions of nitrification whereby the ammonium is converted to nitrite and subsequently nitrate. Nitrification will be discussed in further detail in a following section.

Ammonium in the soil, although subject to rapid nitrification under normal conditions (78) is also prone to several other conversions. The small amounts of ammonium that are generally present are usually associated with the negatively charged clay and organic soil colloids, being held by electrostatic attractive forces, but are readily available for exchange and involvement in reactions (81). Mortland (81) reviewed the various reactions of ammonium in the soil. Microorganisms responsible for immobilization preferentially use ammonium over other inorganic forms in their metabolic assimilation of nitrogen (63). A tie-up of ammonium in the soil can also be incurred by an irreversible fixation of ammonium by certain forms of organic matter, creating a stable ammonium-organic complex (22). Ammonium can be converted to several gaseous forms and completely lost from the soil. This can be incurred through a direct loss of ammonia gas and in the release of other nitrogenous gases as a result of chemical denitrification reactions of ammonium with nitrite (2, 3).

Nitrite is a very transient form of nitrogen in the soil and only under rare conditions is it present in appreciable amounts (65, 96) since it is generally rapidly oxidized to nitrate (78, 96). Plant and microorganisms can utilize nitrite in small amounts (7, 96) but an appreciable

accumulation is highly toxic (96). Under certain circumstances gaseous forms of nitrogen may be released from the soil due to reactions involving nitrite after an abnormally high accumulation of this form (2, 3).

Studies of soil nitrite are however, generally of academic importance because of the specific conditions necessary for this to occur (2, 3, 16).

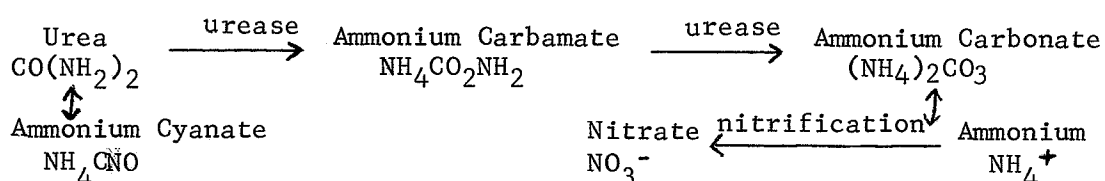
Nitrate is a very important form of inorganic nitrogen since it is the form of nitrogen which is most readily available and utilized to the greatest extent by growing plants (96). In many soils it is the most persistent form of inorganic nitrogen, being the end product of nitrification. Nitrate-nitrogen is however prone to immobilization by microorganisms, but to a lesser degree than ammonium (63). It is also subject to other processes which can reduce its availability to plants. The nitrate ion is highly soluble in water, and is therefore subject to leaching from the soil profile (45). Facultatively anaerobic microorganisms can reduce nitrate to several gaseous forms through denitrifying activity, resulting in a complete loss under certain conditions (16).

B. Fertilizer Nitrogen Reactions in Soil

Nitrogen released by mineralization and through incidental additions (Figure 1) is generally insufficient for successful crop production. This problem is overcome by the addition of nitrogen fertilizers. Most fertilizer nitrogen is in the inorganic nitrate or ammonium form which is readily available or rapidly converted to the available form. Some fertilizers such as urea supply nitrogen as organic compounds and must be converted to available inorganic nitrogen. Although some evidence indicates that small amounts of urea may be absorbed directly, its rapid conversion to inorganic nitrogen under normal growing conditions makes its reaction products more important in plant nutrition (96).

1. Hydrolysis of Urea.

The conversion of urea from the organic amide form to inorganic nitrogen is a hydrolysis reaction. The reactions of urea in the soil and the steps in the hydrolysis process have been outlined by Court et al. (33).



The initial steps of hydrolysis are the conversions of the urea to ammonium carbamate then to ammonium carbonate. These are biochemical enzymatic reactions dependent upon the enzyme urease present in most soils. Urease is secreted by the aerobic soil microorganism Micrococcus Ureae or other Urobacilli bacteria (116). The ammonium carbonate produced is relatively unstable and decomposes readily into ammonium ions (76). Under favorable conditions for microbial and enzyme activity the hydrolysis of urea proceeds rapidly in the soil. Most studies have reported complete hydrolysis in from one day to one week from moderate rates of application (17, 33, 86, 113).

Gasser (49) has stated that the conversion occurs in varying degrees under soil moisture conditions ranging from air dry to waterlogged. In dry soils little reaction has been found (113) and the optimum moisture appears to be in the lower range of available water (25 to 35 per cent field capacity)(98, 116)). Above this, the rate of reaction generally decreases (98, 116) probably because of a decreasing soil oxygen content which has been found to limit the conversion rate (87).

The rate of hydrolysis increases rapidly as the temperature rises above 4°C with an optimum point being around 25°C (49, 50, 87, 98). The

reaction however has been found to occur completely at temperatures as low as 1°C (98) and slightly above 30°C (49).

A neutral to slightly alkaline pH appears to be optimum for hydrolysis, with marked deviations from this point reducing the rate (86, 113, 116). The reaction tends to temporarily raise the pH in the zone of activity and this can aid in providing a pH condition more suitable for the reaction on acidic soils or less suitable on alkaline soils (49).

The presence of readily decomposable organic matter has been found to enhance the reaction rate (50). This may be due to the increase in urease concentration resulting from increased microbial activity and secretion. Also, for a given amount of urease activity in the soil, an increase in the rate of urea application only increases the hydrolysis rate to a maximum point (98, 104). Both of these effects have been explained by theories of enzyme kinetics which deal with reaction rates as affected by substrate and enzyme concentration (104).

2. Nitrification of Ammonium.

The process of nitrification whereby ammonium in the soil from fertilizer or organic nitrogen sources is converted to nitrate is completely accomplished by microorganisms (1). The conversion consists of two separate oxidation steps in which ammonium is converted to nitrite and subsequently to nitrate. Although several autotrophic and heterotrophic microorganisms are known to be capable of nitrifying activity, only the chemoautotrophic bacteria of the genera Nitrosomonas and Nitrobacter (which respectively oxidize ammonium to nitrite and then to nitrate) are considered of importance (1). Both groups complete their reaction independently of the other, except that the Nitrobacter oxidation depends upon the Nitrosomonas production of nitrite. The two genera are physiologically similar requiring

and responding to similar environmental controls (78). Under normal conditions both steps in the nitrification process proceed rapidly (19), as evidenced by the fact that there is generally only traces of ammonium in the soil, and nitrite rarely exceeds one ppm (95). However, under equally favorable conditions indications are that the second oxidation stage proceeds much more rapidly than the first (70). Under certain circumstances one process may proceed much quicker or even to the exclusion of the other which would be evidenced by either a lack of conversion of ammonium or accumulation of nitrite (98).

Since the nitrifying population are mesophilic in nature, optimum activity occurs in the 25°C to 35°C temperature range (44). Any deviation above or below this range causes a rapid decrease in nitrification (44, 94, 116) with a complete halt in activity when the temperature approaches 45° to 50°C (66, 116) or drops to near 0°C (5, 98). Some workers have reported slow nitrifying activity just above freezing at 1° to 3°C (66, 109). Simpson and Melsted (98) did not find this.

Soil pH is a very important consideration in the nitrification process since both nitrifying groups have different optimum pH for activity (in the range of 8.5 to 8.8 for Nitrosomonas and near 7.7 for Nitrobacter (22)). Generally nitrification can proceed to a certain degree in the range of pH 5.0 to 10.0 (1) and has been found to occur at a pH as low as 3.7 (85). Low pH conditions generally hinder the Nitrosomonas activity resulting in slow ammonia oxidation while a high pH reduces or inhibits the Nitrobacter conversion resulting in a nitrite accumulation (22, 55). Nitrite accumulation generally occurs on a strongly alkaline soil or on a poorly buffered soil where activity, such as the hydrolysis of urea, locally increases the pH to the detriment of Nitrobacter (27). High

quantities of ammonium, either added in this form or present as a result of rapid urea hydrolysis can also preferentially limit Nitrobacter activity resulting in a nitrite build-up (1, 105). Once the ammonium concentration has been lowered by the Nitrosomonas oxidation, Nitrobacter activity resumes.

The rate of nitrification can be affected by the moisture status of the soil and has generally been found to increase linearly with increasing soil moisture content between air dry and field capacity (78). The optimum point is considered to be 50 to 75 per cent of field capacity (1) but Wahhab et al. (116) found it to be as low as 35 per cent. Above this optimum the reduced nitrification rate can be attributed to the limited oxygen diffusion into the soil. Since the nitrifying microorganisms are obligate aerobes a reduction in oxygen concentration reduces their activity and has been found to cease if the oxygen in the soil atmosphere drops below 15 per cent (95).

C. Isotopic ^{15}N in Soil Nitrogen Research

An important new technique in soil nitrogen research is the use of isotopic ^{15}N . Techniques are available which differentiate this isotope from the more naturally occurring ^{14}N . Employing it as a tracer allows for detailed study of the fate and reactions of nitrogen fertilizers.

There are two major assumptions which are the basis for work involving ^{15}N . Bremner (13, 15) has reviewed these in detail. The first assumption is that the nitrogen in all naturally occurring nitrogen materials contains 0.366 atom percent ^{15}N . The second assumption is that employing ^{15}N in quantities greater than that which occurs naturally will in no way alter any processes and there is no isotopic discrimination in any physical, chemical or biological processes or reactions between ^{14}N

and ^{15}N .

The use of isotopic nitrogen in research has definite advantages over more conventional methods. With the present techniques and equipment available, accurate measurements can be made on small amounts of ^{15}N present in large amounts of ^{14}N (3, 16). These results are quantitative and reproducible (16, 89). The isotope ^{15}N is stable, making it safe to handle and not restricting the time in which measurements must be made (62). There are however several limitations to the use of isotopic ^{15}N in research. The validity of the fundamental assumptions upon which ^{15}N work is based has not been established and some findings discredit them (13, 15). Bremner (13, 15) quotes some research which shows isotopic fractionation during the physical process of ion exchange in resins. Other researchers have found amounts of ^{15}N in excess of natural abundance in several materials including soils, plants and other organic compounds (13, 15, 88), but rarely has this exceeded 0.380 atom per cent ^{15}N .

Other disadvantages are evident. The cost of ^{15}N enriched materials and the analytical equipment required is high and the equipment is difficult to operate (13, 15, 62). Techniques for analysis are laborious and time consuming (13, 15, 62). There are also several problems and sources of possible error inherent in this equipment and in these techniques which lend some doubt as to the reliability of results obtained (15, 30, 53, 57, 74).

Several other effects must be considered in the interpretation of research dealing with fertilizers containing isotopic ^{15}N . Fertilizer nitrogen added to the soil may result in increased plant yield and nitrogen uptake not only from the increased available nitrogen from the fertilizer but also from that which could be made available by the priming

effects fertilizers have on such processes as mineralization (1). Data from ^{15}N determinations on the plant material would tend to show a lower response to the fertilizer than actually encountered since it would account only for the nitrogen taken up directly from the fertilizer and not for the extra nitrogen assimilated as a result of this stimulatory effect.

Unduly low results from ^{15}N data may also be attributed to isotopic dilution which results from the application of fertilizer containing ^{15}N disproportionate to the amounts naturally occurring. The ^{15}N becomes diluted out of the fertilizer into the other forms of naturally occurring nitrogen as all forms present tend to attain an equal proportion of both isotopes. In doing so, fertilizer ^{15}N is replaced by ^{14}N as exchange of the two isotopes proceeds. Uptake of the fertilizer nitrogen results in smaller quantities of ^{15}N being assimilated than expected. Analysis of plant material would then show a smaller uptake of fertilizer nitrogen than had actually occurred. This problem is encountered to a greater extent on soils having larger quantities of native nitrogen since it allows for greater isotopic dilution (3).

It is evident that difficulties exist with the ^{15}N research technique, but considerable success in studying fertilizer, soil and plant nitrogen relationships has been achieved through its use (3).

D. Nitrogen Fertilization

Most research with nitrogen fertilizer has been devoted to determining the most efficient, practical, and economical methods of supplying it to crops for maximum uptake, yield and quality. It has involved getting the nutrient to the plant in optimum amounts and in the most available form at the time when most effective use can be made of it. In doing so, the nitrogen must be subject to as few as possible mechanisms whereby

it could be lost from or tied up within the soil. Losses most frequently occur from fertilizer sources that require conversion reactions to reach the plant available form. Of major interest has been the comparison of organic fertilizers such as urea with the more conventional inorganic ammonium and nitrate salts, and the times and methods of application.

1. Nitrogen Fertilizer Sources.

Numerous investigations have been conducted comparing crop responses to ammonium and nitrate-nitrogen and urea. Often urea has been found to be a less effective source of nitrogen than the inorganic carriers supplying ammonium or nitrate nitrogen (19). This is especially so for cereals, forages and grasses (49, 73, 106). For some crops and under some conditions however, urea is equally as good (37, 49, 54, 100, 111). The efficiency of urea nitrogen generally decreases with respect to other nitrogen carriers as the rate of nitrogen applied increases (31, 73, 106). At lower rates it can be of equal value (31, 100). Incorporation of the fertilizer into the soil as opposed to surface broadcasting can often increase the efficiency of urea (71, 73).

Certain soil properties affect the relative efficiency of the nitrogen carriers. For example, when soil pH is high, yield response to urea nitrogen is less than for other sources (35, 36, 37). When applied to calcareous soils, as opposed to noncalcareous soils of similar pH, urea is increasingly inefficient relative to the inorganic fertilizers. Similar results have often been found in some studies conducted in Manitoba. On cereal crops, urea has often been found to be less efficient than ammonium nitrate, with its relative efficiency being increased if it is incorporated into the soil rather than broadcasting (29, 93, 99, 107). This has not been conclusively shown in other studies. Ridley (93) in

three years of study has found urea to be less effective than ammonium nitrate in one year, and equally effective in two years.

Variations in the efficiency of nitrogen supplied in ammonium or nitrate forms in inorganic fertilizers have also been found. Greater increases in uptake and effect on yield from nitrate than from ammonium nitrogen have been reported (18, 35, 36, 37, 61). Other researchers have found nitrate and ammonium nitrogen of equal value (54, 71, 100) while some have found ammonium better than nitrate sources (24, 25, 49). The decreased efficiency of ammonium compared to nitrate sources is generally more apparent at higher rates of nitrogen application, when the fertilizer is broadcast and on alkaline and calcareous soils (35, 36, 37, 49). Incorporation of the fertilizer into the soil or application to acidic soils reduces the difference between these two forms (18, 54, 108, 111).

The generally lower efficiency of ammonium forms of nitrogen fertilizers and especially urea may be attributed to several reactions resulting in the complete loss of nitrogen from the soil. Volatilization of ammonia could occur particularly if the fertilizer is broadcast, or the soils are alkaline or calcareous. Chemical denitrification reactions involving ammonium and nitrite could also proceed under conditions favoring nitrite accumulation (2, 3).

Other causes for poorer responses of crops to ammonium fertilizers and especially urea have been established. Several workers have related yield reductions to delays in germination, reductions in numbers of germinating plants and death and damage to established plants (10, 31, 100, 101, 102). This most frequently occurs when ammoniacal fertilizers are placed in contact or close to the seed (33, 34, 36) and may be due to accumulations of ammonia in the soil which is toxic to plants (76, 79, 101).

When urea is the source of nitrogen, biuret may be a problem. Biuret is present in small and varying amounts in urea as a result of the manufacturing process, and is highly toxic to plants (49, 73). Incorporation of urea into the soil or application with the seed generally increases damage by reducing germination when biuret exceeds two pounds per acre (73). However, when urea is broadcast, little damage has been found from urea containing 2.5 percent (73) and even up to 10 percent biuret (10). No problems have been encountered from any application method when the biuret content of urea was less than one percent. McBeath (76) states that there is little cause for concern in Western Canada since locally produced urea contains very small amounts of biuret.

Reduced yields and nitrogen uptake may be due to a nitrite accumulation in the soil after fertilizer application as a result of inhibition of Nitrobacter activity from a locally increased pH or high concentration of ammonium (32, 49, 101). Nitrite in appreciable amounts is toxic to seedlings and can kill established plants. Mixing of urea with acidic potash or phosphate fertilizers to maintain a low pH upon hydrolysis has been found to reduce damage by ensuring Nitrobacter conversion of nitrite to nitrate (49, 73, 101).

2. Methods of Application of Nitrogen Fertilizers.

Three methods of application of nitrogen for crops are generally employed, i.e. broadcasting, applying it with the seed, and uniform incorporation into the topsoil. Incorporation is often better than broadcasting especially for ammonium fertilizers and urea on alkaline or calcareous soils (71, 73, 102). This may be associated with a reduction in loss through ammonia volatilization (49, 50, 59, 67). Poor crop responses from seed drilled and high rates of incorporated ammoniacal nitrogen have

been reported and are attributed to the phytotoxic effects (10, 29, 36, 102, 107). The detrimental effect is reduced if low rates of nitrogen are drilled or fertilizer is not placed in close contact with the seeds (59, 93, 107). Studies in Manitoba indicate that rates of nitrogen greater than forty pounds per acre should not be applied with the seed, and no more than twenty pounds of this should be urea nitrogen (107). Results comparing broadcast and incorporated urea and ammonium nitrate have been inconclusive (93).

3. Time of Application of Nitrogen Fertilizers.

Numerous experiments to determine the optimum time of application of nitrogen fertilizer has been reported in the literature. Results from experiments conducted under a variety of climatic conditions characteristic of England and parts of the United States and Canada, indicate that in the majority of cases spring applied nitrogen is much more efficiently utilized by crops than is fall applied nitrogen (38, 47, 80, 95, 119). Sadler (95) and Welch et al. (119) quote findings which have shown that fall applications were 50 to 65 percent less efficient than spring applications. Results from split applications, i.e. part applied in the fall and part at seeding time indicate yields somewhere between those from fall or spring application (38, 95).

Factors which affect the efficiency of fall applied nitrogen are a combination of temperature, moisture and form of nitrogen applied. Gasser (48) found that under mild winter conditions with heavy precipitation, much nitrate nitrogen, either added as such or nitrified to this form was moved through the soil by percolation. At the lower depths it is less likely to be utilized by plants because of greater dilution with the soil and also due to the detrimental effect of poor aeration on nutrient

absorption (52, 69). Excess soil moisture can also cause denitrification (16).

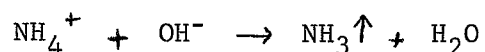
Nitrogen fertilizer applied in the fall as ammonium or urea should be more effective than the nitrate form, provided temperatures are cool enough to prevent nitrification (95), since ammonium is less susceptible to loss by leaching and denitrification. Tyler et al. (109) state that fall application would be questionable where temperatures aren't sufficiently low to prevent nitrification. Also under moderate winter temperature immobilization can proceed and tie up any source of fall applied nitrogen (7).

Several workers have reported that ammonium can be subject to clay fixation through freezing and thawing processes over winter (82, 84). Hinman (56), however reports that alternate freezing and thawing can actually release ammonium by fracturing bonds with colloidal clay and organic matter.

E. Loss of Fertilizer Nitrogen through Ammonia Volatilization

One of the major mechanisms of loss of nitrogen from the soil is through volatilization of ammonia. This is recognized as one of the major contributors to the inefficiency of nitrogen fertilizers especially with increasing rates of application and increasing use made of ammonium type fertilizers (ammonium salts, aqua or anhydrous ammonia and urea (3)). Several workers in the field and laboratory have shown that for most cropping conditions the reduced efficiency caused by this process can amount to 15 to 30 per cent or more of the added nitrogen (2, 3).

Wahhab et al. (117) describe the loss by the chemical reaction:



It is quite evident that pH plays an important role in this reaction especially as it relates to the soil and fertilizer. Ammonia is usually not released from the soil unless the pH condition rises above neutrality (75). Volatilization from soil of less than pH 7.0 is minimal, starts to occur when the pH reaches neutrality and increases in rate and amount with increasing pH beyond this point (67, 75, 116, 117). The results of several workers who found a significant loss as ammonia from slightly to moderately acidic soils are explainable (41, 112, 114, 116, 117). Although soils may be acidic in nature, the application of urea especially at high rates or to poorly buffered soil can result in a local rise in pH above neutrality as a result of the hydrolysis which allows for ammonia volatilization to occur (49). This problem may be overcome by mixing urea with other acidic fertilizers to maintain a low pH and reduce the chances of loss (49, 73).

Volatilization losses are often greater on alkaline soils if calcium carbonate is present especially if finely divided and evenly dispersed (47). This could result from the calcium present saturating the available exchange sites, resulting in a low ammonium absorption capacity (41). Similar high losses have been found on soils with higher base saturation (28). It could therefore be speculated that the increased loss of ammonium fertilizers upon liming of the soil could be due not only to the pH increase but also to the calcium saturation effect.

Although the rate of ammonia evolution and time of occurrence after fertilization varies greatly with external conditions, several studies show a definite pattern of evolution of ammonia from urea and a different pattern for evolution from ammonium sources. Ammonium fertilizers evolve ammonia rapidly after application with the rate of evolution decreasing

with time. From these sources, ammonium is present and subject to volatilization in greatest quantities initially after application. The amount of ammonium present decreases as nitrification proceeds corresponding to a reduction in ammonia evolution (50, 51, 75, 112). Urea, however, has a lag period after application before ammonia volatilization starts due to the time required for hydrolysis to produce appreciable quantities of ammonium. Evolution of ammonia then rapidly reaches a maximum rate before slowly decreasing due to the continual addition of ammonium as hydrolysis proceeds (41, 50, 52, 59, 73). The extent of ammonia volatilization and the length of the evaluation period for urea depends on the relative rates of hydrolysis and nitrification (28, 73). From all ammonium fertilizers, volatilization can occur until all the ammonium has been removed by nitrification (50, 67).

Temperature has a marked effect on ammonia volatilization. Ammonium nitrogen sources like ammonium salts evolve ammonia slowly over an extended period of time at low temperatures (25, 80, 115). Increased temperature increases the rate of ammonia evolution such that volatilization is completed in a shorter time (25, 80, 115). Total ammonia loss is generally greater at the lower temperatures (25, 80, 115). This is attributed to the more rapid nitrification at higher temperatures causing ammonium to be subject to loss for a shorter period.

The effect of temperature on ammonia volatilization from urea is somewhat different. At low temperatures up to 15°C little loss of ammonia has been found from the application of urea. Increased temperatures up to 35°C result in an increased volatilization rate and a decreased evolution period (41, 49, 51, 112). At lower temperatures, bacteria can nitrify ammonia as quickly as it is produced by hydrolysis resulting in little loss (73). With increased temperature, hydrolysis proceeds more rapidly than nitrification yielding ammonium free to be volatilized (73).

The moisture status of the soil can alter the extent of ammonia loss. The amount and rate of ammonia desorption generally decreases as soil moisture content increases from the air dry state (28, 77, 87, 90) with minimum loss occurring in the soil moisture range of 50 to 100 percent of field capacity (6, 116). Water in the soil can dissolve and hold ammonia from potential loss (116). Increasing the water content also reduces the free pore volume through which ammonia diffuses, thus reducing loss (45).

Desorption of ammonia often closely parallels the evaporation of water from soil. Greater loss of ammonia is incurred if the soil dries rather than being held at constant moisture (23, 112). Desorption is also greater if the evaporation rate is slower or if the soils dry from an initially higher moisture content (41). Repeated wetting and drying can increase the loss with the amount evolved decreasing on each subsequent drying cycle (50, 116). Increased air flow over the soil surface creates greater water evaporation and ammonia evolution (68, 87), while plant cover can reduce the occurrence (67).

The cation exchange capacity of the soil plays an important role in retaining ammonium against loss (75). Increased soil cation exchange capacity generally reduces the extent of ammonia volatilization (23, 28, 64). Soils generally have a characteristic quantity of ammonium they can retain on the exchange without loss (90). Amounts of ammonium above this threshold value can be subject to volatilization. This, along with the freer air diffusion in coarse texture soils can explain why clay soils generally release less fertilizer nitrogen as ammonia than sandy soils (77). Organic matter can also aid in reducing ammonia volatilization by increasing the retentive capacity of the soil for ammonium (49, 50).

The increased ability of the soil to retain ammonium along with the more restricted diffusion path for ammonia can explain why placement of fertilizer into the soil compared to broadcast application can reduce ammonia evolution (77, 116). A similar effect is noted if the fertilizer is rapidly leached into the soil by rain after application (50, 113), or if the fertilizer is applied in solution (43).

In addition to soil conditions affecting volatilization, some nitrogen materials are inherently more prone to loss than others. Urea-nitrogen appears to be the most subject to volatilization because of the pH increase during hydrolysis (59, 112, 113, 114). Carriers of acidic nature, such as ammonium sulphate and ammonium nitrate are generally less prone to loss of ammonia (75). Ammonium sulphate-nitrogen generally incurs greater loss than ammonium nitrate nitrogen under similar conditions (114).

F. Loss of Fertilizer Nitrogen through Leaching

Although now recognized to be of less importance than once believed, leaching can still be a source of fertilizer nitrogen loss under some conditions (2, 3). The form most susceptible to this loss is the nitrate ion since it is highly soluble and only very weakly held by chemical or physical forces in the soil (2, 3). Nitrite could also be leached but is generally present in insignificant amounts. Ammonium in the soil generally doesn't move because of electrostatic retention by clays and organic matter (52, 95), unless the exchange capacity is too low (9), or the exchange sites are base saturated (52). Any movement that does occur is by slow exchange reactions (52). With the exception of certain amino acids, most organic forms are relatively unaffected by leaching (52). Urea can readily move since rain immediately after application can leach

it into the soil (73, 76, 112, 113), but generally it is rapidly hydrolyzed to the stable ammonium form.

When movement of nitrogen does occur, especially in the nitrate form, it is closely related to the movement of water in the soil (5). Gardiner (45) has described the process mathematically. Physically, fertilizer applied to the soil causes an osmotic pressure in the region of application. In response, water moves in, dissolves the fertilizer, and establishes a concentration gradient which allows for diffusion outwards of the fertilizer (20). When water movement occurs through the soil, the dissolved nitrate is gradually diluted from the topsoil and moved down in a smooth wave as percolation proceeds (52, 95, 121). This type of movement has been shown mathematically (45) and verified experimentally (8, 52). This is not in agreement with the "drop-out" theory of Burns and Dean (20) which proposed a complete and rapid displacement of the soluble nitrate and not a gradual dilution.

For leaching to occur, the proper combination of conditions must be available for water movement. Rain or irrigation water must occur in sufficient amounts to exceed evapotranspiration, bring the soil to a moisture status greater than field capacity, and then encounter no impermeable layer. Although leaching depends directly on the amount and extent of water movement through the soil, the extent to which nitrate moves in relation to precipitation and water movement is of considerable speculation (83, 97, 118, 121).

The major soil factors influencing the leaching process are its structure and texture. These are particularly important in determining the size and distribution of the soil pore space which is the pathway for water movement (8, 20), and which is of prime importance in controlling

the water holding capacity and hydraulic conductivity. Coarse textured soils which are often without definite structure have a low water holding capacity and water movement is relatively quick through the predominating macropores of the inter particle space (52, 95). Heavy textured soils however are generally well structured, often highly fissured and have a high water holding capacity. Water movement in these soils is relatively slow, especially in the intra particle pores, and is generally limited to the fissures and inter-structural space (52, 95). Studies have found however that the amount of rain required to move fertilizer a given distance through soils of various textures is approximately the same although the rate of movement may differ (46, 47, 97). Heavy, continuous moisture is required to move nitrate to any great extent in any texture of soil (46, 47, 97). Under most arable conditions, several studies have reported that the movement of nitrate is generally less than three feet (46, 47, 97, 121), and although plant roots readily reach this zone, nitrate at this depth is less available. Reverse upward movement of nitrate can occur through capillary rise under dry conditions, but this is usually restricted to the top twelve to eighteen inches of soil (120, 121).

III. FIELD EXPERIMENT

A. INTRODUCTION

Field experiments with urea and ammonium nitrate conducted in 1968 showed that these nitrogen fertilizers were not similar in respect to their effect on barley yields. The data also indicated that the time of application affected the yield response. The order of greatest response was: ammonium nitrate applied in spring > urea applied in spring > ammonium nitrate applied in fall > urea applied in fall. Differences in response to nitrogen carriers may be explained by differences in the nitrogen supplying source; i.e. ammonium and nitrate ions from ammonium nitrate and urea nitrogen. Differences in crop response to similar forms of nitrogen applied at different times are not so readily explained. A field experiment was therefore designed to measure the effect of the different nitrogen supplying sources on response of barley and to determine the relative efficiency of recovery of the various sources.

B. METHODS AND MATERIALS

1. Soils. Two soils were selected for field studies. One was a calcareous Rego Black developed on sandy outwash and was mapped as an Almasippi loamy fine sand by Ehrlich *et al.* (39). The second was an Orthic Black developed on shaly till and was mapped as a Manitou clay loam by Ellis and Shafer (40). Both plot areas had been cropped the previous year. Some pertinent characteristics of the soils are listed in Table I.

2. Experimental Design and Procedure. A randomized block experiment containing four replicates and seven treatments was designed. The overall experimental area was forty feet by thirty-five feet. Treatment plots were individually seven feet long and fifty-six inches wide. Treatment plots were separated by an eight-inch spacing, while replicates were

TABLE I

CHARACTERISTICS OF SOILS IN FIELD EXPERIMENT

Soil Association	Texture	pH	Conductivity (mmhos/cm)	CaCO ₃ equivalent (%)	Organic Matter (%)
Manitou	clay loam	5.90	0.55	0.05	6.88
Almasippi	loamy fine sand	7.85	0.85	12.10	3.96

separated by a three foot roadway.

Treatments in the experiment were as follows:

- 1) Check treatment in which no nitrogen fertilizer was applied.
- 2) Ammonium nitrate (34-0-0) applied at a rate of sixty pounds nitrogen per acre in the spring. The ammonium ion was tagged with $^{15}\text{N}(^{15}\text{NH}_4\text{HO}_3)$.
- 3) Ammonium nitrate (34-0-0). As in treatment number 2 but applied in the fall.
- 4) Ammonium nitrate (34-0-0) applied at a rate of sixty pounds nitrogen per acre in the spring. The nitrate ion was tagged with $^{15}\text{N}(\text{NH}_4^{15}\text{NO}_3)$.
- 5) Ammonium nitrate(34-0-0). As in treatment number 4 but applied in the fall.
- 6) Urea (46-0-0) applied at a rate of sixty pounds nitrogen per acre in the spring. The amide radical was tagged with $^{15}\text{N}(\text{CO}(^{15}\text{NH}_2)_2)$.
- 7) Urea (46-0-0). As in treatment number 6 but applied in the fall.

Each of the tagged fertilizers was prepared by thoroughly mixing weighed amounts of powdered commercial fertilizer with weighed quantities of the corresponding source containing excess ^{15}N so that the final fertilizer applied contained approximately one percent excess ^{15}N (1.072, 1.060 and 1.070 excess ^{15}N in $\text{CO}(^{15}\text{NH}_2)_2$, $\text{NH}_4^{15}\text{NO}_3$ and $^{15}\text{NH}_4\text{NO}_3$ respectively). Fertilizer was broadcast applied and worked into the surface two to four inches of soil with a wheel hoe. Fall applications were near freeze-up time (Oct. 1968) and spring applications were at seeding time (May, 1969). All treatments received phosphate applied as monoammonium phosphate (

(11-48-0) at a rate of forty pounds phosphate per acre drilled with the seed.

Barley (Hordeum Vulgare L. "Conquest") was seeded at seventy-two pounds per acre with an eight-row tractor driven seeder. The plots were sprayed with Bucril-M, T.C.A. and Carbyne as required using recommended rates and procedures for weed control.

Plant samples were taken from each treatment at two periods during the growing season. These samples were cut from two one-foot rows, air-dried, finely ground and analyzed for total nitrogen and ^{15}N .

At maturity, four rows of five-foot length were harvested from the center of each plot. The harvested samples were air-dried, weighed and threshed. The weight of grain and straw were determined individually for yield calculations. A sub sample of each was taken from each treatment and was finely ground and analyzed for total nitrogen and ^{15}N . Total nitrogen uptake was calculated and efficiency of utilization of applied nitrogen was estimated by two methods. One method was the classical approximation where the increase in nitrogen uptake by the treatment over the check was assumed to be from the fertilizer. The equation is as follows:

$$\text{Efficiency or \% recovery} = \frac{\text{N uptake by the treatment} - \text{N uptake by the check}}{\text{N applied}} \times 100$$

The second method involving the use of ^{15}N uptake data will be discussed in a subsequent section.

3. Analytical Procedures.

i) Soil Analysis. Analyses by the following methods were run in duplicate to determine soil characteristics.

a) Soil pH. The electrometric method measuring the pH of a

soil-water suspension described by Peech (91) was used. Fifty grams of soil were shaken in 50 ml of distilled water for thirty minutes and pH was measured with a Fisher Combination Electrode on a Coleman Metrion III pH meter.

b) Soil conductivity. The same soil-water suspension prepared for the pH measurement was used. Electrical conductivity was measured using a CDC 104 cell on a direct reading Radiometer conductivity meter.

c) Soil carbonate content. The gravimetric method reported by Ridley (92) was used. One gram of soil was digested in 10 percent HCl for ten minutes and the CO_2 evolved was drawn through a drying train of concentrated H_2SO_4 , dehydrite and calcium chloride and then absorbed by ascarite in a Nesbitt tube. The weight of CO_2 evolved was determined by weighing the Nesbitt tube before and after absorption. Carbonate content was expressed as percent CaCO_3 equivalent.

d) Soil organic matter content. The dichromate oxidation method of Walkley and Black as described by Allison (4) was used. The organic carbon in a 0.5 g sample of soil was oxidized by excess $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 . The excess $\text{Cr}_2\text{O}_7^{=}$ was titrated with standard FeSO_4 in the presence of H_3PO_4 . Results were expressed as percent organic matter.

ii) Plant Material Analysis

a) Total nitrogen content. A modified Kjeldahl-Gunning method described by Jackson (60) was used in determining the total nitrogen content of plant material. A one-gram sample of finely ground, air-dried plant material was digested in a Kjeldahl flask for one hour using 25 ml of concentrated H_2SO_4 and a No. 2 Kel-pak (containing 0.3g CuSO_4 and 10.0 g K_2SO_4). After cooling, 250 ml of distilled water and 50 ml of 50 percent NaOH was added and the ammonium released was distilled into 25 ml

of 0.1N H_2SO_4 containing methyl red indicator until about 150 ml of distillate was collected. Ammonium content was determined by back titration with standard 0.1N NaOH. Results were expressed as percent nitrogen on an air dry basis.

b) Atom Percent ^{15}N . The atom percent ^{15}N content of plant material was measured by mass spectrometric analysis of a gaseous sample of N_2 derived from oxidation of the ammonium released in the total nitrogen determination. The titrated distillate from the Kjeldahl determination was acidified with a drop of concentrated H_2SO_4 and the solution was evaporated on a hot plate until it was reduced to a volume of approximately 10 ml. This would contain 3 to 5 mg of nitrogen (as ammonia) per ml required for further determination. The sample was stored at $4^\circ C$ for further analysis.

Nitrogen gas was obtained by hypobromite oxidation of the ammonia solution using a vacuum system and method described by Fehr (42) and Pang (89). Mass spectrometric analysis was run on this gas using a MAT GD 1500 mass spectrometer. The atom percent ^{15}N was calculated from measured ion current intensities of mass twenty-eight and twenty-nine using the single collector scanning method which has been shown to give the most accurate results (42, 89). The mathematical formula used was given by Bremner (13):

$$\text{Atom \% } ^{15}N = \frac{100}{2R+1}$$

where R is the ratio of the ion current intensities of the mass to charge (m/e) of $^{28}N_2/^{29}N_2$. This equation holds true only if the equilibrium constant in the system for the following reaction is 4.0:



$$\text{where: } K(\text{eq}) = \frac{(^{14}\text{N} \text{ } ^{15}\text{N})^2}{(^{14}\text{N} \text{ } ^{14}\text{N})(^{15}\text{N} \text{ } ^{15}\text{N})}$$

$$\text{or: } K(\text{eq}) = \frac{(^{29}\text{N}_2)^2}{(^{28}\text{N}_2)(^{30}\text{N}_2)}$$

This value was verified on the apparatus employed using $^{15}\text{NH}_4^{15}\text{NO}_3$ and $(^{15}\text{NH}_4)_2\text{SO}_4$ of known atom percent ^{15}N (42, 89), thereby justifying the use of this equation.

4. Calculations Involving ^{15}N Data

i) Recovery of fertilizer nitrogen. Percent recovery of the various fertilizer nitrogen sources was estimated on the basis of the percent excess ^{15}N contained in the grain and straw samples. Percent excess ^{15}N was calculated by subtracting the value for the percent natural abundance of ^{15}N from the atom percent ^{15}N content determined in each case. Natural abundance was assumed to be 0.366 atom percent ^{15}N since estimates obtained from analysis of twenty-nine plant samples taken from the check treatments at both locations at two intervals during the growing season and at harvest were not significantly different from this value (Table 1A, Appendix).

Uptake of ^{15}N from the fertilizer sources was calculated by:

$$^{15}\text{N uptake} = \frac{X_i \% \text{N} \cdot W}{10^4}$$

where: X_i = % ^{15}N excess in plant material

%N = total % nitrogen in the plant material

W = weight or yield of plant material.

This ^{15}N uptake was calculated separately for the grain and straw and the sum of the two values represented the total ^{15}N uptake of the plants.

Percent recovery of added nitrogen sources was then evaluated by:

$$\% \text{ Recovery} = \frac{T^{15}\text{N}}{Y_i R} \cdot 100$$

where: $T^{15}\text{N}$ = total ^{15}N uptake as calculated

Y_i = % ^{15}N excess in the original fertilizer

R = rate of fertilizer application

Efficiency of uptake of the urea fertilizer was determined by the percent uptake of the tagged urea nitrogen. This represented the only form of nitrogen contained in urea. Uptake of the two species of nitrogen in ammonium nitrate were determined in separate treatments so the overall efficiency of uptake of the ammonium nitrate fertilizer was estimated from an average recovery of the two individually tagged species.

ii) Percent nitrogen derived from the fertilizer. The percent plant nitrogen derived from the various fertilizer sources was also calculated from the atom percent excess ^{15}N content of the plant material. This was calculated by:

$$\% \text{ Ndffs} = \frac{X_i \cdot 100}{Y_i}$$

where: % Ndffs = % nitrogen derived from the fertilizer source.

X_i = % ^{15}N excess in the plant material.

Y_i = % ^{15}N excess in the original fertilizer.

C. RESULTS AND DISCUSSION

Growing conditions were generally favorable for barley during the entire season on the Manitou plot site. Barley on the Almasippi site however was severely affected by extreme wetness in the spring, weed infestation during the summer and hail damage just after heading. As a result, much of the data obtained from this site was not representative

of what could be expected under favorable conditions. All data however was recorded, since definite trends and results were noted in some instances.

1. Effect of Nitrogen on Barley Yields.

Yields of grain and straw for the various treatments at both plot sites are shown in Table II. Grain and straw yields were increased by the application of sixty pounds of nitrogen per acre to the Manitou soil. This was consistent for the urea and ammonium nitrate fertilizers and for spring and fall applications. Yields from spring applied nitrogen treatments were however generally greater than those from fall treatments. This is constant with most findings reported in the literature (38, 47, 80, 95, 119). All spring applied treatments, with the exception of urea, resulted in grain yields that were significantly greater than corresponding fall treatments. Grain yields from fall applied urea were smaller, but not significantly so than any of the spring applied nitrogen treatments.

Yields from spring treated urea and ammonium nitrate plots were not significantly different. Slight yield differences were noted however between the fertilizers when applied in the fall. Treatments of $^{15}\text{NH}_4\text{NO}_3$ tended to give different yield than $\text{NH}_4^{15}\text{NO}_3$ treatments. Such differences appeared consistently in most of the data recorded. This would not be expected since the only difference between the carriers was the tagging and the small amounts of ^{15}N contained should not have affected yields. Similar findings or explanation for this effect could not be found in the literature. However spring applied $\text{NH}_4^{15}\text{NO}_3$ resulted in slight but insignificant higher yields than $^{15}\text{NH}_4\text{NO}_3$. Urea applied in the fall increased yields slightly more than ammonium nitrate. Urea treatment yields were significantly larger than those from $\text{NH}_4^{15}\text{NO}_3$ but not from $^{15}\text{NH}_4\text{NO}_3$. Grain yields from $^{15}\text{NH}_4\text{NO}_3$ appeared to be greater than from

TABLE II

YIELD OF BARLEY AS AFFECTED BY FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE ON MANITOU AND ALMASIPPI SOILS

Treatment ⁽¹⁾	Yield (cwt/acre)			
	Manitou		Almasippi ⁽²⁾	
	Grain	Straw	Grain	Straw
Check	16.0a ⁽³⁾	14.6a	3.8a	5.5a
A) Fall Applied				
$^{15}\text{NH}_4\text{NO}_3$	27.0bc	27.4c	6.4abc	7.7abc
$\text{NH}_4^{15}\text{NO}_3$	23.3b	21.2b	4.9ab	7.1a
$\text{CO}(^{15}\text{NH}_2)_2$	29.9cd	30.5cd	5.9abc	8.4abc
B) Spring Applied				
$^{15}\text{NH}_4\text{NO}_3$	31.7d	33.1d	7.6bc	11.0bc
$\text{NH}_4^{15}\text{NO}_3$	34.4d	34.0d	8.3c	11.2c
$\text{CO}(^{15}\text{NH}_2)_2$	34.0d	32.2cd	6.3abc	7.3ab

- (1) All fertilizer treatments applied at a rate of 60 pounds nitrogen per acre.
- (2) Poor and variable results were obtained on the Almasippi soil due to damage incurred by the crop.
- (3) Any two values in vertical columns not followed by the same letter are significantly different at $p = 0.05$ by Duncan's Multiple Range test.

$\text{NH}_4^{15}\text{NO}_3$ but this was not verified statistically. Straw yields however were statistically different.

Ridley (93) working on several soil types over three years compared urea and ammonium nitrate at rates up to sixty pounds of nitrogen per acre applied in the spring and fall. Results similar to those from the Manitou plot site were found. The data indicated the superiority of spring fertilization with little difference being found between urea and ammonium nitrate in two of the three years. Ammonium nitrate was found to give greater yields than urea in one year. Differences detected between the carriers in one year and not in two other years were attributed to different climatic conditions prevailing in the three years.

Yields on the Almasippi plot site were poor and variable and few significant results were found. Yield increases from the application of nitrogen fertilizers were indicated, with spring fertilization being superior. Little difference in yield due to the nitrogen carriers applied in the fall could be found. However, similar to results from the Manitou site, yields from fall applied $^{15}\text{NH}_4\text{NO}_3$ were slightly larger than from $\text{NH}_4^{15}\text{NO}_3$. Spring applied ammonium nitrate produced larger yield increase than urea but $\text{NH}_4^{15}\text{NO}_3$ treatment yields were slightly greater than from $^{15}\text{NH}_4\text{NO}_3$.

The relative inefficiency of spring applied urea compared to ammonium nitrate indicated on the Almasippi site is consistent with many results documented in the literature. Several workers attributed lower yields from urea to phytotoxic effects which reduced germination as a result of its application (49, 76). Others attributed poor responses to loss of applied urea nitrogen as volatile ammonia (49, 76). Either cause may have been a valid explanation for the results found, but since measurements were not taken to determine either effect, no conclusive reason could be given.

2. Plant Nitrogen.

i) Percent nitrogen content. Data showing the nitrogen content of plant samples taken at two intervals during the growing season and at harvest is presented in Table III. The relatively higher nitrogen content of the plants from the first sampling indicated a rapid assimilation of both fertilizer and native soil nitrogen early in the growth stages of the crop. The slight, although not significantly, higher nitrogen content of the spring fertilized plants over the others, and of the fall fertilized plants over the check plants on both sites at this stage may have reflected the relative availability of the nitrogen in the various treatments. At the seven-week sampling stage on the Manitou site, plants from spring and fall applied urea treatments displayed a slightly lower nitrogen content than comparable ammonium nitrate treatment plants, except from the spring applied $\text{NH}_4^{15}\text{NO}_3$. This could have indicated a slower uptake of urea nitrogen in the early stages of plant growth or greater dilution of assimilated fertilizer nitrogen resulting from increased growth. The second reason appears more probable since final yields and total nitrogen uptake (Table V) were slightly greater in these urea treatments. Slight unexplainable differences were again noted in nitrogen content of plants from the differently tagged ammonium nitrate treatments which may also have reflected the relative rate of fertilizer nitrogen uptake or plant growth. Percent nitrogen content of plants from fall applied $\text{NH}_4^{15}\text{NO}_3$ treatments was larger than from fall applied $^{15}\text{NH}_4\text{NO}_3$. Plants from spring applied $^{15}\text{NH}_4\text{NO}_3$ treatments contained a larger percent nitrogen than those from comparably applied $\text{NH}_4^{15}\text{NO}_3$ treatments.

By the twelfth week sampling time on the Manitou plot, most

TABLE III

NITROGEN CONTENT OF BARLEY AT TWO GROWTH STAGES AND HARVEST AS AFFECTED BY FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE ON MANITOU AND ALMASIPPI SOILS

Treatment	Nitrogen Content (%)							
	Manitou				Almasippi			
	7-week	12-week	Harvest Grain	Harvest Straw	7-week	12-week	Harvest Grain	Harvest Straw
Check	2.28 ⁽¹⁾ _a	1.14a	1.78a	0.33ab	3.54a	1.20a	1.84a	0.77ab
A) Fall Applied								
$^{15}\text{NH}_4\text{NO}_3$	2.68abc	1.08a	1.62b	0.28a	3.81a	1.28a	1.96bc	0.76ab
$\text{NH}_4^{15}\text{NO}_3$	2.88bc	1.04a	1.60b	0.28a	3.60a	1.08a	1.89ab	0.71a
$\text{CO}(^{15}\text{NH}_2)_2$	2.60ab	1.02a	1.67ab	0.30ab	3.64a	1.22a	1.94abc	0.72a
B) Spring Applied								
$^{15}\text{NH}_4\text{NO}_3$	3.14c	1.08a	1.70ab	0.32ab	4.08a	1.38a	2.16e	0.90c
$\text{NH}_4^{15}\text{NO}_3$	2.71abc	1.12a	1.68ab	0.32ab	3.87a	1.29a	2.12de	0.87bc
$\text{CO}(^{15}\text{NH}_2)_2$	2.99bc	1.13a	1.78a	0.35b	4.01a	1.37a	2.03cd	0.88c

(1) Any two values in vertical columns not followed by the same letter are significantly different at $p = 0.05$ by Duncan's Multiple Range Test.

treatments contained a smaller, but not significantly lower nitrogen content than the check. Plants from fall fertilized treatments contained a lower percent nitrogen than those from the spring fertilized treatments. Little difference was detected in nitrogen content of plants from comparably applied urea and ammonium nitrate treatments.

The trends at the twelfth week sampling generally carried through in the harvest grain and straw samples. Fall fertilized treatments contained a smaller percent nitrogen than spring fertilized treatments. Urea treatment samples contained a slightly higher nitrogen content than those from ammonium nitrate applied at the same time. Little difference in percent nitrogen content occurred between the differently tagged ammonium nitrate treatments.

Data from the Almasippi plot site showed that the trend of increased percent nitrogen compared to the check of all nitrogen fertilized plants noted in the first sampling continued through the season. Most differences between treatments also appeared consistently in samples taken at the various stages. Plants from spring fertilized treatments contained a higher nitrogen content than those from the corresponding fall applied treatments. Differences between the differently tagged ammonium nitrate treatments were apparent, but were not significant. Both fall and spring applied $^{15}\text{NH}_4\text{NO}_3$ treatment plants contained a larger percent nitrogen than plants from comparably applied $\text{NH}_4^{15}\text{NO}_3$. Fall applied urea treatments were intermediate in nitrogen content between the two fall applied ammonium nitrate treatments. A similar pattern was noted in the first two samplings of the spring applied treatments, but the nitrogen content of the harvest samples from the urea treatments was lower than from either ammonium nitrate treatments.

ii) Percent nitrogen derived from the fertilizer sources.

The percent plant nitrogen derived from either the urea, ammonium, or nitrate nitrogen applied in the spring and fall as measured by the uptake of these ^{15}N tagged sources is shown in Table IV. In most instances, spring fertilized plants derived a larger percent of their nitrogen from the fertilizer sources than did fall fertilized plants. This was especially noticeable in the data from the Almasippi site. Such differences reflected the relative availability of the nitrogen sources from both times of application.

On the Manitou soil, plants which received ammonium nitrate in the fall derived a significantly larger percent of their nitrogen from the ammonium ion than from the nitrate ion. This indicated that the ammonium ion contributed the greatest amount to the increased yield and nitrogen uptake (Table V) from the ammonium nitrate. Fall applied urea contributed a smaller but generally now significantly lower amount of nitrogen to the plants than the ammonium ion in ammonium nitrate. The amount supplied by urea nitrogen was however, larger than that supplied by the nitrate ion in ammonium nitrate, showing significant difference at harvest time.

The spring fertilized ammonium nitrate treated barley on the Manitou soil derived a larger percent nitrogen from the nitrate ion than the ammonium ion being statistically different in harvest samples. This indicated that nitrate was more responsible for the increased yield and nitrogen uptake from ammonium nitrate. Plants fertilized with urea contained a smaller percent nitrogen derived from this source than plants fertilized with ammonium nitrate contained from the nitrate ion, but a larger percent than ammonium nitrate treated plants contained from the ammonium ion. These trends were consistent but generally not statistically significant at any sample stage.

The percent of fall applied nitrogen contained by barley on the

TABLE IV

PERCENT NITROGEN IN BARLEY DERIVED FROM VARIOUS FORMS OF NITROGEN APPLIED IN UREA AND AMMONIUM NITRATE AS MEASURED BY ¹⁵N UPTAKE

Source	Percent of Nitrogen Derived from Fertilizer Sources									
	Manitou			Almasippi						
	7-week	12-week	Grain	Harvest Straw	Total	5-week	12-week	Grain	Harvest Straw	Total
A) Fall Applied										
¹⁵ NH ₄ in ¹⁵ NH ₄ NO ₃	38.3b ⁽¹⁾	28.0bc	35.9bc	35.1bc	35.9c	8.7a	3.8a	6.1a	5.9a	6.0a
¹⁵ NO ₃ in NH ₄ ¹⁵ NO ₃	15.0a	12.0a	8.0a	7.1a	7.8a	6.1a	5.4a	6.8a	5.4a	6.2a
¹⁵ NH ₂ inCO(¹⁵ NH ₂) ₂	23.7ab	21.2ab	29.5b	25.2b	28.7b	5.4a	4.7a	6.9a	6.5a	6.7a
B) Spring Applied										
¹⁵ NH ₄ in ¹⁵ NH ₄ NO ₃	29.4ab	31.1bcd	39.4bc	36.9cd	39.0cd	13.8a	16.8b	22.3b	20.8b	21.7b
¹⁵ NO ₃ in NH ₄ ¹⁵ NO ₃	43.4b	41.3d	47.0d	52.0e	47.8e	44.7b	41.7d	57.0d	52.7d	55.8d
¹⁵ NH ₂ inCO(¹⁵ NH ₂) ₂	43.6b	39.2cd	44.4dc	42.4d	44.8de	39.7b	33.8c	38.6c	33.7c	36.7c

(1) Any two values in vertical columns not followed by the same letter are significantly different at $p = 0.05$ by Duncan's Multiple Range Test.

Almasippi soil was very small. This was consistent for all forms of nitrogen applied. Barley grown on the spring applied ammonium nitrate treated plots consistently showed a significantly higher percent of the plant nitrogen derived from the nitrate ion than the ammonium ion. This indicated a greater availability of the nitrate ion and a larger contribution made by it on yield and nitrogen content. Urea fertilized plants obtained a significantly smaller amount of nitrogen from the urea than the ammonium nitrate crops obtained from the nitrate ion, but a significantly larger percent than obtained from the ammonium ion. Possible reasons for the differences will be discussed in a later section.

Data from the harvest samples on both plot sites showed that, with one exception, the grain contained a larger percent nitrogen derived from the fertilizer sources than did the straw. This is consistent with data reported by the International Atomic Energy Agency (58) but no explanation was offered for these results. This may have indicated some isotopic discrimination in the biochemical processes occurring in the plant which resulted in the grain containing a higher proportion of the ^{15}N than the straw. However this effect may also have been due to an uptake of fertilizer nitrogen in a certain proportion at a stage in the plant growth when metabolic processes were developing the grain which was different to the proportion of fertilizer nitrogen assimilated at the time of straw development. This would have resulted in differing percentages of fertilizer nitrogen being present in the grain and straw.

iii) Total nitrogen uptake. The nitrogen uptake data at harvest time from the grain and straw samples is shown in Table V. Differences in total nitrogen uptake in the treatments were generally consistent with those found in the yield and percent nitrogen content since these values are

TABLE V

NITROGEN UPTAKE BY BARLEY AS AFFECTED BY FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE ON MANITOU AND ALMASIPPI SOILS

Treatment ⁽¹⁾	Nitrogen Uptake (lb/acre)					
	Grain	Manitou		Grain	Almasippi ⁽²⁾	
		Straw	Total		Straw	Total
Check	28.4a ⁽³⁾	4.7a	33.1a	7.1a	4.2a	11.3a
A) Fall Applied						
$^{15}\text{NH}_4\text{NO}_3$	43.6bc	7.7bc	51.3bc	12.4abc	5.9a	18.3ab
$\text{NH}_4^{15}\text{NO}_3$	37.2b	6.0ab	43.2b	9.2a	5.0a	14.2ab
$\text{CO}(^{15}\text{NH}_2)_2$	50.0cd	9.6cd	59.6cd	11.4ab	6.0a	17.4ab
B) Spring Applied						
$^{15}\text{NH}_4\text{NO}_3$	53.7de	10.5d	64.2de	16.5bc	9.6b	26.3bc
$\text{NH}_4^{15}\text{NO}_3$	56.9de	10.8d	67.7de	17.6c	9.6b	27.2c
$\text{CO}(^{15}\text{NH}_2)_2$	60.6e	11.6d	72.2e	12.6abc	7.0ab	19.6c

- (1) All fertilizer treatments applied at a rate of 60 lb pounds nitrogen per acre.
- (2) Poor and variable results were obtained on the Almasippi soil due to damage incurred by the crop.
- (3) Any two values in vertical columns not followed by the same letter are significantly different at $P = .05$ by Duncan's Multiple Range Test.

closely related. On the Manitou soil, total nitrogen uptake in all fertilized treatments was significantly larger than the check. Spring applied nitrogen resulted in significantly greater nitrogen uptake than corresponding fall applied treatments. Fall applied urea resulted in a lower nitrogen uptake by barley than the spring applied ammonium nitrate sources, but not significantly less. No significant differences were noted between the carriers applied in the spring, but urea appeared to show a slightly larger nitrogen uptake. As noted in previous data, some unexplainable differences were detected between the differently tagged ammonium nitrate fertilizers. Slightly greater nitrogen uptake was apparent from the spring applied $\text{NH}_4^{15}\text{NO}_3$ treatments than from the spring applied $^{15}\text{NH}_4\text{NO}_3$ treatments. Fall applied urea treatments showed a significant increase in total nitrogen uptake compared to $\text{NH}_4^{15}\text{NO}_3$ treatments and a larger but insignificantly greater uptake than $^{15}\text{NH}_4\text{NO}_3$ treatments. The apparently greater nitrogen uptake from the $^{15}\text{NH}_4\text{NO}_3$ treatments over the $\text{NH}_4^{15}\text{NO}_3$ treatments was not significantly different.

The Almasippi plot site results were again inconsistent and only trends could be noted. All fertilized treatments showed a greater nitrogen uptake than the check with larger increases resulting from spring application. Greater uptake of all fall applied nitrogen occurred from the urea and $^{15}\text{NH}_4\text{NO}_3$ treatment over the $\text{NH}_4^{15}\text{NO}_3$ treatments. From spring applied fertilizers, urea treatments showed a smaller uptake of nitrogen than either ammonium nitrate treatments. The uptake from the two ammonium nitrate treatments were only slightly different.

3. Recovery of Applied Nitrogen.

i) Efficiency of nitrogen fertilizers. The efficiency of utilization of the applied nitrogen fertilizers as indicated by the difference in total nitrogen uptake between the fertilized treatment and check plot

plants is shown in Table VI. These results are comparable to data reported in the literature (2, 3). Efficiency of recovery of applied nitrogen was greater on the Manitou than the Almasippi soil presumably due to poor crop growth obtained on the latter site. Nitrogen applied in the spring was more efficiently recovered than fall applied nitrogen. Similar results were found by many researchers who attributed the poorer recovery to a greater loss and tie-up of the fall applied nitrogen resulting in smaller amounts available to the crop (38, 80, 95, 119). Barley on the Manitou plot site recovered a greater amount of spring and fall applied urea nitrogen than comparably applied ammonium nitrate nitrogen. The Almasippi data indicated a possible greater efficiency of spring applied ammonium nitrate over urea. Values from both plots again reflected the unexplainable differences previously noted between the differently tagged forms of ammonium nitrate. Spring applied $\text{NH}_4^{15}\text{NO}_3$ appeared more efficient than $^{15}\text{NH}_4\text{NO}_3$, while a greater efficiency of fall applied $^{15}\text{NH}_4\text{NO}_3$ over $\text{NH}_4^{15}\text{NO}_3$ was apparent.

Table VII shows the efficiency of the fertilizers measured by ^{15}N uptake data. Efficiency of ammonium nitrate was averaged from the uptake of separately tagged ammonium and nitrate treatments. Values calculated by the ^{15}N method were generally lower than the estimates obtained by the first method where efficiency was based on the difference in total nitrogen uptake by the fertilized treatments over the check. Estimates made on this "difference" basis may have included nitrogen which was not only directly obtained from the fertilizer but also from nitrogen made available by the priming effects that fertilizer application had on such processes as mineralization. This would have given an overestimate of fertilizer recovery. Values calculated from the ^{15}N data showed only the

TABLE VI

EFFICIENCY OF UPTAKE OF FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE
NITROGEN AS MEASURED BY NITROGEN CONTENT OF BARLEY ON
MANITOU AND ALMASIPPI SOILS.

Treatment (1)	Efficiency (2) of Applied Nitrogen(%)	
	Manitou	Almasippi
A) Fall Applied		
$^{15}\text{NH}_4\text{NO}_3$	30.3	11.7
$\text{NH}_4^{15}\text{NO}_3$	16.8	4.8
$\text{CO}(^{15}\text{NH}_2)_2$	44.2	10.2
B) Spring Applied		
$^{15}\text{NH}_4\text{NO}_3$	51.8	25.0
$\text{NH}_4^{15}\text{NO}_3$	57.7	26.5
$\text{CO}(^{15}\text{NH}_2)_2$	65.2	13.8

(1) All fertilizer treatments applied at a rate of 60 pounds of nitrogen per acre.

(2) Efficiency was based upon the average yield and nitrogen content of 4 replicates of each treatment and calculated by:

$$\frac{\text{Total N uptake in treatment} - \text{Total N uptake in check}}{\text{Rate of N applied}} \times 100$$

TABLE VII

EFFICIENCY OF UPTAKE OF FALL AND SPRING APPLIED UREA AND AMMONIUM NITRATE NITROGEN AS MEASURED BY ^{15}N CONTENT OF BARLEY ON MANITOU AND ALMASIPPI SOILS.

Carrier	Efficiency ⁽¹⁾ (%)	
	Manitou	Almasippi
A) Fall Applied		
$\text{CO}(\text{NH}_2)_2$	28.5	1.9
NH_4NO_3	18.2	1.7
B) Spring Applied		
$\text{CO}(\text{NH}_2)_{2222}$	52.9	12.1
NH_4NO_3	47.8	17.4

(1) Efficiency of $\text{CO}(\text{NH}_2)_2$ is based upon percent recovery of ^{15}N applied in ($^{15}\text{NH}_2$). Efficiency of NH_4NO_3 is based upon the average of the recovery of $^{15}\text{NH}_4$ and $^{15}\text{NO}_3$ applied separately.

nitrogen assimilated directly from the fertilizer but may be unduly low because of isotopic dilution.

Efficiency calculated from ^{15}N data showed similar trends to those found by the "difference" method. Recovery of nitrogen on the Manitou plot was greater than on the Almasippi plot. Spring applied nitrogen was more completely recovered than that applied in the fall. Urea on the Manitou soil was more completely recovered by the crop than ammonium nitrate from both spring and fall applications. Recovery of fall applied nitrogen sources applied to the Almasippi soil was negligible. Ammonium nitrate nitrogen applied in the spring on this plot was more completely recovered than urea nitrogen.

ii) Recovery of nitrogen fertilizer species. Considerable differences were apparent in the final recovery of the three different nitrogen species present in urea and ammonium nitrate as measured by the uptake of these forms tagged with ^{15}N (Table VIII). Nitrogen recovery trends noted in this data reflected the differences found between percent plant nitrogen derived from the different nitrogen sources previously discussed. Each of the species studied (i.e. ammonium and nitrate in ammonium nitrate and urea nitrogen) was more efficiently recovered from the spring application over the respective form applied in the fall on both plot sites. This indicated that all forms of nitrogen incurred a greater loss or tie-up when applied in the fall. A significantly higher recovery of the ammonium nitrogen from ammonium nitrate than the nitrate nitrogen was evident from the fall applied fertilizer on the Manitou plot. Since relatively little of the applied nitrate was recovered, an extensive loss of this form of nitrogen applied in the fall was apparent. Fall applied urea nitrogen was almost as effectively recovered as the ammonium nitrogen

TABLE VIII

RECOVERY OF VARIOUS FORMS OF NITROGEN FROM FALL AND SPRING APPLIED UREA
AND AMMONIUM NITRATE MEASURED BY ^{15}N CONTENT OF BARLEY ON
MANITOU AND ALMASIPPI SOILS.

Source	Recovery of Applied ^{15}N (%)	
	Manitou	Almasippi
A) Fall Applied		
$^{15}\text{NH}_4$ in $^{15}\text{NH}_4\text{NO}_3$	30.8b ⁽¹⁾	1.8a
$^{15}\text{NO}_3$ in $\text{NH}_4^{15}\text{NO}_3$	5.5a	1.6a
$(^{15}\text{NH}_2)$ in $\text{CO}(^{15}\text{NH}_2)_2$	28.5b	1.9a
B) Spring Applied		
$^{15}\text{NH}_4$ in $^{15}\text{NH}_4\text{NO}_3$	41.9e	9.5a
$^{15}\text{NO}_3$ in $\text{NH}_4^{15}\text{NO}_3$	53.7d	25.3b
$(^{15}\text{NH}_2)$ in $\text{CO}(^{15}\text{NH}_2)_2$	52.9d	12.1a

(1) Any two values in vertical columns not followed by the same letter are significantly different at $P = .05$ by Duncan's Multiple Range Test.

from ammonium nitrate. The excessive loss of the nitrate ion of ammonium nitrate and the relatively similar percent recovery of the ammonium nitrogen to urea nitrogen may explain why the overall efficiency of ammonium nitrate was less than urea and why fall applied urea was closer to spring applied nitrogen treatments in affecting yield and nitrogen uptake. This data is in agreement with the hypothesis of several workers who stated that fall fertilization would be of benefit only if the nitrogen was applied as an ammonium type fertilizer and furthermore, that conditions such as cool temperatures inhibited nitrification (5, 95, 98, 109). A loss or reduction in availability of fall applied or nitrified nitrate, as indicated by this data, could be incurred by leaching of this soluble form by fall rains or downward movement of soil water during the winter or spring (5, 48, 95). Since the fertilizer was applied late in the fall in this experiment it was assumed that temperature was not warm enough to permit nitrification and the extremely poor nitrate recovery may have been due to fall or spring leaching before nitrification of the applied ammonium proceeded to an appreciable degree. Slight nitrification may have occurred however and some loss of the fall applied ammonium could also have been due to this process. Under this assumption conditions must have allowed for hydrolysis of urea to the more stable ammonium form prior to any appreciable leaching, since in the unhydrolyzed form urea could also have been lost by leaching.

Several other workers who found a relatively greater loss of nitrate than ammonium attributed the cause of this loss to denitrification (2, 3, 24, 38, 71). In this experiment, if temperature conditions were not favorable for nitrification of the ammonium it appears unlikely that denitrifying activity could have occurred. However high moisture conditions

in the early spring could have inhibited nitrification through a reduced soil oxygen concentration while permitting denitrification (1).

The extensive loss of all forms of nitrogen applied in the fall to the Almasippi soil indicated that several mechanisms may have contributed to the loss of all nitrogen species. However on this site, nitrification may have occurred and either leaching or denitrification caused the loss of the applied or nitrified nitrate in the fall or during the excessively high moisture conditions encountered in early spring.

The application of nitrogen at seeding time in the spring on the Manitou soil resulted in a significantly larger efficiency of both the nitrate from ammonium nitrate and urea nitrogen than the ammonium nitrogen in ammonium nitrate. Efficiency of uptake of urea and nitrate nitrogen from ammonium nitrate was similar. The slightly smaller relative efficiency of spring applied ammonium nitrate than urea would then be due to the greater loss of the ammonium ion than either nitrate or urea nitrogen. Volatilization of ammonia may have been the cause of this loss. However, this seems unlikely since soil conditions did not appear favorable for this reaction. In addition loss of urea nitrogen did not appear to have been as great as would have been expected had ammonium volatilization occurred. A more probable explanation for the results would be immobilization. Microorganisms would have assimilated all forms of nitrogen but preferentially and more extensively immobilized ammonium prior to nitrification. Urea may have been hydrolyzed at such a rate that any ammonium produced was rapidly nitrified. This would have resulted in little ammonium from this source being subject to immobilization at any time, and resulted in similar recoveries to that from nitrate nitrogen.

Recoveries by barley of the spring applied nitrogen on the

Almasippi soil showed the nitrate form to be more effectively recovered than either the ammonium from ammonium nitrate or urea nitrogen. On this site ammonia volatilization could have been the cause of the excess loss of the ammonium and urea nitrogen. The alkaline pH of this soil would have favored the occurrence of this reaction. Urea nitrogen appeared to be less readily lost than ammonium from ammonium nitrate. Rapid nitrification of the ammonium produced by urea hydrolysis would have resulted in smaller concentrations of ammonium at any time from this source than from ammonium nitrate and therefore less subject to the reaction. Immobilization was probably also in part responsible for the incomplete recoveries, but very low recoveries of all forms may be attributed to poor crop growth and yields.

D. SUMMARY AND CONCLUSIONS

Results from the plot on the Manitou soil showed that the application of both urea and ammonium nitrate at a rate of sixty pounds nitrogen per acre in either the fall prior to seeding or at spring seeding time gave significant increases in yield and total nitrogen uptake of barley. Spring applied fertilizers gave superior responses to fall applied fertilizers. Little difference was detected between the spring applied urea and ammonium nitrate treatments. Yield and total nitrogen uptake in the fall applied urea treatments appeared slightly greater than in fall applied ammonium nitrate treatments. Final percent nitrogen contents of the plants were not significantly different, however spring fertilized crops appeared to contain a slightly larger percent nitrogen than fall fertilized crops. Greater losses of all forms of nitrogen (urea, ammonium and nitrate nitrogen) applied in the fall over those applied in the spring were indicated by the poorer recovery in the crop of these ¹⁵N tagged species from

the fall fertilized treatments. Recovery of fall applied nitrate nitrogen from ammonium nitrate was significantly less than from either the ammonium nitrogen of ammonium nitrate or urea nitrogen. Similar recoveries of the fall applied ammonium and urea nitrogen were found. Spring applied urea and nitrate nitrogen were equally recovered; the recovery of these forms being significantly greater than the ammonium nitrogen.

High variability due to severe crop damage on the Almasippi plot site resulted in few significant findings, but some general trends were noted. The application of both urea and ammonium nitrate in the fall and spring resulted in some increase in yield, percent nitrogen content and nitrogen uptake of barley. The spring applied treatments were definitely superior to fall applied treatment. Recovery of all forms of nitrogen applied in the fall was equally poor. A significantly greater recovery of spring applied nitrate nitrogen from ammonium nitrate was found than either spring applied ammonium or urea nitrogen. Recovery of urea nitrogen was significantly greater than of ammonium nitrogen.

Slight but consistent differences were apparent in the yields and nitrogen uptake of barley from the differently tagged ammonium nitrate fertilizers applied in spring and fall to both plots. These were not significant and could not be explained. Responses in yield and nitrogen uptake were generally greater from fall applied $^{15}\text{NH}_4\text{NO}_3$ than from fall applied $\text{NH}_4^{15}\text{NO}_3$. However spring applied $\text{NH}_4^{15}\text{NO}_3$ appeared better than spring applied $^{15}\text{NH}_4\text{NO}_3$.

IV. LABORATORY EXPERIMENT I

A. INTRODUCTION

The field experiment conducted verified the inefficient recovery of applied fertilizer nitrogen by crops encountered in most research. Several reactions are known to occur in the soil which cause added nitrogen to become unavailable to growing plants. Gaseous release of ammonia from ammonium sources and urea has been credited with the loss of nitrogen from the soil, especially from alkaline and calcareous soils. Results from the field experiment indicated that this reaction may have been a cause of at least part of the low recoveries encountered, especially on the calcareous Almasippi soil. The purpose of this experiment was to determine if ammonia was being released from urea and ammonium sources when applied to a calcareous and a noncalcareous soil and to measure the extent of any loss of urea, ammonium and nitrate nitrogen. Measurements were made when fertilizers were broadcast on the surface and incorporated.

B. METHODS AND MATERIALS

1. Soils.

An Almasippi and a Manitou soil, similar to those used in the field experiment were selected for the laboratory studies. Soil was taken in the fall of 1969 from the 0 to 6 inch depth of cropped fields near the field experimental plots. The soil was air-dried and passed through a one-quarter inch mesh sieve. A representative sample of each soil was taken for analysis. Some characteristics of the soils are listed in Table IX.

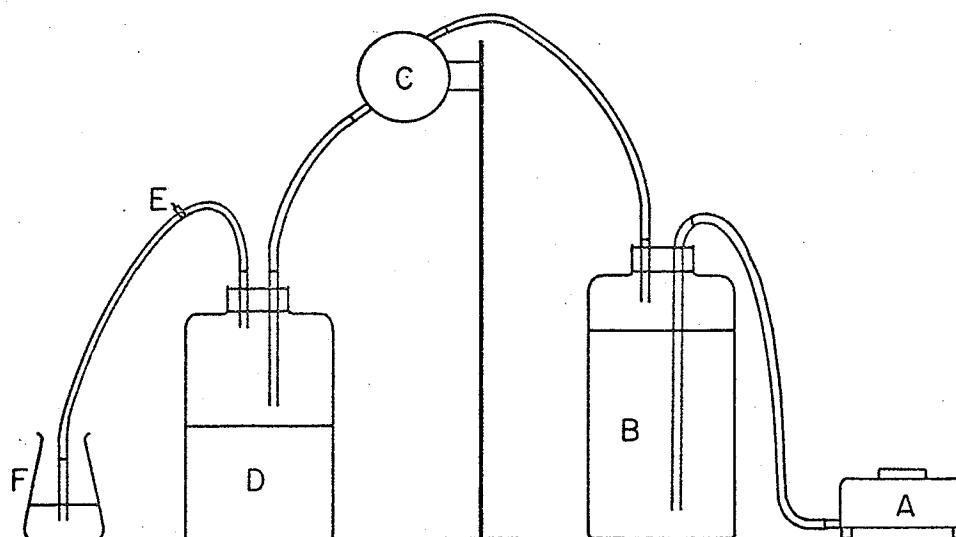
2. Apparatus for Incubation and Collection of Evolved Ammonia.

The apparatus used for incubation of the soil and collection of evolved ammonia, as illustrated in Figure II, was similar to that used by

TABLE IX

CHARACTERISTICS OF SOILS IN LABORATORY EXPERIMENTS

Soil Association	Texture	pH	Conductivity (mmhos/cm)	CaCO ₃ equivalent (%)	Organic Matter (%)	Cation Exchange Capacity (meq/100g)	Field Capacity (%)	Total Nitrogen (%)	NH ₄ -N (ppm)	NO ₃ -N (ppm)	Organic C/N
Manitou	clay loam	6.20	0.30	0.05	6.40	30.6	30.7	.32	25.8	12.5	11.6
Almasippi	loamy very fine sand	7.70	1.75	5.91	3.98	12.3	20.4	1.20	5.8	10.2	11.6



- A - Air Pump
- B - Atmospheric Ammonia Removing Solution
- C - Air Distributing Chamber
- D - Incubating Vessel
- E - Air Flow Control Clamp
- F - Ammonia Collecting Solution

Figure II. Apparatus for incubation and collection of evolved ammonia.

Toews (107). It basically consisted of an air pump (A) which forced air through two inlets into an air distributing chamber (C) made of colorless transparent extruded acrylic plastic tubing. The air was then passed through plastic tubing into a series of twenty 500 ml shaking flasks (D) which were used as incubation vessels. Plastic outlet tubes led from the incubation vessels to 125 ml erlenmeyer flasks (F) which contained an acid solution for collecting ammonia. An aquarium pump was used to provide air flow. Atmospheric air from which ammonia was removed by bubbling it through two liters of $\text{1NH}_2\text{SO}_4$ was passed over the soil in the incubation flasks and into the collecting flasks. The air flow rate was regulated by clamps (E) on the tubes leading to the collecting flasks.

3. Experimental Design and Procedure.

Treatments in the experiment were as follows:

- 1) Check in which no fertilizer nitrogen was applied.
- 2) Urea applied at a rate of 30 ppm nitrogen.
- 3) Urea applied at a rate of 60 ppm nitrogen.
- 4) Ammonium nitrate applied at a rate of 30 ppm nitrogen.
- 5) Ammonium nitrate applied at a rate of 60 ppm nitrogen.
- 6) Ammonium sulphate applied at a rate of 30 ppm nitrogen.
- 7) Ammonium sulphate applied at a rate of 60 ppm nitrogen.
- 8) Potassium nitrate applied at a rate of 30 ppm nitrogen.
- 9) Potassium nitrate applied at a rate of 60 ppm nitrogen.

Each treatment was duplicated and the incubation was run twice, once with the fertilizers broadcast and once with the fertilizers mixed through the soil. A blank was included to check for any contamination.

Two hundred and fifty grams of air-dried soil was weighed into the incubation flasks. Fertilizer was added in the appropriate amounts

and in the manner prescribed using certified A.C.S. grade chemicals. Distilled water was added to bring the soils to field capacity. In the broadcast treatments water was added prior to fertilizer addition while in the incorporated treatments water was added after mixing in the fertilizer. Into each of the ammonia collecting flasks 25 ml of 0.005N H_2SO_4 and 50 ml of distilled water was added. The incubation flasks were attached to the apparatus, the air pump was started and adjustments were made to obtain as near as possible uniform air flow through all sample bottles.

The ammonia collecting solution was changed daily or as deemed necessary by the rate of ammonia evolution. The quantity of ammonia evolved was determined by titration of the acid solution with standardized 0.005N NaOH using a mixed indicator. Temperature was maintained at approximately 22°C.

Soils were allowed to incubate for one week. Each bottle was then disconnected and weighed to determine moisture loss. Since loss never exceeded 0.5 gm, little water was needed to return the soils to field capacity. The soil from each bottle was removed, thoroughly mixed and a sample of each was removed and stored for analysis. Samples were stored in airtight plastic bags at 4°C. This method of storage was found by Carnie (22) to be the best method of maintaining the soil nitrogen status in form and quantity.

4. Analytical Procedures.

i) Soil Characterization. Analyses by the following methods were run in duplicate to determine soil characteristics.

a) Soil pH, conductivity, inorganic carbon and organic matter content: were conducted as outlined in Section III.

b) Soil Cation Exchange Capacity. The ammonium saturation method

outlined by Chapman (26) was used for this determination. The exchange sites of a 10.0 g air-dry soil sample was saturated with ammonium by shaking for one hour in 100 ml of 1N NH_4OAc solution containing 250 ppm Li adjusted to a pH 7 with HCl. The suspension was filtered by suction and further washed with NH_4OAc solution to a filtrate volume of 250 ml. The soil was then washed with 250 ml of 95 percent ethanol. Adsorbed ammonia was displaced with 250 ml of acidified 1N NaCl and the filtrate collected and transferred to an 800 ml Kjeldahl flask. A 25 ml aliquot of 10N NaOH was added to the Kjeldahl flask and the ammonia distilled into 50 ml of 2 percent boric acid solution on a Kjeldahl distillation unit to a volume of 200 ml. The boric acid solution was titrated with standardized 0.1N H_2SO_4 and the cation exchange capacity was calculated as milliequivalents per 100 g of soil.

c) Total Soil Nitrogen. Total nitrogen content of the soil was determined on a 5.0 g sample of air-dried soil as outlined by Bremner (14). This method is similar to the Kjeldahl Gunning method outlined in Section III with the inclusion of a pretreatment to include NO_3^- and NO_2^- . The pretreatment involved the addition of 30 ml of 5 percent KMnO_4 , 30 ml of 50 percent H_2SO_4 , two drops of octanol and 0.5 g of finely ground reducing iron powder to the soil in the Kjeldahl flask and heating for fifteen minutes on the Kjeldahl unit. After cooling the determination was completed by the method outlined in Section III and total nitrogen content expressed as percent dry weight basis.

d) Soil Moisture Content at Field Capacity. Soil moisture content at field capacity was determined by placing a quantity of sieved, air-dry soil into a large beaker. Sufficient water was added and allowed to equilibrate for forty-eight hours so that the wet region did not

reach the bottom of the beaker. A sample was taken above the wetting front, weighed, oven-dried at 105°C for twenty-four hours and reweighed to determine water loss. Moisture content at field capacity was calculated and expressed as percent moisture on an oven-dried basis.

ii) Soil Inorganic Nitrogen. Inorganic ammonium and nitrate-nitrogen of the incubated soils were determined by the method outlined by Bremner (12). Extraction of the inorganic nitrogen was performed on the moist soil sample immediately upon removal from cold storage as suggested by Carnie (22). Soils samples were weighed to give an equivalent of 10.0 g dry soil, placed in a 250 ml erlenmeyer flask along with 100 ml of 2N KCl delivered from a Pyrex automatic pipette and shaken for one hour. The suspension was allowed to settle for a short period of time. Aliquots were taken immediately for analysis by the Magnesium Oxide-Devarda Alloy steam distillation method. A steam distillation apparatus containing a distillation flask fitted with a side arm opening to facilitate addition of chemicals similar to that illustrated by Bremner (12) was employed. A 10 ml aliquot of soil extract was pipetted into the distillation flask and 0.2 g of heavy MgO which had been autoclaved at 650°C for two hours to remove interfering $MgCO_3$ was added. Soil ammonium was then distilled into 5 ml of 2 percent boric acid solution until a distillate volume of 30 ml had been collected. Finely powdered Devarda alloy was then added to the distillation flask to reduce nitrates to ammonia and was similarly distilled into a second collecting flask. Distilled ammonia was determined by titration of the distillates with standardized 0.005N H_2SO_4 and the amount of ammonium and nitrate in the soil was calculated in ppm. Each group of analyses performed included a blank determination on the extractant solution and a periodic check of the apparatus and method was made by

analyzing a sample of a standard solution of ammonium sulphate and potassium nitrate.

C. RESULTS AND DISCUSSION.

1. Ammonia Volatilization.

Data from this experiment indicated that the only instances in which any of the applied nitrogen was released as gaseous ammonia were from the broadcast application of urea and ammonium salts to the Almasippi soil (Tables XI and XII). Ammonia volatilization would have been expected to occur on this soil since several other workers have found that soils with a high pH and calcareous property have favored this reaction (47, 67, 75, 116, 117). Losses however were quite small and reached a maximum of 7.2 percent of the nitrogen applied. Incorporation of the fertilizer into the Almasippi soil and broadcast and incorporation on the Manitou soil resulted in no ammonia liberation. Similar results have been found by numerous researchers who have reported that volatite losses of ammonia were negligible from fertilizers incorporated into the soil (77, 116) or applied to acidic soils like the Manitou where the pH was too low to allow for volatilization to proceed (67, 75).

Ammonia volatilization on the Almasippi soil was slightly greater from ammonium sulphate than from urea treatments, but the amount released from ammonium nitrate was considerably lower. This could be due to the ammonium ion accounting for only about one-half of the nitrogen in ammonium nitrate. Losses of ammonia from ammonium nitrate were similar to losses from the other sources when based on the amount of ammonium added since the quantity evolved from the 60 ppm nitrogen rate of ammonium nitrate (30 ppm ammonium nitrogen) was similar to the quantity evolved from the 30 ppm nitrogen rate of urea and ammonium sulphate. Loss of ammonia was

TABLE X

RATE OF RELEASE OF AMMONIA FROM BROADCAST APPLICATION OF NITROGEN SOURCES ON ALABAMA SOIL
INCUBATED AT 22°C.

Treatment	Amount of NH ₃ -N Evolved (mg)						Total
	0-22 hr.	22-44 hr.	44-69 hr.	69-93 hr.	93-165 hr.	165-180 hr.	
A) 30 ppm N applied							
CO(NH ₂) ₂	0.12	0.10	0.09	0.07	0.06	0.00	0.44
NH ₄ NO ₃	0.07	0.04	0.04	0.03	0.03	0.00	0.21
(NH ₄) ₂ SO ₄	0.19	0.10	0.07	0.06	0.06	0.00	0.48
B) 60 ppm N applied							
CO(NH ₂) ₂	0.27	0.27	0.20	0.10	0.13	0.00	0.97
NH ₄ NO ₃	0.14	0.09	0.07	0.07	0.07	0.00	0.44
(NH ₄) ₂ SO ₄	0.34	0.16	0.13	0.11	0.34	0.00	1.08

TABLE XI

RECOVERY OF NITROGEN ON MANITOU SOIL AFTER ONE WEEK INCUBATION AT 22°C

Treatment	Soil NH ₄ -N (ppm)	Soil NO ₃ -N (ppm)	Gaseous ⁽¹⁾ NH ₃ -N (ppm)	Recovery		Gaseous Recovery (%)	Total Recovery (%)
				Total N (ppm)	Soil ⁽²⁾ Recovery (%)		
A) Fertilizer Incorporated							
Check	1.4	52.1	0.0	53.5	-	-	--
a) 30 ppm N applied							
KNO ₃	0.0	74.5	0.0	74.5	70.0	0.0	70.0
CO(NH ₂) ₂	0.7	67.3	0.0	68.0	48.1	0.0	48.1
NH ₄ NO ₃	0.9	73.8	0.0	74.7	70.6	0.0	70.6
(NH ₄) ₂ SO ₄	0.7	72.2	0.0	72.9	64.6	0.0	64.6
b) 60 ppm N applied							
KNO ₃	1.4	102.7	0.0	104.1	84.4	0.0	84.4
CO(NH ₂) ₂	4.2	96.9	0.0	101.1	79.3	0.0	79.3
NH ₄ NO ₃	0.5	97.1	0.0	97.6	73.4	0.0	73.4
(NH ₄) ₂ SO ₄	6.4	90.4	0.0	96.8	72.0	0.0	72.0
B) Fertilizer Broadcast							
Check	2.1	52.3	0.0	54.4	-	-	-
a) 30 ppm N applied							
KNO ₃	2.1	79.2	0.0	81.3	89.8	0.0	89.8
CO(NH ₂) ₂	0.2	74.7	0.0	74.9	68.1	0.0	68.1
NH ₄ NO ₃	0.9	75.0	0.0	75.9	71.8	0.0	71.8
(NH ₄) ₂ SO ₄	2.1	72.4	0.0	74.5	71.5	0.0	71.5
b) 60 ppm N applied							
KNO ₃	0.0	106.4	0.0	106.4	86.7	0.0	86.7
CO(NH ₂) ₂	7.8	93.4	0.0	101.2	77.8	0.0	77.8
NH ₄ NO ₃	3.9	98.7	0.0	102.6	80.2	0.0	80.2
(NH ₄) ₂ SO ₄	14.1	82.8	0.0	96.9	70.8	0.0	70.8

(1) Gaseous NH₃ was converted to ppm released from the soil to facilitate further calculations.

(2) All recoveries were based on a percent of the total nitrogen applied.

TABLE XII

RECOVERY OF NITROGEN ON ALMASIPPI SOIL AFTER ONE WEEK INCUBATION AT 22°C

Treatment	Soil NH ₄ -N (ppm)	Soil NO ₃ -N (ppm)	Gaseous ⁽¹⁾ NH ₃ -N (ppm)	Recovery			
				Total N (ppm)	Soil ⁽²⁾ Recovery (%)	Gaseous Recovery (%)	Total Recovery (%)
A) Fertilizer Incorporated							
Check	0.0	19.6	0.0	19.6	-	-	-
a) 30 ppm N applied							
KNO ₃	0.0	47.5	0.0	47.5	93.0	0.0	93.0
CO(NH ₂) ₂	0.7	46.4	0.0	47.1	91.7	0.0	91.7
NH ₄ NO ₃	0.0	43.6	0.0	43.6	80.1	0.0	80.1
(NH ₄) ₂ SO ₄	0.0	41.0	0.0	41.0	71.5	0.0	71.5
b) 60 ppm N applied							
KNO ₃	0.4	75.0	0.0	75.4	92.9	0.0	92.9
CO(NH ₂) ₂	0.7	71.7	0.0	72.4	89.5	0.0	89.5
NH ₄ NO ₃	0.0	67.6	0.0	67.6	79.9	0.0	79.9
(NH ₄) ₂ SO ₄	0.0	69.5	0.0	69.5	83.2	0.0	83.2
B) Fertilizer Broadcast							
Check	0.0	19.6	0.0	19.6	-	-	-
a) 30 ppm N applied							
KNO ₃	2.8	48.8	0.0	51.6	107.0	0.0	107.0
CO(NH ₂) ₂	2.8	42.5	1.8	47.1	85.8	5.8	91.7
NH ₄ NO ₃	3.5	48.5	0.8	52.8	108.4	2.7	111.1
(NH ₄) ₂ SO ₄	2.3	44.0	1.9	48.2	88.8	6.3	95.1
b) 60 ppm N applied							
KNO ₃	3.2	74.0	0.0	77.2	95.9	0.0	95.9
CO(NH ₂) ₂	2.1	69.2	3.8	75.1	88.0	6.4	92.4
NH ₄ NO ₃	0.0	76.6	1.8	78.4	93.3	2.9	96.2
(NH ₄) ₂ SO ₄	0.0	67.6	4.3	71.9	80.0	7.2	87.2

(1) Gaseous NH₃ was converted to ppm released from the soil to facilitate further calculations.

(2) All recoveries were based on a percent of the total nitrogen applied.

greater from all sources at the higher application rate.

The rate at which ammonia was evolved from those treatments exhibiting volatilization (Table X) was at a maximum within 22 hours after application of the fertilizer and decreased with time. These results are similar to most reports in the literature where the rate of evolution was found to be related to the amount of ammonium present in the soil and subject to volatilization (50, 51, 75, 112). Greatest quantities of ammonium would be present with the ammonium sources at the time of application when volatilization was most rapid. Nitrifying activity would reduce the concentration of ammonium in the soil which would correspond to the decreasing reaction rate. Cessation of ammonia evolution by the 165th hour after application would probably approximate the time of complete nitrification of ammonium. The smaller initial and less rapidly decreasing volatilization from urea could be related to the hydrolysis process which would release small quantities of ammonium over an extended period of time resulting in a more uniform rate of evolution. Complete hydrolysis and nitrification however had probably occurred by the 165th hour since volatilization from this source had also stopped by this time.

2. Recovery of Applied Nitrogen.

On both soils the majority of the inorganic nitrogen recovered after one week was found as nitrate (Table XI and XII). This was expected because conditions of incubation favored nitrification. Considerable ammonium remained from the higher rates of application of ammonium salts and urea to the Manitou soil, especially in the broadcast treatments. Nitrifying activity was probably not sufficient to convert all of the applied ammonium in these instances since this soil contained high quantities of native ammonium.

The percent recovery of the applied nitrogen was based on the difference in amounts of inorganic nitrogen found in the treated soils over that present in the check at the end of the incubation period. This assumed that any mineralizing activity was similar in all soils and that the application of fertilizer did not result in an enhanced release of nitrogen from the inorganic fraction. Recoveries of greater than 100 percent in a couple of instances may have been due to enhanced mineralization. Generally however, total recovery of applied nitrogen was seldom found. A more complete recovery was obtained in most instances from nitrogen sources, applied to the Almasippi soil than to the Manitou soil, from broadcast treatments over incorporated treatments and from nitrogen treatments containing nitrate than from ammonium or urea treatments. Several possible causes may be apparent for incomplete recoveries found. Denitrification of applied or nitrified nitrate may have reduced recoveries but conditions were generally not conducive to an extensive loss in this manner. Freer diffusion of oxygen through the coarse-textured Almasippi soil would have made denitrifying conditions less probable on the soil, but the pH of the Manitou soil was not as favorable for this activity. Clay fixation of ammonium may also account in part for the lower recoveries of ammonium sources but would be of significance only on the Manitou soil. Although the organic carbon to nitrogen ratio in both soils was approximately 11.5 which would not apparently be conducive to extensive bacterial immobilization of nitrogen, trends in the experiment appeared to indicate this as a possible loss mechanism. A greater reduction in the recovery of ammonium sources would be explained by the fact that bacteria preferentially and more extensively assimilated this form of nitrogen than nitrate which could have occurred prior to nitrification

of the applied ammonium sources. The Manitou soil with a higher organic content would support a greater microbial population than the Almasippi soil and hence more immobilization would result. However the pH of the Almasippi soil was more favorable for immobilization. Incorporation of the fertilizer into the soil would disperse the applied nitrogen more evenly and put it in greater contact with microorganisms than from broadcast application resulting in possibly greater immobilization.

D. SUMMARY AND CONCLUSIONS.

Results of this experiment indicated that ammonia volatilization may be a cause of loss of fertilizer nitrogen broadcast as urea or ammonium salts on calcareous soils. The extent of loss which occurred in this experiment did not appear to be large enough to account for the low efficiencies encountered by growing crops in the field. However, higher rates of fertilization along with other variable factors found under field conditions not studied in this experiment such as fluctuating soil moisture and temperature may result in a larger release of ammonia.

Incomplete recoveries of applied nitrogen found in this experiment indicated that other causes such as denitrification, clay fixation and bacterial immobilization were possibly a more important cause of low recoveries of the fertilizer nitrogen.

V. LABORATORY EXPERIMENT II

A. INTRODUCTION

Results of the field experiment were similar to most findings reported in the literature which indicated that fall application of nitrogen was less effective than spring application. Several processes which the soil undergoes, such as alternate freezing and thawing in the late fall and early spring could create conditions which would result in loss of fall applied nitrogen. A laboratory experiment was designed to measure the effect which alternate freezing and thawing had on the recovery of nitrogen applied as urea, ammonium and nitrate sources in broadcast and incorporation treatments to a calcareous and a noncalcareous soil. The effect which this process had on ammonia volatilization was also to be determined.

B. METHODS AND MATERIALS

1. Soils. Samples of the Almasippi and Manitou soils used in the first incubation experiment and described previously were used in this experiment.

2. Experimental Design and Procedure. This study was designed and conducted in a similar manner to the previous experiment with the same treatments. The apparatus employed was the same as in the first laboratory experiment with the exception that three drying chambers, one of anhydrite and two of anhydrous calcium chloride were inserted between the ammonia removing H_2SO_4 solution and the air distributing chamber. This ensured that moisture in the air would not condense and freeze and plug any air tubes while the apparatus was subjected to cold temperatures. The same procedure was followed as the previous experiment in preparing the soils for incubation.

During the seven day incubation, the soils were subjected to four days of seven hours of cooling to -20°C and seventeen hours at room temperature (22°C). This was followed by an extended twenty-four hour warm period and subsequent sixty-five hour freezing. Freezing was accomplished by placing the apparatus in a standard chest-type deep-freezer. Throughout the incubation, ammonia evolved was collected as described previously. At the end of incubation the soils were checked for moisture loss. Negligible losses occurred. Samples were taken from each treatment and stored at 4°C for analysis. Analysis was performed on the soils for inorganic ammonium and nitrate nitrogen content as outlined in Section II.

C. RESULTS AND DISCUSSION

1. Ammonia Volatilization.

Similar to the results of the first laboratory experiment, the only instances of ammonia volatilization in this experiment were from the broadcast application of urea and ammonium sources to the Almasippi soil (Tables XIV and XV). Under the influence of the alternate freezing and thawing processes however the amounts of ammonia evolved from all nitrogen sources were small, being generally less than one percent of the applied nitrogen.

The rate of volatilization from all sources increased slightly over the first two to four day period, then rapidly dropped and ceased by the end of the 165th hour (Table XIII). In all cases, ammonia evolution probably ceased when the ammonium had diffused into the soil since little nitrification was found to have occurred.

2. Recovery of Applied Nitrogen.

Considerable quantities of both the ammonium and nitrate forms of nitrogen were found in various treatments on both soils (Tables XIV and XV).

TABLE XIII

RATE OF RELEASE OF AMMONIA FROM BROADCAST APPLICATION OF NITROGEN SOURCES ON
ALMASIPPI SOIL SUBJECT TO ALTERNATE FREEZING AND THAWING

Treatment	Amount of NH ₃ -N Evolved (mg)					Total
	0-21 hr.	21-45 hr.	45-93 hr.	93-165 hr.	165-189 hr.	
A) 30 ppm N applied						
CO(NH ₂) ₂	0.00	0.05	0.02	0.00	0.00	0.07
NH ₄ NO ₃	0.00	0.00	0.02	0.00	0.00	0.02
(NH ₄) ₂ SO ₄	0.02	0.01	0.02	0.01	0.00	0.06
B) 60 ppm N applied						
CO(NH ₂) ₂	0.01	0.04	0.10	0.04	0.00	0.19
NH ₄ NO ₃	0.01	0.02	0.06	0.01	0.00	0.10
(NH ₄) ₂ SO ₄	0.01	0.04	0.05	0.01	0.00	0.11

TABLE XIV

RECOVERY OF NITROGEN ON MANITOU SOIL AFTER ONE WEEK INCUBATION WITH ALTERNATE FREEZING AND THAWING

Treatment	Soil NH ₄ -N (ppm)	Soil NO ₃ -N (ppm)	Gaseous ⁽¹⁾ NH ₃ -N (ppm)	Total N (ppm)	Recovery ⁽²⁾		Total Recovery (%)
					Soil Recovery (%)	Gaseous Recovery (%)	
A) Fertilizer Incorporated							
Check	21.9	20.5	0.0	42.0	-	-	-
a) 30 ppm N applied							
KNO ₃	15.5	47.9	0.0	63.4	69.9	0.0	69.9
CO(NH ₂) ₂	47.2	21.9	0.0	69.1	89.0	0.0	89.0
NH ₄ NO ₃	33.6	36.4	0.0	70.0	92.5	0.0	92.5
(NH ₄) ₂ SO ₄	47.0	20.8	0.0	67.8	84.8	0.0	84.8
b) 60 ppm N applied							
KNO ₃	19.3	75.6	0.0	94.9	87.5	0.0	87.5
CO(NH ₂) ₂	66.9	21.8	0.0	88.6	77.1	0.0	77.1
NH ₄ NO ₃	46.4	49.6	0.0	96.0	89.3	0.0	89.3
(NH ₄) ₂ SO ₄	69.6	23.2	0.0	92.8	84.0	0.0	84.0
B) Fertilizer Broadcast							
Check	20.6	21.9	0.0	42.5	-	-	-
a) 30 ppm N applied							
KNO ₃	21.6	46.9	0.0	68.5	86.5	0.0	86.5
CO(NH ₂) ₂	39.0	22.1	0.0	61.1	61.7	0.0	61.7
NH ₄ NO ₃	32.9	36.3	0.0	69.2	88.7	0.0	88.7
(NH ₄) ₂ SO ₄	47.7	22.6	0.0	70.3	92.3	0.0	92.3
b) 60 ppm N applied							
KNO ₃	25.0	73.9	0.0	98.9	94.1	0.0	94.1
CO(NH ₂) ₂	69.0	22.7	0.0	91.7	81.8	0.0	81.8
NH ₄ NO ₃	51.9	48.7	0.0	100.5	96.6	0.0	96.6
(NH ₄) ₂ SO ₄	67.7	23.5	0.0	91.2	81.0	0.0	81.0

(1) Gaseous NH₃ was converted to ppm released from the soil to facilitate further calculations.

(2) All recoveries were based on a percent of the total nitrogen applied.

TABLE XV

RECOVERY OF NITROGEN ON ALMASIPPI SOIL AFTER ONE WEEK INCUBATION WITH ALTERNATE FREEZING AND THAWING

Treatment	Recovery						
	Soil NH ₄ -N (ppm)	Soil NO ₃ -N (ppm)	Gaseous NH ₃ -N (ppm)	Total N (ppm)	Soil Recovery (%)	Gaseous Recovery (%)	Total Recovery (%)
A) Fertilizer Incorporated							
Check	2.9	19.3	0.0	22.2	-	-	-
a) 30 ppm N applied							
KNO ₃	0.3	46.7	0.0	47.0	82.7	0.0	82.7
CO(NH ₂) ₂	25.0	20.6	0.0	45.6	77.8	0.0	77.8
NH ₄ NO ₃	10.5	31.3	0.0	41.8	65.1	0.0	65.1
(NH ₄) ₂ SO ₄	22.7	22.6	0.0	52.3	76.7	0.0	76.7
b) 60 ppm N applied							
KNO ₃	1.0	77.8	0.0	78.8	94.2	0.0	94.2
CO(NH ₂) ₂	49.1	21.6	0.0	70.7	80.7	0.0	80.7
NH ₄ NO ₃	21.8	48.2	0.0	70.0	79.4	0.0	79.4
(NH ₄) ₂ SO ₄	46.4	21.3	0.0	67.7	75.7	0.0	75.7
B) Fertilizer Broadcast							
Check	5.2	19.5	0.0	24.7	-	-	-
a) 30 ppm N applied							
KNO ₃	33.2	46.2	0.0	49.4	82.8	0.0	82.8
CO(NH ₂) ₂	27.7	20.3	0.3	48.3	77.8	0.8	78.6
NH ₄ NO ₃	16.0	33.4	0.1	49.5	82.2	0.3	82.5
(NH ₄) ₂ SO ₄	29.5	23.5	0.2	53.2	94.5	0.7	95.2
b) 60 ppm N applied							
KNO ₃	2.6	75.1	0.0	77.7	88.3	0.0	88.3
CO(NH ₂) ₂	54.6	20.5	0.7	75.8	84.3	1.2	85.5
NH ₄ NO ₃	27.1	47.2	0.4	74.6	82.6	0.6	83.3
(NH ₄) ₂ SO ₄	56.4	18.9	0.4	75.7	84.2	0.7	84.9

(1) Gaseous NH₃ was converted to ppm released from the soil to facilitate further calculations.

(2) All recoveries were based on a percent of the total nitrogen applied.

Ammonium sulphate and potassium nitrate treatments contained a proportionally larger amount of their inorganic nitrogen in the same form in which it was applied (i.e. ammonium and nitrate-nitrogen, respectively). Ammonium nitrate treated soils contained larger amounts of both ammonium and nitrate-nitrogen than the check soils. Urea treated soils contained most of the inorganic nitrogen in the ammonium form. This data indicated that extensive nitrification of the applied ammonium had not occurred. However, larger quantities of nitrate in the check and ammonium sulphate and urea treated soils after incubation than were present in the original soils prior to incubation (Table IX) indicated that some nitrifying activity had occurred. A greater decrease in the ammonium contents of most of the potassium nitrate treated soils along with a larger increase in the nitrate contents of the urea and ammonium sulphate treatments than was found in the check soils also indicated a slight enhancement of nitrification through the application of fertilizers. It was apparent however that the warm period between freezings was not long enough to allow for appreciable nitrification or else the alternate freezing and thawings inactivated the bacteria capable of nitrifying activity before considerable nitrification had occurred. This has been found previously by Campbell *et al.* (21). Although the urea treated soils were not analyzed for urea nitrogen contents, and small amounts may have remained in the unhydrolyzed form, the recovery of urea nitrogen in the ammonium form in similar proportions to the recovery of nitrogen in other treatments indicated that hydrolysis had not been halted by the freezing and thawing processes before hydrolysis had been nearly completed.

Total recovery of the applied nitrogen in all treatments was less than 100 percent. No trends were noticeable in the recoveries of the

various forms applied and recoveries were in a similar range for all carriers on both soils and applied by both methods. Since, as indicated by the lack of appreciable nitrification, bacterial activity was minimal both immobilization and denitrification can apparently be eliminated as possible causes for incomplete recoveries. Clay fixation may be a possible cause of ammonium loss since freezing and thawing may enhance this occurrence (84), but this would only be of importance on the Manitou soil.

D. SUMMARY AND CONCLUSIONS

Results of this experiment indicated that ammonia volatilization was negligible from soils treated with urea and ammonium fertilizers and subjected to alternate freezing and thawing. This process also appears to have considerably restricted microbial activity since nitrification of applied or native soil ammonium was negligible, however urea hydrolysis was not halted. No specific cause was apparent for the incomplete recoveries found of all forms of nitrogen applied to the soils under these experimental conditions.

VI. LABORATORY EXPERIMENT III

A. INTRODUCTION

Leaching has been accredited as a major mechanism creating loss of fertilizer nitrogen especially the nitrate form (2, 3). Under moisture conditions present during the growing season in Manitoba, there is little possibility of this occurrence. However, heavy fall precipitation or water from spring precipitation or melting snow could cause some movement of fall applied fertilizer and contribute to the extremely poor recoveries found of fall applied fertilizers. This experiment was conducted to investigate the movement and recovery of various forms of nitrogen applied to a coarse-textured calcareous and a fine-textured noncalcareous soil under leaching conditions.

B. MATERIALS AND METHODS

1. Soils.

Manitou and Almasippi soils used in the previous laboratory experiment were again selected for this experiment.

2. Apparatus for Study of Nitrogen Movement.

The apparatus designed for the study of nitrogen movement consisted of two-foot cast acrylic plastic cylinders with a $2\frac{1}{2}$ inch inside diameter. These were cut into four six-inch segments and bound together with waterproof tape. This facilitated dismantling of the apparatus for soil sampling. Each cylinder was set on top of a 65 mm plastic funnel which was secured with glue and tape. Soil in the cylinders were held in by a 12.5 cm #30 Whatman filter paper placed in the funnel. Ten such columns were constructed and held by clamps on a filter stand. Plastic bags were placed over the top of the cylinders to eliminate external air contamination and the funnels were set into 250 ml erlenmeyer collecting flasks.

3. Experimental Design and Procedure.

Treatments in the experiment included:

- 1) Check in which no fertilizer nitrogen was applied.
- 2) Urea applied at a rate of 60 ppm nitrogen incorporated in the top four inches of soil.
- 3) Ammonium nitrate applied at a rate of 60 ppm nitrogen incorporated in the top four inches of soil.
- 4) Ammonium sulphate applied at a rate of 60 ppm nitrogen incorporated in the top four inches of soil.
- 5) Potassium nitrate applied at a rate of 60 ppm nitrogen incorporated in the top four inches of soil.

All treatments were run induplicate for each soil type.

The weight of soil required to fill the bottom three segments (18 inches) was placed in each column and distilled water was added to bring the soils to a point where movement of water out of the columns would just start. The amount of soil required for the top four-inch depth was weighed for each column, along with the fertilizer necessary for the different treatments. The soils and fertilizers were mixed and placed as a surface layer on the soils in the appropriate columns. Water was added to bring this surface soil to field capacity and the soils were allowed to equilibriate for one day. At 24-hour intervals for five days, a volume of water comparable to two inches of precipitation was added to the soils and the leachate collected. The leachate was stored at 4°C prior to analysis. After five successive water additions, the soils were allowed to stand for two days. The cylinders were then dismantled and sectioned into the four segments and the weight of soil in each segment was determined. The soil from each section of the cylinders was removed separately,

mixed and two samples were taken. One was placed in an air-tight plastic bag and stored at 4°C for analysis. The second sample was placed in a 50 ml beaker, weighed, oven-dried at 105°C, reweighed and the moisture content determined.

The leachate collected daily from each treatment was measured volumetrically and an aliquot was taken for analysis for inorganic ammonium and nitrate nitrogen by the Magnesium Oxide-Devarda Alloy steam distillation method similar to that outlined in Section IV. Soil samples were analyzed for inorganic ammonium and nitrate nitrogen by the same method described in Section IV. The amount of nitrogen collected in the leachates along with the percent recovery of the fertilizer nitrogen in the leachate and soil columns was calculated. Graphs were drawn to show the distribution of ammonium, nitrate and total inorganic nitrogen in the various treatments on both soils after leaching.

C. RESULTS AND DISCUSSION

1. Nitrogen Distribution.

The distribution of ammonium, nitrate and total inorganic nitrogen in the soil columns after leaching is shown schematically in Figures III to VIII. (Table IIA, Appendix). The distribution of ammonium in the Manitou clay loam soil (Figure III) indicated that very little movement of this form of nitrogen had occurred. A small increase in ammonium with depth in the check and potassium nitrate treatments however indicated a slight downward movement. The larger amounts of ammonium in all depths of the potassium nitrate treatments than in the check was probably due to the priming effect which the added nitrate had on the ammonification process. Little movement of the applied ammonium from the ammonium sulphate and ammonium nitrate treatments was apparent since they contained larger

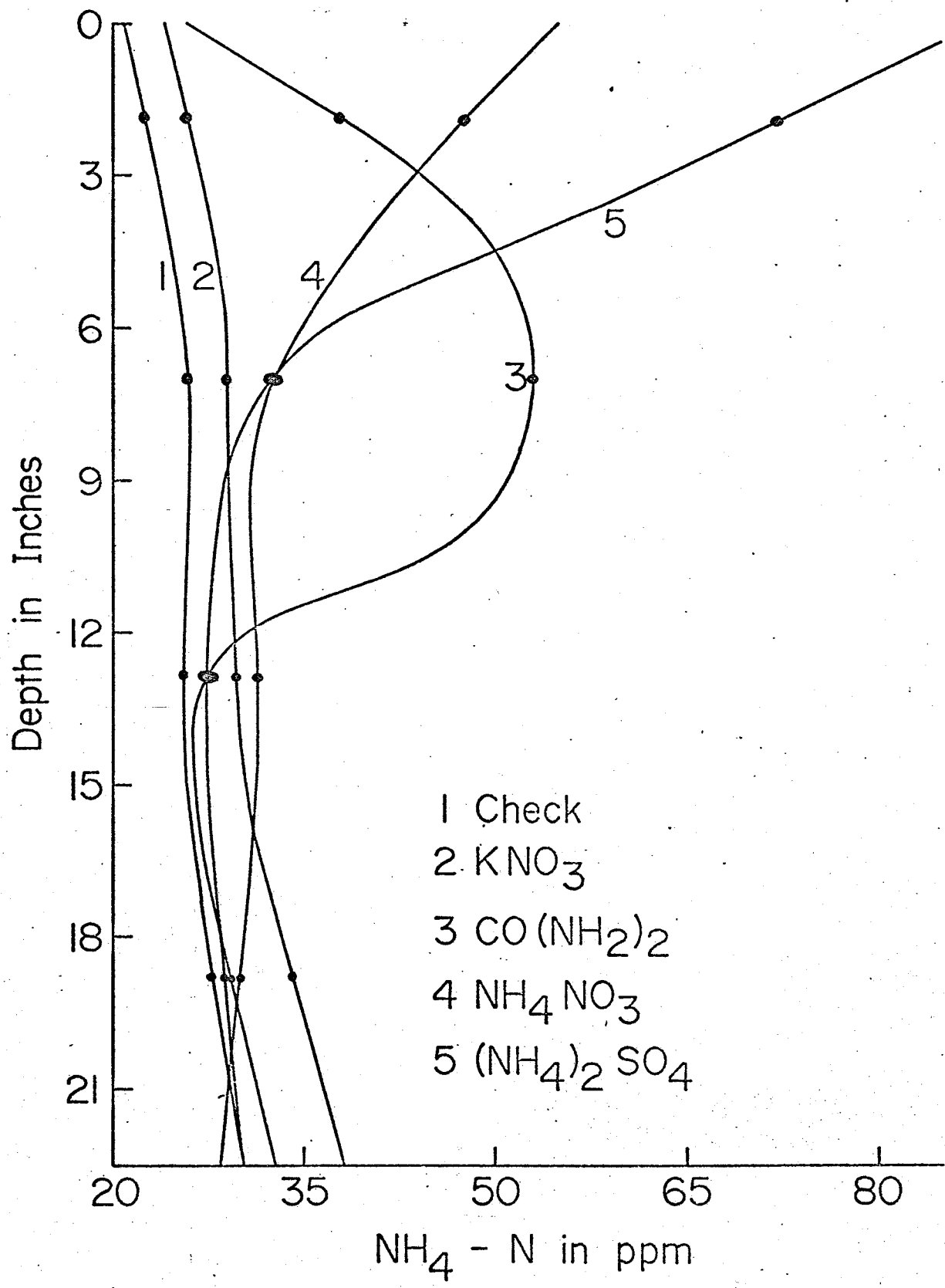


Figure III. Distribution of ammonium nitrogen in columns of Manitou soil after leaching with ten inches of water.

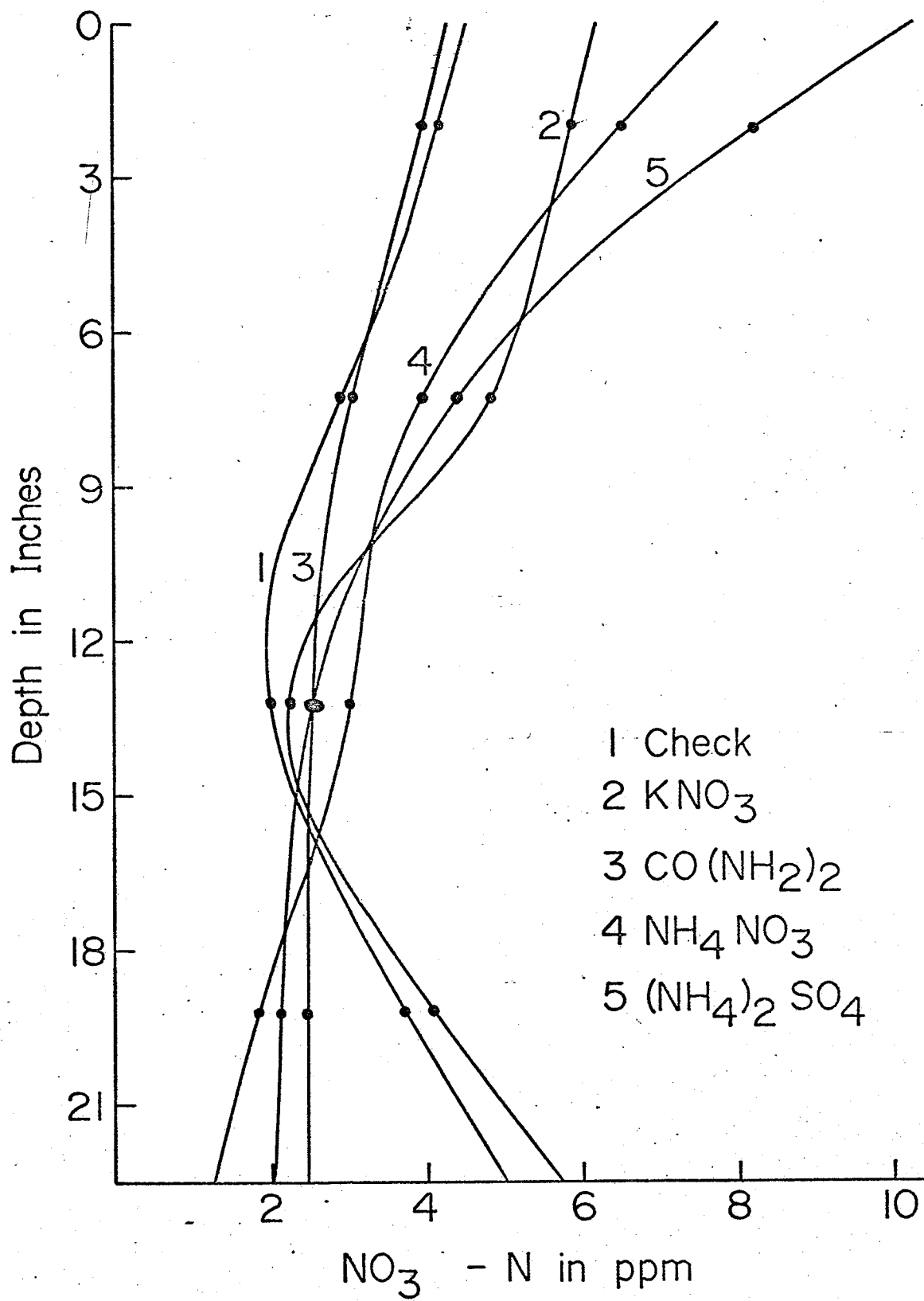


Figure IV. Distribution of nitrate-nitrogen in columns of Manitou soil after leaching with ten inches of water.

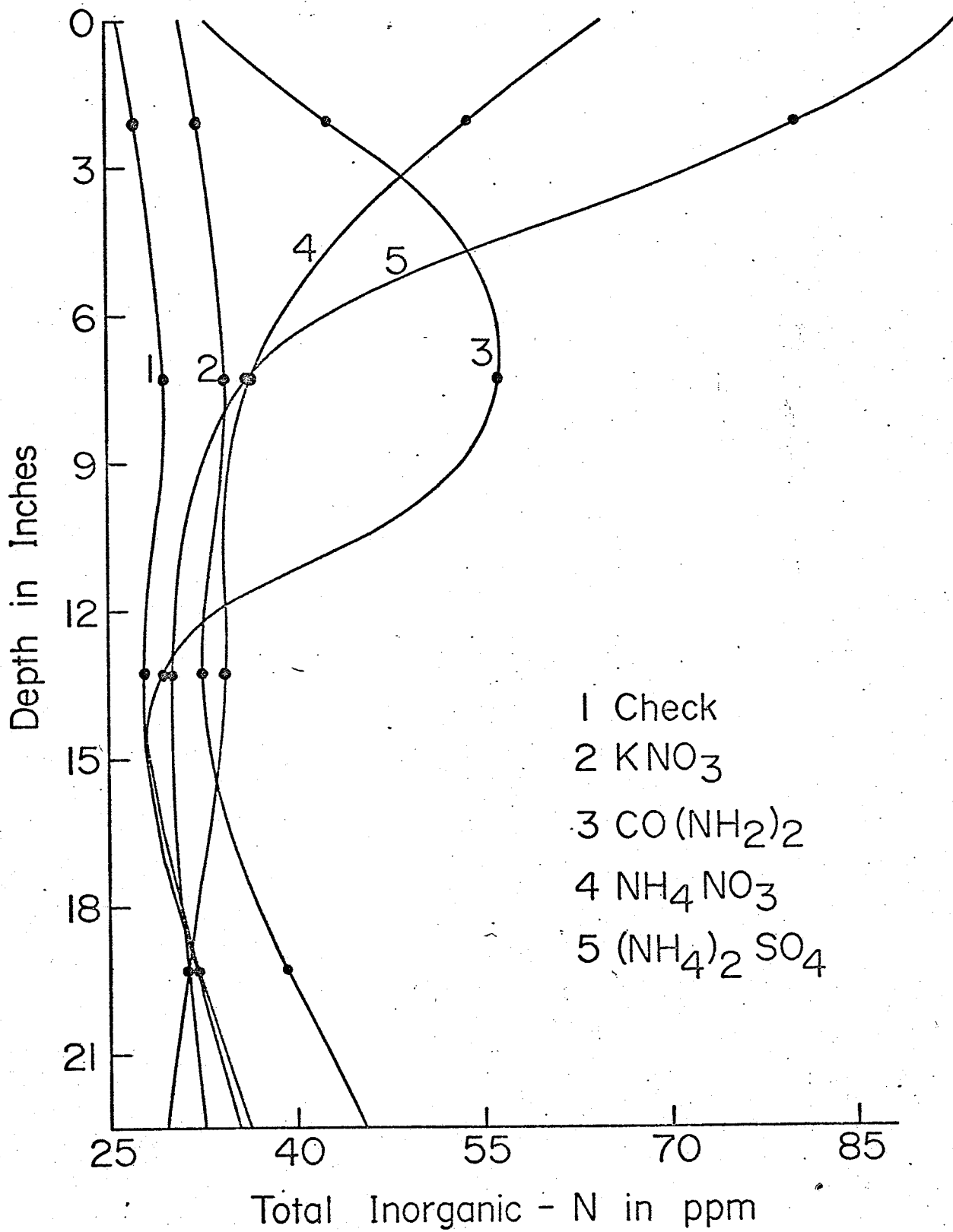


Figure V. Distribution of total inorganic nitrogen in columns of Manitou soil after leaching with ten inches of water.

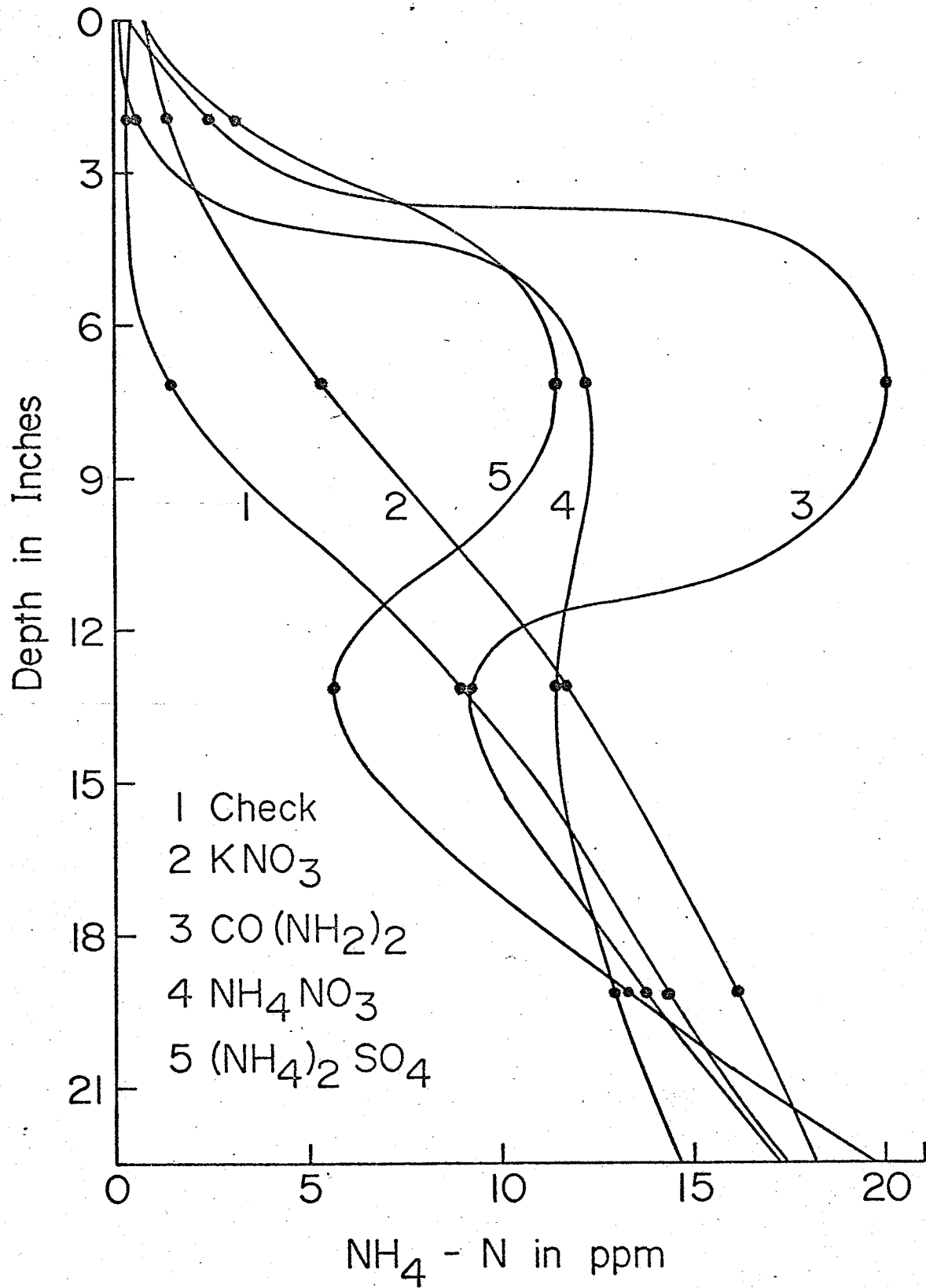


Figure VI. Distribution of ammonium nitrogen in columns of Almasippi soil after leaching with ten inches of water.

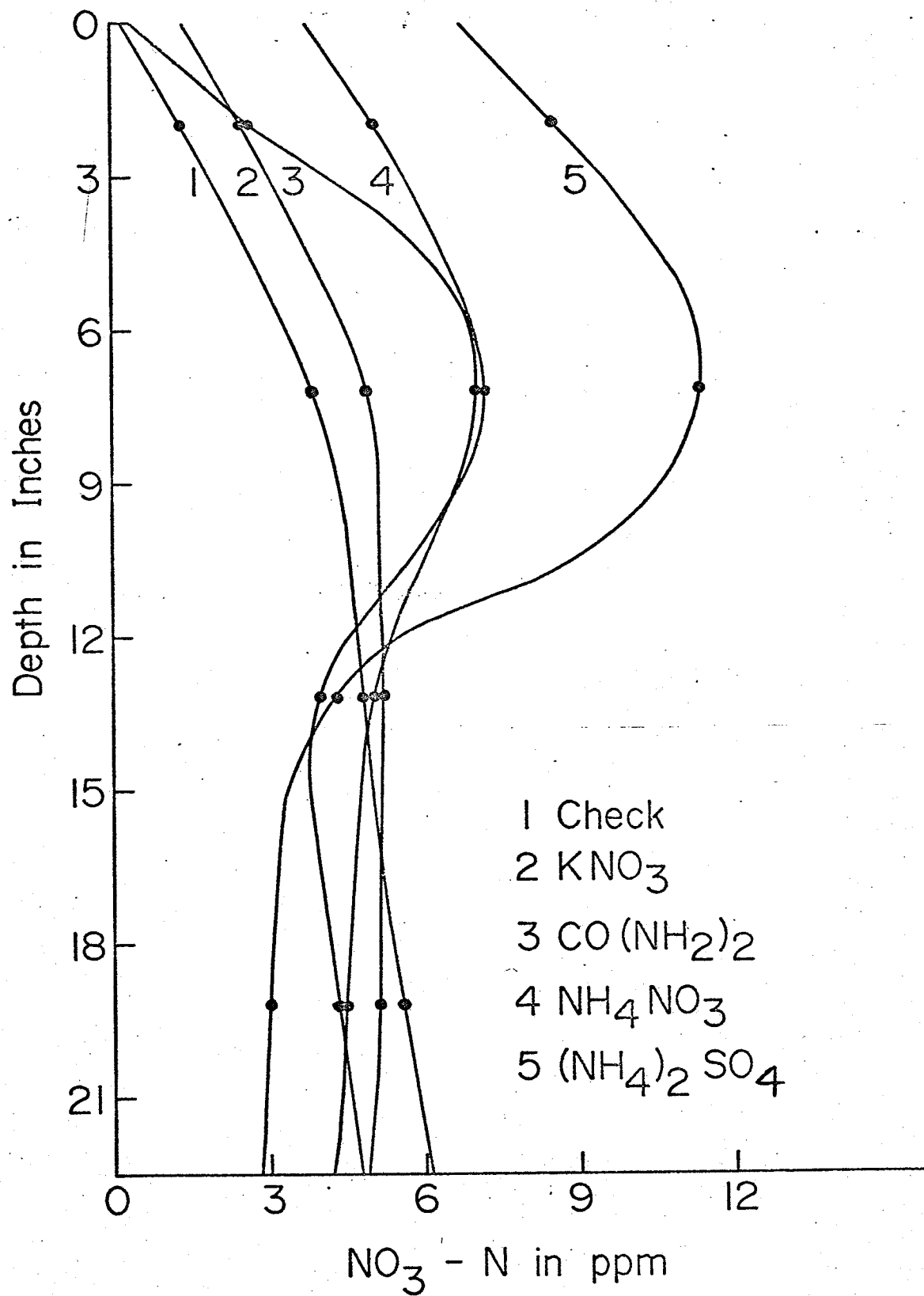


Figure VII. Distribution of nitrate-nitrogen in columns of Almasippi soil after leaching with ten inches of water.

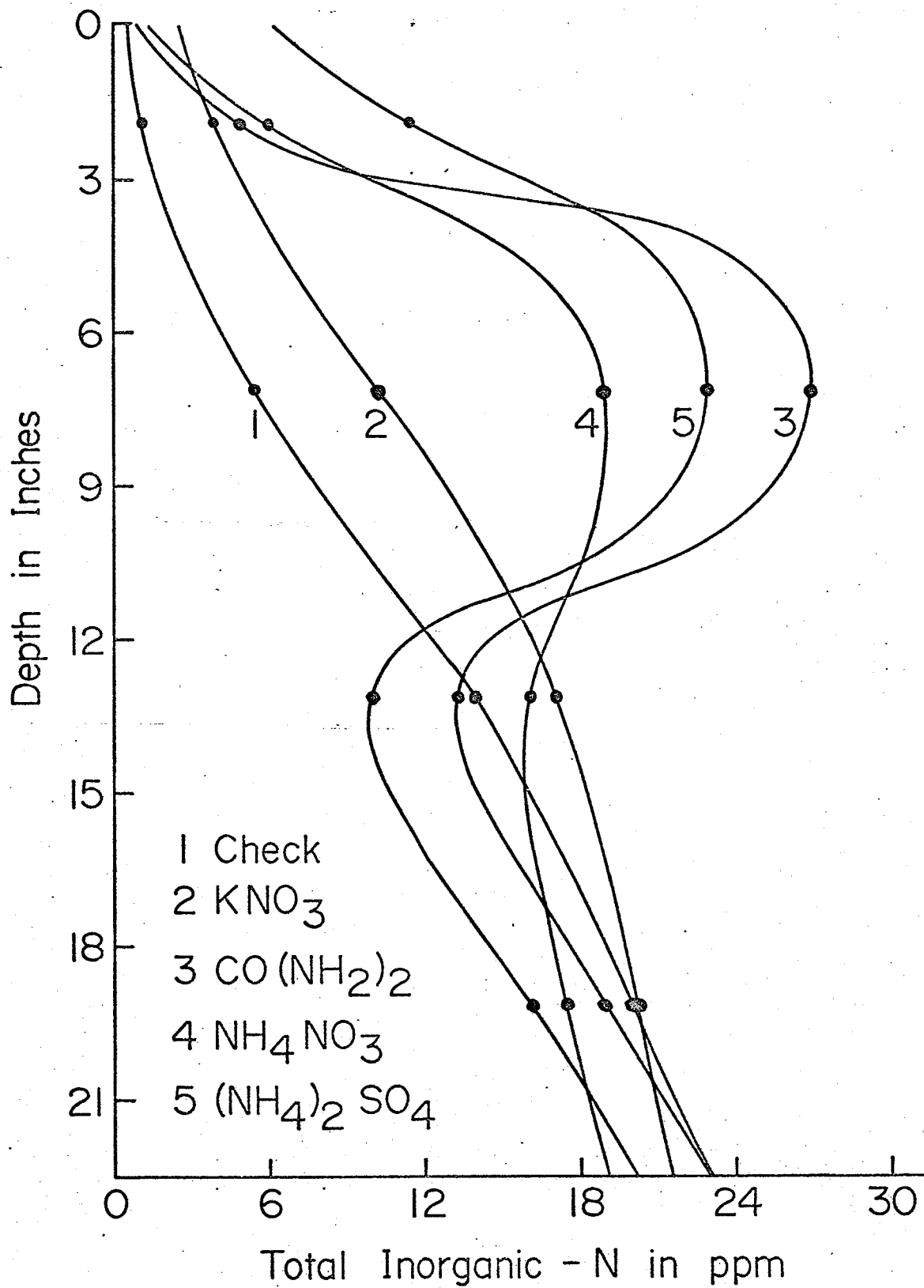


Figure VIII. Distribution of total inorganic nitrogen in columns of Almasippi soil after leaching with ten inches of water.

concentrations of ammonium in the top four inches of soil while in the lower levels of the columns, ammonium concentrations were similar to those in the check and potassium nitrate treatments. Urea treatments showed a large concentration of ammonium in the 4 to 10 inch depth which may have indicated an initial downward movement of urea to this level in the unhydrolyzed form, then relatively little movement of ammonium after hydrolysis since movement of ammonium from ammonium fertilizers was negligible.

Nitrate distribution (Figure IV) in the check and potassium nitrate treatments on the Manitou soil showed a decrease in nitrate concentration with depth in the first 12 inches of soil and subsequent increasing concentration with depth in the next 10 inches. The nitrate contained in the lower depth probably represents that moved down from the upper soil zones. Total displacement of the nitrate initially present or added to the top soil level would not be expected since the total amount of water added was insufficient to cause a complete displacement of the water initially present prior to leaching. The nitrate present in the upper soil zones was probably due to nitrification after leaching had ceased. The remaining urea, ammonium nitrate and ammonium sulphate treatments showed a constant decline in nitrate contents with depth. The presence of most of the nitrate-nitrogen in these treatments located in the same zone as the large concentrations of ammonium again indicated that nitrification of the ammonium had occurred after water additions had ceased.

The distribution of total inorganic nitrogen in all treatments on the Manitou soil (Figure V) was similar to the distribution pattern of the ammonium since nitrate generally contributed very little to the total inorganic nitrogen and its distribution followed a similar curve to the ammonium ion distribution.

Considerable movement of ammonium nitrogen was apparent in the Almasippi loamy fine sand soils as shown in Figure VI. The rapid increase in ammonium concentration with depth in the check and potassium nitrate treatments indicated that native soil ammonium initially present in the top soil levels of the columns had been moved down to lower levels. The larger amounts of ammonium present in the potassium nitrate treatments were again attributed to enhanced microbial ammonification due to the addition of the fertilizer. Added fertilizer ammonium nitrogen from the ammonium sulphate, ammonium nitrate and urea treatments was also displaced from the zone in which it had been added and most was located in the 4 to 10 inch depth. Below this zone ammonium contents in these treatments were similar to the treatments to which no ammonium had been added. Ammonium movement was probably facilitated in this soil by the low cation exchange capacity and possible calcium saturation of the relatively few exchange sites available.

Nitrate distribution in the check and potassium nitrate treatments on the Almasippi soil showed a slight increase with depth (Figure VII). The remainder of the treatments contained most of their nitrate in the same zone where ammonium had accumulated which again indicated that nitrification had proceeded following the final water addition.

Similar to the findings on the Manitou soil, the pattern for the distribution of the total inorganic nitrogen in the Almasippi soil columns closely followed that of the ammonium nitrogen in all treatments (Figure VIII). Although nitrate generally contributed a larger proportion of nitrogen to the total inorganic nitrogen in the treatments on the Almasippi soil than on the Manitou soil, the distribution curves for nitrate were similar to those for ammonium.

2. Leached Nitrogen.

Table XVI shows the amount of inorganic nitrogen leached from the various treatments on both soils. All treatments on the Manitou soil showed a large quantity of inorganic nitrogen leached from the soil columns upon the addition of the first two inches of water. This probably represented native soil nitrate which had been leached downward upon adding the water to bring the columns to field capacity and which subsequently moved rapidly out with the first volumes of water which were collected. Considerably smaller quantities of nitrogen were collected with each subsequent addition of water. The total amount of nitrogen leached was greatest from the potassium nitrate treatments. Urea treatments were second in total amounts of nitrogen moved out of the soil but in all but the first day leachates collected from the ammonium nitrate treatments contained more nitrogen than those from the urea treatments. Smaller quantities were collected from the ammonium sulphate and check treatments. On these soil treatments, the major form of nitrogen which was leached from the soil was probably nitrate since the distribution curves indicated that this was the only form appreciably displaced in the soils. Since the total amount of water added was insufficient to completely displace all of the water initially present, most of the leached nitrogen in all cases was probably native soil nitrogen. However small amounts of fertilizer nitrogen may have moved out in the latter two water additions.

The Almasippi soil treatments showed no initial flush of leached nitrogen that was encountered on the Manitou soil treatments. A gradual increase in the amounts of nitrogen moved out of the soil upon subsequent additions of water was generally found. Again most of the nitrogen recovered in the leachate was probably native soil nitrogen with fertilizer

TABLE XVI

AMOUNT OF NITROGEN COLLECTED IN LEACEATE AFTER ADDITIONS OF WATER TO COLUMNS OF SOIL TREATED WITH NITROGEN FERTILIZERS

Treatment ⁽¹⁾	Amount of Nitrogen Collected (mg)					Total
	First 2 in. of Water	Second 2 in. of Water	Third 2 in. of Water	Fourth 2 in. of Water	Fifth 2 in. of Water	
A. Manitou Soil						
Check	16.33	0.31	0.07	0.13	0.17	17.01
KNO ₃	16.26	0.18	0.11	2.14	1.85	20.54
CO(NH ₂) ₂	17.48	0.12	0.09	0.12	0.19	18.00
NH ₄ NO ₃	16.72	0.32	0.17	0.42	0.28	17.91
(NH ₄) ₂ SO ₄	16.12	0.14	0.04	0.12	0.26	16.68
B. Almasippi Soil						
Check	0.70	0.90	1.03	1.19	1.19	5.01
KNO ₃	0.82	1.18	1.27	1.90	1.39	6.56
CO(NH ₂) ₂	0.88	1.08	1.19	1.20	1.20	5.55
NH ₄ NO ₃	0.74	1.11	1.22	1.75	1.38	6.20
(NH ₄) ₂ SO ₄	0.75	1.05	1.07	1.15	1.19	5.21

(1) All treatments applied at a rate of 60 ppm nitrogen in the top 4 inches of soil.

nitrogen moving out only in the latter water additions as the initial water present was being displaced. The potassium nitrate treatments had the largest amount of nitrogen leached from the columns followed in order by the ammonium nitrate, urea, ammonium sulphate and check treatments. Although most nitrogen leached from the soils would be expected to have been in the nitrate form, some might also have been ammonium since the distribution curves for this ion on this soil showed downward displacement of ammonium nitrogen.

3. Recovery of Applied Nitrogen.

Most of the nitrogen which remained in the columns of both soils was found to be in the ammonium form (Table XVII). The presence of larger quantities of ammonium in the potassium nitrate treatments than in the check soils indicated that fertilizer additions had probably resulted in an enhanced bacterial release of ammonium from the organic fraction (ammonification). Since all soils contained considerable quantities of ammonium, and treatments in which ammonium was applied contained correspondingly larger amounts, nitrification appears to have been minimal. Restricted oxygen concentration in the soils as a result of the high water contents probably limited the activity of the nitrifying population since they are aerobic microorganisms. The larger proportion of nitrate to ammonium in the Almasippi soil compared to the Manitou soil may have reflected greater nitrifying activity brought about by freer diffusion of oxygen into this coarse-textured soil between water additions, and following the final water addition, than into the heavier clay loam Manitou soil.

Percent recoveries of nitrogen in the various treatments were based on the difference in nitrogen contents between the treatment and check samples. This method of calculation may give an overestimation of the

TABLE XVII

RECOVERY OF NITROGEN APPLIED TO COLUMNS OF SOIL AND LEACHED WITH TEN INCHES OF WATER

Treatment	Recovery							
	Soil NH ₄ -N (mg)	Soil NO ₃ -N (mg)	Total Soil N (mg)	Leachate N (mg)	Total N (mg)	Soil ⁽¹⁾ Recovery (%)	Leachate Recovery (%)	Total Recovery (%)
A. Manitou Soil								
Check	49.10	5.86	54.96	17.01	71.97	-	-	-
KNO ₃	56.99	77.59	64.58	20.54	85.12	50.1	18.5	68.6
CO(NH ₂) ₂	68.34	5.45	73.79	18.00	91.79	98.0	5.1	103.1
NH ₄ NO ₃	63.65	6.60	70.25	17.91	88.16	79.5	4.7	84.2
(NH ₄) ₂ SO ₄	70.38	7.41	77.79	16.68	94.47	118.9	- 2.0	116.9
B. Almasippi Soil								
Check	13.69	8.85	22.54	5.01	27.55	-	-	-
KNO ₃	20.81	9.17	29.98	6.56	36.54	33.5	7.1	40.6
CO(NH ₂) ₂	27.41	10.85	38.26	5.55	43.81	70.8	2.4	73.2
NH ₄ NO ₃	23.07	11.52	34.59	6.20	40.79	54.3	5.4	59.7
(NH ₄) ₂ SO ₄	19.78	14.05	33.83	5.21	39.04	50.8	1.0	51.8

(1) All recoveries were based on the percent of the total nitrogen applied.

recoveries since it may include nitrogen released by enhanced nitrification resulting from fertilizer addition. Results indicated this may have occurred. However, since ^{15}N tagged nitrogen sources had not been used, it was not possible to determine the actual recovery of the applied nitrogen. This method did however show relative amounts of nitrogen recovered. Recovery of nitrogen from all sources was greater on the Manitou soil than on the Almasippi soil. Within the soil columns, recoveries of nitrogen were generally poorest from those treatments in which nitrate had been applied which indicated a more extensive loss of this form of nitrogen. Ammonium nitrate treatments which contained only half of the applied nitrogen in the nitrate form showed greater recoveries than the potassium nitrate treatments in which all of the applied nitrogen was nitrate. Greater recoveries of applied nitrogen were found from the ammonium sulphate and urea treatments on the Manitou soil. However, nitrogen recovery from ammonium sulphate on the Almasippi soil however was very low.

Recovery of applied nitrogen in the leacheate was low and could not account for the losses of applied nitrogen in the treated soils. Evidence apparent in the data tended to indicate the losses could be due to bacterial denitrification. The restricted oxygen content of the soils caused by the repeated additions of water would have produced conditions favorable for this loss. Denitrification may explain why the nitrate sources, especially potassium nitrate showed severe loss of the applied nitrogen on both soils. Little nitrification was found to have occurred on the Manitou soil, hence the applied ammonium sources were not converted to nitrate and subject to denitrification resulting in a complete recovery of nitrogen from the ammonium sulphate and urea sources. Slight nitrification of the ammonium sources on the Almasippi soil, noted in previous

data would have resulted in a certain degree of loss by denitrification in these treatments. Greater denitrification and the subsequent greater losses encountered in the Almasippi soil than on Manitou soil would have been favored by the alkaline pH of the former soil which is more conducive to the denitrifying bacteria.

No explanation for the excessively poor recovery of the nitrogen in the ammonium sulphate treatments on the Almasippi soil could be found. Volatile losses of ammonia would have been expected to be negligible since the fertilizer was incorporated into the topsoil and results of the first laboratory experiment found little ammonia volatilization under these conditions.

D. SUMMARY AND CONCLUSIONS

Results of this experiment minimize leaching as a cause for appreciable loss of fertilizer nitrogen. Under the influence of ten inches of water, little movement of ammonium was found on the Manitou soil, but a certain amount of displacement of this form of nitrogen appeared on the Almasippi soil. Movement of nitrate in both soils was indicated. Such extensive water movement through Manitoba soils is not normal and although small amounts of nitrogen did move through the columns, only a small percent of it was fertilizer nitrogen.

Data indicated that microbial denitrification may have been a more important source of loss of fertilizer nitrogen under the experimental conditions.

VII. SUMMARY AND CONCLUSIONS

A field study was conducted on a calcareous and a noncalcareous soil to determine the effectiveness of ammonium, nitrate and urea nitrogen applied in the fall and spring. Crop yields and total nitrogen uptake from the various nitrogen carriers was determined. Labelling of the fertilizer with ^{15}N permitted an assessment of the effect of specific nitrogen species from ammonium nitrate and urea. Results showed that spring applied nitrogen was more efficiently recovered by barley than fall applied nitrogen and yields were greater. Yields and total nitrogen uptake by barley on the Manitou clay loam soil were similar for urea and ammonium nitrate. However some differences were detected between ammonium, nitrate and urea nitrogen with respect to their uptake and recovery by barley. Nitrate-nitrogen was found to be the most efficiently utilized form applied in the spring and ammonium nitrogen was the least with urea nitrogen being intermediate. Ammonium and urea nitrogen applied in the fall showed similar recovery being significantly greater than nitrate-nitrogen. Although yield results from the plots on the calcareous Almasippi loamy fine sand were poor and variable due to crop damage, some definite patterns were noted in respect to the individual nitrogen species. Uptake of nitrogen applied in the spring appeared greatest for the nitrate-nitrogen with recovery of urea nitrogen being significantly less but slightly greater than that of ammonium nitrogen. All three forms of nitrogen applied in the fall were recovered in equally low amounts.

Laboratory experiments were subsequently conducted to determine possible nitrogen loss processes. In one experiment, the extent of volatilization of ammonia and the recovery of nitrogen in the soil from the broadcast and incorporation application of various nitrogen sources

was measured. Manitou and Almasippi soils were used and incubation was conducted at a constant warm temperature (22°C). Results of the experiment indicated that volatile losses of ammonia may be the cause of fertilizer inefficiency from the broadcast application of urea or ammonium sources to a calcareous soil. Incomplete recovery of the applied nitrogen may have been due to clay fixation, denitrification and bacterial immobilization, but the latter cause appeared most probable.

A second laboratory experiment was conducted to determine the effect of alternate freezing and thawing of fertilized soils on nitrogen losses. This is a natural condition soils are subjected to in fall and spring. The loss of applied fertilizer as gaseous ammonia was found to be negligible under these conditions. Microbial activity appeared to have been minimal in the soils so the losses of applied nitrogen encountered could not be attributable to immobilization or denitrification. No other mechanism was apparent for the incomplete recoveries.

A third laboratory experiment was conducted to determine if leaching was a significant loss pathway for fall applied fertilizer. Since little applied nitrogen was recovered in the leachates collected from the treated soils after leaching with ten inches of water, it was concluded that denitrification of nitrate-nitrogen rather than leaching was the probable cause of the poor recoveries encountered. The lower recoveries of fertilizers containing nitrate-nitrogen than ammonium sources and urea and the greater recoveries on the Manitou than on the Almasippi soils appeared to be explainable by the denitrification process.

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IX. APPENDIX

TABLE IA

^{15}N CONTENT OF BARLEY FROM SEVERAL SAMPLES OF PLANT MATERIAL FROM CHECK TREATMENT PLOTS ON MANITOU AND ALMASIPPI SOILS

<u>Manitou</u>		<u>Almasippi</u>	
Plant Material Sample	Atom % ^{15}N	Plant Material Sample	Atom % ^{15}N
7 weeks after seeding	0.373	5 weeks after seeding	0.380
	0.380		0.375
	0.385		0.369
	(1)		(1)
12 weeks after sampling	0.375	10 weeks after seeding	0.369
	0.372		0.386
	0.368		0.382
	0.399		(1)
Harvest grain	0.379	Harvest grain	0.381
	0.376		0.375
	0.378		0.377
	0.386		0.379
Harvest straw	0.379	Harvest straw	0.399
	0.362		0.383
	0.371		0.366
	0.379		0.367
Average Atom % ^{15}N			0.378
Standard Deviation			0.009

(1) Samples lost prior to analysis.

TABLE IIA

DISTRIBUTION OF NITROGEN IN COLUMNS OF SOIL AFTER LEACHING
WITH TEN INCHES OF WATER

Treatment ⁽¹⁾	Depth (inches)	Manitou Soil			Almasippi Soil		
		NH ₃ -N (ppm)	NO ₃ -N (ppm)	Total N (ppm)	NH ₄ -N (ppm)	NO ₃ -N (ppm)	Total N (ppm)
Check	0-4	22.8	4.2	27.0	0.6	1.2	1.8
	4-10	26.6	3.1	29.7	1.2	4.0	5.2
	10-16	25.7	2.0	27.7	9.1	4.9	14.0
	16-22	28.4	3.7	32.1	14.4	5.5	19.9
KNO ₃	0-4	26.5	5.8	32.3	1.4	2.5	3.9
	4-10	29.5	4.9	34.4	5.5	4.8	10.3
	10-16	30.1	2.2	32.3	11.7	5.2	16.9
	16-22	34.9	4.0	38.9	16.0	4.9	20.2
CO(NH ₂) ₂	0-4	38.4	4.0	42.4	2.2	2.5	4.7
	4-10	53.7	3.2	56.9	20.2	7.2	27.4
	10-16	27.2	2.5	29.7	9.4	4.0	13.4
	16-22	29.7	2.5	32.2	13.7	5.1	18.8
NH ₄ NO ₃	0-4	47.8	6.5	54.3	0.6	4.9	5.5
	4-10	32.4	4.0	36.4	12.2	6.9	19.1
	10-16	31.5	3.1	34.6	11.5	4.9	16.4
	16-22	30.0	1.8	31.8	12.9	4.5	17.4
(NH ₄) ₂ SO ₄	0-4	73.5	8.3	81.8	2.8	8.6	11.4
	4-10	32.3	4.5	36.8	11.8	11.4	23.2
	10-16	27.7	2.6	30.3	5.7	4.2	9.9
	16-22	29.2	2.2	31.4	12.8	3.1	15.9

(1) All treatments applied at a rate of 60 ppm nitrogen in the top 4 inches of soil.