EXCHANGEABLE AMMONIUM AND ITS AVAILABILITY TO PLANTS

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ABSTRACT

The aim of this investigation was to evaluate exchangeable ammonium as a source of nitrogen in the soil and to study its interconversion to other forms of nitrogen. Three sources of added nitrogen were used, namely ammonium nitrate, ammonium sulphate and urea.

Preliminary investigations showed that, to obtain an accurate estimate of the exchangeable ammonium present in the soil in its natural state, determinations should be made on the fresh soil immediately after sampling. Least change in ammonium occured with storage at 2°C.

Under good growing conditions the ammonium ion is rapidly converted to nitrate; the conversion rate is slower in acid soils than in alkaline soils. If soil samples are taken in the spring before all the ammonium has been nitrified, some allowance for this exchangeable ammonium should be made when making estimations of available nitrogen.

In field trials urea was found to cause reduced germination and yield, particularly when drilled in with the seed. This was thought to be due to ammonia or nitrite toxicity. That nitrite does accumulate in alkaline soils was shown in an incubation experiment. By contrast, in a greenhouse experiment, higher yields of plant material were obtained from urea than from ammonium sulphate. With the alkaline soils this was attributed to volatile loss of nitrogen from the ammonium sulphate treated soils. No loss occured from the urea. In the incubation experiment loss of nitrogen occured with both carriers. The overall evidence suggests that the mode of application of the fertilizer and the general soil conditions are highly important with respect to loss of nitrogen.

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CHAPTER I

Introduction

Nitrogen is essential to plant growth and is frequently the factor controlling crop yields. In recent years many arable soils in Manitoba have been found to be deficient in this element and increasing use is now being made of nitrogeneous fertilizers. To facilitate economic use of these fertilizers, investigations were made by Huang (44) into the various methods of predicting soil nitrogen requirements. He established that only the determination of accumulated nitrate-nitrogen in the profile at seeding time appeared to have any real value for predicting nitrogen needs for cereals for Manitoba soils.

This method assumes that the form of nitrogen being used by the plants is nitrate-nitrogen and that other forms of inorganic nitrogen are of negligible importance or are directly related to nitrate-nitrogen in some manner. However, plants are known to be capable of utilizing other forms of inorganic-nitrogen. Since recent investigations (72) have shown that fairly high levels of exchangeable ammonium-nitrogen exist in some Manitoba soils, this investigation was initiated to evaluate the importance of this form of inorganic-nitrogen to crop growth.

As the inorganic forms of nitrogen in soil are subject to rapid changes through ammonification, nitrification and other microbial processes, preliminary investigations were made to establish the best method of sample storage. This was to ensure that the values obtained

were true estimations of the exchangeable ammonium in the soil and did not result from changes which had taken place after the soil had been sampled.

The main problem was approached by following the changes in inorganic -nitrogen in the soil with and without an actively growing crop. From this it was hoped to establish the importance of exchangeable ammonium to plant growth and development. Crop response to different ammonium sources was also evaluated.

CHAPTER II

Review of Literature

A. Reactions of Ammonia in Soils

Under natural conditions the main source of ammonium in the soil system is the nitrogen containing organic compounds. Microorganisms living on the organic matter produce ammonia when they set free more nitrogen than they can assimilate into their own protoplasm (79).

Small quantities of ammonia are also carried into the soil by rainwater. The amount of nitrogen brought to the soil varies with rainfall, general climatic conditions and the habits and occupation of the population. Eriksson (33), in a review of this topic, showed values to vary from two to twenty pounds per acre per annum across the world.

In cultivated areas large quantities of inorganic nitrogen are added to the soil in the form of fertilizers. These are principally of two types, ammonium salts, such as ammonium sulphate and ammonium nitrate, and nitrates, such as potassium nitrate and calcium nitrate. However, increasing use is now being made of liquid ammonia and urea.

Free ammonia can interact with the soil components in a variety of ways. It may be dissolved in the soil moisture, sorbed on the soil particles by chemical or physical mechanisms or a combination of both, or fixed by organic matter and certain clay minerals.

Smith (80) gives the following equations as being partially representative of the ammonia equilibria in the soil.

$$\operatorname{NH}_{\underline{\mu}}OH + H - \operatorname{soil} \longleftrightarrow \operatorname{NH}_{\underline{\mu}} - \operatorname{soil} + HOH$$

The proportion of the total ammonia ionized depends on the dissociation constant for the molecule and the pH of the soil system.

Physical sorption of ammonia is thought to occur by two main mechanisms, hydrogen bonding and ammonate formation. For hydrogen bonding the usually proposed bond is between the oxide or hydroxyl group of the clay lattice surface and the hydrogen of the ammonia (Coffee and Bartholomew (25), Smith (80)).

$$MH_3 + OX \leftrightarrow MH_3 - - OX$$

Young and McNeal (98) also proposed bonding between the hydrogen of the clay lattice and the nitrogen of the ammonia.

$$\operatorname{NH}_{3}$$
 + HOX \longleftrightarrow H₃N---HOX

Ammonia can react with various salts to form ammonates in a manner similar to hydrate formation. That this mechanism of ammonia sorption may be quite extensive has been suggested by Brown and Bartholomew ((20),(21)) and Young and McNeal (98). Physical sorption of ammonia by clays and clay minerals has been demonstrated by Mortland (67) and Jenny et al.(47).

Chemisorption is the term used when the ammonia is held by the

soil material with relative stability. Exchangeable ammonium falls into this category.

Two mechanisms for the retention of ammonia on the exchange sites of the clay minerals have been proposed by Brown and Bartholomew (21). The first is the reaction of ammonia with exposed lattice hydroxyls and the second involves the water of hydration of the exchangeable cations and the tendency of cation hydrolysis products to be stable in the clay system. This reaction can be represented by the following equation.

 $Al(H_2O)_6^{3+} + 3NH_3 \longrightarrow 3NH_4^+ + Al(OH)_3 + 3H_2O$

Fixation is defined as the condition wherein the ion can not be exchanged with other cations under ordinary conditions of cation exchange. (Mortland <u>et al.</u>(68)). Ammonia fixation by clay minerals is thought to occur by a mechanism similar to potassium fixation. (Bremner (14)). The occurence of fixed ammonia is now well established (Rodrigue (78), Stevenson (86), Bremner (14)).

Interaction of ammonia with organic matter to form stable complexes has been reported by Broadbent <u>et al.(16)</u> and by Sohn and Peech (82). Mattson and Koutler Anderson (60) concluded that lignin is the chief constituent of organic matter responsible for ammonia fixation, an idea that is supported by Bennet's (7) methylation studies.

Ammonia in the soil solution and retained by physical sorption is in dynamic equilibrium with the gaseous phase. (Coffee and Bartholomew (25)). In this form it is subject to movement and it is mainly in this way, and to a limited extent by solution diffusion, that ammonia moves

from the sites of addition <u>or</u> production and either finds stable sorption sites or enters the atmosphere above the soil.

From this it is apparent that no sharp dividing line can be drawn between the various forms in which ammonia is retained in the soil. Ammonia sorption, retention and fixation are transient conditions in a system that is constantly changing. Exchangeable ammonium is itself an arbitrary term used to differentiate between ammonium readily extractable by a salt solution and "fixed" ammonium. The most widely used definition of exchangeable ammonium is "that portion of the ammonium-nitrogen in the soil that is extractable with a lN potassium chloride solution (Adams and Stevenson (1)).

B. <u>Methods</u> of <u>Sample</u> Storage

The level of exchangeable ammonium in the soil system is subject to rapid change due to physical, chemical and microbiological activity. As a result difficulty is encountered in estimating the amount of exchangeable ammonium present in the soil at any one time. Generally the most accurate values are considered to be obtained when determination is made on the fresh soil immediately after sampling (Bremner (13)). Since this is rarely possible, a variety of methods of pre-treatment and storage have been used.

Microbial inhibitors such as toluene and chloroform have been tried by several workers. Piper (77) suggested toluene but had some doubts concerning its efficiency. When using chloroform as a fungicide, Lewis (54) found that it interfered quite seriously with the determination of inorganic-nitrogen. This type of method is often ineffective and,

as pointed out by Gasser (38), changes the balance of the soil microorganisms.

Inhibition of microbial activity by low temperatures is another frequently recommended method of storage. Anderson and Purvis (4), using acid soils, noted that the rate of nitrification was very slow at $37^{\circ}F$. Gasser (38), however, found that the mean ammonium and nitrate nitrogen content of soils increased on storage at $2^{\circ}C$. With continuous storage at $-10^{\circ}C$ there was no change in mineral nitrogen, although two days at each of $-10^{\circ}C$ and $2^{\circ}C$ led to a marked increase in inorganicnitrogen levels. Increase in extractable ammonium nitrogen due to low temperature storage was also observed by Allen and Grimshaw (2). They attributed this change to increased microbial activity while the sample was still only partly thawed. Low temperature storage would appear to be a method which produced little change in exchangeable ammonium (Soulides and Allison (83), Paul and Tu (73)).

The most convenient and most widely used method of sample storage is in an air or oven dried condition. Where immediate analysis can not be made on the fresh soil, Piper (77) recommends rapid oven drying at 55°C. However, drying of soil samples has been shown by many workers (Cooke and Cunningham (31), Birch (9), Gasser (39), Walsh and Murdock (94), Soulides and Allison (83)) to lead to significant changes in exchangeable ammonium nitrogen. In particular Cunningham (27) noted that air-dried storage produced a marked increase in mineral nitrogen and ammonium nitrogen.

Several reports of changes in exchangeable ammonium levels in soils stored in a dried condition have been made. Timmons et al.(90)

noted contamination of samples stored in paper cartons in a laboratory in which ammonia was used regularly. Olsen $\underline{et al}.(71)$ compared paper bag with jar storage of air dried samples. They attributed greater accumulation with paper bag storage than with bottle storage to ammonium absorption from the atmosphere and to greater ammonification occuring in the more exposed, well aerated soil samples. This idea is supported by the work of Gasser (39) who found that soils stored in sealed polythene bags changed less than those stored in paper bags.

Bremner (13), quoting from the unpublished works of Edwards and Bremner, confirms that air-dried soils can sorb significant amounts of ammonia from the atmosphere and that results of soil nitrogen investigations using air-dried soils may be seriously affected if the soils used are exposed to the atmosphere for significant periods of time during their drying, grinding and storage.

At present information on the effects of drying on inorganic forms of nitrogen in soils is limited. Bremner points out that observed changes may be the net result of losses due to volatilization and gains due to sorption of atmospheric ammonia during drying. Bremner and Keeney (13) have recently shown that loss of inorganic nitrogen was particularly marked with samples containing both ammonium and nitrite, presumably because these react during air-drying to liberate nitrogen gas (NH_{4} + $NO_{2} \longrightarrow N_{2}$ + $H_{2}O$). Their findings show that drying of soil can lead to chemical as well as biological transformations of inorganic forms of nitrogen.

C, Exchangeable Ammonium and Its Availability to Plants

In the soil system mineral nitrogen is present in two main forms, as the nitrate ion and as the ammonium ion. The nitrate ion is normally dissolved in the soil solution and makes up the larger portion of the inorganic nitrogen; most of the ammonium ions are absorbed on the exchange sites of the soil particles.

Russell (79) gives the average nitrate nitrogen content of arable soils of temperate regions as 2 to 20.p.p.m.; exchangeable ammonium levels are usually much lower than this, and normally less variable. More recently evidence has been presented which shows that, in certain soils, exchangeable ammonium values may be much higher than nitrate-nitrogen values. Young, (97) working with seventeen Pacific Northwest soils, found their exchangeable ammonium contents ranged between 5 and 83 p.p.m. in the surface horizons and 1 to 84 p.p.m. in the sub-surface horizons. In all cases the nitrate-nitrogen content was less than 15 p.p.m.. For Manitoba soils, Patil (72) gives the average range of exchangeable ammonium as 5 to 35 p.p.m.

That the ammonium ion does not move readily through the soil has been shown by Carleton (22), by Benson and Barnette (8) and by Nelson (69). Krantz and Ohlrogge (50) attributed this immobility of the ammonium cations to the fact that they are absorbed by the base exchange complexes while the nitrate anions move freely with the soil moisture. McDowell and Smith (61) point out that soil texture has a pronounced effect on ammonia movement and retention. Greatest movement occurs in sand and silt loam soils, least in clays.

A review of the persistence of the ammonium ion and its effect

on soil properties has been carried out by Fox <u>et al.(36</u>). From the various results two main conclusions can be drawn. Firstly the ammonium ion acts as a dispersant, causing a deterioration of soil structure and a reduction in soil permeability. Secondly, the ammonium ion persists in the soil for extended periods, especially if the pH is not high and the soil is low in organic matter and phosphate.

Under natural conditions the main source of ammonium to the soil is the soil organic matter, and its production and conversion to other nitrogen compounds is dependent on the soil microbial population. The transformations take place through the stages

organic-nitrogen \rightarrow ammonia \rightarrow nitrite \rightarrow nitrate. (79). Because of the importance of this reaction to nitrogen availability and hence to plant growth, extensive study has been made of the micro-organisms bringing about these changes and the factors affecting them.

Two genera of bacteria are definitely known to convert ammonium to nitrite, namely <u>Nitrosomonas</u> and <u>Nitrosococcus</u> and one genera to oxidise nitrite to nitrate, namely <u>Nitrobacter</u> (Meiklejohn (64)). Lees and Quastel (52),(53)) studied the biochemistry of nitrification in soil in considerable detail. From their results they concluded that the entire process of conversion of ammonium to nitrate in the soil is accomplished by micro-organisms. Under similar experimental conditions the conversion of nitrite to nitrate proceeds at a much faster rate than ammonium to nitrite. The nitrifying bacteria nitrify on the surface of soils, in the vicinity of receptor sites where ammonium is combined <u>or</u> adsorbed. Conditions which lead to an increase <u>or</u> diminution of these

receptor sites likewise leads to an increase <u>or</u> diminution in the rate of nitrification.

The rate of nitrification is also greatly affected by the acidity <u>or</u> alkalinity of the soil system. According to Olsen (70) ammonification can take place in soils with pH between 3.7 and 9.0, and nitrification between pH 3.7 and 8.8. Meek and Lipman (62) give the optimum pH range for nitrification as 8.5 to 8.8. This corresponds to the optimum pH given by Hofman and Lees for <u>Nitrosomonas</u> activity. However, for <u>Nitrobacter</u> they quote an optimum pH of 7.7 which is in agreement with the results of Martin <u>et al</u>.(58). They found that ammonia is not completely oxidised to nitrate in alkaline desert soils until the pH has been reduced to a threshold value of 7.7.

Soil reaction and ammonium concentration appear to be the key factors involved in nitrite accumulation. As early as 1930 Fraps and Sterges (37) had noted that considerable amounts of nitrite may be present in nitrification experiments. From field and laboratory studies on nitrite accumulation in soils, Chapman and Leibig (24) concluded that wherever fairly high ammonium concentrations and neutral or alkaline soil conditions occur, more or less nitrite accumulation may be expected. Martin <u>et al.</u>(58) also found that nitrites could accumulate even in well aerated alkaline soils under favourable conditions of temperature and moisture, but that they decreased to trace quantities almost immediately after nitrates began to form.

Studies of the effect of the nitrite ion on the conversion of nitrite to nitrate by Stojanovic and Alexander (88) showed that the nitrite ion itself did not inhibit the transformation. They

concluded that the accumulation of nitrites in soils of high pH to which a high concentration of ammonium-nitrogen had been applied resulted from inhibition of the <u>Nitrobacter</u> by free ammonia.

Much support is lent to this idea by Warren's results (95). He showed that a pK_a 9,0, the percentage of non-ionised ammonia in solution at pH 6.0, 7.0, 8.0 and 9.0 respectively is 0.1, 1.0, 10.1 and 50.0. The ammonium ion is not generally toxic to plants because it does not cross cellular barriers at any appreciable rate, but ammonie does so freely. In low concentrations ammonia can be tolerated by most living organisms because of their highly efficient detoxifying systems in which urea, glutamine and asparagine are formed. However, at high pH's there may be such large amounts of free ammonia in solution that it may enter the plants so rapidly that their protective mechanisms are overwhelmed.

Although most plants absorb their nitrogen in the form of nitrates, it is well established that many plants, when grown in ' sand and solution cultures under suitable conditions, can develop as well <u>or</u> better when supplied with ammonium salts rather than nitrates (Meyer and Anderson (65)). On the basis of experiments with excised plant roots, Jenny <u>et al.(47)</u> concluded that ammonium adsorbed on clays can be readily utilized. Peterburgskii <u>et al.(75)</u> also found that ammonium adsorbed on exchange resins, soils and peats was available to a variety of plants, but less so than the water soluble form.

That a proportion of ammonium in the nitrogen nutrition of plants may be beneficial has been shown by Blanc (10) and by Andrews <u>et al.(5)</u>. The latter found that young corn and cotton plants prefer ammonium-nitrogen to nitrate-nitrogen and that they grow more rapidly

when ammonium is available than when the sole source of nitrogen is nitrate. In general older plants prefer nitrate-nitrogen. In certain types of soil it is probable that ammonium compounds are the chief form in which nitrogen is available to plants. Acid podsolic soils of northern latitudes and many uncultivated soils in the southern U.S.A. contain little nitrate, but considerable quantities of ammonium compounds. Plants growing on these soils apparently obtain their nitrogen in the latter form. (Meyer and Anderson (65)).

Nitrogen in the soil in forms available to plants is also available to the soil micro-organisms. Broadbent and Tyler (18) found that competition for added tracer nitrogen between a growing crop and the immobilizing flora emphasized preferential utilization of the ammonium-nitrogen by soil micro-organisms and of nitrate-nitrogen by the crop. This preference for ammonium rather than nitrate by the microbes has also been shown by Winsor and Pollard (96) and Jansson <u>et al.(46)</u>. The latter noted that ammonium promoted a greater total immobilization. In general immobilization reaches a maximum in two days then mineralization predominates.

Higher amounts of soluble nitrogen were transformed to microbial protein in planted than in unplanted pots, due to the intensive microbial activity of the rhizosphere (Gerretsen (41)). Nearly fifty per cent of the total available nitrogen was monopolized by the microorganisms in some natural soils. From the overall evidence it is apparent that considerable competition exists between the plants and the microbes for the available nitrogen. Under certain conditions this may limit the growth of the plants.

D. Effects of, and Response to Added Nitrogen Fertilizers

One of the main sources of ammonia to the soil to-day is the ammonium producing nitrogen fertilizer. The most common form of these fertilizers are salts such as ammonium sulphate, ammonium nitrate and urea.

This added ammonium nitrogen is subject to the same type of reaction in the soil system as naturally produced ammonium-nitrogen. In a study of the nitrification of ammonium sulphate on calcareous soils, Justice and Smith (49) found that the rate of conversion of ammonium to nitrate was affected by temperature and by moisture content. Conditions unfavourable for nitrification were high levels of ammonium nitrogen, low temperatures, low moisture levels and temperatures above twenty five degrees centigrade. These tended to lead to an accumulation of nitrite-nitrogen. Incomplete recovery of mineral nitrogen under unfavourable conditions was attributed to ammonia volatilization.

Mehendrappa <u>et al.(63)</u> also noted that nitrites accumulate under temperature conditions less favourable for nitrification. Optimum temperatures for nitrification were found to vary with latitude, being twenty to twenty five degrees centigrade for northern soils of western U.S.A. and thirty-five to forty degrees centigrade for southern soils.

Under optimum conditions nitrification is rapid. (Broadbent et al.(19)). However, when fertilizers are applied the ammonium ion is rarely uniformly distributed throughout the soil. Localised high concentrations usually occur where nitrification may be inhibited if the soil is poorly buffered. Inhibition results from the production of

areas of excessively high or low pH, high concentrations of free ammonia or high salt concentrations. The most common conditions under which inhibition may occur are high concentrations of any type of ammoniacal fertilizer, with alkaline soil reaction. In calcareous soils the problem is aggravated.

The hydrolysis of urea in fertile soils proceeds rapidly, where conditions of temperature and moisture favored the activities of aerobic soil micro-organisms. A few days after application only small amounts of urea remain in the soil (Court <u>et al.(30)</u>). Broadbent <u>et al.</u> (17) also found that urea was rapidly nitrified in all soils at moderate levels of application. However, an 800 p.p.m. application to a poorly buffered Hanford sandy loam caused inhibition due to the production of a high pH. Other factors affecting rate of nitrification include soil type and season (Stojanovic (87)) and temperature and rate of application (Fisher and Parks (34)). The average amount of hydrolysis increased with increasing urea application at all temperatures except ten degrees centigrade. At ten degrees centigrade nitrification rate was nearly constant, being about twenty-five pounds per acre per week at 100 and 200 pound rates of urea application. The transformations of urea and products of hydrolysis in soils are summarized below (Court <u>et al.(30)</u>).

UREA	\rightarrow	AMMONIUM CA	RBAMATE	\longrightarrow	AMMONI	IUM CARBONATE
co(№2)2 ↑		NH4CO2NH2			(NH ₄)	2 ^{CO} 3
AMMONIUM C	YANATE				NH ⁺ 4	solution
NH ₄ CNO		bacterial oxidation		bacte	rial	1
NIT	RATE ION NO ₃ -	< <u>by</u>	NITRITE I NO _O -	$ON \leftarrow by$		\iff NH ₃
	5	Nitrobacter	2	Nitros	omonas	
					11111	ausprned

The results of field and greenhouse experiments comparing the efficiency of urea with other nitrogeneous fertilizers brings out several interesting points. These can be illustrated in the work of Devine and Holmes (32), Templeman (89), Court <u>et al</u>.(28) and Stephen and Waid (84).

The conclusions of Devine and Holmes (32) are based on twenty one field trials carried out in various parts of England and Scotland, in which several nitrogen sources were combined drilled with spring barley. Ammonium sulphate and ammonium nitrate at rates of thirtyfive to 105 pounds per acre of nitrogen checked early growth slightly in some experiments but no important difference was obtained between the two sources. Urea at forty-five pounds per acre of nitrogen had no large effect on early growth while at seventy to ninety pounds per acre braiding was seriously delayed and plant population reduced in many experiments. In many of the experiments where early growth was affected yields were lower than with ammonium sulphate or ammonium nitrate and at all rates of application mean yields were lower. With broadcast application all sources gave similar yields; combine drilling gave slightly smaller yields than broadcasting with ammonium sulphate and ammonium nitrate and markedly smaller yields with urea.

The results of various grassland experiments also show that urea is slightly less efficient than conventional materials (Templeman (89)). Inefficiency was more frequent at high rates of application; least inefficiency occured when growing conditions were most favourable.

Glasshouse experiments carried out by Court <u>et al.(28)</u> and by Stephen and Waid (84) provide supporting evidence of the inefficiency

of urea compared with ammonium sulphate and ammonium nitrate. Similar yields were obtained at low application rates, slightly lower yields at intermediate rates, and much lower yields at highest rates of application. Urea adversly affected plant development to a greater extent on light soils than on heavy soils and peats. (28). In many crops smaller yields were associated with urea induced damage which was followed by death of established plants (84).

This association of lower yields with damage and death of plants was also noted by Court <u>et al.(29)</u> and by Cooke (26). Possible causes of plant damage have been reviewed by Low and Piper (55) and by Court <u>et al.(30)</u>.

The available evidence suggests than neither 'biuret', when less than one per cent is present in the urea, nor cyanate is responsible for damage arising from the use of urea. High levels of ammonia are known to be toxic to both plants and micro-organisms. The increase in pH caused by the hydrolysis of urea may be sufficient to raise the pH above seven and allow ammonia concentrations sufficient to damage plants. Inhibition of Nitrobacter activity also occurs at high pH values and high ammonia concentrations, leading to an accumulation of nitrite. Lowering of the pH by the accumulated nitrite may retard nitrification still farther. At the lower pH values the toxicity of the nitrite to the plants is likely to be greater. Damage to plants due to application of urea is most commonly attributed to local accumulations of free ammonia (Stephen and Waid (85), Low and Piper (55), Devine <u>et al.(32),</u> Cooke (26), Court <u>et al.(30)</u>) and subsequent death of established plants to nitrite accumulation in the soil. (Stephen and Waid (85), Court <u>et</u>

<u>al.(29)).</u>

The presence of high levels of volatile ammonia in the soil system is also important in relation to loss of applied nitrogen. Volatile loss of ammonia is most marked when the fertilizers are broadcast ((66), (51)), when soil pH is greater than seven ((66), (59),(49),(93)) and when the level of fertilizer application is high ((51), (66),(93)). Martin and Chapman (59) compared the losses of applied nitrogen from a variety of carriers in soils ranging from pH 4.5 to 8.0. They concluded that nine to fifty-one percent of nitrogen added in the form of ammonium hydroxide was lost and one to twenty-seven percent was lost from ammonium sulphate. Except in poorly buffered soils, where ammonia formation could increase the pH sufficiently to allow volatilization of ammonia, losses from urea and dried blood were comparatively small. By contrast, Gasser (40) found losses were similar from urea and from ammonium sulphate applied to calcareous soils. Ammonia was lost at twenty-five degrees centigrade from calcareous soils until all the ammonium nitrogen had been nitrified, from the slightly alkaline clay soils until nine-tenths had been nitrified and from neutral sandy soils until half had been nitrified.

Losses of fertilizer nitrogen in forms other than ammonia have been noted by Carter and Allison (23) and by Wagner and Smith (92). The latter found greatest loss from usea and attributed the main loss to nitrous oxide (NO). Smith <u>et al.(81)</u> suggested that loss of nitrogen other than by ammonia volatilization may be due to reduction of nitrogen dioxide (NO₂) to nitrogen gas (N₂) by some component of the soil complex.

At lowest levels of application recovery of added nitrogen may be greater than the amount added. This type of result was obtained by Broadbent <u>et al.(19)</u> who found recoveries of nitrogen from ammonium nitrate and ammonium sulphate were greater than the added 50 p.p.m. due to ammonification and subsequent exidation of organic nitrogen as well as quantitative exidation of ammonium nitrogen. This stimulating effect was also observed in soils receiving no organic amendment and in which no plants were grown indicating that it can not be attributed solely to the activity of rhizosphere microflora.

Recovery of added nitrogen by plants is relatively low. Allison (3) gives a value of fifty percent as the amount of available nitrogen recovered by plants. Using tagged nitrogen, Tyler and Broadbent (91) compared the recovery from ammonium sulphate, ammonium hydroxide and ammonium nitrate. They found that considerable tagged nitrogen was immobilized soon after application as shown by relatively low crop recovery of added fertilizer in all but the ammonium sulphate treated pots. Total recovery from the plant and soil varied from eighty-three to ninety-seven percent of the tagged nitrogen applied. According to Bartholomew <u>et al.</u>(6) only eleven to twenty-nine percent of the total nitrogen adsorbed by oats was derived from applied fertilizer.

Hunter and Carter (45) found that the higher the fertilizer level, the greater the proportion of nitrogen uptake derived from the fertilizer. Their data suggests that N-values, indigenous ammoniumnitrogen, and indigenous ammonium-nitrogen and nitrate nitrogen may all be of value in predicting nitrogen needs for Oregan soils.

CHAPTER III

Methods and Materials

A. Determination of Exchangeable Ammonium Nitrogen in Soils

The technique used involved the displacement of the ammonium ion from the exchange complex by some other exchangeable cation such as sodium <u>or</u> potassium. The extract was then distilled and the concentration of ammonium in the distillate determined by Nesslerization or by titration. Direct Nesslerization was not possible as high concentrations of other cations in the extract interfered with the Nessler's reaction. Unless otherwise indicated, extraction was made on the fresh soil.

(1) Preparation of Samples

Details on the handling of the soils are given along with each experiment.

(2) Extraction

In the initial experiments an acidified 10% NaCl (pH 2.0 - 2.5) solution was used for extraction of the exchangeable ammonium. Later it was found desirable to use 2NKCl in place of 10% NaCl.

No generally acceptable definition of exchangeable ammonium is available. The most widely used definition is that ammonium which can be extracted by a KCl. solution at room temperature. Use of 2NKCl makes comparison with other workers' results much easier. The advantages and disadvantages of the two reagents are listed below.

			21
EXTRACTANT	ADVANTAGES		DISADVANTAGES
2NKC1	1. Extracts can be stored	1.	Possibility of reduced
	2. Extracts can be used		ammonium release due
	for nitrate and nitrite		to potassium fixation.
	determinations.	2.	Possibility of loss
			of ammonia by
			volatilization on
			high alkaline soils.
			(Bremner detected no
			loss with soils
			containing 10% CaCO ₃)
	l. Does not undergo	 1.	Difficult to store
(pn 2.))	fixation.	2.	Risk of hydrolysis
	2. The lower pH		of organic-nitrogen
	reduces risk of		compounds particularly
	volatilization.		with acid soils.
		3.	Can not be used for
			nitrate <u>or</u> nitrite

determinations.

Two experiments were run to compare these extractants. In the first experiment results were inconclusive. With eight out of twelve soils exchangeable ammonium values were the same, within the limits of experimental error. The second experiment, in which four soils were used, gave similar results with both extractants. However, recovery of added ammonium was considerably better with 2NKCl than with acidified 10% NaCl. Bremner obtained comparable results with 2NKCl, acidified 1NKCl and 1NNaCl. He recommends equilibrium extraction with 2NKCl and distillation with MgO, which was the method adopted here. As distillation with MgO is difficult in the Micro-Kjeldahl apparatus, 40% NaOH was used in its place. This gave similar results to distillation with MgO.

(3) Distillation

The Markham Micro-Kjeldahl (57) apparatus was used.in the first three experiments and a special steam distillation unit, similar to that modified by Bremner (13), in the fourth experiment. With the latter unit the distillate was collected in boric acid containing mixed indicator, as modified by Ma and Zuazaga (56), and titrated with standard acid.

(4) Nesslerization

The method described by Yuen and Pollard (99), modified for a 100 ml instead of 50 ml volume, was used.

B. Determination of Nitrate-Nitrogen in Soils

Two procedures were used for nitrate-nitrogen determination.

- The colorimetric phenoldisulphonic acid method as modified by Harper (42).
- (2) The magnesium oxide steam distillation method describedby Bremner (13).

C. Determination of Nitrite-Nitrogen in Soils

Bremner's magnesium-oxide - Devarda's alloy steam distillation procedure was used.

D. Determination of Soil pH

pH measurement was made in water using a glass electrode and a l:l soil solution ratio as described by Peech (74).

E. Determination of Total Nitrogen in Plant Material

Total nitrogen was determined by the Kjedahl-Gunning method.

CHAPTER IV

A Comparison of Several Methods of Storage of Samples for Exchangeable Ammonium Determinations

One of the main difficulties encountered in the determination of exchangeable ammonium nitrogen in soils is the alteration in the inorganic-nitrogen levels caused by sample transportation and storage. The aim of this experiment was to determine the method of storage which would produce least change in the exchangeable ammonium in the soil.

Α.

Experimental Procedure

In the fall of 1964 soil samples were taken from a variety of sites in Manitoba. These samples were transported in closed plastic bags and extraction and analysis was carried out as soon as possible after their arrival in the laboratory. Where immediate extraction could not be made, storage was at 2°C. Sub-samples were taken and treated as follows:-

- (a) Stored in closed plastic bags at 2°C for eight weeks.
- (b) Stored in plastic bags at -15°C for three months.
- (c) Air-dried in the greenhouse.
- (d) Oven dried at 55°C.

Analysis on the dried samples was carried out immediately drying was complete. Samples (a) and (b) were weighed and extracted as soon as they were sufficiently defrosted to handle. Increase in

exchangeable ammonium on storage at low temperature is thought to be due to the flush of microbial activity as the sample attains room temperature (2). By extracting the soils before they reached room temperature it was hoped to reduce this effect.

Exchangeable ammonium-nitrogen was determined by the procedure given on page 21. All results are expressed as parts per million ovendried soil.

Results and Discussion

The soil types and exchangeable ammonium values are given in Table 1. The eleven soils used include representatives of the Black, Dark Grey and Grey-wooded soil zones. Textures range from loamy sand to silty clay and pH from 6.9 to 8.0. Soils of a high pH were chosen because most available information deals with neutral to acid soils. Many Manitoba soils have a high pH, and later work was intended to be mainly with these soils.

Despite the fact that a variety of soil types and textures was used, all soils were found to be low in exchangeable ammonium. Nor did any of the treatments tested raise the exchangeable ammonium level in any of the soils above 6 p.p.m.

On comparison of the average values of the eleven soils, least change is seen to occur with storage at 2°C. This contrasts with Gasser's (38) findings in which storage at 2°C led to an increase in exchangeable ammonium. However, Soulides and Allison (83) and Paul and Tue (73) also reported that low temperature storage produced least change in exchangeable ammonium. Three months storage at -15°C reduced the exchangeable ammonium in most of the soils to a negligible level.

Gasser (38) reported no change with continuous storage at -10°C.

Drying increased exchangeable ammonium values, air drying causing a greater increase than oven-drying at 55°C. Increases in exchangeable ammonium on drying soils have been reported by a variety of workers (9,27,31,38,83,94).

Β.

Experimental Procedure

In the spring of 1965 soil samples were collected from four of the plots on which field trials were to be run during the summer. Samples were taken from the 0-6, 6-12,12-24,24-36, and 36-48 inch depths, twelve sets from each plot. These were transported to the laboratory in closed plastic bags and treated as follows.

- (a) Half the samples, 6 sets per plot, were oven dried at 50°C for nitrate-nitrogen determinations and stored in paper bags. Exchangeable ammonium determinations were made after four to eight weeks storage.
- (b) Composites were prepared from the remaining samples and sub-samples immediately taken for extraction and ammonium determination. At the same time a second sample was oven-dried at 55°C and extractable ammonium determined on the dried soil.

Exchangeable ammonium was determined as previously described.

Results and Discussion

Some of the characteristics of the soils used are given in Table 5 and exchangeable ammonium values in Table 2. The range of exchangeable ammonium levels in the fresh soil is considerably greater in this part of the experiment than in part A. As in the initial experiment oven drying at 55°C has caused a marked increase in ammonium extractable from the soils. Statistics run on these soils showed the difference between the means to be significant at the 1% level.

Table 3 gives the levels of exchangeable ammonium in the samples which had been oven dried and stored in paper bags. Considerable variation is seen to occur between the six samples from the same plot. This variability is greater in the 0-6 inch samples than in the 6-12 inch samples. In all but one set of samples, air drying has increased the level of exchangeable ammonium. With the Altona soil four of the six samples from the 0-6 inch horizon gave lower values. This was the only set of samples which showed a high level of exchangeable ammonium in the fresh soil. The possibility of loss of ammonia by volatilization would therefore have been much greater.

On average the samples which were oven dried and stored show a lower level of exchangeable ammonium than the corresponding oven dried composite samples (Table 2). Bremner (13) has suggested that changes in stored samples are the net result of losses due to volatilization of ammonia and gains due to sorption of atmospheric ammonia during drying. In this case the free circulation of air allowed by the paper bags may have permitted sufficient loss to counterbalance a portion of the ammonia sorbed during drying.

Conclusion

Drying soils of neutral to alkaline reaction produces an increase in exchangeable ammonium. To obtain a valid estimation of the exchangeable

ammonium present in the soil in its natural state, determination should be made on the fresh soil samples, with the minimum of delay between sampling and extraction. Where this is not possible, the fresh soil should be stored at 2° C.

On the basis of these results later samples for exchangeable ammonium determinations were stored, where necessary, at $2^{\circ}C$. Extraction and determination was always made, however, within one week of sampling.
TABLE 1 SOIL CHARACTERISTICS AND EXCHANGEABLE AMMONIUM VALUES

				MC	JIST SOIL		DRY	SOIL
				A	д	C	Q	된
SOIL	GENETIC CLASS	TEXTURE	Hď	Initial P.P.M.	8 weeks at 2°C P.P.M.	3 months at -15 ^o C P.P.M.	Air Dried P.P.M.	Oven Dried P.P.M.
WELLWOOD	ORTHIC BLACK	VERY FINE SILT LOAM	6.9	2.4	2.5	0.7	4.8	2.8
GARSON	ORTHIC GREY WOODED	FINE SANDY LOAM	7.3	3.8	2.5	5.2	5.6	4.6
GARSON	ORTHIC GREY WOODED	LOAMY SAND	7.7	1.6	1.9	0.6	5.8	4.0
GARSON	ORTHIC GREY WOODED	SANDY LOAM	7.8	1.8	1.9	1.0	5.2	3.6
PORTAGE	ORTHIC BLACK	SILT	7.5	2.7	4.2	1.0	6.0	4.4
ALTONA	ORTHIC BLACK	VERY FINE SANDY CLAY LOAM	7.5	1.9	3.8	1.3	5.2	3.0
RIVERDALE		VERY FINE SANDY CLAY	7.8	2.3	2.9	0.8	6.0	4.0
INWOOD-NARCISSE COMPLEX	GLEYED DARK GREY	SILTY CLAY	7.8	1.0	3.0	0.0	5.8	3.6
RED RIVER	REGO BLACK	SILTY CLAY	7.9	3.7	3.2	1.7	4.4	3.6
LAKELAND	CAL.REGO BLACK	SANDY CLAY	7.8	4.3	2.6	0.8	5.8	4.8
LAKELAND	CAL.REGO BLACK	VERY FINE SANDY CLAY	8.0	2.0	2.1	1.0	5.6	4.0
AVERAGE				2.5	2.8	1.3	5.4	з . 8

			TREATMENT	
SOIL	SAMPLING DEPTH (INCHES)	COMPOSIT FRESH P.P.M.	TE SAMPLES OVEN- DRIED P.P.M.	OVEN- DRIED AND STORED P.P.M.
ALTONA	0 - 6 6 - 12 12 - 24 24 36 36 - 48	17.4 9.5 4.2 3.3 2.2	23.6 11.2 7.4 5.0 4.4	15.0 11.45
ALMASIPPI	0 - 6 6 - 12 12 - 24 24 - 36 36 - 48	1.6 0.7 0.0 0.6 0.0	6.2 6.0 4.4 5.2 4.4	3.9 3.7
LAKELAND	0 - 6 6 - 12 12 - 24 24 - 36 36 - 48	5.0 2.4 0.8 0.4 1.0	9.0 7.4 4.6 4.6 4.2	8.0 5.3
WELLWOOD	0 - 6 6 - 12 12 - 24 24 - 36 36 - 48	6.1 1.2 0.0 0.8 0.0	7.4 5.6 4.0 3.8 3.8	9.07 5.17
MEAN		2.87	6.61	

-

TABLE 2 EXCHANGEABLE AMMONIUM IN SPRING SAMPLES

TABLE 3 EXCHANGEABLE AMMONIUM IN SAMPLES DRIED AT 50°C

AND STORED IN PAPER BAGS

11.45 AVERAGE 9.07 5.17 15.0 9**.**9 8.0 3.7 5.3 20.02 10.0 4.8 3.8 8.2 8 7.8 10.0 6.0 TΛ EXCHANGEABLE AMMONIUM IN P.P.M. 11.6 16.2 0.8 .0 4.4 12.2 3.6 8.0 3.4 \succ 4.0 20.02 11.2 3.0 5.0 4.8 6.8 3.2 LV III 7.6 10.0 о.с 2.5 6 5.6 6.6 10.0I 4.4 13.6 13.0 3.4 2.0 7.8 5.0 10.2 5.0 П 12.6 13.0 4.0 0.6 6.2 7.4 9.4 6.8 н 6-12" 6-12" 6-12" 6-12" DEPTH ..9-0 ..9-0 ..9-0 ..9-0 ALMASIPPI LAKELAND WELLWOOD ALTONA SOIL

CHAPTER V

Field Experiment

Experimental Procedure

In 1965 field trials were conducted at four locations in Manitoba to study the response of barley to certain nitrogeneous fertilizers. Some of the characteristics of the soils at these sites are presented in Tables 4 and 5. Seeding and harvesting dates are shown in Table 4.

A randomized block design with nineteen treatments and six replicates was used. Nitrogen was applied in three forms, ammonium nitrate (33.5-0-0), urea phosphate (23-23-0) and urea (46-0-0) and phosphate as ammonium phosphate (11-48-0). All phosphate was drilled in with the seed and nitrogen was either broadcast <u>or</u> drilled in as indicated in Table 6. Rate of nitrogen application varied from 0 to 90 pounds per acre and phosphate rates were 0, 20 and 30 pounds per acre. Details of all treatments are listed in Table 6. All plots were seeded to Conquest barley.

At about the four leaf stage of development germination counts were made. These were based on the number of plants in a ten foot portion of the central two rows in each treatment. The check was used as 100 per cent.

Per cent germination =

Treatment count. (2-10 ft. rows/Rep.) (Total of 6 Reps. x 100 Check count

The same portion of each treatment was harvested for yield determinations when the crop had reached maturity. The barley plants were air-dried, threshed and weighed to give both grain and straw yields. Portions of both the grain and the straw were retained for total nitrogen determinations. Composites were prepared from the six replicates in each treatment for this purpose.

Where possible, response to nitrogen fertilizer was determined by the percent yield suggested by Bray (12). Because 11-48-0 was used as the phosphate source, the percent yield was calculated as follows:

Per cent yield =
$$\frac{\text{Yield from 20 lb N + 30 lb P_20_5 treatment}}{\text{Yield from 7 lb N + 30 lb P_20_5 treatment}}$$

With treatments in which only 20 lb per acre phosphate was used, percent yield could not be calculated.

Soil samples were taken at intervals of 0-6, 6-12, 12-24, 24-36 and 36-48 inches from all plot sites at seeding time and at harvesting time and stored in closed plastic bags at 2°C for exchangeable ammonium determinations. At the same time a corresponding set of samples was taken and dried at 50°C for nitrate nitrogen determinations.

Results and Discussion

Determinations on the soils are summarized in Table 7 and yield, nitrogen uptake and germination data in Tables 9 to 13. Figures 1 to 4 are diagramatic representations of the distribution of exchangeable ammonium and nitrate nitrogen in the four profiles.

From these diagrams the level of exchangeable ammonium in the soil is seen to decrease with depth in the profile. This pattern was

not affected by time of sampling. The ammonium ion is absorbed by the base exchange complexes in the soil (50) and therefore would not be readily subject to movement by leaching. Carleton (22), Benson and Barnette (8) and Nelson (69) found that the ammonium ion does not move readily through the soil.

The nitrate nitrogen showed a similar distribution except in the spring samples of the Wellwood and Altona soils and the fall sample of the Altona soil. In both the spring samples the nitrate nitrogen was uniformly distributed down the profile, except at the 6-12 and 12-24 inch levels where the nitrate nitrogen contents were slightly higher. With the fall sample of the Altona soil the nitrate decreased down to the 24 inch depth and then increased sharply at the 36 inch depth. This pattern is not unexpected as the nitrate ion exists mainly in the soil solution and would therefore be readily subject to movement and redistribution throughout the profile.

In all cases the total exchangeable ammonium and total nitrate nitrogen to the 48 inch depth has decreased over the growing season. The largest decrease in total inorganic nitrogen occured in the Altona soil, where approximately half the inorganic nitrogen had been removed over the growing season. It is interesting to note that ammonium nitrogen made up approximately five-sixth of the total loss. With the Almasippi soil, which was very low in both ammonium and nitrate nitrogen initially, all the ammonium was lost and half the nitrate nitrogen. In the Lakeland and Wellwood soils, the decrease in ammonium nitrogen was approximately equal to the decrease in nitrate nitrogen. This is also true of the Almasippi soil. The loss from the Lakeland

soil was extremely low.

Greatest decrease occured in the soil with the most inorganic nitrogen. Although the Lakeland and Wellwood soils contained similar amounts of inorganic nitrogen in the spring, by the end of the growing period the Wellwood soil had lost most of its ammonium nitrogen and half its nitrate nitrogen, whereas the Lakeland soil had lost little of either. Three out of the four soils showed a marked decrease in ammonium nitrogen between the spring and the fall.

On the basis of these results, the following explanation for the observed changes is suggested. During the winter and early spring conditions are such in the soil that breakdown of organic matter and release of ammonium is likely to be more rapid than the oxidation of ammonium to nitrate. In the spring, conditions are more suited to nitrification, crops are planted and, in general, the conversion of ammonium to nitrate is stimulated. The Lakeland soil is calcareous, a condition which favours the rapid breakdown of organic matter. Ammonium released during this reaction will help to maintain a constant level of exchangeable ammonium in the soil over the summer. However, in the other three soils, utilization of nitrate would appear to be more rapid than the production of ammonium from the organic matter. The level of exchangeable ammonium in the soil would therefore drop. The exchangeable ammonium present in the soil in the spring appears to be the main reserve of utilizable nitrogen used to maintain the nitrate nitrogen levels in the soil. Under conditions of rapid nitrogen uptake by the crop, some direct utilization of exchangeable ammonium itself may occur. The overall evidence indicates that the exchangeable

ammonium present in the soil in the spring can not be ignored when making determinations of available nitrogen. The amount of exchangeable ammonium present and its extent of utilization is highly dependent on the nature of the soil itself and the conditions in the soil during the spring and summer.

Correlations (Table 8) were run to determine whether yield or nitrogen uptake could be directly related to exchangeable ammonium, nitrate nitrogen, total inorganic nitrogen or N-values. The highest correlation obtained was between exchangeable ammonium and nitrogen uptake. None of the values were significant above the 10 per cent level.

For treatments 2 to 9 and 17 to 19 yield was calculated on a per cent basis as previously mentioned. These values are shown in Table 14. Figures 5, 6, and 7 are graphs of the same data plotted against added nitrogen.

Figure 5, which is based on T2 to T6, shows that the per cent yield increased linearly for all four soils up to the 60 lb per acre level of fertilizer application. At this point the yield leveled off on the Almasippi, Wellwood and Altona soils. With the Lakeland soil a more gradual decrease took place. Greatest response to added fertilizer occured on the Almasippi soil, least on the Altona. The individual points plotted on this figure represent treatment 7,8 and 9. Points for the broadcast urea all fall below the ammonium nitrate lines, with the exception of the 40 lb per acre treatment on the Lakeland soil. Working in the urea gave the same response, except in the Wellwood soil, where a marked increase in yield occured. Figure 6, which shows the

per cent grain yields against added nitrogen, is similar to Figure 5. The point of interest here is that the grain yield for the Lakeland soil was still increasing linearly, even at the highest level of nitrogen application.

The total percent yields for T17,18 and 19, in which the nitrogen source was drilled in with the seed, are plotted against added nitrogen in Figure 7. Comparison of this figure and figure 5 shows that a higher percent yield was obtained when the fertilizer was drilled in rather than broadcast on the Almasippi and Lakeland soils. This effect was less marked in the Wellwood soil and on the Altona soil the response appeared to be poorer. With the Almasippi and Lakeland soils, the lower yields obtained when the fertilizer was broadcast may have resulted from volatile loss of nitrogen, possibly in the ammonia form.

Nitrogen uptake, calculated on a percent basis, is shown in Table 15. Values are seen to vary widely, not only between the soils but also within the soils. With the Wellwood soil all but four treatments have nitrogen uptake values between 59 and 73 per cent. Low recovery was obtained with 40 lb per acre urea, both drilled in and broadcast. By contrast, a higher than average recovery was obtained when 40 lb per acre urea was worked in. Omission of phosphate lowered the nitrogen recovery to 55 per cent.

The average range of values for the Lakeland soil, 50 to 66 per cent, is considerably lower than the average range for the Wellwood soil. In this soil five treatments lie outside the average range; four of the five are above this range. Recovery from 40 lb per

acre urea phosphate, drilled in, was only 45 per cent. Drilling in 20 or 40 lb per acre ammonium nitrate, on the other hand, increased the recovery considerably. High recovery was also obtained from the lowest level of added nitrogen, that is, the 7 lb per acre ammonium phosphate treatment.

No average range of values for nitrogen uptake exists with the Altona soil. In this soil the percent nitrogen uptake varies from 17.5 to 133. Highest uptake occured with the lowest rates of nitrogen application. Very low recovery was obtained from 90 lb of broadcast ammonium nitrate, 40 lb of drilled in urea <u>or</u> urea phosphate and when no phosphate was added. Comparison of T11 and 12 with T13 and 14 and T15 and 16 shows that nitrogen uptake was greater from ammonium nitrate than from urea <u>or</u> urea phosphate.

With the Almasippi soil two average ranges can be distinguished. With broadcast application nitrogen uptake varied between 35 and 59 per cent; when the fertilizer was drilled in, this range was 60 to 80 per cent. Again treatments 14 and 16 fall well outside this range with a 32.5 per cent nitrogen uptake. The value for the 30 lb per acre urea application was also low in this soil. That the difference between drilled in and broadcast application was most noticeable in this soil is to be expected, since the Almasippi soil has a lighter texture than the other three. In this soil the number of exchange sites available for the absorption of the ammonium ions will be fewer than in the heavier soils. Drilling in the fertilizer brings it into contact with a far greater volume of soil than when it is broadcast on the surface. More nitrogen will therefore be retained.

One of the main objectives of these field trials was to evaluate urea and urea phosphate as fertilizers and to compare them with another nitrogen source, in this case ammonium nitrate. Grain and straw yields for each treatment are given in Tables 9 and 10. Each value is an average of the six replicates. Throughout the following discussion all comparisons are between the urea treatment and the equivalent ammonium nitrate treatment.

From Table 9 urea is seen to have caused significant reductions in grain yields on the Wellwood and Altona soils. Sixty pounds per acre of broadcast urea yielded 9.4 bushels per acre less than a similar application of ammonium nitrate on the Wellwood soil. The significantly lower yield obtained when phosphate was not applied indicates that this plot responded to the phosphate application. On the Altona soil a significant decrease in yield occurred with both broadcast and worked in urea at the 60 lb. per acre rate of application.

When the fertilizers were drilled in with the seed, reductions in yield were obtained with the urea treatments on three of the four soils. On the Lakeland soil a reduction in yield of 6.5 bushels per acre was recorded when 40 lb. per acre urea phosphate was used. Significant reductions in yield occurred on the Altona soil with the 20 and 40 lb. per acre urea phosphate treatments and with the 20 and 40 lb. per acre urea treatments. The urea and urea phosphate treatments also reduced the yield on the Almasippi soil, but only significantly at the 40 lb. per acre rate of application.

Significant reductions in yield resulting from the use of urea or urea phosphate occurred most frequently on the Altona soil. This may

have been because this soil had both a high pH and high level of exchangeable ammonium initially. Most of the exchange sites in the soil would be already occupied and the addition of more ammonium ions would result in a high concentration of ammonium in the soil solution. Combined with the high pH, this would lead to high concentrations of free ammonia in the soil. Since free ammonia is toxic to plants, damage and possible death of plants would follow. This effect would be more marked with the drilled in fertilizer because of the closeproximity of the urea to the seeds. In the case of the Almasippi soil, the initial level of exchangeable ammonium was quite low. However, as this soil was more sandy in texture, the amount of available exchange sites would be quite low. Combined with the high pH, a similar situation as in the Altona soil would exist.

These results agree well with the conclusions of Court <u>et al.</u>(28), Templeman (89) and Cooke (26) that inefficiency of urea is most marked at higher levels of fertilizer application and when the urea is drilled in with the seed rather than broadcast. Support for the idea that the reduction in yield on the Altona and Almasippi soils with the drilled in fertilizers may be due to ammonia damage to the seed and due to reduced germination can be obtained from the germination counts. In five out of the six cases of reduced yield, significant reductions in germination had also occured. However, the evidence strongly suggests that some other factor was also involved, as out of the ten cases of reduced yield which can be attributed to urea <u>or</u> urea phosphate, only five showed reduced germination.

Some support for the idea that reduction in germination was

due to ammonia toxicity is obtained from the germination counts. As shown in Table 13 counts were made on twelve of the nineteen treatments, and of these only four were ammonium nitrate treatments. Out of the sixteen values from the latter, only one case of a significant reduction in germination occurred, namely on the Wellwood soil where 40 lb. per acre ammonium nitrate had been drilled in with the seed. On the Lakeland soil, germination was reduced by more than 10 per cent with all ammonium nitrate treatments, although in no case was this reduction statistically significant. The Lakeland soil has a high pH and is highly calcareous; under these conditions high levels of free amounts are likely to accumulate in the soil (95). Although both the Altona and Almasippi soils are also of alkaline pH, neither soil is calcareous. Nor was the level of added ammonium very high in any of the ammonium nitrate treatments when allowance is made for the fact that approximately half the nitrogen was in the nitrate form. With the Wellwood soil, the reduction in germination only occurred where the ammonium nitrate was actually drilled in with the seed. Since the ammonium ion tends to persist in acid soils (36), a high concentration of ammonium would tend to develop. Although the proportion of nitrogen in the ammonia form would be considerably lower at this lower pH (95), the toxicity of free anmonia is very much greater under acid conditions.

Significant reductions in germination with urea only occurred when the urea was drilled in with the seed. The average germination for the four drilled in urea and urea phosphate treatments were Almasippi, 69.4 per cent, Altona 75.6 per cent, Lakeland 75.1 per cent and Wellwood 94.1 per cent. Least reduction occurred with the only

acid soil used. From the twelve treatments on the four soils, a total of twelve cases of significant reduction in germination were recorded. Of these, seven recovered sufficiently to show no significant reduction in yield.

Numerous causes have been suggested for the reduction in yield so often obtained with urea. The most widely accepted explanation is nitrite accumulation. With the alkaline soils in this experiment the pH is already above the threshold value of 7.7 given by Martin <u>et al</u>. (58) for the oxidation of nitrite to nitrate. The addition of urea will further raise the pH, thus slowing down the nitrite oxidation to an even greater extent. Ammonium nitrate, on the other hand, would be more likely to lower the pH and facilitate nitrite oxidation. With the acid Wellwood soil, its lower initial pH would counteract the effects of the urea and reduce the probability of nitrite accumulation. This seems a possible explanation for the yield reductions obtained in this experiment with the three alkaline soils and the higher yield obtained with the acid soil when urea was used as nitrogen carrier.

Conclusions

From this experiment the following conclusions can be drawn.

- Ammonium nitrogen does not move down the soil profile as readily as nitrate nitrogen.
- (2) Both the ammonium and nitrate nitrogen levels in the soil decrease over the growing period; evidence suggests that, although nitrate nitrogen is the most important portion of the inorganic nitrogen for crops, the exchangeable ammonium nitrogen can not be completely

ignored when making determinations of available nitrogen.

- (3) On the Almasippi and Lakeland soils drilling in the ammonium nitrate source gave higher yields than broadcasting. With the Altona and Wellwood soils, no difference was observed between the two modes of application.
- (4) Nitrogen uptake values varied widely between treatments and between soils. Lowest values occured with the highest rates of nitrogen application, the urea and urea phosphate treatments and where no phosphate was added.
- (5) Significant reductions in yield as compared with the ammonium nitrate treatment occured with the 60 lb per acre broadcast urea treatment on the Wellwood and Altona soils. No corresponding reduction in germination was noted. More cases of reduced yield occured with drilled in urea or urea phosphate than when urea was broadcast.
- (6) Significant reductions in germination only occured when the fertilizer was drilled in with the seed. Only one case of significantly reduced germination was noted with ammonium nitrate, all others occuring with the urea or urea phosphate treatments. Reduced germination was more common on the three alkaline soils than on the acid Wellwood soil.

TABLE 4

SOIL TYPES, SEEDING AND HARVESTING DATES

CO-OPERATOR	SOIL ASSOCIATION	TEXTURE	SEEDING DATE	HARVESTING DATE
HUMESTON	WELLWOOD	SILTY CLAY LOAM	June 5	Sept. 2
MOELLER	LAKELAND	SILTY CLAY	June 1	Aug. 19
WIEBE	ALTONA	VERY FINE SANDY LOAM	May 19	Aug. 10
MURTA	ALMASIPPI	LOAMY FINE SAND	June 3	Aug. 13

TABLE 5

SOIL CHARACTERISTICS

SOIL TYPE	Hď	о . м.	caco ₃ EQUIV. %	NaHCO3 EXTÁCT- ABLE P P.P.M.	EXCH. K P.P.M.	"utronomic of the second secon	ITRATE TROGEN s/acre 0 - 48"	EXCHAN AMMONI 1bs/a 0 - 24"	IGEABLE UM cre cre 0 - 48"
WELLWOOD	6.3	5.8	ΤΪ	14.5	266	50	31	15	17
LAKELAND	7.9	8.0	28.5	20.1	275	1 6	21	18	24
ALTONA	7.7	6.1	0.36	6.5	339	34	64	ΤŢ	93
ALMASIPPI	7.8	2.2	0.91	17.0	100	ŢŢ	18	ŝ	7

TABLE	6
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BARLEY TREATMENTS

NUMBER	FERTILIZER CARRIERS	NI lb	TROGEN s/acre	(P ₂ 0 ₅) lbs/acre
7				
T				
2	11 - 48 - 0		7	30
3	33.5-0-0 + 11-48-0		20	30
4	33.5-0-0 + 11-48-0		40	30
5	33.5-0-0 + 11-48-0		60	30
6	33.5-0-0 + 11-48-0		90	30
7	UREA -+ 11-48-0		40	30
8	UREA + 11-48-0		60	30
9	UREA + 11-48-0	60 worked	in	30
10	33.5 - 0-0		60	0
11	33.5-0-0 + 11-48-0		20D	20
12	33.5-0-0 + 11-48-0		40D	20
13	UREA PHOSPHATE	:	20D	20
14	UREA PHOSPHATE		40D	20
15	UREA + 11-48-0 + FILLER	:	20D	20
16	UREA + 11-48-0 + FILLER		40D	20
17	33.5-0-0 + 11-48-0	2	20D	30
18	33.5-0-0 + 11-48-0		30D	30
19	33.5-0-0 + 11-48-0	j	40D	30

Note:- D - Drilled in

TABLE 7

INORGANIC-N IN SPRING AND AUTUMN SOIL SAMPLES

	SAMPLE	S	SPRING AMPLES			AUTUMN SAMPLES	- <u></u>	
SOIL TYPE	DEPTH in inches	NH4-N lbs/acre	NO ₃ -N lbs/acre	total lbs/acre	NH4-N lbs/acre	NO3-N lbs/acre	total lbs/acr	е
WELLWOOD	0-6 6-12 12-24 24-36 36-48	12.2 2.4 0.0 2.4 0.0	1.9 6.3 13.1 6.7 3.2	13.1 8.7 13.1 9.1 3.2	4.0 0.0 0.0 0.0 0.0	4.8 2.8 2.0 1.6 0.8	8.8 2.8 2.0 1.6 0.8	
LAKELAND	0-6 6-12 12-24 24-36 36-48	10.0 4.8 3.2 1.6 4.2	9.0 6.6 4.3 2.9 2.4	19.0 11.4 7.5 4.5 6.6	3.8 2.8 1.6 1.6 12.4	10.4 4.8 2.0 1.6 2.0	14.2 7.6 3.6 3.2 14.4	
ALT O NA	0-6 6-12 12-24 24-36 36-48	34.8 19.0 16.8 13.2 8.8	7.4 7.3 19.6 14.4 15.0	43.2 26.3 36.4 27.6 23.8	7.2 4.0 4.8 10.4 3.6	9.8 4.2 5.2 4.8 24.8	17.0 8.2 10.0 15.2 28.4	
A IMA SI PPI	0-6 6-12 12-24 24-36 36-48	3.6 1.4 0.0 2.4 0.0	4.3 1.8 2.8 2.8 3.8	7.9 3.2 2.8 5.2 3.8	0.0 0.0 0.0 0.0 0.0	3.0 0.8 0.0 1.6 1.6	3.0 0.8 0.0 1.6 1.6	











TABLE 8

CORRELATIONS BETWEEN YIELD AND N-UPTAKE AND

 $\text{NH}_{4}\text{-}\text{N}\text{, NO}_{3}\text{-}\text{N}\text{, TOTAL INORGANIC-N AND N-VALUES}$

	······································	
	YIELD	N-UPTAKE
YIELD	1.000	0.743
N-UPTAKE	0.743	1.000
NH4-N 0-48"	0.747	0.750
NH4-N 0-24"	0.748	0.748
NO ₃ -N 0-48"	0.732	0.716
N03-N 0-24"	0.729	0.701
TOTAL INORGN	0.745	0.740
N VALUES	0.580	0.671

Note:- No value was significant above the 10% level.

GRAIN AND STRAW YIELDS FROM FIELD TRIALS

TABLE 9

(FERTILIZER BROADCAST)

lb/acre STRAW 982 1166 1525 2232 2885 2028 2762 2778 2662 2303 ALMASIPPI bu/acre GRAIN 22.6 20.7 39.6 27.2 48.8 51.5 35.0 48.4 47.2 6.6 43.4 5.4 lb/acre STRAW 2769 3173 3492 3228 3548 3459 4184 3904 3561 3085 ALTONA bu/acre GRAIN 51.1 58.9 **64.3 61.3 61.5 69.7 66.8 60.5 4.2 **62.4 3.6 **52.4 lb/acre STRAW 1871 2376 3039 4110 3251 3974 3362 3773 3798 3767 LAKELAND GRAIN S bu/acre 27.0 31.3 36.8 45.2 55.l 65.8 49.8 51.7 53.8 6.6 7.8 55.4 STRAW lb/acre 1496 172**2** 2112 2811 3070 2393 3311 2914 3452 2684 WELLWOOD bu/acre GRAIN 26.6 32.9 38.3 44.0 56.4 53.9 *47.0 39.1 56.6 *46.7 0.0 10.8 N lbs /acre 0.01** 60W 0.05* 60 0 20 40 90 \sim 8 40 3 33.5-0-0 + 11-48-0 33.5-0-0 + 11-48-0 33.5-0-0 + 11-48-0 33.5-0-0+11-48-0 Urea + 11-48-0 Urea + 11-48-0 Urea + 11-48-0 SOIL TYPE CARRIERS FERTILIZER **11-**48-0 33.5-0-0 L.S.D.

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TABLE 10 GRAIN AND STRAW YIELDS FROM FIELD TRIALS

(FERTILIZER DRILLED IN)

STRAW lb/acre 982 1980 2725 2460 1926 2096 17741797 2511 2782 ALMASIPPI bu/acre GRAIN 31.8 **32.0 20.7 50.7 30.4 29.3 36.2 38.0 **35.0 47.1 STRAW lb/acre 2769 3193 3315 3047 3193 3222 3182 3362 3603 3517 ALTONA bu/acre GRAIN 51.1 59.4 62.6 *55.2 **58.2 *55.8 62.3 61.4 66.1 **51.8 STRAW lb/acre 1871 2892 3488 2617 3050 2599 3262 2496 3017 4069 LAKELAND bu/acre GRAIN 27.0 6.44* 36.9 37.6 51.4 37.2 45.6 44.l 42.9 52.2 lb/acre STRAW 1496 14 2508 2776 1926 2140 2655 2502 2102 2681 2941 WELLWOOD bu/acre GRAIN 26.6 39.3 47.6 46.9 38.4 49.5 40.0 38.7 43.0 43.6 20/20 20/20 40/20 40/20 20/20 40/20 20/30 30/30 40/30 acre P_{2}^{05} lbs/ acre N Lbs/ 0 33.5-0-0 + 11-48-033.5-0-0 + 11-48-0 33.5-0-0 + 11-48-0 33.5-0-0 + 11-48-0 33.5-0-0 + 11-48-0 Urea Phosphate Urea Phosphate + filler + filler Urea + 11-48-0 Urea + 11-48-0 CARRIERS FERTILIZER SOIL TYPE

L.S.D. given in Table 9

TABLE 11 N-UPTAKE OF GRAIN AND STRAW FROM FIELD TRIALS WITH BROADCAST FERTILIZER

(in lbs per acre)



X - T7

0 — тв - Lakeland L 🗆 — Т9 Α — Altona AL — Almasippi





N-UPTAKE OF GRAIN AND STRAW FROM FIELD TRIALS IN WHICH THE FERTILIZER TABLE 12

WAS DRILLED IN WITH THE SEED (in lbs/acre)

SOIL TYPE	N lbs/ acre	M	ELLWOOD			LAKELAN	Q		ALTONA		ALM	IdgISA	
	r2 ^U 5 ^{LDS} /acre	GRAIN	STRAW	TOTAL	GRAIN	STRAW	TOTAL	GRAIN	STRAW	TOTAL	GRAIN	STRAW	TOTAL
	0	18	L	25	21	10	31	51	25	76	17	9	23
33.5-0-0 + 11-48-0	20/20	28	TT	39	28	16	44	64	30	д	25	IO	35
33.5-0-0 + 11-48-0	40/20	37	1.5	52	39	ΤŢ	56	65	59	β	μŢ	14	55
Urea phosphate	20/20	28	σ	37	28	13	41	56	29	85	25	12	37
Urea phosphate	40/20	39	15	54	34	15	49	59	30	89	26	10	36
Urea + 11-48-0 filler	20/20	29	10	39	29	15	11 11	58	29	87	53	IO	e S S
Urea + 11-48-0 filler	40/20	35		116	36	ΤŢ	53	51	32	83 83	28	12	⁴⁰
33.5-0-0+11-48-0	20/30	28	6	37	35	J2	μŢ	65	32	76	29	σ	38
33.5-0-0+11-48-0	30/30	32	12	717	32	15	47	65	32	97	31	14	45
33.5-0-0 + 11-48-0	40/30	36	16	52	40	20	60	69	36	105	38	ЪЦ	52

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PLOT	FERTILIZER	N 1b/		· <u></u>	SOIL		
NO.	TREATMENT	acre	WELLWOOD	LAKELAND	ALTONA	ALMASIPPI	MEAN
1	Check	0	100.0	100.0	100.0	100.0	100.0
2	11-48-0	7	101.1	85.1	100.4	104.2	97.7
5	33 ¹ / ₂ -0-0 + 11-48-0	60	96.9	90.0	102.0	113.5	100.6
8	Urea + 11-48-0	60	104.2	-	93.8	110.4	102.4
9	Urea + 11-48-0	60W	99.3	96.6	92.8	106.4	98.8
11	33늘-0-0 + 11-48-0	20D	101.8	87.4	98.4	101.8	95•9
12	33½-0-0 + 11-48-0	4 OD	95.0	87.4	92.7	102.1	94.3
13	Urea phosphate	20D	90.7	86.4	92.8	90.1*	90.0
14	Urea phosphate	40D	90.7	59.6**	70.8**	40.2**	65.3
15	Urea + 11-48-0 filler	20D	104.2	76.6 *	79.6**	89.1**	87.4
16	Urea +11-48-0 fil le r	40D	86.4*	77.9*	69.3**	58.1 **	72.9
19	$33\frac{1}{2}-0-0+11-48-0$	40D	86.4*	82.2	95.9	101.1	91.4
	L.S.D.	0.05*	12.8	19.3	13.2	7.8	
		0.01**	17.1	26.5	17.4	10.2	

GERMINATION AS INFLUENCED BY FERTILIZER TREATMENT (PERCENT)

D - Drilled in W - Worked in

TABLE 14 GRAIN, STRAW AND TOTAL YIELDS (PER CENT)

TABLE 15

NITROGEN UPTAKE BY BARLEY (PER CENT)

				SOIL		
No.	TREATMENT	NITROGEN lbs/acre	WELLWOOD	LAKELAND	ALTONA	ALMASIPPI
2	11-48-0	7	71.4	85.7	133	42.8
3	$33\frac{1}{2}$ -0-0 + 11-48-0	20	65.2	65.0	105	35.0
4	33 <u>2</u> -0-0 + 11-48-0	40	65.0	52.5	50.0	52.5
5	$33\frac{1}{2}-0-0+11-48-0$	60	6 8. 3	61.7	55.0	58.3
6	$33\frac{1}{2}-0-0 \div 11-48-0$	90	58.9	61.1	34.4	45.6
7	Urea + 11-48-0	40	50.0	65.0	60.0	40.0
8	Urea + 11-48-0	60	68.3	55.0	50.0	55.0
9	Urea + 11-48-0	боw	86.7	66.0	48.3	53.3
10	33 ¹ / ₂ -0-0	60	55.0	53.3	21.7	43.3
11	33 ¹ / ₂ -0-0 + 11-48-0	20D	70.0	65.0	90.0	60.0
12	33 ¹ / ₂ -0-0 + 11-48-0	4 _{OD}	67.5	87.5	45.0	80.0
13	Urea phosphate	20D	60.0	50.0	45.0	70.0
14	Urea phosphate	40D	72.5	45.0	32.5	32.5
15	Urea +11-48-0 + filler	20D	70.0	65.0	55.0	50.0
16	Urea +11-48-0 + filler	40D	52.5	55.0	17.5	32.5
17	33 ¹ / ₂ -0-0 + 11-48-0	20D	60.0	80.0	105	75
18	33 1 -0-0 + 11-48-0	30D	63.3	53.2	70.0	73.3
19	$33\frac{1}{2}$ -0-0 + 11-48-0	40D	67.5	72.5	72.5	72.5

W - Worked in D - Drilled in

CHAPTER VI

Greenhouse Experiment

This experiment was designed to follow the changes in the levels of exchangeable ammonium and nitrate.nitrogen in the soil under an actively growing crop. Evidence has already been presented to show that a marked decrease in both these forms of inorganic-nitrogen in the soil occurs between the spring and the fall. By actually determining the pattern of this decrease, and by comparing it with changes in a noncropped soil, it was hoped to obtain some idea of the relative importance of these two forms of nitrogen.

The four soils from the field trials were chosen for this experiment so that comparisons could be made between the field trials and the greenhouse experiment. Two sources of nitrogen were used, ammonium sulphate and urea, both of which supply inorganic nitrogen in the ammonium form. Ammonium sulphate decomposes in solution with the release of free ammonium. Urea, on the other hand, hydrolysis slowly with the release of the ammonium over a period of several days.

Experimental Procedure

In the fall of 1965 soil samples were collected from the four chosen sites, air dried in the greenhouse, ground and sieved.

2000 grams of air-dried soil were weighed into pots and dipotassium phosphate solution added at the rate of 30 mg.P per pot at about the 2 inch depth. Test treatments were as follows:-

Treatment Code	Number of pots	Nitrogen Source	Crop
Ac	10	(NH4)2SO4	Barley
А	24		None
Bc	10	Urea	Barley
В	24		None
Cc	10	None	Barley
С	24		None

Twelve barley seeds were planted in the indicated pots approximately one half inch below the surface of the soil. Nitrogen source was added as a solution to the surface of the soil at the rate of 50 p.p.m. nitrogen. Sodium sulphate was added prior to planting to treatments Bc, Cc, B and C in amounts such that the level of added sulphate was the same in all pots. All pots were then wetted to their field capacity.

Germination was complete within four days. Four days after complete germination, when the plants were about five inches tall, the number of plants per pot was reduced to six.

The above ground portion of the plants was harvested from one pot in each of treatments Ac, Bc and Cc at the following intervals - 12, 16, 20, 24, 28, 32, 36 and 41 days after germination. The final two sets of pots were harvested 46 days after germination. The soil from each pot was transferred to a plastic bag and retained for analysis.

At the same time soil samples were taken from the incubated pots (treatments A, B and C). To ensure that the sample was representative of the entire depth of the soil and not just the
surface soil, a core sample was taken by using a cyclindrical metal tube. A composite was made of the four samples from each treatment and stored in plastic bags for analysis.

The plant material was cut into small pieces, air-dried and weighed. Total nitrogen determinations were made using the Kjeldahl-Gunning procedure.

Exchangeable ammonium determinations were made on the fresh soil as soon after sampling as possible. Where determinations could not be made immediately samples were stored at 2°C. Sub-samples were oven-dried at 50°C for nitrate and pH determinations.

Development of Browning and Nitrogen Deficiency

At a very early stage in the development of the plants browning was noted on the leaves. To try to determine if this was related in any way to the test treatments, the number of pots with affected plants were recorded at regular intervals. This data is summarized below.

No. of days after germination	Total no. of pots affected	Ratio treatments (NH ₄) ₂ SO ₄ urea control	Ratio soils W:L:AL:AM	Degree
4	one <u>or</u> tr	wo plants slightly	affected.	
7	12	2:7:3	2:2:4:4	mild
11	15	2:10:3	1:3:5:6	fairly
15 ¹	26	3:9:4 5:11:10 2:2:6	7:4:5:10	marked badly mild
20 ²	55	13:17:26	13:10:10:23	
24 ³	64	14:17:32	10:5:7:10	(A and B only)

- 1 Nitrogen deficiency had started to develop on treatment Cc.
- 2 Nitrogen deficiency symptoms had become quite marked on treatment Cc.
- 3 Out of a total of seven remaining pots in each treatment, twenty one pots with no added nitrogen were showing nitrogen deficiency symptoms. Six were affected on the Wellwood and Almasippi soils, five on the Lakeland and four on the Altona soil.

By twenty eight days after germination marked purpling could be seen at the base of the plants growing on the Wellwood soil, treatment B. This effect was not so marked on treatment A.

From the overall picture browning appears to have been more prevalent on those soils treated with usea than on the ammonium sulphate treated soils. By twenty four days after germination browning symptoms could no longer be distinguished as nitrogen deficiency had become fairly widespread.

Results and Discussion

Results of determinations on soils and plant material are given in Tables 17 - 21 and the Appendix. In the aid of clarity, the discussion has been split into the following sections.

- 1. Exchangeable ammonium nitrogen in the soil.
- 2. Nitrate-nitrogen in the soil.
- 3. Soil pH
- 4. Plant Material Yield and Nitrogen Uptake.
- 5. General.

1. Exchangeable Ammonium Nitrogen in the Soil

From Tables 17 and 18 it can be seen that in all treatments, except A and Ac on the Wellwood soil, the added nitrogen did not persist in the ammonium form. Similar results were obtained from both cropped and incubated soils. With the exception of the Wellwood soil, there was no difference between the two nitrogen sources. By the end of the forty six days the level of exchangeable ammonium had been reduced to less than 2 p.p.m. in all treatments with all four soils.

Persistence of the ammonium ion occured in the Wellwood soil where the added nitrogen was ammonium sulphate. Fireman and his coworkers (35) found that the ammonium ion persists in acid soils low in organic matter and phosphate. Also Pillsbury (76) has shown that high concentrations of ammonium sulphate can cause acidity, thus slowing down the conversion of ammonium to nitrate.

In this experiment the degree of acidity was not excessive nor was the level of added ammonium sulphate very high. However, the method of addition of the fertilizer to the soil would have created localised areas of high fertilizer concentration. In these areas conditions would be such that retardation of nitrification would occur. This is a possible explanation for the fairly high level of exchangeable ammonium found to be present in the Wellwood soil sixteen days after the addition of the ammonium sulphate.

To confirm that ammonium sulphate produced a lowering of pH, pH determinations were made on the first set of soil samples. The original pH and pH values sixteen days after the addition of the fertilizers are given below.

SOIL	INITIAL	AFTI	ER 16 DA	YS
	CONTROL	$(\mathrm{NH}_4)_2 \mathrm{SO}_4$	UREA	CONTROL
Wellwood	6.6	6.5	6.9	7.2
Lakeland	8.0	7.8	7.9	8.1
Altona	7.4	7.2	7.2	7.4
Almasippi	7.8	7.6	7.8	-

Comparison of the pH of the control soil with the pH of the ammonium sulphate treated soil shows that, with the Wellwood soil, the addition of ammonium sulphate has lowered the pH by 0.7 units. With the three alkaline soils, only a slight lowering of pH has occured. These figures confirm that addition of ammonium sulphate to a soil produces a lowering of the soil pH. Further discussion of the changes in pH during this experiment are given in section five.

The level of exchangeable ammonium twelve days after germination was considerably higher in the incubated soil than in the cropped soil. Two possible explanations exist. Firstly, in the cropped soil the nitrate nitrogen was being removed from the system by the plants. This reduction in the level of nitrate nitrogen may have stimulated the conversion of ammonium to nitrate. Microbial activity is known to be greater in the rhizosphere area of a cropped soil than in a fallow soil. On the other hand, direct utilization of the ammonium nitrogen by the plants may also have occured. Jenny <u>et al.</u>(47) using excised plant roots, found that ammonium absorbed by clays could be used by plants. Availability of exchangeably absorbed ammonium to

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TREATMENT

a variety of plants grown on exchange resins, soils and peats partially saturated with ammonium has been reported by Russian (75) workers. Sufficient evidence exists to indicate that plants can utilize exchangeable ammonium under certain conditions. Some direct utilization of ammonium may have occured here during the early stages of plant growth.

Figure 8 represents the changes in exchangeable ammonium with time. Twenty eight days after the addition of the ammonium sulphate, the level of exchangeable ammonium had been reduced in both the incubated and cropped soils to less than 4 p.p.m. The time taken for the ammonium ion to be removed from the system appeared to be the same whether or not a crop was grown on the soil. The graph shows that a sudden marked decrease in the level of exchangeable ammonium in the incubated soil occured between sampling dates two and three. This did not correspond to any marked increase in nitrate nitrogen. However, an increase in nitrate nitrogen did occur several days hater, between sampling dates four and five. Broadbent and Tyler (18) also noted that several days elapsed between the disappearance of the ammonium nitrogen and the appearance of the nitrate nitrogen.

2. Nitrate-Nitrogen in the Soil

From Table 19 it can be seen that for all three treatments on the cropped soils the nitrate nitrogen has been reduced to less than 4 p.p.m. by the end of the growing period. With the exception of the Altona soil, the nitrate nitrogen values are higher in the urea treated soils than the ammonium sulphate treated soils up to 36 days after germination. The graphs of nitrate-nitrogen against time show this more clearly (Figures 9 and 10). With the Altona soil the levels are

6.9

the same, within the limits of experimental error.

In all cases the level of nitrate nitrogen at the first sampling date lay between 40 and 50 p.p.m. for the urea treated soils. With the ammonium sulphate treatment, only the Altona soil gave this type of value. The Wellwood, Lakeland and Almasippi soils showed levels of 37, 29 and 24 p.p.m. respectively.

In the control soils, incubation for a period of 46 days in the greenhouse produced a marked increase in nitrate nitrogen levels for all four soils. The Altona soil increased from 5 to 45 p.p.m., the Lakeland from 9 to 36 p.p.m., the Wellwood from 1 to 23 p.p.m. and the Almasippi from 1 to 20 p.p.m. Table 20

On comparison of the incubated soils to which fertilizers had been added, the nitrate nitrogen levels are seen to be considerably higher in the soils treated with urea than in those treated with ammonium sulphate. This difference may be due to nitrogen loss.

Fifty parts per million nitrogen was added to each soil initially. If allowance is made for the natural increase in nitrate-nitrogen due to incubation and the original amounts of nitrate nitrogen in the soils, the amounts of nitrogen remaining in the soils after 41 and 46 days incubation are as follows:

 $m D Tr \Lambda m \Lambda Tr \Lambda m$

SOIL

	(NH	4)2804	UR	EA
	*p.p.m.	per cent	*p.p.m	per cent
WELLWOOD	45.8	91.6	52.8	105.6
LAKELAND	33.6	67.2	51.8	103.6
ALTONA	38.3	76.6	47.8	95.6
ALMASIPPI	30.5	61.0	51.4	102.8

These values show that, with the three soils of alkaline pH, a marked loss of inorganic nitrogen occured from the ammonium sulphate treatment, but little loss from the urea treatment. With the Wellwood soil, the recovery from the urea treatment was only slightly higher than the recovery from the ammonium sulphate treatment.

This loss of nitrogen from the alkaline soils was probably due to ammonia volatilization. Conditions which tend to cause volatilization of ammonia are surface application of the fertilizer (51,66) on soils of pH greater than seven (49,59,66,93). Both these conditions were present in this experiment. These results, in fact, agree well with the findings of Martin and Chapman (59) that 1 to 27 per cent of the nitrogen is lost from ammonium sulphate; except in poorly buffered soils losses from urea are quite small. With the Wellwood soil, loss of nitrogen in some form other than ammonia may have occured.

The greater than 100 per cent recovery with three of the urea treated soils can be attributed to stimulation of microbial activity by the added fertilizer. Broadbent <u>et al</u>.(19) obtained similar results at the 50 p.p.m. level of fertilizer application.

3. Soil pH

Incubation of the control soil, to which potassium dihydrogen phosphate and sodium sulphate had been added, led to a marked increase in pH with the Wellwood soil. With the three alkaline soils, there was little change in pH (Table 21).

^{*}Based on the average of the nitrate nitrogen values after 41 and 46 days incubation.

In the soils to which ammonium sulphate and urea had been added only a slight lowering of pH was noted with the three alkaline soils. However, with the acid Wellwood soil, incubation with ammonium sulphate resulted in an average pH *0.65 units lower than the control, and incubation with urea an average pH *0.32 units lower than the control. By the final sampling date the difference in pH between the three treatments had decreased considerably. At this point pH values were 7.05 for treatment A, 7.07 for treatment B and 7.30 for treatment C.

This lowering of pH as a result of the addition of ammoniacal fertilizers to soil has been attributed to the formation of nitrous and nitric acids (17). Broadbent <u>et al</u>.(17) found that changes were most marked with poorly buffered acid soils, whilst in calcareous soils little change occured. Similar results were obtained in this experiment.

The difference in pH between treatments A and B can be explained from a consideration of the intermediate products of the nitrification of urea. One of these intermediate products is ammonium carbonate, which would tend to increase the soil pH. This will partially counteract the lowering of pH caused by the nitrification of the ammonium.

Serious inhibition of nitrification is thought to occur when the pH is less than 5.1 (5). In this experiment the lowest pH recorded was 6.52, which would not be expected to greatly reduce the rate of

Based on first seven values.

nitrification. The persistence of the ammonium ion, however, can still be attributed to the lowering of the pH if allowance is made for the fact that, in localised zones, much greater pH changes may have occured. Soils in the vicinity of added fertilizer may become quite acid as a result of nitrification even though the main body of the soil is unaffected.

4. Plant Material - Yield and Nitrogen Uptake

Dry matter yields, on a per cent basis, are shown in Table 22, and figures 11 to 14 show actual yields against time. From these graphs the urea treated soils are seen to give higher barley yields than the ammonium sulphate treated soils at nearly every stage of development, with the exception of the Altona soil. This difference in yield becomes more marked at later stages of development. With the Altona soil, treatment B yielded slightly higher at the intermediate stages of development, but the difference decreased as the plants matured.

The average per cent yield over the entire system for treatments A and B are 57.2 and 50.6 respectively. For all four soils the urea treatment has given a higher average yield than the ammonium sulphate treatment. Greatest response to added nitrogen occured on the Wellwood soil, least on the Altona.

The average nitrogen uptakes by the barley for treatments A, B and C are 76, 110 and 27 mg. nitrogen per pot respectively. To determine whether the higher nitrogen uptake from the urea treated pots was entirely due to the greater amount of available nitrogen or whether, in fact, the actual uptake was greater from the urea than the ammonium sulphate, the percentages of available nitrogen utilized were calculated.

For this purpose it was assumed that all the nitrate nitrogen was available to the plants.

Per cent utilized	=	N content of p	lants x 100
		Nitrate content	Nitrate content
		incubated pots -	cropped soil
		(average)	(final)

The values obtained are given in Table 23. These figures show that the percent utilized from the urea was greater than the percent utilized from the ammonium sulphate for all four soils.

5. General

The initial aim of this experiment was to determine which was the main portion of the soil inorganic nitrogen being used by the plants. Early in the experiment it was apparent that the ammonium ion did not persist in alkaline soils for any appreciable length of time. Plants growing on these soils would therefore be expected to absorb their nitrogen as nitrate nitrogen. On the acid Wellwood soil, the ammonium ion only persisted where ammonium sulphate was added. When the ammonium ion did persist, the plants had two possible sources of nitrogen, nitrate and exchangeable ammonium.

The nitrogen uptake figures Appendix IV for the plant material show that a sharp rise in nitrogen content occurred between days sixteen and twenty. At the same time there was a marked drop in nitrate nitrogen in the soil. When the decrease in soil nitrate nitrogen is plotted against the increase in nitrogen in the plant material, a linear relationship is obtained. However, the point for the Wellwood soil, treatment A, does not fall on this line. When the decrease in ammonium nitrogen is added to the decrease in nitrate nitrogen, a much closer fit is obtained (Figure 15).

Statistical analysis run on these figures show that the correlation between nitrogen uptake by the plant and decrease in soil inorganic nitrogen is significant at the one percent level.

These results strongly suggests that the main form of nitrogen taken up by the plants was nitrate nitrogen, except where there was an appreciable proportion of exchangeable ammonium present. Where exchangeable ammonium was present part of the nitrogen may have been absorbed from this source. With soils in which an appreciable portion of the inorganic nitrogen is in the exchangeable ammonium form, this nitrogen should be taken into consideration when determinations of available nitrogen are being made.

Conclusion

From the results of this experiment the following conclusions can be drawn.

(1) The occurrence of "browning" on barley plants grown on soils which had recently been cropped to barley was more common where urea was used as nitrogen source than when ammonium sulphate was used.

(2) Exchangeable ammonium nitrogen does not persist for any appreciable length of time in alkaline soils under good growing conditions.

(3) Exchangeable ammonium nitrogen persists in acid soils where the pH is very low naturally <u>or</u> is reduced to a fairly low level by added fertilizers.

(4) A short time lag exists between the disappearance of the ammonium ion and the appearance of nitrate ion.

(5) Loss of nitrogen from surface application of ammonium sulphate occurs with soils of high pH, presumably due to the volatilization of ammonia. This does not happen when a solution of urea is applied to the soil surface.

(6) On acid soils ammonium sulphate produces a marked lowering of pH; with urea only a slight lowering of pH occurs. On alkaline soils there is little change with either nitrogen source.

(7) In this experiment higher yields and nitrogen uptakes were obtained from unea than from ammonium sulphate. For the alkaline soils, this may be due to the lower amount of available nitrogen, as a result of the volatile loss of ammonia. With the acid soil, the influence of the two carriers on the soil pH may have been the controlling factor.

(8) Only part of the extractable nitrate nitrogen in the soil can be readily utilized by the above ground portion of the plants, the proportion used being strongly dependent on the nature of the soil itself.

(9) Where exchangeable ammonium is present in the soil it appears to be available to the plants when the demand for nitrogen is at its highest. In soils containing a fairly high level of exchangeable ammonium, some allowance must be made for this nitrogen when making determinations of available nitrogen.

TABLE 16 SOIL CHARACTERISTICS

P.P.M. NH4 – N 3.0 3.1 3.4 2.4 P.P.M. AVAIL. NO3-N 0.96 8.99 5.19 1.44 K P.P.M. 236 300 407 22 P.P.M. O.M. AVAIL 14.58 4.86 7.99 5.29 5.8 8.0 6.1 50 8 caco₃ Equiv. 0.36 0.91 28.5 Nil 8.0 Ηđ 6.6 7.8 7.4 VERY FINE SANDY CLAY LOAM TEXTURE SILTY CLAY LOAM LOAMY FINE SAND ALMASTPPI SOIL TYPE LAKELAND WELLWOOD ALTONA FARMER HUMESTON MOELLER WIEBE MURTA

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EXCHANGEABLE ANMONIUM IN POTS CROPPED WITH BARLEY (p.p.m.) TABLE 17

trace trace trace trace trace trace trace trace 1.2 ч. Ч 7.5 1.0 46 Ц trace trace TIIV trace trace trace trace trace 7†] 2.0 0.0 0.0 0.0 0.0 TIΛ 1.2 ч. Г 1.2 4.0 1.6 1.6 1.6 1.6 1.6 2.8 1.2 1.2 36 trace 32 а. С 4.8 4.0 4.0 2.4 3.2 0.0 2.4 0.0 1.6 2.4 ΓΛ trace trace trace 1.6 28 ч. Ч 1.2 2.4 1.2 0.0 2.4 0.0 2.4 \triangleright trace trace trace trace trace trace 1.6 0.0 0.0 5 0.0 0.0 0.0 PI 0.0 trace TIT 0.0 2.0 0.0 20 10.2 3.6 2.0 0.0 0.0 0.0 0.0 16 trace 17.6 2.0 0.0 0.0 1.6 Ц 0.0 2.4 0.0 2.0 ь. С 0.0 trace 3.6 Ч 5.1 2.0 3.6 26.7 4.3 5.1 4.0 3.6 5.00 2.8 н SOURCE OF ADDED N (NH4)2SO4 $(\mathrm{NH}_{\mathrm{h}})_{2}\mathrm{SO}_{\mathrm{h}}$ (NH4)2SO4 (NH4)2SO4 NUMBER OF DAYS AFTER UREA NONE UREA NONE UREA NONE UREA NONE GERMINATION ALMASIPPI **WELLWOOD** LAKELAND ALTONA SOIL

TABLE 18 EXCHANGEABLE AMMONIUM IN INCUBATED POTS (p.p.m.)

trace trace trace trace 0.0 0.0 1.6 0.0 0.0 0.0 0.0 ч. Ч 46 trace trace trace trace trace trace trace 0.0 0.0 1.6 0.0 0.0 41 4 trace trace 1.6 1.6 1.6 1.6 1.6 1.6 1.2 1.2 Ч.2 1.2 36 trace 1.6 2.0 а. С 3.6 2.0 1:6 0.0 0.E 0.0 6.4 2.4 32 trace trace 1.6 1.2 4.0 1.6 1.2 1.2 0.0 1.2 0.0 1.6 28 0.0 trace trace 4.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 24 14.8 0.0 0.0 2.0 2.0 0.0 2.0 0.0 0.0 5.2 0.0 2.4 20 trace 4.8 4.8 1.6 4.8 1.6 0.0 0.0 0.0 42.0 0.0 0.0 16 4.0 3,8 4.2 5.0 53.3 6.0 4.8 3.6 0.0 7.6 3.6 പ്പ trace SOURCE OF ADDED N. (NH4)2SO4 (NH4)2SO4 (NH4)2SO4 $(\mathrm{NH}_{\mathrm{l}})_{2}\mathrm{SO}_{\mathrm{l}}$ NUMBER OF DAYS AFTER NONE NONE NONE UREA UREA UREA UREA NONE GERMINATION ALMASIPPI LAKELAND WELLWOOD ALTONA SOIL



TABLE 19 NITRATE-NITROGEN IN POTS CROPPED WITH BARLEY (p.p.m.)

8.3 م.3 2.2 1.5 1.8 2.0 1.8 2.8 ی. 8 0 0 1.8 а. В 1.4 46 Ц VIII 4 I 3.6 7.3 5.0 3.5 2.6 د.ع 1.9 1.3 1.8 9.5 1.0 2.1 2.9 4.9 3.6 2.6 а. С 3.1 5.0 3.7 2.2 10.2 3.8 1.3 36 LIV 5.4 6.9 5.2 1.9 6.8 4.2 6.8 4.3 5.3 3.5 6.0 3.5 32 TΛ 9.9 3.6 8.6 6.2 6.3 5.8 3.5 5.3 1.3 4.3 28 14.7 11.7 \geq 25.0 4.9 9.6 11.9 4.0 14.0 9.1 20.2 2.7 6.1 16.3 Σ 5.7 57 26.1 23.9 39.2 5.4 5.6 18.2 18.0 13.2 2.7 17.3 4.7 8.1 III 20 6.9 29.6 36.8 46.6 с. 9 6.8 22.8 6.6 17.3 34.3 50.4 46.7 Ъб II 9.4 6.6 4.0 43.8 35.6 39.4 24.2 41.0 43.3 Ц 2.92 47.7 10.7 н $(\mathrm{NH}_{4})_{2}\mathrm{SO}_{4}$ (NH4)2SO4 SOURCE OF ADDED N. $(\mathrm{NH}_{l_{4}})_{2}\mathrm{SO}_{l_{4}}$ $(\mathrm{NH}_{\mathrm{h}})_{2}\mathrm{SO}_{\mathrm{h}}$ NUMBER OF DAYS AFTER NONE NONE NONE UREA UREA UREA UREA NONE GERMINATION ALMASIPPI **WELLWOOD** LAKELAND SOIL ALTONA

TABLE 20 NITRATE NITROGEN IN INCUBATED POTS (p.p.m.)

89.6 65.8 35.5 74.2 96.0 23.1 7.97 75.2 81.0 45.2 60.7 20.3 46 Ц TIIV 73.1 85.8 36.3 55.9 23.1 40.8 90.9 63.7 63.7 20.3 104.3 44.4 41 91.9 29.0 97.0 66.0 21.8 69.1 45.7 56.0 145.3 106.7 40.9 14.7 36 TIΛ 111.3 76.5 119.1 62.0 168.7 32.5 65.0 7.06 21.3 19.3 93.2 37.1 32 TΛ 115.8 124.0 83.3 28.2 18.5 54.6 81.0 20.6 86.9 67.1 88.1 36.3 28 ⊳ 35.6 19.3 62.0 60.2 15.2 81.0 85.6 76.5 22.6 78.7 60.2 69.1 57 Σ 86.6 35.6 85.6 90.7 21.3 68.4 17.0 41.8 80.9 15.8 133.1 20 83.3 III 22.0 101.5 116.3 44.5 83.2 95.7 77.5 101.5 35.6 14.5 14.1 98.0 Ч Т ΤI 58.0 129.9 18.2 114.O 132.2 15.6 66.1 66.1 47.3 119.7 27.4 12 н 1 SOURCE OF ADDED N (NH4)2SO4 $(\mathrm{NH}_{\mathrm{l}})_{2}\mathrm{SO}_{\mathrm{l}}$ $(\mathrm{NH}_{\mathrm{l}_{\mathrm{l}}})_{2}\mathrm{SO}_{\mathrm{l}_{\mathrm{l}}}$ host (IHI) NUMBER OF DAYS AFTER NONE NONE UREA UREA NONE UREA NONE UREA GERMINATION ALMASIPPI LAKELAND WELLWOOD SOIL ALTONA





SOIL	NUMBER OF DAYS AFTER GERMINATION	А	В	С
LAKELAND	0	8.0	8.0	8.0
	12	7.84	7.85	8.07
	28	7.80	7.90	8.00
	46	7.83	7.78	7.86
ALTONA	0	7.40	7.40	7.40
	12	7.15	7.18	7.42
	28	7.20	7.25	7.54
	46	7.25	7.26	7.38
ALMASIPPI	0	7.80	7.80	7.80
	12	7.63	7.79	-
	28	7.57	7.64	7.80
	46	7.64	7.73	7.80
WELLWOOD	0 12 16 20 24 28 32 36 41 46	6.60 6.52 6.70 6.90 6.85 6.60 6.60 6.60 7.05 7.05	6.60 6.90 7.15 7.20 7.10 7.00 7.00 7.00 7.20 7.07	6.60 7.22 7.40 7.42 7.50 7.32 7.35 7.35 7.35 7.32 7.30

SOIL pH AT SEVERAL SAMPLING DATES

TABLE 22 BARLEY YIELDS ON A PERCENT BASIS

61.8 40.6 46.2 75.3 69.1 56.7 36.1 45.4 Αν. 25.6 51.8 52.8 25.6 17.6 32.7 49.0 40.4 46 Ц 70.8 30.8 24.9 26.1 66.8 50.0 48.9 31.0 IIIV 41 54.8 60.9 65.6 50.9 35.9 25.5 35.1 31.3 TIΛ 36 32.0 30.0 61.5 53.0 50.5 51.0 49.0 43.5 IΛ 32 29.8 68.5 36.2 35.5 50.7 X 100 27.6 58.2 62.4 28 ⊳ CONTROL YIELD TREATMENT YIELD 59.8 37.9 81.9 57.6 53.0 52.0 60.2 36.4 ΓΛ 5 67.6 42.0 29.9 63.6 44.2 54.0 95.4 60.4 III 20 80.9 96.1 81.3 75.4 П 57.5 80.0 70.1 62.7 16 HI PERCENT YIELD 6.09 57.0 55.0 124.4 108.7 77.1 72.5 72.7 5 н (NH4)2SO4 (NH4)2SO4 SOURCE OF ADDED N. $(\mathrm{NH}_{\mathrm{tl}})_{2}\mathrm{SO}_{\mathrm{tl}}$ $(\mathrm{NH}_{4})_{2}\mathrm{SO}_{4}$ NUMBER OF DAYS AFTER GERMINATION UREA UREA UREA UREA ALMASIPPI LAKELAND WELLWOOD SOIL ALTONA

		NITRATE ¹ LOSS FROM THE SOLL	NITROGEN ² IN ABOVE GROUND PORTION	PERCENT NITROGEN UTILIZED BY PLANTS
SOIL		Mg	PLANTS (Mg)	ACTUAL
LAKELAND	A	132	68	51.5
	В	178	106.9	60.1
	С	48.2	30.2	62.7
WELLWOOD	А	174	72.7	41.8
	В	183	110.7	55.0
	С	35.2	17.3	49.1
ALMASIPPI	А	100	57.4	57.4
	В	138.2	95.4	69.0
	С	28.8	16.7	58.0
ALTONA	A	190	106.6	56.1
	В	201.2	128.4	63.8
	C	71.6	43.5	60.8

NITROGEN UTILIZATION BY PLANTS (PER CENT)

Note: 1 Nitrate loss from soil = nitrate content incubated pots (average)

- nitrate content cropped soil (Final)

2 Based on final harvest

1.5



Figure II. Increase in Barley Yields With Time - Lakeland Soil.











	1)					
SOIL	LA	KELAN	ים	WE	LLWOO	D	I AL	ASIPI	PI	i 1. '	ALTON	A
TREATMENT	A	B	<u>C</u> 1	A	в	С.	I. I.A.	B	С	, A	в	С
INCREASE IN NITROGEN	29.4	128.0	1 1	21.2	46.1	10.9	1 15.6	1 1 42.5	1 1 12.3	 37.1	 17.2	1
DECREASE IN NITROGEN (NO3-N) NH4-N	24.6	21.4	2.41	9.21 14.81 14.81	57.2	13.8 1 1	1 1 18.4 1 1	1 42.2 1 1	1 10-4 1	38.8	 15.0 	 3.0

CHAPTER VII

Incubation Experiment

Exchangeable ammonium has been shown to be rapidly converted in an alkaline soil but to persist in an acid soil. This experiment was set up to follow the changes in exchangeable ammonium, nitrate nitrogen and nitrite nitrogen in these two soil types and to compare their rates of interconversion over a short period of time. Two of the four soils used in the greenhouse experiment were chosen, namely the Wellwood and Lakeland soils.

Experimental Procedure

Samples of the two soils were air-dried in the greenhouse and ground to pass a 2 mm. sieve. The main characteristics of the soils are given in Table 16 on page 77.

Fifty gram portions of soil were weighed into 500 ml bottles and 50 p.p.m. nitrogen added, in solution, to the surface of the soil. Similar amounts of phosphate and potassium were added as in the greenhouse experiment and the moisture level adjusted to 25 per cent by weight. The same two nitrogen sources, urea and ammonium sulphate, were used and a control with no added nitrogen was also included. Duplicate samples were prepared, sealed and placed in an incubator at 20°C.

The jars were opened after four and eight days and the air in each jar completely exchanged by using a squeeze bulb. The lid of each jar was moistened with a fine mist at the time of aeration to maintain the high humidity inside the jars.

Duplicate samples were taken after 0, 2, 4, 8 and 12 days of incubation. Sufficient jars were prepared to allow one jar for every set of determinations, each jar being removed from the incubator after sampling. The following determinations were made on a 2 NKCl extract ammonium, nitrite and nitrate nitrogen using the steam distillation procedure described by Bremner (13). pH was determined as previously indicated.

Results and Discussion

The results for the inorganic nitrogen and pH determinations on the two soils are given in Tables 24 and 25. In both control soils incubation has increased the total inorganic nitrogen and decreased the exchangeable ammonium. Exchangeable ammonium does not persist in the soil when moisture and temperature conditions are suited to microbial activity.

Breakdown of urea was extremely rapid in both soils. As the procedure used for extraction and determination of the ammonium does not decompose the urea (13) , the slightly higher exchangeable ammonium values in these soils compared with the control soils indicates that, even during the short period between the addition of the urea and the extraction with 2NKC1, some breakdown had occured. Within two days all the urea was converted to ammonium, although little nitrate had been produced. These results agree with the work of Broadbent <u>et al.(17)</u> and Low and Piper (55) who found that, under optimum moisture and temperature conditions, urea was hydrolysed within two days.

Under the conditions of temperature and moisture used, the conversion of exchangeable ammonium to nitrate nitrogen appears to have

been quantitative in the acid soil (Table 24). In the calcareous soil, however, considerable loss of inorganic nitrogen occured. Slightly higher nitrate production than ammonium decrease in the ammonium sulphate treated Wellwood soil during the first two days of incubation can be attributed to microbial production from the organic matter. The effect was not so clearly seen on the urea treated soil because of the ammonium production from the urea itself. However, the quantity of ammonium produced was in excess of the amount of nitrogen added as urea. Both fertilizers initially stimulated microbial production of ammonium, urea having a much greater effect than ammonium sulphate. With no process for the removal of the nitrogen, the production of additional inorganic nitrogen from the organic matter was inhibited after two days. A similar reaction was obtained with the calcareous soil.

Removal of exchangeable ammonium produced from both carriers was more rapid in the Lakeland than in the Wellwood soil. A marked lag period occured with the Wellwood soil before ammonium conversion reached an appreciable rate. Under the conditions of the experiment, the time lag between the ammonium disappearance and nitrate appearance was quite small. Broadbent and Tyler (18) noted an initial four day lag period before ammonium disappearance became rapid. As in this experiment, the production of nitrate nitrogen began to increase rapidly at this same time.

With the Wellwood soil, incubation caused a slight increase in pH initially, then the value dropped back to its original level. The urea treatment also produced an increase in pH on the Wellwood soil, but this gradually dropped to the same level as the ammonium sulphate

treatment as nitrate nitrogen was produced. With the Lakeland soil, the pH dropped off in a similar manner with both carriers. The rapid rate of conversion of the ammonium from the urea, and the presence of nitrite nitrogen in the Lakeland soil may explain this effect.

Accumulation of nitrite nitrogen occured on the Lakeland soil with both carriers, but not on the Wellwood soil. Nitrite persistence is generally considered to occur in neutral to alkaline soils, where a considerable concentration of ammonium ions exist (24). The highly calcareous nature of the Lakeland soil would further encourage nitrite nitrogen accumulation. As incubation conditions were good, this nitrite nitrogen had nearly all been removed by the end of the twelve day incubation period. However, it did not reappear in the system as nitrate nitrogen. Broadbent and Tyler noted that under optimum incubation conditions, nitrite nitrogen did not persist for any appreciable length of time. Nitrite nitrogen was considerably greater in the urea treated soil than in the ammonium sulphate treated soil.

By the end of the twelve day incubation period, all the ammonium nitrogen had been nitrified in the Lakeland soil. In the Wellwood soil nitrification was slower and some exchangeable ammonium was still present twelve days after the addition of the fertilizers.

Conclusion

The results of this experiment can be summarized as follows.

(1) Urea did not persist in the soil and was completely converted to ammonium within two days.

(2) Oxidation of exchangeable ammonium was more rapid in the calcareous than in the acid soil.

(3) In the acid soil the total inorganic nitrogen reached a maximum within two to four days and did not change markedly during the rest of the experiment. Decrease in exchangeable ammonium was balanced by an increase in nitrate nitrogen.

(4) In the calcareous soil the total inorganic nitrogen decreased with time. The most marked decreased occured after the appearance of nitrite nitrogen. The urea treatment produced a greater concentration of nitrite nitrogen than the ammonium sulphate treatment, but this may have been due to the higher initial level of ammonium.

(5) On both soils, ammonium sulphate and urea produced a decrease in pH in comparison with the control soil. The decrease was greater with the ammonium sulphate than with the urea.

(6) An accumulation of nitrite nitrogen occured on the calcareous soil. By the end of the twelve day incubation period, however, this had almost completely disappeared again. This nitrogen did not reappear in the system as nitrate nitrogen.

INORGANIC NITROGEN AND pH VALUES AFTER VARIOUS INCUBATION PERIODS

WELLWOOD SOIL

INCUBATION PERIOD IN DAYS	TREATMENT	EXCHANGEABLE NH ₄ -N p.p.m.	NO3-N p.p.m.	TOTAL INORGANIC NITROGEN	рH
0	CONTROL	7.8	3.0	10.8	6.66
2		7.8	7.8	15.6	6.80
4		7.4	11.8	19.2	6.66
8		3.6	17.2	20.6	6.63
12		1.2	20.4	21.6	6.71
0	(NH ₄) ₂ SO ₄ (50 ppm)	52.4	2.4	54.8	6.58
2		50.4	10.4	60.8	6.61
4		46.4	12.8	59.2	6.54
8		35.4	22.6	58.0	6.48
12		8.8	51.6	60.4	6.33
0	UREA (50 ppm)	14.8	1.8	16.6	6.64
2		70.0	7.2	77.2	6.89
24		66.2	13.5	79.7	6.87
8		45.4	32.8	78.2	6.55
12		17.2	58.0	75.2	6.38

Note: Only a trace of NO_2 -N was ever detected.

INORGANIC NITROGEN AND pH VALUES AFTER VARIOUS INCUBATION PERIODS

LAKELAND SC

INCUBATION PERIOD IN DAYS	TREATMENT	EXCHANGEABLE NH4-N p.p.m.	NO3-N p.p.m.	NO2 -N p.p.m.	TOTAL p.p.m.	рH
0	CONTROL	6.4	5.4	trace	11.8	8.2
2		4.6	17.0	-	21.6	8.14
4		4.2	15.0	-	19.2	8.09
8		0.6	20.4	-	21.0	8.12
12		0.6	21.2	trace	21.8	8.13
0	(NH4)2SO4 (50 ppm)	56.0	5.6		61.6	8.10
2		48.8	13.0	-	61.8	7.98
4		30.8	26.2	2.8	59.8	7.85
8		5.4	38.8	9.6	53.8	7.83
12		0.0	38.9	-	38.9	7.85
0	UREA (50 ppm)	21.0	7.6	-	28.6	8.14
2		61.8	14.4	7.0	83.2	8.07
4		40.8	20.0	7.1	67.9	7.93
8		12.4	33.1	37.3	82.8	7.83
12		0.0	51.2	3.9	55.1	7.86

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TREATMEN	Г	(NH		UREA			
	TIME DIFFER- ENCE	NH4-N DECREASE р.р.т.	NO3-N INCREASE p.p.m.	NO2-N CHANGE p.p.m.	NH4-N DECREASE p.p.m.	NO ₃ -N INCREASE p.p.m.	NO ₂ -N CHANGE p.p.m.
WELLWOOD	0-2	2.4	8.0			5.4	
	2-4	4.0	2.4	-	3.8	6.3	
	4-8	11.0	9.8	-	20.8	19.3	-
	8-12	26.6	29.0		28.2	25.2	-
TAL	2-12	41.6	41.2	0	52.8	50.8	-
AKELAND	0-2	7.2	7.4			6.8	7.0
	2-4	18.0	13.2	_	21.0	6.6	0.1
	4-8	25.4	12.6	2.8	28.4	13.1	30.2
	8-12	5.4	0.1	6.8	12.4	18.1	-33.4
OTAL	2-12	48.8	25.9	9.6	61.8	37.8	- 3.1
TOTAL NO3	NO2		35-5	5		34.1	7

CHANGES IN INORGANIC NITROGEN WITH TIME
CHAPTER VIII

Summary and Conclusions

The aim of this investigation was to evaluate exchangeable ammonium as a source of nitrogen in the soil and to study its persistance and its interconversion to other forms of inorganic nitrogen. As many soils are deficient in nitrogen, the effects of added nitrogeneous fertilizers were also considered. Since the ammonium ion was the portion of the inorganic nitrogen of primary interest, three ammonium releasing fertilizers were used, namely ammonium nitrate, ammonium sulphate and urea.

An initial investigation was carried out to ensure that accurate determinations of exchangeable ammonium were being made. From this experiment it was concluded that, to obtain a valid estimation of the exchangeable ammonium present in the soil in its natural state, determination should be made on the fresh soil samples, with the minimum of delay between sampling and extraction. Where this is not possible, the fresh soil should be stored at 2° C.

In the spring of 1965 field trials were set up at four sites in Manitoba. The four soil types used for these trials were calcareous Lakeland soil, an acid Wellwood soil and two alkaline soils, an Almasippi and an Altona. In these particular field trials higher barley yields were obtained when the ammonium nitrate was drilled in with the seed rather than broadcast on the Lakeland and Almasippi soils. No significant difference between the two methods of application could be

seen with the other two soils.

When the yields from broadcast urea and ammonium nitrate at several rates of application were compared, no significant difference between the two carriers existed, except on the Wellwood and Altona soils at the 60 lb. per acre rate of application. At this level ammonium nitrate was superior to urea. Drilling in the fertilizers with the seed, however, produced greater yield differences between carriers. On the Altona soil 20 and 40 lb. per acre applications of urea and urea phosphate gave lower yields than similar ammonium nitrate application. With the Almasippi soil only the 40 lb. per acre urea and urea phosphate rates yielded lower than ammonium nitrate, and on the Lakeland soil only the 40 lb. per acre urea phosphate treatment. All three carriers yielded similarly on the acid soil.

Another difficulty frequently encountered when using urea containing fertilizers is poor germination. In these particular field trials significant reductions in germination only occured when the fertilizer was drilled in with the seed. One case of reduced germination with an ammonium nitrate treatment was noted. From the four urea containing treatments on the four soils, eleven showed significantly reduced germination. This effect was more common on the three alkaline soils than on the acid Wellwood soil.

Soil samples were taken from the four field trial locations and analysed, both before and after cropping, for exchangeable ammonium and nitrate nitrogen. Exchangeable ammonium values varied from quite low in the Almasippi soil to very high in the Altona soil. Nitrate nitrogen showed a similar pattern, but the range of values was narrower than for the exchangeable ammonium. Both exchangeable ammonium and nitrate nitrogen levels decreased over the growing season.

In a greenhouse experiment the changes in nitrate and exchangeable ammonium nitrogen were followed more closely. This experiment showed that exchangeable ammonium nitrogen does not persist in alkaline soils under good growing conditions. Further support for this conclusion was obtained from an incubation experiment where ammonium nitrogen was all found to be nitrified in an alkaline soil within twelve days. On the other hand, in both experiments exchangeable ammonium persisted for a considerably longer time in an acid soil.

As in the field trials both forms of inorganic nitrogen decreased over the growing period. The overall evidence from the field trials and greenhouse experiment suggests that, although nitrate nitrogen is the most important portion of the inorganic nitrogen for barley, the exchangeable ammonium nitrogen can not be completely ignored when making determinations of available nitrogen. Where exchangeable ammonium is present in the soil, it appears to be available to the plants when the demand for nitrogen is at its highest.

Conversion of exchangeable ammonium to nitrate nitrogen was more rapid in the alkaline soils than in the acid soil. Both the greenhouse and incubation experiments showed that loss of nitrogen occured when ammonium sulphate was applied to the surface of an alkaline soil. This was not the case with the acid soil. The lower yields obtained in the field trials when the fertilizer was broadcast rather than drilled in with the seed may result from this volatile loss of nitrogen from the soil surface.

Surface application of urea showed little to no loss of nitrogen in the greenhouse experiment. However, in the incubation experiment, nitrogen loss occurred on the alkaline soil from both the urea and the ammonium sulphate. In this case the loss of nitrogen appeared to be related to nitrite nitrogen accumulation. The difference in results obtained with the two experiments can probably be attributed to the differences in environmental conditions.

Although the same soils were used, direct comparisons between the field trials, greenhouse and incubation experiments are difficult to make because of the differences in environmental conditions; the latter are highly important to plant growth and microbial activity. However, the incubation experiment does confirm that nitrite nitrogen can persist in these alkaline soils and that nitrite levels are higher with urea than with ammonium sulphate. This gives considerable support to the idea that the lowered yields obtained with the urea and urea phosphate treatments in certain of the field trials may be due to nitrite accumulation. With the greenhouse experiment, the urea gave higher yields than the ammonium sulphate, indicating that the mode of application of the fertilizers is highly important in this respect. In the field trials the urea was applied in pellet form, thus increasing the likelihood of localised high concentrations of fertilizers; in the greenhouse experiment the fertilizers were applied in solution, which would give a better distribution of the carrier throughout the soil. Further support for this idea is obtained from the Wellwood soil, the soil which gave the greatest difference in yields between the two carriers in the greenhouse experiment. When the urea was worked in on

the field trial, the yield was similar to that from the ammonium nitrate.

The results of these investigations open up several possible lines for future investigations. With the acid soil the use of ammonium sulphate was found to give lower yields than urea. This appeared to be related to ammonium ion persistence. Further work is needed to elucidate the cause of this ammonium ion persistence in acid soils when an acid based ammoniacal fertilizer is applied and to investigate the possibility of counteracting this effect by using urea.

On the alkaline soils a marked loss of nitrogen occurred. Investigations could be made into the possibility that this is due to ammonia volatilization and that the reduced germination obtained in several cases may be due to ammonia toxicity. The mode of application of the fertilizers seems to be very important in this respect since no loss of nitrogen occurred when the urea was applied in solution. Study of nitrate nitrogen persistence as a probable cause of the reduced yields with urea and urea phosphate and the possibility of adding an ameliorating substance to counteract this effect could also be made.

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Statistics From Experiment 1.

Α.

	A	В	С	D	E
Standard Deviation	3.26	2.35	4.72	1.62	1.96

To determine whether the various treatments had produced any significant difference in exchangeable ammonium levels as compared with the initial level, "t" values were calculated.

 B
 C
 D
 E

 t
 0.394
 1.01
 4.64**
 2.00*

 *
 significant at the 5% level.
 **
 significant at the 1% level.

в.

		Fresh	Oven-Dried
Standard	Deviation	18.4	19.4

The difference between the means is significant at the 1% level.



APPENDIX III BARLEY YIELDS IN GREENHOUSE EXPERIMENT (in grams)

4.90 2.40 5.04 3.48 4.89 7.09 6.78 5.94 1.25 5.73 1.47 6.82 46 Ц 4.90 1.22 5.42 3.62 4.03 4.00 4.75 5.12 TIIV 1.97 1.24 3.97 3.94 41 3.38 0.98 4.08 2.62 1.72 2.73 3.85 3.14 3.55 1.10 3.67 2.24 36 TTV2.23 1.26 2.39 2.69 1.17 2.61 2.78 0.84 2.78 1.71 2.47 3.23 32 ΓΛ 2.38 3.00 1.28 2.42 0.86 2.22 2.20 2.05 2.52 2.72 0.75 1.52 28 ⊳ l.66 1.60 1.76 0.61 1.00 1.15 l.50 2.35 1.22 1.67 l.11 0.64 24 ΔI 0.49 1.11 1.06 l.53 0.68 1.80 1.31 0.67 l.l4 1.24 1.24 1.64 20 III 16 0.55 0.62 0.44 0.67 0.73 0.42 0.60 0.48 0.78 0.92 0.75 0.64 НЦ 0.48 0.46 0.28 0.48 0.49 0.40 0.46 0.51 0.38 0.37 0.27 0.50 Ц Н SOURCE OF $(\mathrm{NH}_{4})_{2}\mathrm{SO}_{4}$ (NH4)2SO4 (NHI)2SO4 (NH4)2SO4 ADDED N NUMBER OF DAYS AFTER UREA NONE NONE NONE UREA UREA UREA NONE GERMINATION ALMASTPPI WELLWOOD LAKELAND ALTONA Soll

APPENDIX IV TOTAL NITROGEN IN PLANT MATERIAL (mg. per pot)

NUMBER OF GERMI	DAYS AFTER NATION	12	1 6	20	24	28	32	36	μ 1	46	
SOIL	SOURCE OF ADDED N		ΠI	III	IV	Δ	TΛ	IIA	ΛΙΙΙ	IX	1
LAKELAND	(NH4)2SO4	27.4	27.7	57. I	66.8	69.3	79 - 9	65.0	72.9	68.1	I
	UREA	23.0	33.9	61.9	4.77	90.2	92.9	101.4	107.2	106.9	
	NONE	20.6	22.6	27.8	32.9	29.4	28.1	31.0	25.1	30.2	
WELLWOOD	(NH4)2SO4	22.7	36.3	51.5	59.3	75.3	76.0	50.5	79.2	72.7	
	UREA	28.1	32.0	78.1	85.7	90.8	99.5	102.8	108.7	7.0LL	
	NONE	14.1	12.2	13.1	16.1	18.4	19.5	15.8	17.0	17.3	
ALMASIPPI	$(\rm NH_{l})_2SO_{l}$	28.9	35.3	50.9	58.1	66.2	53.7	54.6	59.2	51.4	
	UREA	28.2	34.3	76.8	78.2	86.6	88.4	90.5	91.6	95.4	
	NONE	11.1	12.5	14.8	11.0	15.4	14.0	15.0	15.7	16.7	
ALTONA	(NH4)2SO4	23.2	h2.8	6.67	70.5	89.7	100.7	102.8	7.411	106.6	
	UREA	26.1	49.6	66.8	99.2	106.2	109.2	114.5	116.0	138.7	
	NONE	24.9	31.4	31.5	36.5	37.1	36.2	32.5	47.1	43.5	