THE UNIVERSITY OF MANITOBA

COMPARISON OF UREA AND AMMONIUM NITRATE AS

DETERMINED BY YIELD DATA, NITROGEN UPTAKE

AND AMMONIA VOLATILIZATION IN FIELD, GREENHOUSE

AND LABORATORY EXPERIMENTS

by

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ABSTRACT

Field experiments were conducted in 1968 and 1969 to study the relative efficiency of urea and ammonium nitrate as sources of nitrogen at eight locations representing seven Manitoba soil types. A greenhouse experiment was also conducted to study plant uptake of tracer nitrogen applied as urea and ammonium nitrate. Finally, a laboratory experiment was conducted to determine the magnitude of ammonia losses from urea and ammonium nitrate treated soils.

The field experiments showed that damage to barley seedlings was inversely related to the cation exchange capacity of the soils when urea was applied with the seed up to rates of 53 lb/Ac. Yield increases from uniform incorporation of NH_4NO_3 with the soil caused greater yield increases than urea on a two year average, but the differences varied with soil type and year of application. The coarse textured Almasippi soil with a high pH showed the greatest differences in carriers. Drilling ammonium nitrate with the seed caused greater yield increases than uniform incorporation up to 60 lb N/Ac.

The greenhouse experiment showed that plant uptake of tracer nitrogen applied as urea and NH_4 was less than that applied as NO_3 indicating a preferential immobilization of NH_4 N over NO_3 N.

The laboratory experiments showed that a decrease in temperature from $25°$ to $15°C$ caused a marked delay in initiation of ammonia volatilization and a decrease in total

ammonia volatilized. Losses of ammonia from urea were much larger than from NH_4NO_3 and were greatest on soils of high pH. Cation exchange capacity also exerted an influence on the amount of ammonia lost.

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I   INTRODUCTION

Nitrogenous fertilizer application to agricultural soils is often the single most significant agronomic practice used to increase crop production. Hence, it is important to evaluate the relative efficiency of the most commonly used nitrogen carriers in Manitoba, namely, urea, urea products and ammonium nitrate. Recent unpublished work in Manitoba (11) has indicated that these carriers are not necessarily equal as sources of nitrogen for field crops, a fact which has been amply documented in the literature (18, 20, 31, 33, 34, 43, 48, 67, 68, 69, 72, 78, 79, 80, 82). It was felt, therefore, that a comprehensive study on Manitoba soils was necessary in order to obtain more complete information. Previous evidence suggested that differences in efficiency of the nitrogen carriers was related to soil pH and texture. The soils used in this study were therefore chosen with a range in these variables.

The study was conducted in the field, greenhouse and laboratory. The field studies were conducted over two successive growing seasons and the evaluation of the nitrogen sources was made by measuring seedling emergence, nitrogen uptake and crop response of barley. In the greenhouse, labelled nitrogen carriers were used in an attempt to locate the path of fertilizer nitrogen and to evaluate the labelling technique for field studies. Laboratory incubation experiments were conducted to measure volatile losses of ammonia nitrogen, a mechanism suspected to account for the differences found

between the two nitrogen sources in the field and green-
house.

II   LITERATURE REVIEW

Unlike other commonly used nitrogen carriers, urea is an organic compound which is hydrolyzed by the soil enzyme urease to form ammonia and carbon dioxide (28) (62) (66) (15) (31).

$$\begin{array}{c} NH_2 \\ \diagdown \\ \diagup \\ NH_2 \end{array} C = 0 + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2$$
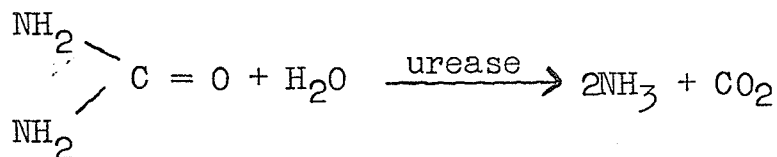
These products can be further hydrolyzed to form ammonium carbonate.

Experimentally, soil pH has been shown to increase from 5.5 to 9.0 near the zone of urea hydrolysis (21) (81). This may result in loss of N   as NH_3, ammonia toxicity to plants and to ammonia sensitive nitrifiers such as Nitrobacter. Bates and Pinching (2) found that in aqueous solution, 99% of the ammonia is present in the protonated form at pH 7.0 whereas 50% is present in the protonated form at pH 9.0. In a soil system this relationship is affected by the soil exchange sites and other salts present, although even in the soil solution, increasing pH results in a decrease in the protonated form.

Although ammonia in solution is often written as a solution of the weak base ammonium hydroxide, Cotton and Wilkinson (16) state that it does not exist as such and the relationship between ammonia and water should be written

$$NH_3 \text{ (aq.)} + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (pKb = 4.75).$$
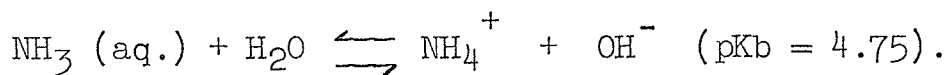
They also state that ammonia exists as one of the two hydrated forms $2NH_3 \cdot H_2O$ or $NH_3 \cdot H_2O$.

Although initially urea results in an increase in pH, its final effect is to reduce soil pH as NH_3 is oxidized to NO_3. In reducing pH, its behaviour is similar to that of NH_4NO_3 and $(NH_4)_2SO_4$ (77).

Factors Affecting Urea Hydrolysis

The hydrolysis of urea is the most significant factor differentiating it from carriers such as ammonium nitrate and ammonium sulphate.

Chemical hydrolysis in soils is exceedingly slow relative to enzymatic hydrolysis (13). This discussion will therefore pertain to the latter.

Soils vary in their ability to hydrolyze urea (63). On some soils, the reaction is first order (40) (44) (54). On others, the enzyme saturation level is reached and no rate increase occurs beyond a particular rate of urea application (63) indicating that the soils ability to hydrolyze urea will depend on the inherent urease activity of each soil.

Conrad (14) and Gibson (32) reported a direct relationship between soil organic matter content and urease activity. The increased organic matter was believed to be associated with greater microbiological activity and urease production. The addition of energy materials such as glucose has been shown to markedly increase urease activity (13). A

similar effect was observed by the addition of urease to the soil (49). The increase in hydrolysis was immediate upon application to the soil whereas the addition of energy sources requires a lag period in which the microbial population increases. Soils with higher clay contents were also observed to exhibit higher urease activity (57). This is due to a clay-urease complex which slowly releases urease upon the addition of urea.

A number of reports (6) (29) (63) indicate a direct relationship between temperature and urease activity from $1^{\circ}C$ to $30^{\circ}C$. This corresponds with the effect of temperature on the increase in growth rate of microorganisms and subsequent increase in urease production. This is an important consideration in Manitoba since fertilizers for cereals are usually applied when soil temperatures are relatively low $(5 - 15^{\circ}C)$. At $25^{\circ}C.$, urea hydrolysis can be 100% completed within two days but at $1^{\circ}C$ it can take two weeks or more depending on the concentration of urea and urease (13).

The effect of pH on urease activity is not very marked within a range of $\pm$ 2 units of pH 7.0. Urea is hydrolyzed rapidly at pH's as low as 3.1 or as high as 9.2 (12) (32) (46) (63). Soulides and Clark (65) and Gibson (32) reported slower hydrolysis rates with increasing alkalinity but another report indicates slightly more rapid hydrolysis with increasing pH (63). The apparent discrepencies could be due to the kinds of urease producing microbes present in the different soils. Bacillus pasteurii thrives in soils

high in pH and ammonia concentration (66). Since it is a major urease producing organism, a soil with a large population of this organism would be expected to show a positive correlation between pH and hydrolysis rate. Since high concentrations of ammonia are toxic to most other microbes, soils populated with microbes other than Bacillus pasteurii would be expected to show a negative correlation between hydrolysis rate and pH. Since the pH falls within a fairly narrow range in most agricultural soils in Manitoba, it should not be a major factor influencing urea hydrolysis.

Moisture content in the available water range has very little effect on urease activity (39) (63) (79). Urea hydrolyzes quite rapidly at moisture contents as low as 1% based on an air dry sample (78). It appears that for most practical purposes, soil moisture is not a critical factor governing the rate of urea hydrolysis.

Ammonia Retention

Although ammonia is very soluble in water, constant gaseous losses would occur from soil except for the adsorptive capacity of soil colloids and the utilization of ammonia by plants and soil microbes. The adsorption complex is made up of clay and organic material which can adsorb ammonia either physically or chemically. Mortland and Walcott (50) state that physical adsorption is characterized by easy reversibility, low heat of adsorption and does not require

any specific adsorption sites. Any compound that is phys-
ically adsorbed by a colloid is quite easily removed by a
reduction in the pressure or concentration of the adsorbate.
Chemically adsorbed compounds are characterized by a degree
of irreversibility and require specific adsorption sites.
They also state that as the process of adsorption progresses,
a range from chemical to physical adsorption will occur due
to the interaction of molecules already adsorbed with those
in the process of being adsorbed. In a review of the liter-
ature Mortland and Walcott (50) conclude:

> "(1) The ammonium ion is formed when
> ammonia is adsorbed by acid clay minerals. (2)
> The ammonium ion is also formed when certain base-
> saturated clay minerals adsorb ammonia. The source
> of the proton for the latter reaction is thought to
> be provided by water molecules which have been alt-
> ered in their dissociation properties by the polar-
> ization effects of the exchangeable cation augment-
> ed by the clay mineral surface itself. (3) Ammine
> type (coordination) bonds may be formed upon amm-
> onia adsorption if appropriate cations are present
> on the exchange complex. This ion-dipole inter-
> action varies greatly in stability depending on
> the nature of the ion. Hydrogen bonding of amm-
> onia to surface oxygen atoms of clay lattices and
> of various oxides existing in soils is another
> adsorption mechanism. Hydrogen bonding between
> NH_3 and NH_4^+ and between H_2O and NH_4^+ also takes
> place. (4) Pure physical adsorption of ammonia
> represents the least energetic adsorption mechanism."

Volatilization

Most of the research on factors affecting urea
hydrolysis has included studies of factors affecting ammonia
volatilization. The literature comparing sources of nitrogen
and determining gaseous ammonia losses is quite voluminous.

Field and greenhouse comparison of these sources often indicate that urea is as effective as other sources of nitrogen in increasing crop production. A summary of the work done in the Soviet Union from 1958 to 1964 indicated that urea and ammonium nitrate were equal sources of nitrogen (41). However, a significant portion of the literature indicated that urea is not necessarily as effective as ammonium nitrate or sulfate. The differences were usually associated with specific soil characteristics which induce ammonia volatilization.

Factors Affecting Ammonia Volatilization

Chin and Kroontje (13) applied ammonium carbonate to soils and upon incubation found that the rate of ammonia volatilization was related directly to ammonium concentration. Parr and Papendick (56) studied the desorption of ammonium from the soil under continuous aeration and found that the rate of desorption was an increasing function of the ammonium concentration previously applied to the soil. They also found characteristic threshold values for initial ammonia concentrations below which the rate of ammonia desorption fell markedly. They concluded that the rate of desorption was governed by the strength of the various NH_3 - adsorbent bonds. They also suggested that at low moisture levels competition for adsorbent sites occured between water and ammonia which agreed with the conclusion of Jones and Harvard (41). The rate of desorption at the start of aeration was inversely

related to the moisture level and ammonia was rapidly dis-
placed from an air dry soil by water vapour from moist air.

Results similar to those of Chin and Kroontje (13)
were reported by Gasser (30) for ammonium sulfate. Similar
functions are shown for volatilization from urea, although
the rate of volatilization is governed to some extent by
the rate of urea hydrolysis. If hydrolysis is slow, the
ammonia concentration may not reach the critical levels
reported by Parr and Papendick (56) and little ammonia volat-
ilization would occur since the urea would diffuse from the
initial point of contact and hydrolyze where urea concent-
ration was lower. However, a prolonged period of volatiliza-
tion has been shown to occur even when hydrolysis was slow (49).

Ernst and Massey (26) found that the total ammonia
loss was related to the moisture content of the soil before
drying. This was in agreement with Martin and Chapman (45)
and Jewitt (38). Ernst and Massey (26) found, however, that
the amount of ammonia volatilized from urea was not necess-
arily a function of the rate of drying when the soil was ini-
tially at field capacity. Rapid drying to air dryness halted
urea hydrolysis, thus allowing only small amounts of ammonia
to volatilize. Losses up to 10% of the applied nitrogen
occured when no evaporation took place, but although evapora-
tion was considerably more rapid at 50 - 55% than at 85 - 90%
relative humidity, ammonia volatilization was the same.
Wahhab et al. (73) subjected urea treated soils to wetting
and drying cycles and found decreasing amounts of ammonia

volatilized with each drying until the fifth cycle when no ammonia was lost. The amount lost increased with increasing moisture content. When constant moisture context is maintained, more ammonia is lost from soils with a lower than those of a higher initial moisture content (26).

There is agreement on the effect of pH on ammonia volatilization. The results of Bates and Pinching (2) and Ernst and Massey (26) indicate that the concentration of ammonia is increased exponentially as the pH of an aqueous solution is increased above 7. This was related to ammonia losses from soils by Gasser (30) and Ernst and Massey (26). Although ammonium sulfate has been reported to be subject to greater losses of ammonia than urea on soils of pH 7 due to downward movement of urea before hydrolysis (30), in most instances urea is subject to greater losses of ammonia due to the increase in pH as urea hydrolyzes.

Chin and Kroontje (13) suggested (without experimental evidence) that according to the Arrhenius equation, the rate of ammonia volatilization from the soil should be higher at higher temperatures. Total losses do not necessarily increase with temperature, however, as Gasser (30) has shown. Martin and Chapman (45) studied the loss of ammonia from ammonium sulfate, ammonium nitrate, ammonium hydroxide and urea applied to soils which were alternately wetted and dried and varied in temperature. A linear relationship between total ammonia lost from the inorganic carriers and temperature was found. The relationship of temperature to urea

nitrogen volatilization appeared exponential. Although exceptions do occur (30) most researchers report greater losses of ammonia from urea with higher temperatures. This is theoretically sound since a slower hydrolysis time allows greater urea and ammonia diffusion in the soil.

Overrein and Moe (54) reported an approximately linear relationship between the depth of soil with which urea was mixed and total ammonia volatilization for moisture contents of 10 and 20%. There was a significant difference in ammonia volatilization between the two moisture levels due to the solubility of ammonia in water. These results are similar to those of Ernst and Massey (26) who found that 5% of the urea nitrogen was lost when mixed with the surface $1\frac{1}{2}$ inches of soil and 18% when urea was applied to the soil surface. This experiment was performed with a silt loam soil with pH adjusted to 6.5. Gasser (30) found that mixing ammonium sulfate with the soil decreased losses but mixing urea with the soil and applying it to the soil surface result-ed in similar ammonia losses. The latter results can be explained by the ability of urea to diffuse from the soil surface before hydrolysis occurs. Meyer and Olson (48) concluded that nitrogen fertilizers, particularly urea and ammonium containing compounds should be incorporated with the soil when irrigation or rain do not follow application.

Gasser (30) combined his results with those of Volk (78) and Martin and Chapman (45) to show the relationship between cation exchange capacity and ammonia losses. The

results indicated that at cation exchange capacities greater
than 30 meq/100g, only small losses occur. As cation
exchange capacity decreased, the degree of ammonia loss
increased rapidly.

However, Wahhab et al (73) compared two soils of
differing texture and reported losses from the sandy loam
were nearly double that of the sand. Since the sandy loam
contained three times more organic matter than the sand,
it may have been able to hydrolyze urea more rapidly causing
a greater temporary ammonia concentration. Cation exchange
capacity was not determined, however, so the two determining
factors (available energy and cation exchange capacity) could
not be compared.

Ammonia Toxicity

The application of fertilizer in a band with small
grain seed is known to increase yields and nitrogen uptake
to a greater extent than an equivalent broadcast application.
However, at the higher practical rates of application sign-
ificant stand reduction can occur due to the osmotic effect
of the fertilizer. This often results in yield reductions.

Urea applied with the seed causes a special problem
since toxic amounts of ammonia are released near the germinat-
ing seeds. This fact is well documented (4, 15, 18, 19, 20,
34, 47, 67, 69, 76, 81). When the pH rises to 8 or 9, the
presence of ammonia in the soil is highly toxic due to its
rapid diffusion through cell membranes and the inability of

the detoxifying mechanism in the cell to cope with large amounts of ammonia (75). Ammonia is also toxic to the nitrite nitrifier Nitrobacter causing the accumulation of high concentrations of nitrite (19) (22) (64) (75). Smith (64) related lower cation exchange capacities to the accumulation of nitrite in the soil. He suggested that this was due to the greater concentration of ammonia on soils of low cation exchange capacity. Court et al. (17) (19) suggested that the accumulation of nitrite caused toxicity to maize seedlings. The toxicity symptons they noted occurred after high ammonia concentrations had been oxidized to nitrite.

Immobilization of Ammonium and Nitrate

Ammonium and nitrate nitrogen carriers have been considered equally available to micro-organisms (60). Richards and Shicklande (61) first suggested that ammonium was absorbed more rapidly than nitrate, particularly during the early stages of decomposition of cereal straw. Jannson (37) states that "although ammonium and nitrate have generally been considered of about equal value as fertilizer materials under a wide range of conditions, there may be peculiar sets of circumstances where each would have advantages over the other." Using labelled nitrogen as a tracer, he found that if both ions were added in sufficient quantity, the organisms utilized ammonium almost exclusively. He also found that during periods of high immobilization when ammonium was likely

to be low, nitrate nitrogen was extensively absorbed, but when ammonia was being liberated more rapidly than nitrogen was being absorbed, nitrate was utilized only to a minor extent. Overrein (53) studied the path of tracer inorganic nitrogen on forest raw humus with similar results to those of Jansson. He found, however, that at higher temperatures (20 vs. 4 and 12°C) the preferential utilization of ammonium decreased. Urea nitrogen was immobilized to a greater extent than nitrate and also more rapidly than from an ammonium source. He suggested that this was due to the temporary pH increase associated with urea hydrolysis being more conducive to increased biochemical activity. This effect was also reported by Jansson (37) and Broadbent and Tyler (10). Jansson suggested that this might be due to marked differences in microflora. Broadbent and Tyler considered the physiological acidity or alkalinity of the nitrogen source. The possibility of more rapid absorption of ammonia at a higher pH due to a higher concentration of non-protonated ammonia was not suggested.

Broadbent and Tyler (9) studied the relative immobilization of ammonium and nitrate in two soils taking into account net nitrogen changes as well as tracer nitrate. On a sandy soil low in organic matter, the nitrifying population was unable to compete with the heterotrophs whereas on the heavier textured soil with high organic matter content, a higher portion of the added ammonium appeared as nitrate. Nitrate was also immobilized on the sandy soil to a greater extent than

on the clay. The release of labelled immobilized nitrogen
was negligible over a period of sixty days, however, a portion
of this was replaced by non labelled mineralized nitrogen.
Other investigators (7) (36) also reported the relative
unavailability of immobilized nitrogen which is released at
a rate approaching that of mineralization, i.e., the immob-
ilized nitrogen rapidly becomes stabilized. Broadbent and
Tyler (9) reported the release of non-labelled ammonium ten
days after the addition of labelled ammonium. Stojanovic
and Broadbent (70) also reported a net immobilization of
labelled nitrogen which was partially replaced by non-labelled
nitrogen. They stated that nitrogen used by plants is partly
produced by soil organisms even when fertilizer nitrogen is
recently applied to the soil. In greenhouse studies, various
investigators (8) (9) (36) reported this occurrence. Nitrogen
immobilization was of little consequence in crop production
if immobilized nitrogen was rapidly replaced by mineralized
nitrogen.

However, the literature reviewed indicates that
immobilized nitrogen is not rapidly nor totally replaced in
the growing season of cereal crops. Considering that ammonia
is often immobilized preferentially over nitrate, the choice
of nitrogen carrier appears quite important.

III   FIELD EXPERIMENTS

Introduction

The purpose of the field experiments conducted in 1968 and 1969 were threefold. They were primarily designed to study the effect of soil pH and cation exchange capacity on the relative efficiency of urea and NH_4NO_3 applied to a barley crop. In addition, comparisons were made between incorporating nitrogen fertilizers uniformly with the soil (broadcast) and applying them with the seed (drilled). Finally, the response of the barley crops to various rates of nitrogen application was studied.

Methods and Materials

Soils

The soils chosen for the field plot sites are described in some detail in the Manitoba Soil Survey reports numbers 4, 5, 7 and 12 (23) (24) (25) (59). They were selected for their range in pH, cation exchange capacity and low nitrate nitrogen content. A summary of the soil character-istics is given in Tables I and II. Texture ranged from loamy very fine sand to a clay with a corresponding range in cation exchange capacity from 11.3 to 37.1   meq/100g. Soil pH ranged from 6.0 on the 1969 Stockton soil to 8.2 on the Plum Ridge soil. The Plum Ridge and Lakeland soils were highly calcareous ($CaCO_3$ equiv. $\geq$ 10%) in the 0-6" soil layer. All other soils had 1.0% or less except the

TABLE I   PLOT LOCATIONS, SOIL NAMES AND TEXTURES,
SEEDING AND HARVEST DATES

	Cooperator	Legal Loc.	Soil Association or Series*	Texture	Seeding Date	Harvesting Date
1968	Murta	S. E. 22-6-6 W	Almasippi	L V F S	May 28	August 28
	Hockin	S.E. 16-13-15 W	Stockton	F S L	May 30	August 30
	Hawkins	S.W. 7-15-2 E	Plum Ridge*	V F S L	May 22	August 25
	Janick	S.E. 5-4-4 W	Altona	V F S C L	May 29	August 29
1969	Hockin	N.E. 16-13-15 W	Stockton	F S L	May 14	August 14
	Sirrette	S.W. 5-14-16 W	Newdale	C L	May 16	August 15
	Moeller	N.E. 19-16-3 E	Lakeland*	C L	May 17	August 19
	Toews	S.W. 1-5-3 W	Red River	C	May 20	August 18

TABLE II

SUMMARY OF ANALYSES CONDUCTED TO
CHARACTERIZE SOILS FROM EXPERIMENTAL SITES

Year	Soil Type	Nitrate Nitrogen lb/acre to 2'*	NaHCO$_3$ Ext. P (ppm)	Exch. K (ppm)	pH	CaCO$_3$ Equiv. %	OM %	Cond. mmhos/cm	C.E.C. meq/100g
1968	Almasippi	11.9	6.3	112	8.0	1.0	2.9	.40	11.3
1968	Stockton	9.2	5.9	260	6.3	0.5	3.7	.34	14.3
1968	Plum Ridge	5.2	8.9	114	8.2	11.0	4.6	.41	17.0
1968	Altona	10.5	11.0	290	7.3	0.5	3.3	.32	22.0
1969	Stockton	15.0	7.0	376	6.0	0.3	5.2	.34	15.9
1969	Newdale	8.0	8.4	336	7.4	1.7	5.3	.39	24.8
1969	Lakeland	7.6	18.9	451	8.0	15.6	6.9	.57	29.4
1969	Red River	21.0	4.1	685	7.6	0.5	7.0	.39	37.1

* Other soil characteristics to 6"

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Newdale which had 1.7%. Organic matter content varied from a low of 2.9% on the Almasippi soil to a high of 7.0% on the Red River. The order corresponded roughly to texture and cation exchange capacity. Soluble salt content was low on all soils as indicated by the conductivity of the saturation extract.

All soils were low to very low in nitrate nitrogen (in the 0-24" zone) indicating that barley should respond well to nitrogen fertilizer application.

Description of Field Experiments

Conquest barley (Hordeum vulgare) was used as a test crop. Seeding was performed with a six-row double disc type seeder with seven inch spacing. Fertilizer materials were either drilled with the seed, broadcast and incorporated with the surface 2.5 inches of soil, or banded approximately one inch to the side of the seed after seeding. Each treatment consisted of an area $3\frac{1}{2}$ x 20 ft. Seeding and harvest dates are listed in Table I.

The experimental design in the 1968 trials was a six replicate split-plot type with the comparisons between carriers receiving greatest precision, i.e., N carriers were paired at similar rates of N and methods of application to reduce variability. The second order of precision was given to treatments which were similar in method of applicat-ion (either broadcast or drilled). The 1969 experimental design was also the split-plot type but carriers were not paired. Instead, sub-plots consisted of treatments with

equal rates of N regardless of N carrier or method of application. Treatments were replicated four times. Intra and inter-subplot randomization was performed within replicates in both years. The treatments used in the experiment are listed in Tables III and IV. The treatments with 20, 40 and 60 lb/Ac of broadcast N are listed twice in Table III to simplify the statistical analyses and interpretation of data from the 1968 experiments.

Seedling emergence counts were taken at the three to four leaf stage of growth. At maturity samples of barley straw and grain were taken by cutting the stems just above ground level from the two center rows of each treatment area. The samples were dried at a temperature of approximately $80^{\circ}F$. The grain was separated from the straw and each weighed separately. Replicate samples were bulked and analyzed for nitrogen by the Kjeldahl procedure.

The difference in seedling emergence between urea and ammonium nitrate treatments and between urea and the phosphorous only treatment were related to cation exchange capacity by regression analysis.[1] Using differences in nitrogen uptake between treatments receiving phosphorous only and those receiving nitrogen and phosphorous the efficiency of the fertilizer nitrogen was determined.

$$N \text{ efficiency } \% = \frac{N \text{ uptake from N treat.} - N \text{ uptake from P only treat.}}{Rate \text{ N applied}} \times 100$$

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[1] The standard (check) treatment of 60 lb/Ac of mono-ammonium phosphate (30 lb/Ac P_2O_5) is referred to as the phosphorous only treatment even though it had a small amount of nitrogen.

Analytical Procedures

The NO_3 - N content of the soils was determined colorimetrically using the phenoldisulfonic acid method described by Black (3). Available phosphate was measured by the $NaHCO_3$ extraction method described by Olsen (52). Exchangeable potassium was extracted with a 1N ammonium acetate solution containing 250 ppm lithium. Potassium content of the extract was determined on a Baird Atomic Flame Photometer. Soil pH was measured with a universal pH meter on a saturated soil water paste. Carbonate content was determined by the gravimetric measurement of CO_2 liberated by digestion with HCl as described by Black (3). Organic matter content was determined by chromic acid digestion as described by Walkey and Black (74). Conductivity was measured on saturated soil paste using a Radiometer type CDM 104 conductivity cell. The total nitrogen content of the plant material was determined by the macro-Kjeldahl method described by Black (3). Cation exchange capacity was determined using the 1N ammonium acetate saturation method described by Atkinson et al. (1).

Results and Discussion

Barley Response to Nitrogen

The yield of barley increased with increasing rates of broadcast NH_4NO_3 to 60 lb N/Ac on all soils as predicted by the soil test results (Tables III and IV). (There were

carrier and method of application differences which will be
discussed in a later section). In 1968, only the Plum Ridge
soil which was very low in NO_3 - N responded beyond 60/lb
N/Ac. In 1969, barley responded to 90 lb N/Ac even though
the NO_3 - N content was 18.0 and 21.0 lb/Ac on the Stockton
and Red River soils, respectively. In both years, however,
barley response to N may have been limited considerably by
lodging which occurred at the 90 lb N/Ac rate and beyond.
The fact that barley responded quite markedly up to 60 lb
N/Ac on all soils aided in the carrier and method of applic-
ation comparisons.

Seedling Emergence

The effects of drilling NH_4NO_3 and urea with the
seed on seedling emergence as compared to the phosphorous
only treatment as 100 per cent are outlined in Figures 1 and
2. Urea caused greater reductions in emergence than ammonium
nitrate on soils and at all rates except the 13 lb N/Ac
rate on the Altona soil.[2] The extent of seedling emergence
reductions from the urea treatments was related to the cation
exchange capacities of the eight soils. The following relation-
ships were obtained:

_____

2.
  This rate does not include the 7 lb N/Ac as $NH_4H_2PO_4$
  which was applied with all treatments. i.e., this rate
  is actually 20 lb N/Ac but only 13 lb N/Ac as urea.
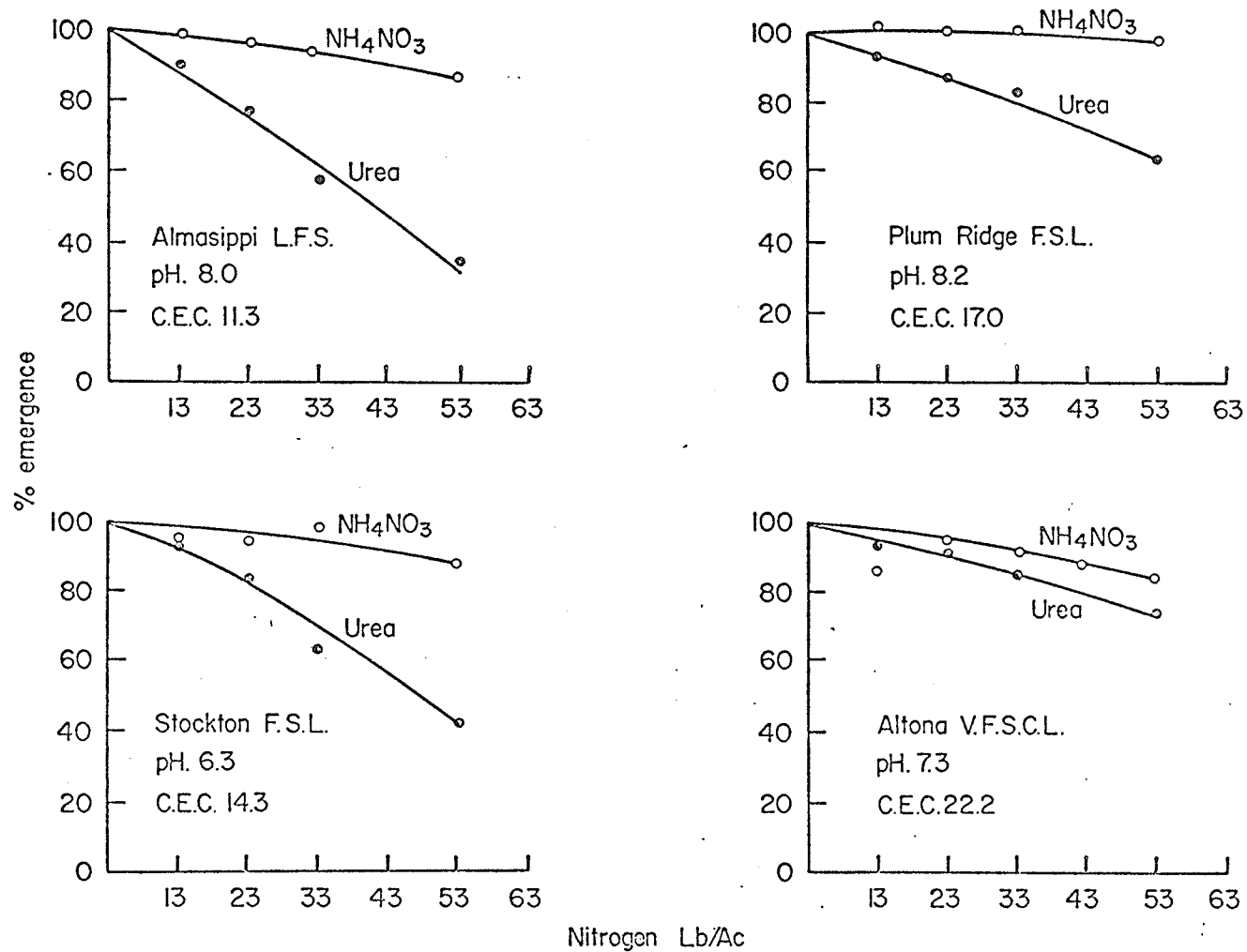
FIGURE 1   SEEDLING EMERGENCE OF BARLEY AS INFLUENCED BY SOIL TYPE
AND BY UREA AND NH₄NO₃ DRILLED WITH THE SEED IN 1968

23
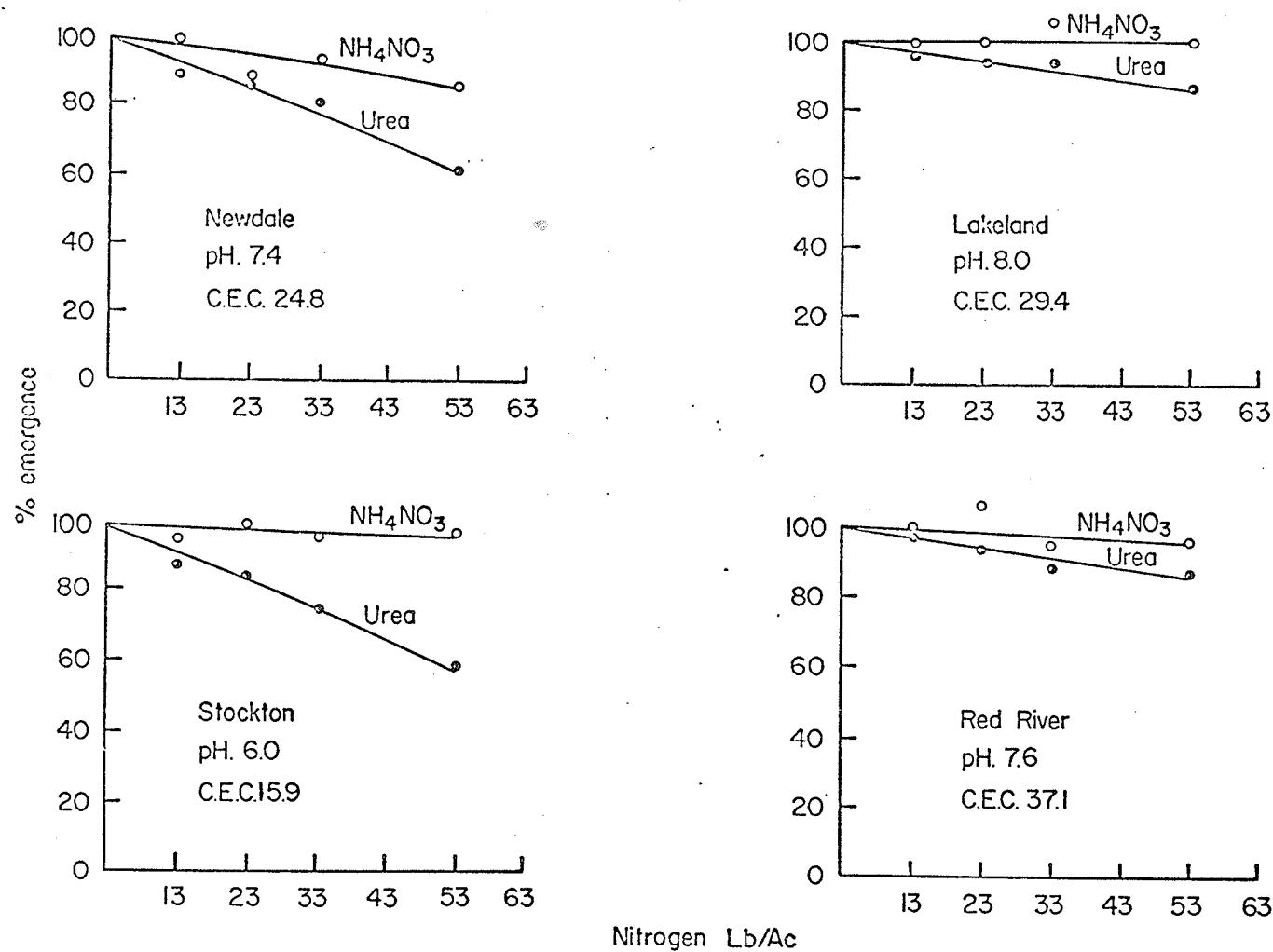
FIGURE 2   SEEDLING EMERGENCE OF BARLEY AS INFLUENCED BY SOIL TYPE
AND BY UREA AND NH₄NO₃ DRILLED WITH THE SEED IN 1969

Urea N lb/Ac		r^2 x 100
13	Eq. 1 (a) $Yc = .14 + 129\ x^{-1}$	81
23	(b) $Yc = {}^-2.19 + 294\ x^{-1}$	90
33	(c) $Yc = -4.56 + 484\ x^{-1}$	88
53	(d) $Yc = -9.55 + 859\ x^{-1}$	88

Yc = % emergence phosphorous treat. - % emergence
urea treat.

x = cation exchange capacity meq/100 g

The constants A and B of the general equation
$Yc = A + B\ x^{-1}$ were linearly related to the rate of urea N
application (Figure 3). By substitution an equation relating
reductions in emergence to cation exchange capacity and rate
of urea nitrogen application was then determined to be

Eq. 2 $Yc = 3.25 - 120\ x^{-1} + 18.4\ Rx^{-1} - 0.34\ R$

where R = rate of urea N (lb/Ac) and Yc and
x are the same as in Equation 1.

The literature reviewed indicated that toxic quant-
ities of ammonia could accumulate when urea is placed in a
band with the seed. Assuming this to be true in this case,
the equations indicate that the cation exchange capacity of
the soil exerts a strong negative influence on the amount of
free ammonia present in the soil. Although both ammonia and
nitrite have been shown to be toxic to seedlings, the accumu-
lation of nitrite is not likely to occur unless concentrations
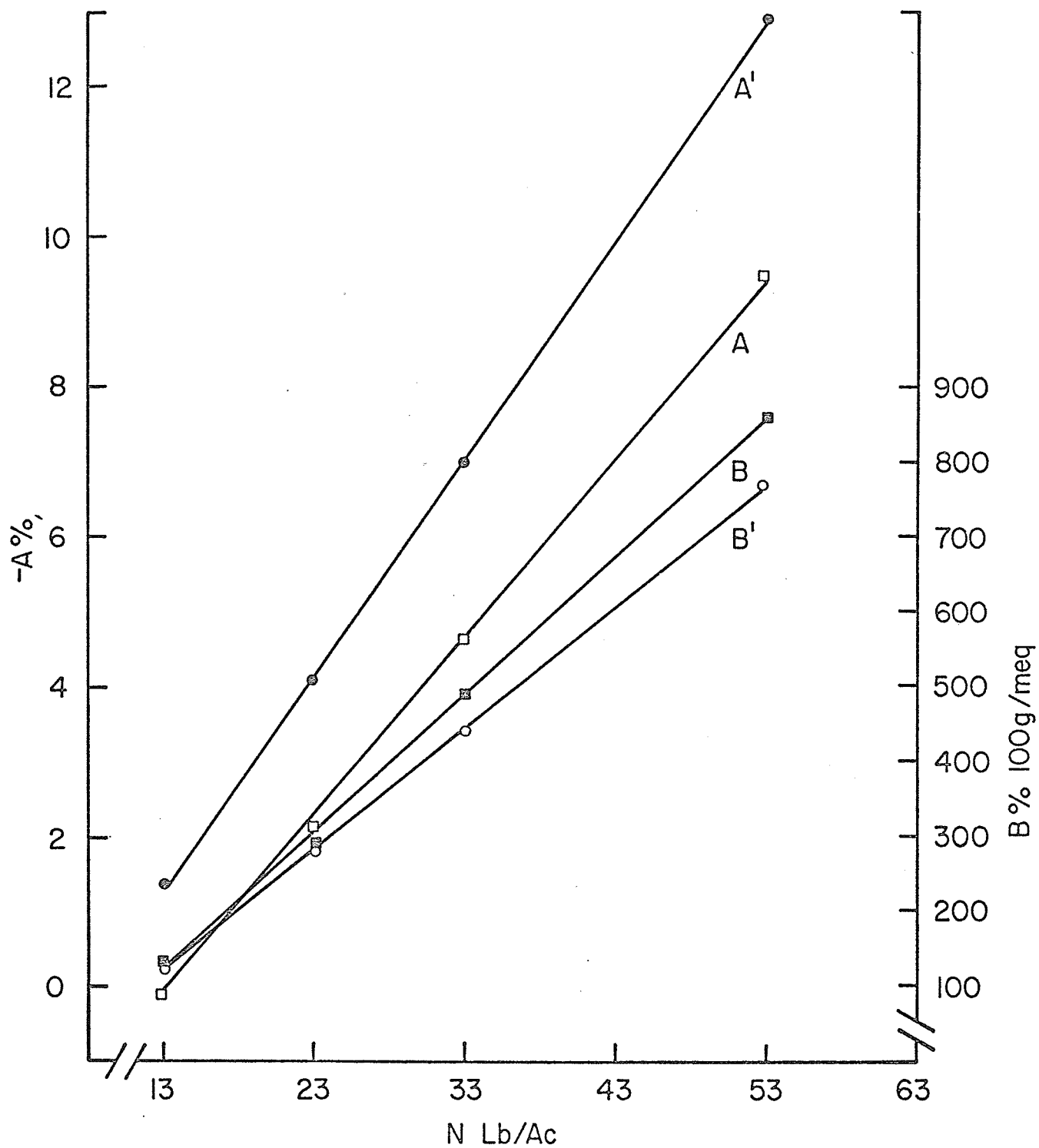
FIGURE 3   RELATIONSHIP OF CONSTANTS A, B, A',
            AND B' TO RATE OF N APPLICATION

Note   A' and B' are constants for the equations
            on page 27.

of ammonia which are toxic to <u>Nitrobacter</u> are present in the soil. Therefore the presence of nitrite would also be indirectly related to soil cation exchange capacity.

Calculating the seedling reductions caused by urea relative to those caused by NH_4NO_3 at the equivalent rates of N offered a more practical application of the seedling emergence data since differences in yield increases caused by the application of the two carriers could be related to differences in seedling emergence. The equations are of the same form as Equation 1.

N lb/Ac				r^2 x 100
13	Eq. 3	(a)	$Y_N = -1.4 + 130\ x^{-1}$	80
23		(b)	$Y_N = -4.1 + 276\ x^{-1}$	93
33		(c)	$Y_N = -7.0 + 446\ x^{-1}$	93
53		(d)	$Y_N = -12.8 + 774\ x^{-1}$	89

Y_N = % emergence NH_4NO_3 treat. minus % emergence urea treat.

x = cation exchange capacity (meq/100g)

The convergence of these equations at 0% emergence reduction (Figure 4) indicates that the difference in % emergence between urea and NH_4NO_3 treatments would become 0 on soils with a cation exchange capacity of 86 meq/100g. The validity of this extrapolation is doubtful however, since further extrapolation suggests that damage caused by NH_4NO_3 treatments would be greater than that caused by urea treatments. Also one would not expect that emergence reductions even at
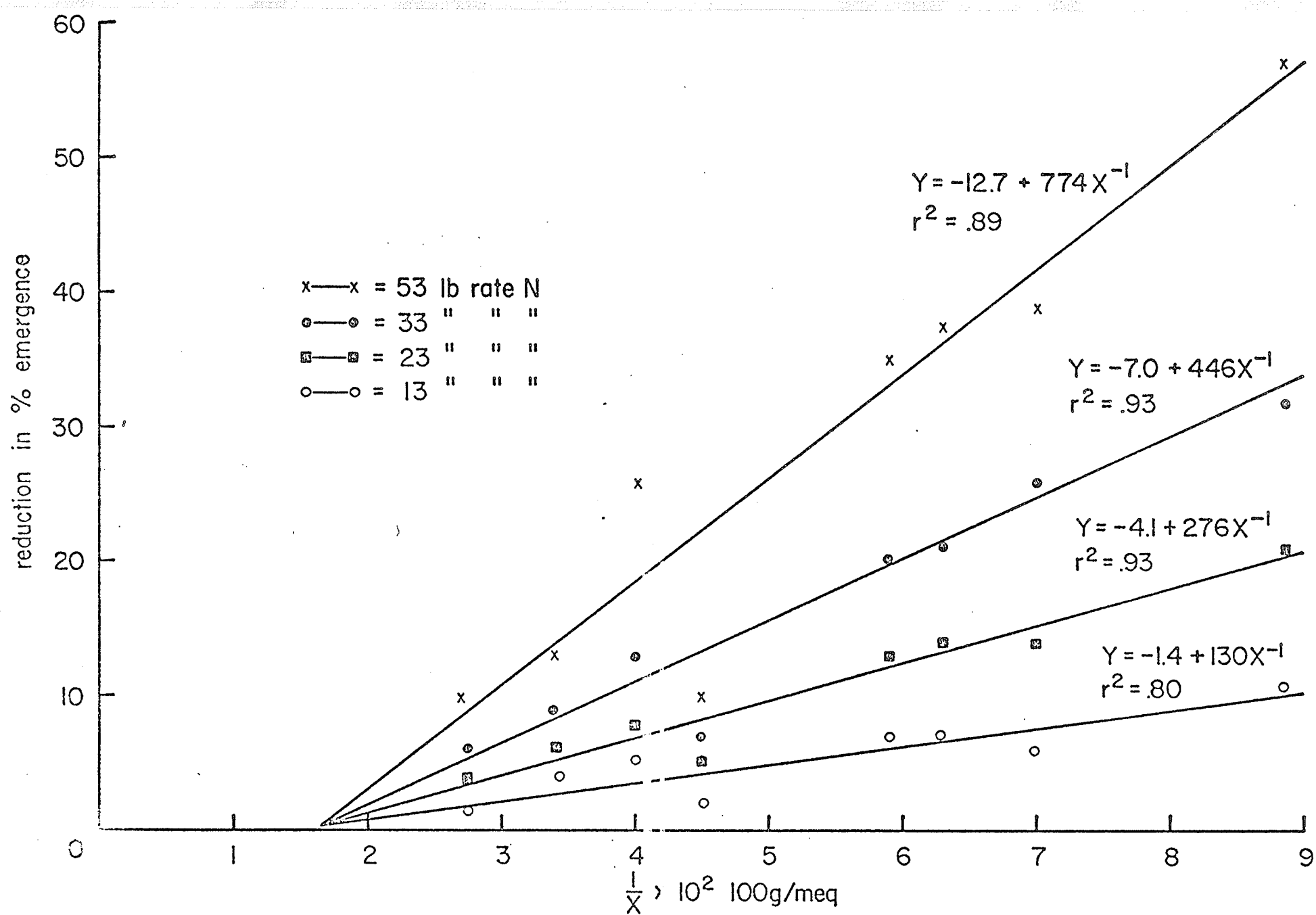
FIGURE 4 RELATIONSHIP OF REDUCTIONS IN EMERGENCE OF BARLEY DRILLED WITH UREA
TO CATION EXCHANGE CAPACITY (X) OF EIGHT SOILS

high cation exchange would be independent of rate. A more
likely equation would tend to approach the abscissa exponent-
ially at each rate with convergence taking place at the origin.
The author suggests that although the equations are valid over
the range of cation exchange capacities studied, at the higher
values of exchange capacities, the equation might not hold.
The cation exchange capacities studied, however, cover a wide
range of agricultural soils in Manitoba and the results are
practically useful in determining what rate of urea can be
applied with the seed on various soils without causing sign-
ificant seedling damage. The high r^2 values for each equa-
tion suggest that very little variability could be accounted
for by factors such as pH or moisture content in this exper-
iment. Since the constants A' and B' of the general equation
$Y_N = A' + B' x^{-1}$ were linearly related in Equations 3a to 3d
(similar to Equations 1a to 1d), an equation relating the
reductions in emergence caused by urea relative to NH_4NO_3
treatments to the rate of N and cation exchange capacity
could be written:

Eq. 4 $Y_N = 2.3 - 80 x^{-1} + 16.1 R x^{-1} - 0.28R$

where Y_N = % emergence NH_4NO_3 treat. - % emergence urea treat.

x = cation exchange capacity (meq/100g)

R = rate of N as urea or NH_4NO_3(lb/Ac)

By substituting values for R and x in Equation 4 the %
reduction in seedling emergence expected by applying urea with
the seed rather than NH_4NO_3 can be determined.

The % reductions in emergence and the reductions in yield caused by urea relative to NH_4NO_3 treatments were correlated in a linear manner (Figure 5). The resulting equation was:

$$\text{Eq. 5} \quad W = -2.4 + 0.65Y_N \qquad\qquad r^2 \times 100 = 75$$

where W = yield NH_4NO_3 treat. - yield urea treat.

$\qquad$ Y_N = % emerg. NH_4NO_3 treat. - % emerg. urea treat.

Relatively small reductions in emergence caused by urea treatments were related to substantial reductions in yield, e.g., a difference in emergence of 20% was related to a yield difference of 10 bus/Ac. This yield reduction is higher than expected since seeding rates can be varied considerably without affecting yield. This indicates that the toxicity to seedlings caused by applying urea with the seed results not only in reduced seedling emergence but also in a reduction in potential yield of the plants which do emerge.

Combining Equation 5 and Equation 4, an equation relating reductions in grain yield caused by urea to N rate and cation exchange capacity of the soil was obtained.

$$\text{Eq. 6} \quad W = -52\,x^{-1} + 10.5\,R\,x^{-1} - 0.18\,R - 0.9$$

This equation can be used to predict the type of yield decrease one can expect from drilling urea with the seed rather than NH_4NO_3.

Since urea phosphate fertilizers 23-23-0 and 27-27-0 are also commercial sources of nitrogen fertilizer, they were

$$Y = -2.4 + 0.65\,X$$
$$R^2 = .75$$

FIGURE 5   CORRELATION OF REDUCTIONS IN SEEDLING
EMERGENCE TO REDUCTIONS IN YIELD

included in the experiment at two rates for comparison pur-
poses. Discounting the 1969 data,[3] the above equations
appear to be valid for the urea phosphates although the
extent of damage is not as severe as from urea. This appears
reasonable since at the lower rates of urea phosphate appli-
cation which were used in this experiment, the amount of urea
in the urea phosphates is nearly as high as urea combined
with the phosphorous only treatment.

Effect of Drilled vs. Broadcast N on Yield

Drilling urea or urea phosphates at the 20 lbN/Ac
rate on the medium to fine textured soils resulted in as high
or higher yields than broadcasting urea or NH_4NO_3. The
increased availability of drilled nitrogen evidently more than
offsets the harmful effect of ammonia at these rates. This is
not true on the coarser textured soils used in 1968 in which
damage was considerable (Table III).

Considerable plant damage at the 60 lb N/Ac rate of
drilled NH_4NO_3 occurred on the coarse textured Almasippi
soil resulting in grain yields of 5.5 bu/Ac less than broad-
casting the same N carrier.   On all other soils barley
response to drilling 60 lb N/Ac as NH_4NO_3 was equal to
or better than broadcasting.   This was also true of the

3.
    The validity of the 1969 23-23-0 data is questionable
    since seedling reductions are much higher than expected.
    This combined with very high nitrogen efficiency and
    high grain yields indicates an error in initial fert-
    ilizer weight.

90 lb N/Ac rate on the soils which received this treatment,
the Stockton (1969), Newdale, Lakeland and Red River. On the
average (Figure 6 and 7), drilling ammonium nitrate up to 60 lb
N/Ac resulted in substantially higher grain yields than
broadcasting with the greatest difference occurring at the
40 lb N/Ac rate. These results are consistent with the
view that placing fertilizers in a band makes it more avail-
able to the plant roots and less available to competing weeds.
The nitrogen efficiency figures (Table V) also indicate that
broadcasting NH_4NO_3 results in less fertilizer N utiliz-
ation up to rates of 60 lb N/Ac except on the Almasippi
soil.

Comparison of Broadcast Urea and NH_4NO_3 on Yield

The grain yields from broadcasting urea in 1968
were less on all soils than from broadcasting NH_4NO_3 up
to 60 lb N/Ac (Table III). The greatest differences occurred
on the coarse textured Almasippi Soil. At the 60 lb N/Ac
rate of application, NH_4NO_3 caused barley yields to be 9.1
bu/Ac higher than urea.   On the other three soils,
the differences averaged 4.1 bu/Ac. At the higher rate of
application, the response curve levelled off and differences
between carriers were not meaningful.

The individual plots in 1969 were subject to con-
siderable variability and differences between broadcast
sources were not statistically significant. The averaged
results of the yields (Figure 7) however, suggest that at
60 and 90 lb N/Ac, urea was not as effective as NH_4NO_3.

The relationship of pH or cation exchange capacity on the effectiveness of broadcast urea relative to NH_4NO_3 is not readily apparent in this experiment except for the Almasippi soil where large differences between the carriers was noted. This could be related to the low cation exchange capacity and high pH. The other soils used in 1968, although considerably different in both pH and cation exchange capacity, had relatively similar values for differences between urea and NH_4NO_3.

Split Applications

The 1969 trials included split applications of 40 drilled and 20 broadcast, 40 drilled and 50 broadcast, 60 drilled and 30 broadcast and 60 drilled and 60 broadcast lb N/Ac as ammonium nitrate. The 1968 drilled results had indicated that toxicity of 60 lb N/Ac as ammonium nitrate drilled with the seed may have been the cause of the sharp decrease in response from the 40 to 60 lb N/Ac rate. Drilling lower amounts of nitrogen with the seed and broadcasting the remainder was considered a possible improvement over drilling or broadcasting alone. No consistent improvements were recorded using this procedure in 1969, however (Table IV). The yields from the split applications of 40 lb N drilled and 20 lb. N broadcast were similar to drilling ammonium nitrate at 60 lb N/Ac. Drilling 50 and broadcasting 40 lb N/Ac appeared better than drilling 60 and broadcasting 30 lb N/Ac on three of the four trials but differences were not significant

at the 5% level. Neither of these split applications was
significantly different than drilling or broadcasting 90 lb.
N/Ac. Drilling 60 and broadcasting 60 lb N/Ac was also very
similar to broadcasting 120 lb N/Ac.

Banding Urea

Banding urea 1 inch to the side of the seed caused
no apparent injury to the barley seedings on any of the soils
which received this application. Yields were comparable to
those of NH_4NO_3 drilled. This is consistent with the
results of Uliddowson and Penny (76).

TABLE III

EFFECT OF FERTILIZER TREATMENTS
ON GRAIN AND STRAW YIELDS IN 1968

Fertilizer Carrier	SOIL TYPE N/P_2O_5 lb/acre	ALMASIPPI Grain bu/Ac	Straw cwt/Ac	STOCKTON Grain bu/Ac	Straw cwt/Ac	PLUM RIDGE Grain bu/Ac	Straw cwt/Ac	ALTONA Grain bu/Ac	Straw cwt/Ac
Urea Phosphate (23-23-0)	20/20 D	40.6	17.9	44.8	19.6	27.9	16.3	46.0	22.5
Urea Phosphate (27-27-0)	20/20 D	39.5	12.0	44.4	21.5	28.8	15.6	40.1	19.1
NH_4NO_3 + $NH_4H_2PO_4$	20/20 D	42.4	18.2	46.3	20.5	30.0	14.3	38.4	17.7
Urea + $NH_4H_2PO_4$	20/20 D	35.7	16.5	45.7	20.4	29.7	15.2	41.3	16.2
Urea Phosphate (23-23-0)	30/30 D	41.7	19.2	52.1	25.9	33.1	19.3	52.0	28.1
Urea Phosphate (27-27-0)	30/30 D	39.1	19.5	52.3	24.1	29.4	19.5	48.7	24.8
NH_4NO_3 + $NH_4H_2PO_4$	30/30 D	49.1	20.8	58.8	22.7	40.0	20.1	48.3	23.6
Urea + $NH_4H_2PO_4$	30/30 D	41.6	19.5	48.2	22.0	31.0	20.4	52.6	24.5
L S D 5%		3.7		5.0		5.2		6.8	
NH_4NO_3 + $NH_4H_2PO_4$	20/30 D	40.1	17.1	49.1	22.7	28.4	14.4	40.7	18.7
Urea + "	20/30 D	38.0	16.2	47.3	19.6	28.1	15.3	40.5	18.6
NH_4NO_3 + "	20/30 B	39.2	16.1	45.0	19.0	32.3	14.0	38.7	16.1
Urea + "	20/30 B	38.6	16.3	44.1	18.4	30.8	14.0	41.8	18.7
NH_4NO_3 + "	40/30 D	55.8	24.2	66.4	28.8	46.3	28.1	58.1	27.6
Urea + "	40/30 D	39.2	22.6	53.1	27.1	37.1	25.2	57.0	27.9
NH_4NO_3 + "	40/30 B	51.1	22.2	55.4	20.5	45.3	22.1	42.3	21.7
Urea + "	40/30 B	47.6	21.1	49.6	21.1	44.3	21.6	37.9	22.2
NH_4NO_3 + "	60/30 D	57.8	27.5	63.8	30.3	60.6	32.5	59.8	33.5
Urea + "	60/30 D	25.5	21.8	48.0	34.3	20.5	36.8	63.4	37.2
NH_4NO_3 + "	60/30 B	63.3	28.3	59.5	25.5	60.1	26.7	58.0	27.5
Urea + "	60/30 B	54.2	25.2	55.7	23.5	56.5	26.8	53.2	24.8
L S D 5%		4.8		6.8		7.2		6.5	

...

TABLE III (continued)

Fertilizer Carrier	SOIL TYPE N/P$_2$O$_5$ lb/acre	ALMASIPPI Grain bu/Ac	ALMASIPPI Straw cwt/Ac	STOCKTON Grain bu/Ac	STOCKTON Straw cwt/Ac	PLUM RIDGE Grain bu/Ac	PLUM RIDGE Straw cwt/Ac	ALTONA Grain bu/Ac	ALTONA Straw cwt/Ac
NH$_4$NO$_3$ + NH$_4$H$_2$PO$_4$	20/30 B	39.2	16.1	45.0	19.0	32.3	14.0	40.5	16.1
Urea + "	20/30 B	38.6	16.3	44.1	18.4	30.8	14.0	41.6	18.7
NH$_4$NO$_3$ + "	40/30 B	51.1	22.2	55.4	20.5	45.3	22.1	42.3	21.7
Urea + "	40/30 B	47.6	21.1	49.6	21.1	44.3	21.6	37.9	22.2
NH$_4$NO$_3$ + "	60/30 B	63.3	28.3	59.5	25.5	60.1	26.7	58.0	27.5
Urea + "	60/30 B	54.2	25.2	55.7	23.5	56.5	26.8	53.2	24.8
NH$_4$NO$_3$ + "	90/30 B	64.0	29.6	61.8	27.0	70.9	36.9	61.5	35.5
Urea + "	90/30 B	58.2	28.4	57.8	24.0	73.0	34.8	58.4	31.1
NH$_4$NO$_3$ + "	120/30 B	57.8	28.9	67.4	32.2	69.7	39.3	66.5	37.2
Urea + "	120/30 B	59.7	29.3	65.3	30.0	79.1	41.7	57.8	31.0
NH$_4$NO$_3$ + "	240/30 B	59.0	33.8	73.5	39.6	68.4	56.6	53.5	38.1
Urea + "	240/30 B	57.4	35.7	67.8	42.2	55.3	50.1	68.9	39.1
L S D 5%		5.4		6.7		13.0		8.8	
NH$_4$H$_2$PO$_4$	7/30 D	33.4	14.9	41.2	21.7	24.6	10.8	33.8	15.7
NH$_4$NO$_3$ + NH$_4$H$_2$PO$_4$ + KCl	90/30/30 B	65.1	40.0	62.4	32.4	73.8	40.0	66.4	32.4
NH$_4$NO$_3$ + "	400/140/130 D	59.7	48.1	89.5	43.3	65.2	62.2	67.8	42.3
NH$_4$NO$_3$	90/0 D	50.0	26.2	42.3	22.2	64.4	41.2	61.0	30.0

All Phosphate Drilled with Seed

D = Nitrogen Drilled

B = Nitrogen Broadcast

TABLE IV

EFFECT OF FERTILIZER TREATMENTS ON GRAIN AND STRAW YIELDS IN 1969

Fertilizer Carrier	SOIL TYPE N/P_2O_5 lb/Ac	STOCKTON Grain bu/Ac	Straw cwt/Ac	NEWDALE Grain bu/Ac	Straw cwt/Ac	LAKELAND Grain bu/Ac	Straw cwt/Ac	RED RIVER Grain bu/Ac	Straw cwt/Ac
Urea Phosphate (23-23-0)	20/20 D	34.6	15.2	33.2	14.2	30.8	16.9	55.8	27.8
Urea Phosphate (27-27-0)	20/20 D	33.0	13.4	25.5	10.8	26.2	16.5	51.2	25.6
NH_4NO_3 + $NH_4H_2PO_4$	20/20 D	38.0	15.5	30.1	10.8	25.2	13.0	56.3	28.8
L S D 5%		6.0		7.7		3.7		11.4	
Urea Phosphate (23-23-0)	30/30 D	47.6	24.5	39.9	18.4	39.7	22.9	59.1	30.8
Urea Phosphate (27-27-0)	30/30 D	48.1	20.6	28.1	11.0		15.1	57.4	28.7
NH_4NO_3 + $NH_4H_2PO_4$	30/30 D	47.1	20.4	37.7	17.3	32.6	17.0	60.1	31.6
Urea + "	30/30 D	43.7	20.2	37.2	16.6	28.6	15.4	58.4	28.9
Urea + "	30/30 S	41.7	17.6	39.4	16.7	30.1	14.6	63.5	31.6
L S D 5%		8.7		11.2		9.1		5.8	
NH_4NO_3 + $NH_4H_2PO_4$	20/30 D	42.3	18.1	29.7	13.7	21.4	11.0	51.0	25.9
Urea + "	20/30 D	40.9	22.0	27.9	11.9	20.0	10.9	50.4	25.4
NH_4NO_3 + "	20/30 B	40.9	14.3	27.1	11.2	19.0	12.4	45.9	22.5
Urea + "	20/30 B	40.3	14.3	27.4	11.5	17.0	8.4	51.0	24.8
L S D 5%		6.6		4.2		6.2		7.5	
NH_4NO_3 + $NH_4H_2PO_4$	40/30 D	54.6	22.7	47.4	21.0	39.4	20.6	65.3	33.7
Urea + "	40/30 D	46.1	18.3	40.7	18.5	37.0	17.5	58.6	29.5
NH_4NO_3 + "	40/30 B	45.2	17.9	44.3	16.2	31.7	16.5	69.2	33.1
Urea + "	40/30 B	43.5	17.5	41.3	14.5	35.8	17.5	73.1	44.5
Urea + "	40/30 S	48.3	20.1	48.3	20.6	35.3	19.4	66.3	31.8
L S D 5%		8.3		6.8		7.0		13.7	

TABLE IV (continued)

Fertilizer Carrier	SOIL TYPE N/P$_2$O$_5$ lb/Ac	STOCKTON Grain bu/Ac	Straw cwt/Ac	NEWDALE Grain bu/Ac	Straw cwt/Ac	LAKELAND Grain bu/Ac	Straw cwt/Ac	RED RIVER Grain bu/Ac	Straw cwt/Ac
NH$_4$NO$_3$ + NH$_4$H$_2$PO$_4$	60/30 D	65.4	26.2	54.6	23.9	47.4	27.3	69.5	35.1
Urea + "	60/30 D	40.4	18.9	45.5	17.8	41.3	24.6	57.5	32.5
NH$_4$NO$_3$ + "	60/30 B	54.1	17.7	53.6	16.5	31.7	24.8	76.9	35.3
Urea + "	60/30 B	53.9	21.9	54.4	20.5	36.1	16.4	72.8	37.0
Urea + "	60/30 S	66.1	26.9	57.7	24.0	45.0	25.8	74.5	35.8
NH$_4$NO$_3$ + "	60/30 S$_{p1}$	61.7	26.4	54.6	25.4	42.8	25.1	74.0	32.2
L S D 5%		7.9		12.6		10.0		11.4	
NH$_4$NO$_3$ + NH$_4$H$_2$PO$_4$	90/30 D	72.8	29.8	67.8	29.4	55.1	31.5	77.8	43.1
NH$_4$NO$_3$ + "	90/30 B	62.8	24.2	70.6	28.0	53.3	30.7	82.5	43.6
Urea + "	90/30 B	65.4	27.4	63.3	24.8	55.1	30.8	77.8	38.2
NH$_4$NO$_3$ + "	90/30 S$_{p2}$	70.0	29.4	65.8	27.8	60.3	35.9	80.3	42.5
NH$_4$NO$_3$ + "	90/30 S$_{p3}$	70.9	29.7	63.7	27.9	53.9	33.0	75.4	41.2
L S D 5%		4.1		10.6		11.3		11.4	
NH$_4$NO$_3$ + NH$_4$H$_2$PO$_4$	120/30 B	63.4	27.6	73.3	28.8	62.0	33.4	76.7	37.9
Urea + "	120/30 B	66.3	28.0	67.6	28.5	61.3	32.3	79.3	42.5
NH$_4$NO$_3$ + "	120/30 S$_{p4}$	70.0	30.2	75.0	30.1	60.6	34.2	76.4	41.4
L S D 5%		17.0		16.2		12.9		17.9	
NH$_4$H$_2$PO$_4$	7/30 D	31.0	15.3	20.7	9.2	14.4	8.4	47.1	21.8

All Phosphate Drilled with Seed

D = Nitrogen Drilled

B = Nitrogen Broadcast

S = banded 1" to side of seed

   S$_p$ = Split Application   S$_{p1}$ = 40D + 20B   S$_{p2}$ = 40D + 50B   S$_{p3}$ = 60D + 30B   S$_{p4}$ = 60D + 60B

TABLE V

NITROGEN FERTILIZER UPTAKE IN PERCENT OF THAT APPLIED.
CALCULATED FROM THE DIFFERENCE IN NITROGEN UPTAKE BETWEEN
PLOTS RECEIVING NITROGEN AND PHOSPHORUS
AND THOSE RECEIVING PHOSPHATE ONLY

SOIL TYPE Fertilizer Carrier	N lb/acre		ALMASIPPI	STOCKTON (1968)	PLUM RIDGE	ALTONA	STOCKTON (1969)	NEWDALE	LAKELAND	RED RIVER
NH_4NO_3	20	D	31.5	3.8	4.6	11.5	67.7	66.9	30.0	15.4
Urea	20	D	25.7	-10.0	7.7	3.1	63.8	50.6	28.4	-28.4
NH_4NO_3	20	B	40.8	-12.2	30.8	-3.8	73.8	43.1	36.2	-17.7
Urea	20	B	30.0	-19.4	26.1	22.3	66.2	56.1	20.0	0.0
Urea Phosphate (23-23-0)	30	D	21.7	23.0	19.6	72.2	93.9	78.3	97.0	55.8
Urea Phosphate (27-27-0)	30	D	13.0	27.4	7.4	48.3	64.3	30.9	–	20.8
NH_4NO_3	30	D	47.6	35.8	42.6	45.2	67.5	68.4	56.5	48.3
Urea	30	D	33.0	9.3	14.3	65.0	53.0	64.4	37.8	16.5
Urea	30	S					56.5	71.0	49.2	62.2
NH_4NO_3	40	D	66.0	63.3	50.0	59.4	73.0	70.4	55.1	57.0
Urea	40	D	33.7	36.4	28.4	55.5	55.4	54.8	53.7	36.1
NH_4NO_3	40	B	59.4	35.1	43.4	28.2	48.4	61.0	42.4	63.6
Urea	40	B	45.2	14.8	42.1	10.9	44.8	55.5	52.1	61.5
Urea	40	S					63.9	82.1	48.2	
NH_4NO_3	60	D	56.1	46.4	53.8	53.5	73.6	63.2	57.9	60.0
Urea	60	D	5.7	38.5	7.7	60.0	27.5	49.2	50.7	33.2
NH_4NO_3	60	B	70.8	39.4	50.0	51.2	56.2	58.3	54.5	60.1
Urea	60	B	47.4	26.8	48.2	38.3	63.8	65.4	37.8	65.5
Urea	60	S					81.6	70.5	53.3	66.1
NH_4NO_3	60	S_{Pl}					68.9	64.4	53.1	54.0

. . .

TABLE V (continued)

SOIL TYPE Fertilizer Carrier	N lb/acre		ALMASIPPI	STOCKTON (1968)	PLUM RIDGE	ALTONA	STOCKTON (1969)	NEWDALE	LAKELAND	RED RIVER
NH_4NO_3	90	D					70.6	60.5	50.1	65.5
NH_4NO_3	90	B	66.0	34.6	58.5	62.0	62.4	68.1	52.1	80.5
Urea	90	B	43.0	27.1	60.0	53.1	63.9	59.7	59.2	73.3
NH_4NO_3	90	S_{p_2}					67.1	62.5	63.5	65.5
NH_4NO_3	90	S_{p_3}					67.6	58.3	54.4	67.2
NH_4NO_3	120	B	45.3	44.0	48.8	59.0	53.9	61.1	53.2	56.4
Urea	120	B	40.2	41.0	64.5	38.5	63.9	56.3	51.8	65.2
NH_4NO_3	120	S_{p_4}					61.7	57.2	46.2	52.8

D = Drilled

B = Broadcast

S = Sideband

S_p = Split application S_{p_1} = 40D + 20 B S_{p_2} = 40D + 50B S_{p_3} = 60D + 30B

S_{p_4} = 60D + 60B
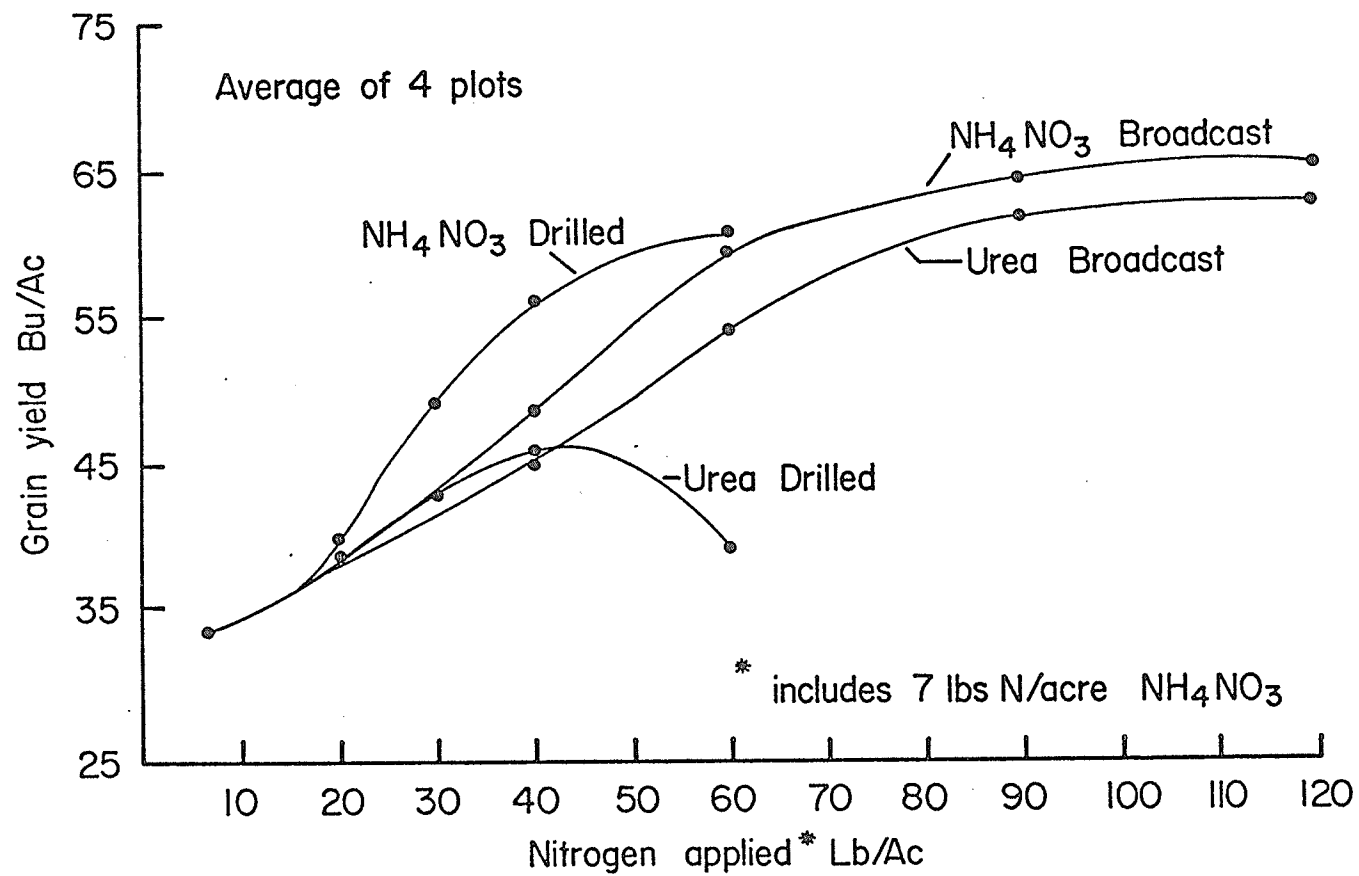
FIGURE 6   INFLUENCE OF RATE OF NITROGEN, NITROGEN SOURCE AND METHOD OF APPLICATION ON GRAIN YIELD IN 1968
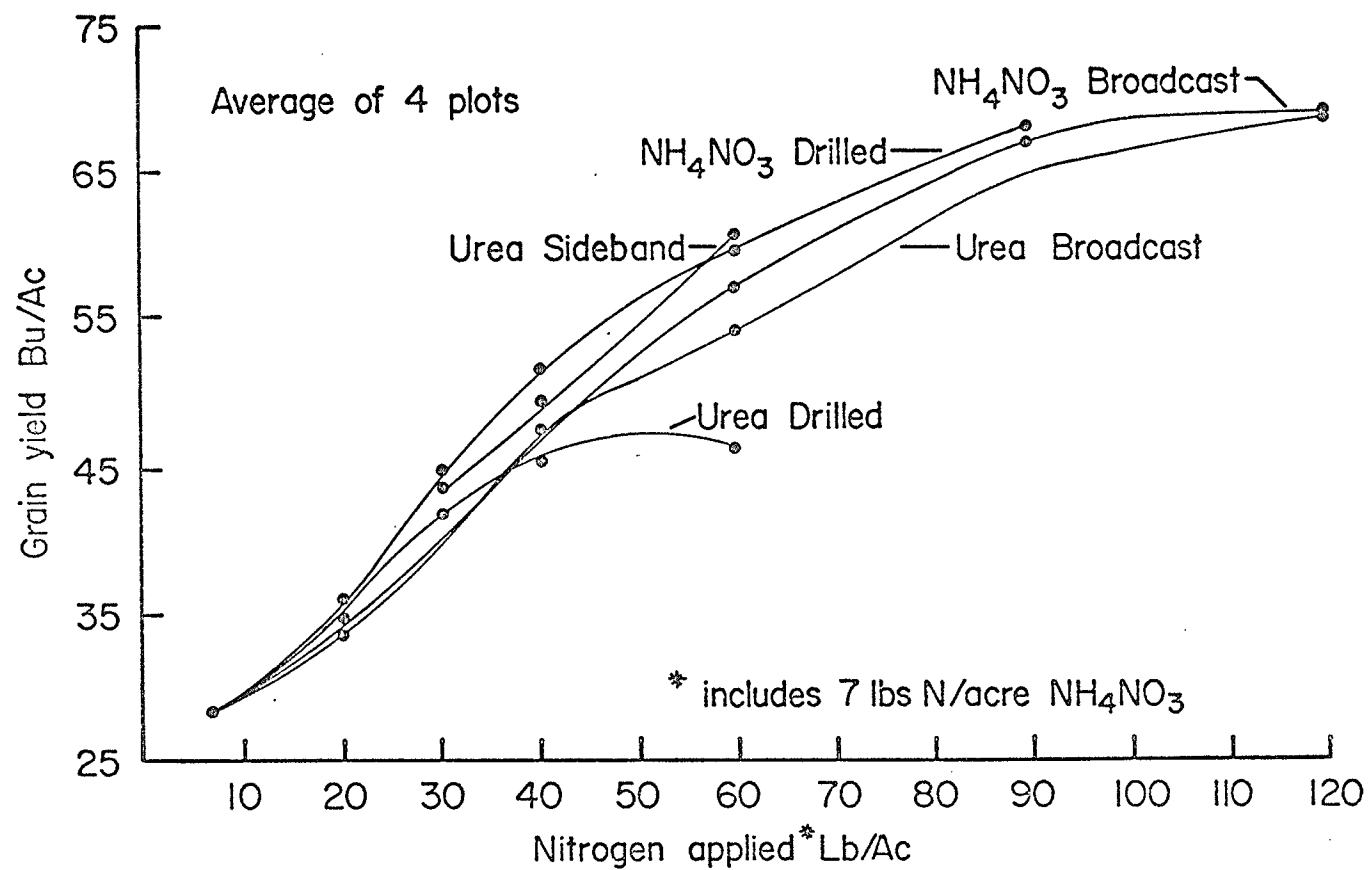
FIGURE 7   INFLUENCE OF RATE OF NITROGEN, NITROGEN SOURCE AND
METHOD OF APPLICATION ON GRAIN YIELD IN 1969

IV   GREENHOUSE EXPERIMENT

Introduction

The purpose of the greenhouse experiment was to study the fate of urea, ammonium and nitrate nitrogen when added to a soil plant system. The purpose was to determine reasons for the differences in crop response to urea and NH_4NO_3 in the field experiments. This experiment also permitted a comparison of the difference technique[1] and the tracer technique for measuring fertilizer nitrogen efficiency.

Methods and Materials

$$^{15}NH_4NO_3 \, , \quad NH_4 \, ^{15}NO_3 \quad \text{and} \quad \begin{matrix} ^{15}NH_2 \\ \\ NH_2 \end{matrix} \Big\rangle C = 0 \text{ (urea)}$$
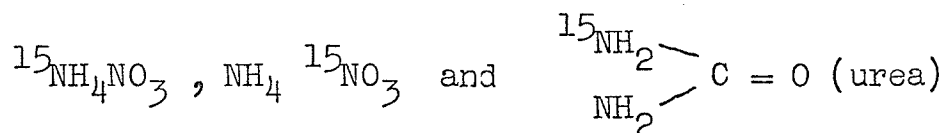
with approximately 1.0% ^{15}N excess[2] were used as nitrogen sources for conquest barley (Hordeum vulgare) grown on two soils (Table VI) which had been used in the field experiments. The Almasippi soil was chosen for its low cation exchange capacity of 11.3 meq/100g and high pH of 8.0, characteristics which made significant losses of ammonia likely. The Stockton soil was chosen for its lower pH of 6.0 and higher cation exchange capacity of 15.9, characteristics which make ammonia

---

1.

Described in Table XI

2.

The low % ^{15}N excess material used in this experiment limited the analysis for ^{15}N to plant material only.

TABLE VI   CATION EXCHANGE CAPACITY, $CaCO_3$ EQUIVALENT, PH, NH_4 AND NO_3-N

AND MOISTURE AT FIELD CAPACITY OF SOILS USED IN GREENHOUSE EXPERIMENT

Soil Type	C.E.C. meq/100g	$CaCO_3$ equivalent %	pH	NH_4-N ppm	NO_3-N ppm	Moisture at Field Capacity %
Almasippi L V F S	11.3	1.0	8.0	3.3	2.9	23
Stockton F S L	15.9	0.3	6.0	8.7	13.0	28

losses less likely than on the Almasippi soil. The 1968
field results had indicated that NH_4NO_3 was a better
source of nitrogen than urea on both soils, but on the
Stockton soil the differences were not as great as on the
Almasippi. In 1969 the results on the Stockton soil were
similar for both urea and NH_4NO_3. The cause of the differ-
ences in 1968 was not determined but ammonia losses were
suspected.

The treatments (Table VII) were randomized within
blocks and replicated three times. Treatments were shifted
every three to four days. Block positions were rotated each
week.

Before seeding, all the soil (5 Kgm) except an
amount equal to the surface two inches was added to the
plastic containers. The moisture level of the soil in the
pots was brought up to field capacity and a basal dressing of
potassium, sulfur and phosphorous was applied in solution form
in the following amounts.

$$15 \quad ppm \quad P \quad as \quad K_2HPO_4$$

$$20 \quad ppm \quad S \quad as \quad K_2SO_4$$

Fifteen barley seeds were planted on the surface of the soil
and covered with a two inch layer of soil which had been
thoroughly mixed with the nitrogenous fertilizer material.
The latter was in powder form when mixed. Water was again
applied until field capacity was reached. After one week,
the number of barley seedlings emerging was very low and
therefore the pots were reseeded. After emergence of the

second seeding, the plants were thinned to six plants per pot. Soil and plant samples were taken at three and eight weeks after emergence. The soil samples were composites of four core samples from each pot. The soil was then analyzed for ammonium and nitrate nitrogen by the method described by Bremner and Keeney (5). Plant samples were analyzed for Kjeldahl plus nitrate nitrogen (55). The per cent ^{15}N excess in the plant samples was determined after replicates were bulked (27).

Results and Discussion

Plant Yields

The plant yields of the two ammonium nitrate sources should theoretically have been the same in all treatments since they differed only in respect to the labelled ion. The differences found in these yields (Table VII) must be attributed to uncontrolled variability.

The early harvest yields from these two sources were quite similar but the late harvest yields were quite variable which made comparison between ammonium nitrate and urea on this basis less meaningful. The yields of the plants harvested three weeks after emergence indicate that on the Almasippi soil, urea was less effective in causing high yields than ammonium nitrate even at this early stage of growth. The results from the Stockton soil indicate this at the 30 ppm rate but not at the 75 ppm rate of application. Although a statistical analysis indicates a significant carrier effect

TABLE VII   INFLUENCE OF NITROGEN SOURCE AND HARVEST DATE
ON TOTAL BARLEY YIELD (G/POT).

SOIL		ALMASIPPI		STOCKTON	
		Yield g/pot		Yield g/pot	
Rate N (ppm)	N Source	Early Harvest	Late Harvest	Early Harvest	Late Harvest
0		0.72	3.85	1.59	11.06
30	$NH_4\,^{15}NO_3$	1.17	8.56	1.91	14.93
	$^{15}NH_4\,NO_3$	1.21	9.96	1.80	15.66
	Urea	0.94	8.52	1.57	15.31
75	$NH_4\,^{15}NO_3$	1.35	14.26	1.76	17.29
	$^{15}NH_4\,NO_3$	1.45	14.31	1.71	18.64
	Urea	1.03	11.92	1.91	16.65

on yields from the early harvest, the results on the Stockton
soil at the two rates differ. The results from the Almasippi
soil were consistent at both rates, however, and are likely
true effects.   There is a highly significant soil effect on
plant yields which is predictable from the initial soil inorg-
anic nitrogen content of the two soils (Table VIII). No sign-
ificant source x soil interaction was present in the early
harvest yield results indicating that the differences between
urea and ammonium nitrate are not affected by the soil type.
This suggests that the difference between nitrogen sources
at the early harvest is of little consequence.

A statistical analysis of the late harvest yields
indicates a highly significant source effect. The significant
rate x source interaction indicates that at the 75 ppm rate
of application, there is a difference in sources. The variat-
ion in yields between the two NH_4NO_3 carriers at the 30 ppm
rate precludes a comparison of urea and ammonium nitrate. A
highly significant soil effect on late harvest plant yields is
predicted by the initial NO_3 - N content of the two soils
similarly as the early harvest yields.

Nitrogen Uptake

The nitrogen uptake data is less variable than the
yield data, therefore more easily interpreted (Table IX). The
soil inorganic nitrogen values which appear in the same table
are quite variable and present difficulties in interpretation.
The values for the ammonium nitrate sources are considerably

TABLE VIII   MINERAL NITROGEN OF SOILS USED IN
GREENHOUSE EXPERIMENT AT TWO HARVEST DATES (ppm)

SOIL		ALMASIPPI			STOCKTON		
		Early Harvest					
Rate N ppm	Source	NH_4^+	NO_3^-	Total	NH_4^+	NO_3^-	Total
0		4.1	2.2	6.3	10.4	25.6	36.0
	$NH_4\ ^{15}NO_3$	4.6	17.1	21.7	9.6	57.3	66.9
30	$^{15}NH_4\ NO_3$	4.7	12.6	17.3	13.0	54.3	67.3
	Urea	3.7	11.0	14.7	12.9	57.5	70.4
	$NH_4\ ^{15}NO_3$	4.6	55.7	60.3	9.8	99.5	109.3
75	$^{15}NH_4\ NO_3$	4.2	55.7	59.9	11.1	97.5	108.6
	Urea	4.9	40.9	45.8	12.5	87.4	99.9
		Late Harvest					
0		4.2	6.4	10.6	9.7	4.9	14.6
	$NH_4\ ^{15}NO_3$	5.1	2.0	7.1	11.8	3.7	15.5
30	$^{15}NH_4\ NO_3$	3.0	1.4	4.4	11.8	5.5	17.3
	Urea	5.8	4.6	10.4	9.8	4.1	13.9
	$NH_4\ ^{15}NO_3$	6.1	5.8	11.9	12.9	6.2	19.1
75	$^{15}NH_4\ NO_3$	4.3	3.2	7.5	11.4	4.6	16.0
	Urea	5.4	2.4	7.8	11.3	4.6	15.9

TABLE IX — SOIL MINERAL NITROGEN AND PLANT NITROGEN AT TWO HARVEST DATES   (mg/pot)

		ALMASIPPI			STOCKTON		
Rate N ppm	Source	Inorganic Soil N	Plant N	Soil + Plant N	Inorganic Soil N	Plant N	Soil + Plant N
		Early Harvest					
0		31.5	25.8	57.3	180.0	86.6	266.6
	NH_4 $^{15}NO_3$	108.5	63.5	172.0	334.5	110.0	444.5
30	$^{15}NH_4$ NO_3	86.5	65.0	151.5	336.5	104.1	440.6
	Urea	73.5	50.2	123.7	352.0	89.3	441.3
	NH_4 $^{15}NO_3$	301.5	77.0	378.5	546.5	103.0	649.5
75	$^{15}NH_4$ NO_3	299.5	82.1	381.6	543.0	100.0	643.0
	Urea	229.0	56.6	285.6	499.5	111.6	611.1
		Late Harvest					
0		53.0	56.0	109.0	73.0	220.9	293.9
	NH_4 $^{15}NO_3$	35.5	128.2	163.7	77.5	312.5	390.0
30	$^{15}NH_4$ NO_3	22.0	132.7	154.7	86.0	332.6	418.6
	Urea	52.0	111.2	163.2	69.5	322.4	391.9
	NH_4 $^{15}NO_3$	59.5	259.5	319.0	95.5	471.4	566.9
75	$^{15}NH_4$ NO_3	37.5	260.5	298.0	80.5	474.3	554.8
	Urea	39.0	183.3	222.3	79.5	470.1	549.6

51

different in some cases which must be attributed to experimental error. The soil data does, however, support to some extent the nitrogen uptake data. It is readily evident in Table IX from the early harvest data that the urea treated Almasippi soils contained less inorganic nitrogen and produced plants with less nitrogen than did the ammonium nitrate treated soils. This appears to be the cause of the lower plant yields discussed under the previous section. Since this type of soil has been characterized as the type in which ammonia losses occur, this is suggested as a cause in this case. Further evidence that ammonia losses from this soil occur is presented in the next chapter. The results on the Stockton soil are not very consistent at the early harvest, but plant nitrogen plus soil inorganic nitrogen total was approximately 30 mg/pot less on the 75 ppm urea treated soil. At the 30 ppm rate there is no difference between sources in plant nitrogen plus inorganic soil nitrogen. The final harvest results reveal only small differences between urea and ammonium nitrate labelled at the ammonium end. The differences are smaller than the difference between the two ammonium nitrate sources which are attributed to uncontrolled variability. The late harvest results on the Almasippi soil indicate that soil plus plant nitrogen was 90 mg/pot higher from the ammonium nitrate than from the urea amended soils at the 75 ppm rate. This is mainly accounted for by the difference in plant uptake of nitrogen from the urea and ammonium nitrate sources. At the 30 ppm rate, soil plus plant nitrogen totals are the same

although the plant nitrogen alone is approximately 20% greater
from ammonium nitrate than from urea. Considering the early
harvest results and the fact that there should theoretically
be little nitrate nitrogen left in a soil on which nitrogen
deficient plants have been growing, the reported value of
52 mg/pot appears high. Using plant nitrogen only as a
criterion for available nitrogen, the data becomes more consis-
tent and the previous observation of the relative availibility
of nitrogen from the urea and ammonium nitrate soils becomes
more conclusive.

Plotting the nitrogen uptake values for the observed
check (0 nitrogen), 30 ppm and 75 ppm treatments (Figure 8)
resulted in curves designated as type 3 by Terman and Brown
(71). That is, the observed check is the same as that des-
cribed by regression. This indicates that the efficiency of
nitrogen uptake doesn't change with rate of application and
no net immobilization or mineralization has occurred due to
treatment at harvest time. Similar results were obtained in
the Almasippi soil although the regression curves do not pass
exactly through the observed check values. The relative
inefficiency of urea on this soil is also apparent from these
curves.

Tracer Nitrogen Uptake

The use of isotopes to study soil-fertilizer react-
ions has become widespread and highly regarded as an experi-
mental method. Broadbent and Nakashima (8) state that the
use of ^{15}N labelled fertilizer has made it possible to obtain
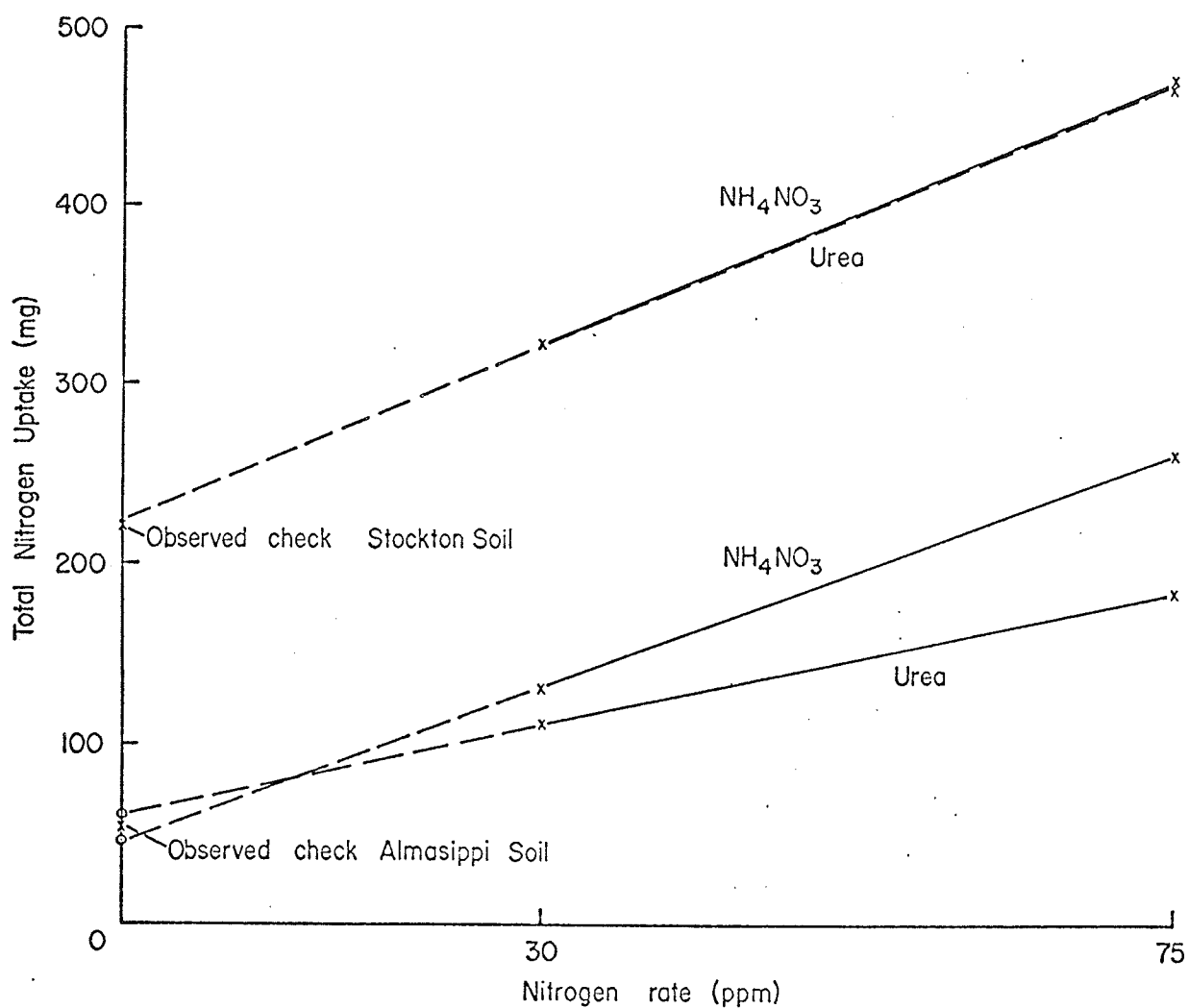
FIGURE 8   NITROGEN UPTAKE OF PLANTS IN GREENHOUSE EXPERIMENT
AS INFLUENCED BY SOIL TYPE, RATE AND SOURCE OF N

much better estimates of nitrogen losses than are possible
with conventional techniques. It is important, however, to
interpret this type of data correctly or it may be less use-
ful than using nontracer methods.

A comparison of the two NH_4NO_3 sources (Table X)
indicates that a greater per cent of the plant nitrogen is
derived from tracer $NO_3 - N$ than $NH_4 - N$ on all treat-
ments except the plants harvested at the early date with 75
ppm N applied to the Stockton soil. The differences bet-
ween the sources on the Almasippi soil are considerably
larger than on the Stockton. In all cases, the per cent
derived from the tracer ammonium source is approximately 50%
of that derived from the urea source. This result would be
expected if the ammonia released upon urea hydrolysis is
available to the plant to the same degree as the ammonium
from the ammonium nitrate source since there was exactly twice
as much tracer urea N applied as tracer $NH_4 - N$. The total
amount of tracer nitrogen (as opposed to % of plant nitrogen)
taken up by the plants on the Almasippi soil was less than
twice that of tracer $NH_4 - N$ indicating the disappearance
of tracer urea N by soil fixation or gaseous loss. This
did not occur to a great extent on the Stockton soil. In
order to compare tracer urea with $NH_4 NO_3$ tagged on both
ions, the results of $^{15}NH_4 NO_3$ and $NH_4 {}^{15}NO_3$ were summed
and presented under the heading $^{15}NH_4 {}^{15}NO_3$ in Table X.
In all cases, tracer ammonium nitrate was present in the plant
tops in greater amounts than tracer urea. This is mainly due

TABLE X   TRACER NITROGEN IN PLANT TOPS FROM
UREA AND AMMONIUM NITRATE

SOIL	RATE N	HARVEST DATE[+]	SOURCE							
			Urea		$^{15}NH_4NO_3$		$NH_4{}^{15}NO_3$		$^{15}NH_4{}^{15}NO_3$	
			%*	mg/pot	%	mg/pot	%	mg/pot	%	mg/pot
Almasippi										
	30	E	42.1	21.1	20.2	13.1	30.7	19.5	50.9	32.6
		L	35.6	39.6	18.3	24.3	25.2	32.4	43.5	56.7
	75	E	57.7	32.6	27.2	22.4	39.8	30.6	67.0	53.0
		L	55.0	101.0	27.7	71.0	40.2	103.0	67.9	174.0
Stockton										
	30	E	21.9	19.5	11.7	12.4	15.5	17.1	27.2	29.5
		L	19.9	64.2	9.5	31.6	15.6	48.6	25.1	80.2
	75	E	40.1	44.6	22.7	22.7	22.1	22.9	44.8	45.6
		L	40.3	189.5	20.1	99.5	23.9	112.5	44.0	212.0

$$* \quad \% = \frac{\text{Tracer N in plant tops}}{\text{Total N in plant tops}}$$

+ E = 3 weeks after emergence

  L = 8 weeks after emergence

to the presence of the nitrate ion in ammonium nitrate.

The per cent nitrogen recovery results (Table XI) of the urea and ammonium sources determined by the tracer technique were quite similar on the Stockton soil but not on the Almasippi. This indicates that urea N disappeared in greater amounts than $NH_4 - N$ from NH_4NO_3 to a greater extent on the Almasippi soil than on the Stockton. A likely mechanism for this disappearance would be ammonia volatilization as urea hydrolyzes since the Almasippi soil characteristics are conducive to this occurrence whereas on the Stockton soil this is not the case. The percentage utilization of tracer $NO_3 - N$ was higher than either urea or $NH_4 - N$ and was more similar to the efficiency of NH_4NO_3 measured by the difference (Table X) method. Since total nitrogen uptake from the Stockton soil (Table IX) was similar for both the NH_4NO_3 and urea sources, the lower per cent utilization of tracer urea or $NH_4 - N$ was not likely due to volatilization of ammonia from the soil. Two possibilities are ammonia fixation and/or immobilization. Ammonium fixation to any large extent does not appear likely since the soils remained moist from the time of fertilizer application to harvest (51). Preferential microbial immobilization of ammonium over nitrate has been shown to occur (8) (37) (61) and appears to have occurred in this experiment. To account for the similarity in total nitrogen uptake from the urea and NH_4NO_3 sources, mineralization of non-tracer nitrogen would have to occur to an extent equal to that immobilized, i.e., the tracer ammonium

TABLE XI

FERTILIZER NITROGEN RECOVERY BY PLANTS
IN GREENHOUSE EXPERIMENT (per cent)

SOIL	RATE	HARVEST DATE[+]	Urea ^{15}N	Urea Diff.*	NH_4 ^{15}N	NO_3 ^{15}N	NH_4NO_3 ^{15}N	NH_4NO_3 Diff.*
						SOURCE		
Almasippi	30	E	14.1	16.3	17.5	26.0	21.7	25.6
		L	26.4	36.8	32.4	43.2	37.8	49.7
	75	E	8.7	8.2	12.0	17.4	14.1	14.3
		L	26.9	34.0	37.9	55.0	46.4	54.3
Stockton	30	E	13.0	1.8	16.6	22.8	19.7	13.6
		L	41.4	67.5	42.2	64.8	53.5	67.5
	75	E	11.9	7.2	12.1	12.2	12.2	4.0
		L	50.5	66.5	53.1	60.0	56.5	67.2

*   % recovery by difference method = $\dfrac{\text{N uptake of N treatment} - \text{N uptake of O N treatment}}{\text{N added}}$

+   E = 3 weeks after emergence
    L = 8 weeks after emergence

immobilized was replaced by non-tracer nitrogen.

V   AMMONIA VOLATILIZATION STUDIES

Introduction

The results of the field and greenhouse experiments indicated that urea was considerably less efficient than ammonium nitrate in supplying nitrogen to plants. This was particularly noticeable on the course textured Almasippi soil. A review of the literature indicated that the lower efficiency of urea could be due to volatilization of ammonia as urea hydrolyzed. Thus, several experiments were conducted to determine the influence of temperature, soil type and method of fertilizer placement on ammonia loss from urea and NH_4NO_3.

Methods and Materials

An apparatus was designed to pass ammonia free air over a soil surface and into an ammonia absorbing medium (Figure 9). Air was passed by pressure through a bottle (bottle A) containing boric acid to remove any ammonia which may have been present in the air entering the apparatus. The air was then passed through water (bottle B) to increase the moisture content of the air. This prevented excess moisture loss from the soils. The air was then passed through a 500 ml bottle containing soil (bottle C) and finally passed through a bottle containing 25 ml of 0.1N H_2SO_4 diluted to 75 mls in which the volatilized ammonia was trapped (bottle D). The apparatus was designed to accomodate 21 treatments.

Air →

Boric
Acid

H_2O

Soil

.I N.
H_2SO_4

A

B

C

D
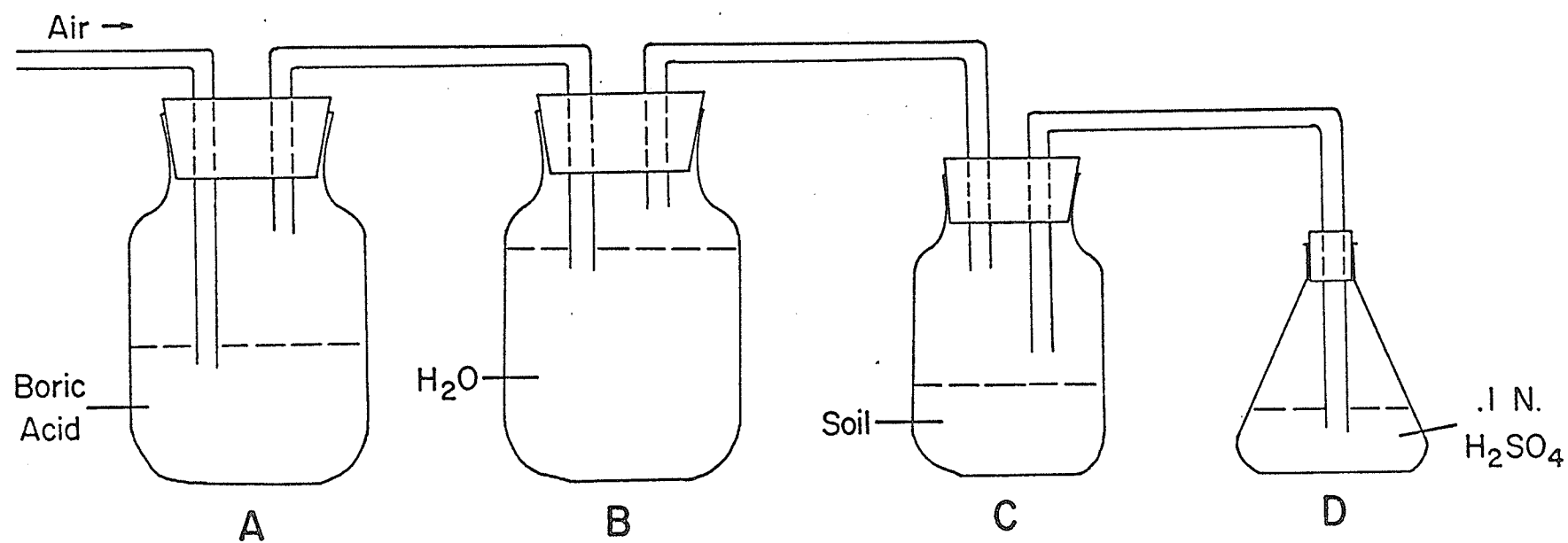
FIGURE 9   APPARATUS USED FOR MEASURING AMMONIA LOSS FROM SOILS

Following construction of the apparatus, an experiment was conducted to determine if the apparatus would function properly. The treatments used are listed in Table XIII. 250g of Almasippi soil were placed into the glass jar. One jar contained only standard NH_4NO_3. This treatment was used to test the efficiency of the apparatus in recovering volatilized NH_3. The soils were then wetted to field capacity and a urea nitrogen solution added uniformly over the soil surface. The jars were stoppered and the air inlet tube connected to the air supply. Sufficient air was passed through the jar so that the air above the soil was replaced approximately five times per minute. 20 ml of 0.1N NaOH was added to the jar containing only NH_4NO_3. The jars were immediately sealed and the collection of ammonia initiated. The incubations were conducted at 25°C. The ammonia absorption flasks were replaced with jars containing unreacted acid every 24 hours. The reacted acid was then titrated with 0.1N NaOH and the amount of ammonia volatilized calculated.

The characteristics of the soils used in the various ammonia volatilization studies are outlined in Table XII.

Results and Discussion

The amounts of ammonia N volatilized from the soil after 120 hours was nearly linear with rate of application (Figure 10). After 24 and 48 hours, however, volatilization was less complete and the curves have a large inflection

TABLE XII   CATION EXCHANGE CAPACITY, pH, $CaCO_3$ EQUIVALENT AND % MOISTURE AT FIELD CAPACITY OF SOILS USED IN THE AMMONIA VOLATIZATION EXPERIMENTS

Soil Type		C.E.C. (meq/100g)	pH	$CaCO_3$ equiv. (%)	Moisture content at field capacity (%)
Almasippi	L V F S	11.3	8.0	1.0	23
Stockton	F S L	15.9	6.0	0.3	28
Altona	V F S C L	22.0	7.3	0.5	34
Lakeland	C L	29.4	8.0	15.6	40

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if extrapolated to 0. The total N volatilized after 120 hours was not a direct function of the amount of urea N added since at the 25 ppm rate of application 2.9 mg of N was volatilized but at the 100 ppm rate, 9.46 mg was volatilized. This is clearly indicated in Figure 11 which shows the inverse relationship of per cent N volatilization to the rate of urea N application (curves 4, 5 and 6). Curves 1, 2 and 3 show that 85% of the ammonia volatilization from the 25 ppm rate of urea N occurred within the first 24 hours but at the 50 and 100 ppm rates only 65 and 42%, respectively, volatilized within this time period. Only after 72 hours did the 100 ppm rate, curve (3), show a marked decrease in volatilization rate.

The fact that a lower percentage of N was volatilized at higher rates of urea application could be due to a limitation of the urease enzyme in the soil at higher rates of urea application. The urea would therefore be able to diffuse into the soil where volatilization was less likely to occur.

The results of the field experiments in Chapter III indicated that barley response to an NH_4NO_3 application was 43% higher than that from a urea application at the 60 lb N/Ac rate on the Almasippi soil. The ammonia losses which occurred from this soil in the incubation experiments could account for this difference assuming that very little ammonium nitrate would have been lost under the same conditions. This could also account for the differences between urea and

TABLE XIII   VOLATILIZATION OF AMMONIA N FROM UREA APPLIED TO AN
ALMASIPPI SOIL AT RATES OF 25,   50 and 100 ppm N

Treatment	NH_3 N Volatilized (mg) Time (hour)				
	24	48	72	96	120
Control (ON)	-	0.10	0.10	0.10	0.10
Urea 25 ppm (6.25 mg)	2.51	2.74	2.86	2.90	2.90
Urea 50 ppm (12.50 mg)	3.48	4.64	4.99	5.14	5.14
Urea 100 ppm (25.00 mg)	4.43	7.41	8.91	9.39	9.46
NH_4NO_3 + NaOH(6.45 mg NH_4 N)	6.27	6.38	6.40	6.40	6.40

Statistical analysis of urea treatments

Source of variance	Variance	F
Treatments	22.1	110.5 **
Replications	0.3	1.5
Error	0.2	
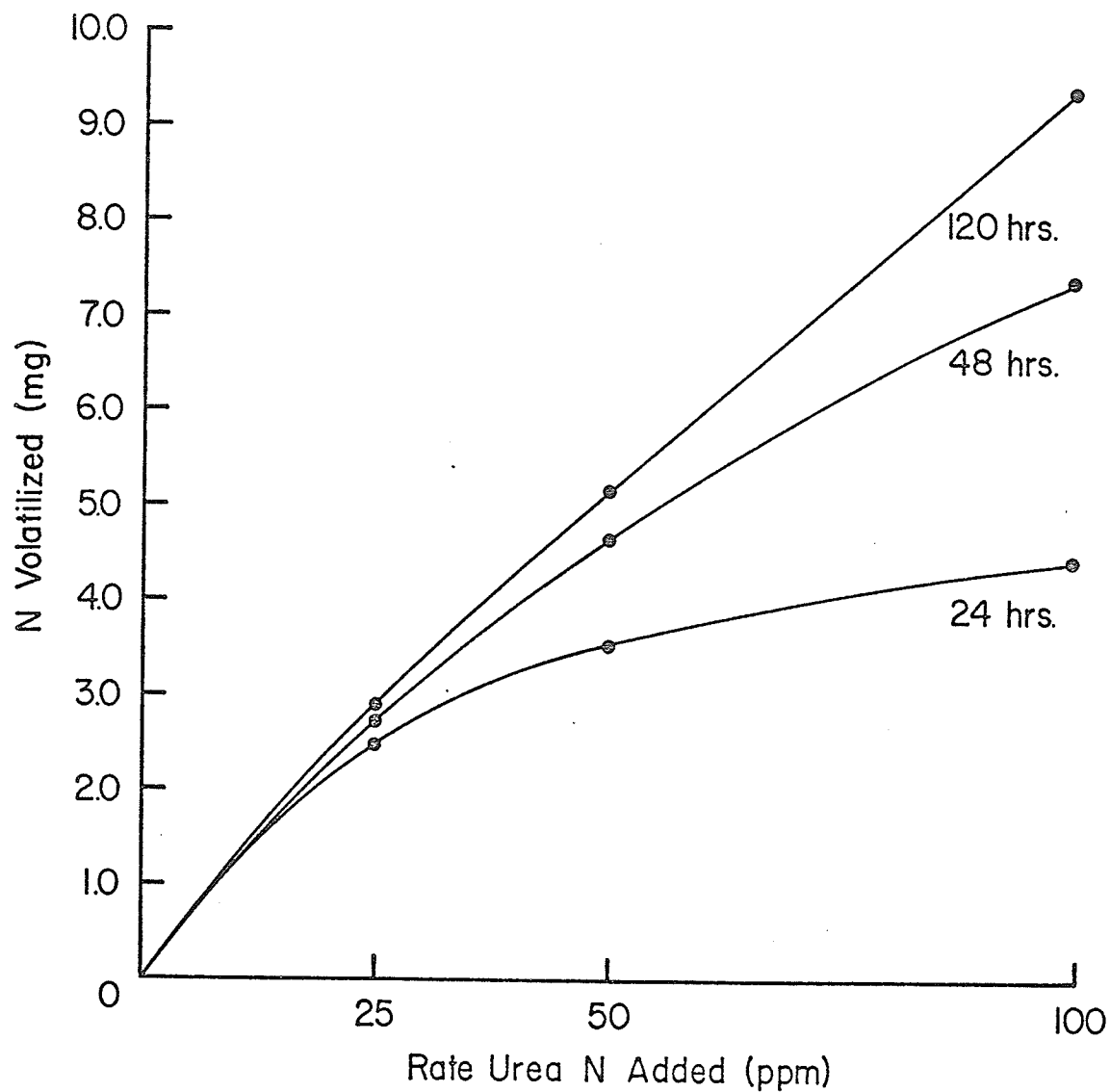
FIGURE 10   VOLATILIZATION OF NH_3 N FROM UREA APPLIED TO THE ALMASIPPI SOIL AS INFLUENCED BY RATE OF APPLICATION
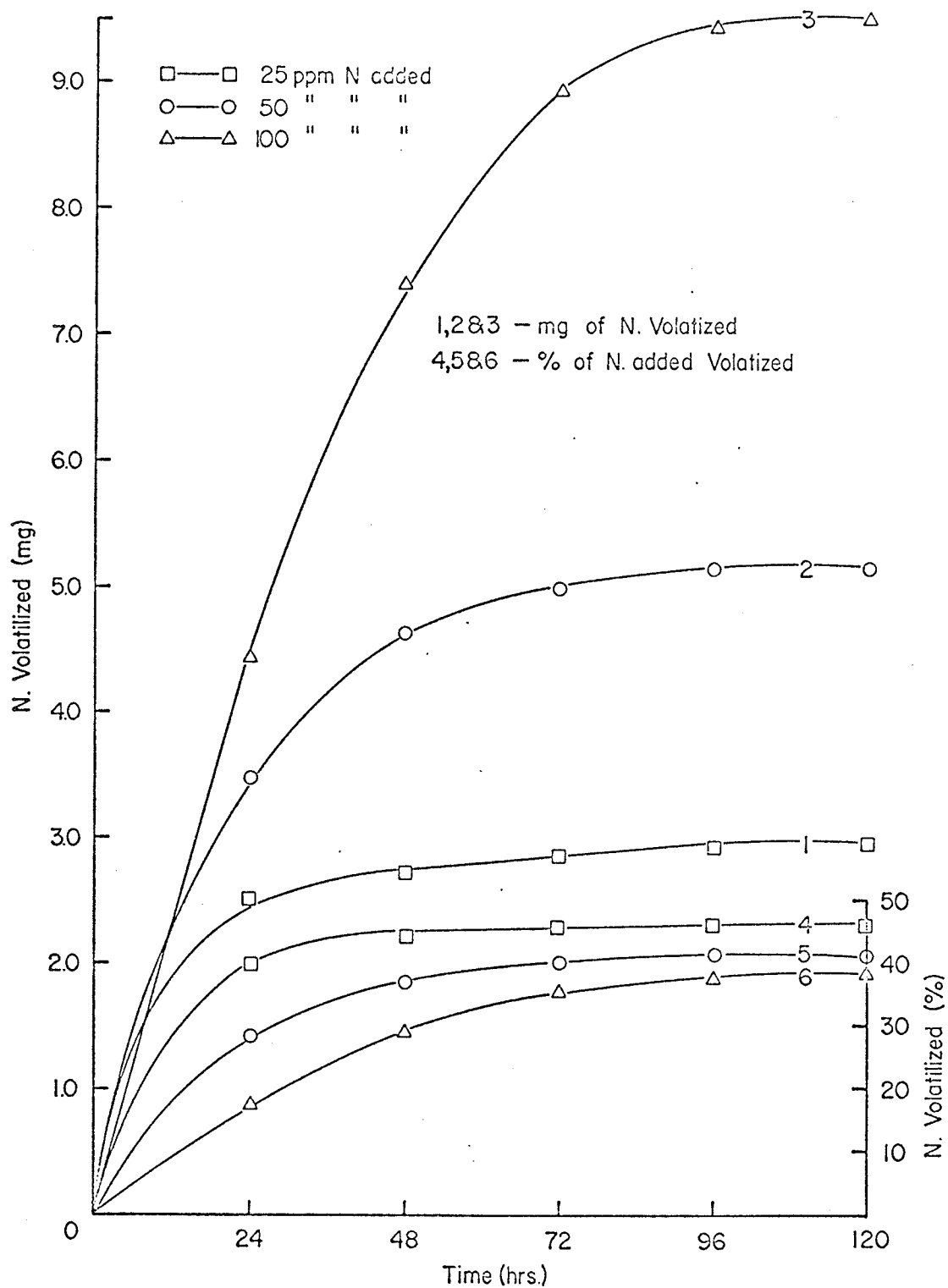
FIGURE 11   VOLATILIZATION OF NH_3 N FROM UREA WITH TIME
ON THE ALMASIPPI SOIL AT THREE RATES OF APPLICATION

ammonium nitrate found in the greenhouse studies.

The smooth curves showing the amount of nitrogen volatilized with time and the 99.2% recovery of N from the standard ammonium nitrate solution indicates that the experimental apparatus worked well and could be expected to detect small differences between treatments. Statistical analysis of the 25, 50 and 100 ppm urea treatments which were replicated twice indicates a low variance due to replications and experimental error. Therefore, to accomodate more treatments, the treatments were not replicated in the following experiments.

A second experiment was performed to determine the effect of placement, N source, rate of N applied and soil type on the amount of ammonia volatilized. The experimental method was as previously described. An incubation temperature of $15^{\circ}C$ was selected. Thus, a comparison of the data in this experiment with that obtained in the previous experiment would yield some information on the influence of temperature on NH_3 volatilization. The experiment was terminated after the ninth day of incubation due to an accidental restriction of the air flow. However, the rate of ammonia being volatilized after nine days of incubation was extremely low and the losses occurring after this time would be small relative to those measured during the first few days of incubation. However, a very low rate of volatilization could have occurred for a considerable period of time (13).

Temperature had a marked effect on the rate of

TABLE XIV INFLUENCE OF PLACEMENT AND SOIL TYPE
ON THE VOLATILIZATION OF NH_3 N

Soil Type	Method of Application	N source	Rate of N applied (ppm)	Total NH_3 N Volatilized mg	%
Almasippi			0	0	0
"	Surface	Urea	75	0.59	3.2
"	"	"	150	2.53	6.7
"	"	"	300	3.54	4.7
"	1" depth	"	75	0.10	0.5
"	"	"	150	0.88	2.3
"	"	"	300	0.78	1.0
"	Surface	NH_4NO_3	150	0.46	1.2
"	"	"	300	1.33	1.8
"	"	"	600	0.70	0.5
Altona			0	0	0
"	Surface	Urea	75	0.45	2.4
"	"	"	150	1.61	4.3
"	"	"	300	2.56	3.4
"	1" depth	"	75	0.06	0.3
"	"	"	150	0.30	0.8
"	"	"	300	0.21	0.3
"	Surface	NH_4NO_3	300	0.05	0.1
"	"	"	600	0.47	0.3

ammonia volatilization from urea (Tables XIII and XIV). In
the previous experiment (Table XIII), conducted at 25°C, the
percentage of added nitrogen lost in 24 hours was 28% and
17% when 50 and 100 ppm N as urea was added, respectively.
The greatest loss after nine days of incubation at 15°C was
6.7% and occurred when 150 ppm N as urea was added to the
Almasippi soil (Table XIV). The soils lost no or very little
nitrogen during the first 24 hours of incubation. Loss of
ammonia from urea was 3 to 6 fold lower when placed into the
Almasippi soil at a depth of one inch than when applied to
the soil surface. Placing urea at a depth of one inch on
the Altona soil reduced losses approximately 5 to 10 fold.
Losses from surface applied urea varied only from 2.4 to 4.3%
on the Altona soil. The lowering of ammonia volatilization
by placing the nitrogen fertilizers into the soil has been
noted by other workers (11) (35). Total losses of ammonia
from urea increased with rate of application on both soils
when placed on the soil surface. This trend was not evident
when the fertilizers were placed into the soil.

The largest volatilization of N, expressed as a
percentage of the amount of urea N added, occurred when
150 ppm N was added to both soils and with both methods of
application. However, the per cent N volatilized was usually
greater when 300 ppm N was added than when 75 ppm N was
added. The per cent of added nitrogen volatilized from the
Almasippi soil treated with NH_4NO_3 was the highest when
300 (150 ppm NH_4 N) ppm N was added. The per cent N volat-
ilized from the Altona soil treated with NH_4NO_3 was greatest

at the 600 ppm N rate (300 ppm NH_4 N). Ammonia N volat-
ilization from NH_4NO_3 applied at 150 ppm N (75 ppm NH_4 N)
was approximately 20% of that volatilized from the equivalent
rate of urea N on the Almasippi soil. Volatilization of
NH_4NO_3 N from the Altona soil was very low. The lower
pH and higher cation exchange capacity of the Altona soil
accounts for these results.

A third experiment was conducted to study the volat-
ilization of ammonia from pelleted commercial grade urea and
NH_4NO_3 mixed with the surface one inch of soil. The Almasippi,
Stockton, Altona and Lakeland soils which were used in the
field experiments were used in this experiment. The treat-
ments used are listed in Table XV. A constant relative
humidity of 31% at $25^{\circ}C$ was maintained over the soil samples
by passing air through a saturated solution of $CaCl_2$ prior
to passing the air over the soil samples. The soils were
wetted to field capacity and incubation initiated. The exper-
iment was stopped after 11 days of incubation when ammonia
volatilization became negligible.

The results are presented in Table XV and Figure 12.
Except for the Almasippi soil, losses of nitrogen during the
first day of incubation were negligible (Figure 15). The rate
of ammonium volatilization increased rapidly between the first
and third day of incubation and then decreased rapidly on the
Stockton and Altona soils but on the Almasippi and Lakeland
soils considerable volatilization occurred until the ninth
day of incubation.

Approximately 20% of the 300 ppm urea N added to the

TABLE XV — AMMONIA N VOLATILIZED AND MOISTURE LOSS FROM FOUR SOILS TREATED WITH PELLETED UREA AND NH_4NO_3

Soil Type	N Source	Rate N Applied (ppm)	Ammonia N volatalized (mg)	(%)	Moisture content at Field capacity g/jar	Moisture loss (g)
Almasippi		0	0	0	69.0	22.7
	Urea	75	1.3	5.8	"	37.1
	"	150	3.5	7.9	"	33.6
	"	300	18.5	20.5	"	42.3
	NH_4NO_3	600	3.0	1.6	"	24.0
Stockton		0	0	0	84.0	36.4
	Urea	75	0.03	0.13	"	33.5
	"	150	0.13	0.29	"	38.8
	"	300	3.10	3.44	"	34.5
	NH_4NO_3	600	0.07	0.04	"	36.6
Altona		0	0	0	102.0	52.9
	Urea	75	0.25	1.10	"	46.1
	"	150	0.50	1.10	"	53.5
	"	300	4.45	4.84	"	59.2
	NH_4NO_3	600	0.14	0.07	"	56.6
Lakeland		0	0	0	120.0	41.6
	Urea	75	0.33	1.47	"	47.7
	"	150	1.83	4.10	"	49.8
	"	300	6.60	7.20	"	47.0
	NH_4NO_3	600	1.09	0.54	"	42.6
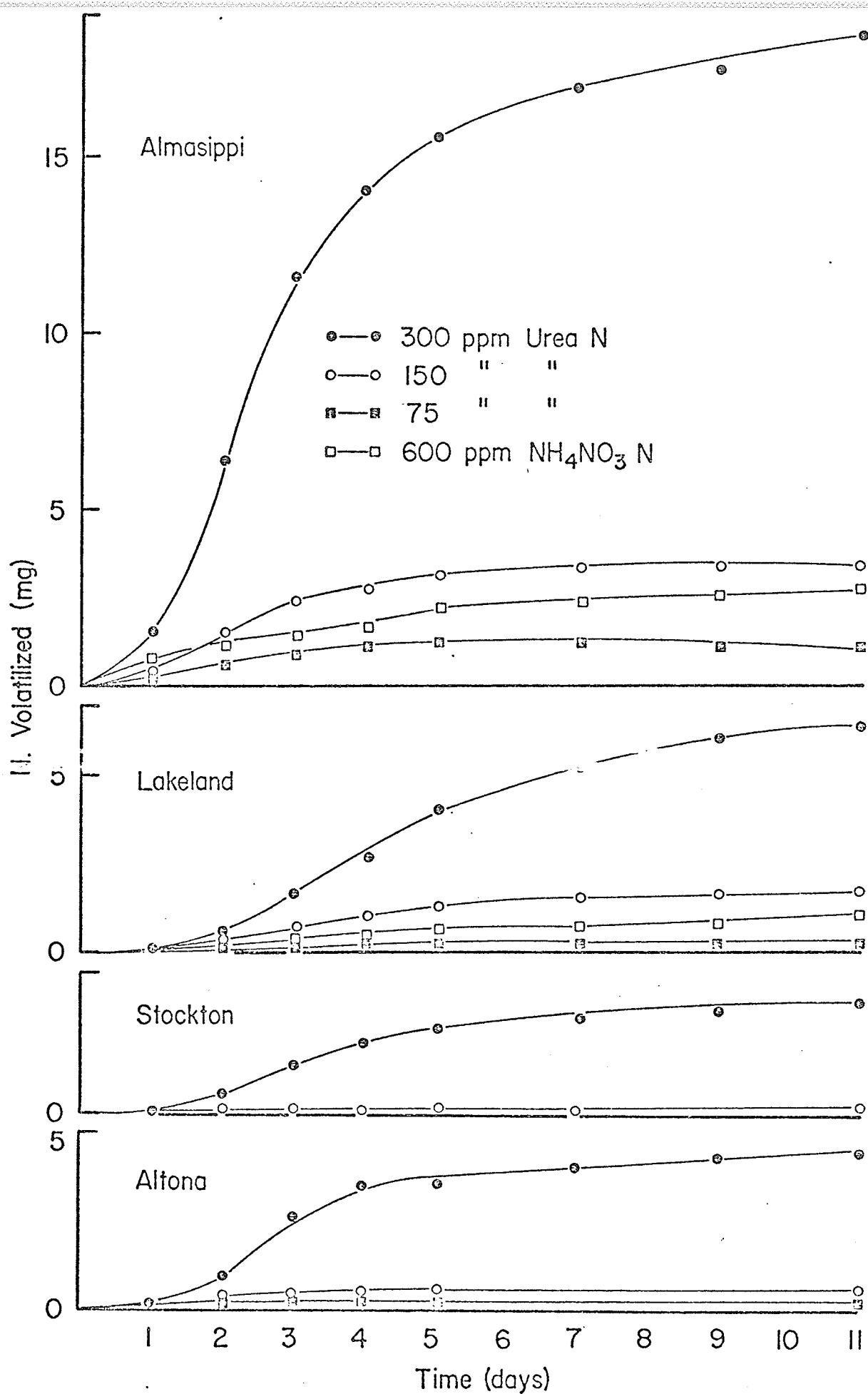
FIGURE 12   VOLATILIZATION OF NH_3 N FROM FOUR SOILS TREATED
WITH UREA AND NH_4NO_3

Almasippi soil was volatilized after 11 days of incubation.
This was over 3 times that volatilized from any of the other
soils at this rate of application. This is probably due to
the high pH and carbonate content and low cation exchange
capacity of this soil. The Lakeland soil which also had a
high pH and carbonate content volatilized much less N. This
soil however, had a larger cation exchange capacity than the
Almasippi soil. Volatilization of N from the Lakeland soil
was greater than from the Stockton and Altona soils from which
little or no ammonia was volatilized at the 75 and 150 ppm
rate of N application. The lower pH and the low carbonate
content of the latter two soils probably restricted losses
even though their cation exchange capacities were lower than
that of the Lakeland.

The magnitude of ammonia volatilized from NH_4NO_3
relative to soil type decrease in the order Almasippi, Lake-
land, Altona and Stockton. This was the same order as ammonia
volatilized from urea. The total N volatilized from the
NH_4NO_3 source, however, was much less than the total losses
from the urea. The volatilization of N from NH_4NO_3 applied
to the Almasippi soil at 600 ppm N (300 ppm NH_4 N) was approx-
imately 1.6% of that applied whereas urea applied at 300 ppm N
resulted in approximately 20% of that added volatilized. On a
field basis these rates of application are equivalent to 320
and 160 lb N/Ac, respectively. Thus, the losses from the
Almasippi soil were 10.5 pounds of NH_4NO_3 N and 32 pounds of
urea N per acre. The difference in volatilization losses

from the urea and NH_4NO_3 sources is probably due to the increase in pH associated with urea hydrolysis which causes higher concentration of free ammonia in the soil. The pH effect on ammonia volatilization was also shown by the higher NH_4NO_3 N losses from the Almasippi and Lakeland soils than on the Stockton and Altona.

VI   SUMMARY

Field experiments were conducted in 1968 and 1969
to study the relative efficacy of urea and ammonium nitrate
as sources of nitrogen for barley at eight locations repre-
senting seven Manitoba soils using various methods of
nitrogen application. The soils ranged in pH from 6.0 to
8.0 and in cation exchange capacity from 11.3 to 37.1
meq/100 g. A greenhouse experiment was conducted to study
plant uptake of tracer nitrogen applied as urea and ammonium
nitrate from soils used in the field. Finally, a laboratory
experiment was conducted to determine the magnitude of
ammonia losses from urea and ammonium nitrate treated soils
which had been used in the field and greenhouse.

The field results showed that drilling urea caused
seedling emergence reductions which were related to the rate
of nitrogen applied and the cation exchange capacity by the
equation

$$Y_c = 3.25 - 120 \, x^{-1} + 18.4 \, Rx^{-1} - 0.34R$$

where Y_c = reduction in seedling emergence (%)

x = cation exchange capacity meq/100g

R = rate of urea N application lb/Ac

Drilled ammonium nitrate caused a large reduction in emergence
only on the coarse textured soil at the 60 lb N/Ac rate of
application. Grain yield reductions caused by the drilled
urea treatments relative to the drilled ammonium nitrate

treatments were higher than that expected from the reduction
in stand. This indicated damage to plants which did emerge.
Banding urea one inch to the side eliminated all evidence
of damage to the seed and grain yields were similar to those
obtained with ammonium nitrate treatments at the same rate.
Uniform incorporation of ammonium nitrate caused greater
yield increases than equivalent urea treatments in 1968 but
not in 1969. The greatest differences occurred on the coarse
textured Almasippi soil which had a pH of 8.0. Differences
also occurred on the coarse textured Stockton in 1968 which
had a pH of 6.3 but to a lesser extent. Drilling ammonium
nitrate with the seed was generally superior to uniform
incorporation up to 60 lb N/Ac except on the Almasippi
soil where considerable seedling damage occurred at this rate.

In the greenhouse experiment nitrogen uptake and
yields of barley were lower with urea than with ammonium
nitrate on the Almasippi soil. The differences in tracer
NH_4 N and urea N uptake indicated that this was due to a
loss of ammonia. On the Stockton soil which also showed this
effect in the field in 1968 but not in 1969, urea and ammon-
ium nitrate supplied equal amounts of nitrogen. Considerably
less tracer urea N and ammonium N from ammonium nitrate
was found in the plant tops indicating that ammonium was
preferentially immobilized over nitrate on both soils. The
results also indicated that the difference found in measuring
nitrogen efficiency by the tracer and the difference methods
was in part due to the immobilization of nitrogen fertilizer.

The laboratory experiment showed that ammonia

volatilization from urea treated soils was responsible for
the field and greenhouse results which had indicated a low
efficiency of urea relative to ammonium nitrate on the
Almasippi soil. A surface application of urea on this soil
resulted in losses of up to 47%. Placing urea at a one
inch depth and decreasing temperature from 25 to $15^{O}C$ reduced
ammonia losses. At the $15^{O}C$ temperature a very low percentage
loss occurred within the first 24 hours at all rates of N
application whereas at $25^{O}C$, 85% of total volatilization
occurred within this period at the 25 ppm N rate. Small
losses of ammonia from ammonium nitrate also occurred on
the calcareous soils.

VII   CONCLUSIONS

1.   Cation exchange capacity of the soil has a marked effect
      on the ability of the soil to reduce the toxicity to plants
      caused by applying urea with the seed.

2.   The inefficiency of broadcast urea relative to ammonium
      nitrate under field conditions varies from year to year
      but the possibility of this occurring is greater on coarse
      textured soils of high pH than on finer textured soils
      of lower pH.

3.   Drilling ammonium nitrate with the seed causes greater
      yield increases than uniform incorporation up to a rate of
      60 lb N/Ac.

4.   Incorporation of urea with the soil reduces ammonia
      losses considerably thus improving its relative efficiency.

5.   The difference in nitrogen efficiency as measured by
      tracer nitrogen and the difference method is due in part
      to the immobilization of fertilizer nitrogen with the
      subsequent mineralization of non tracer nitrogen. When
      ammonia nitrogen, which is preferentially immobilized as
      compared to nitrate, is used the difference between the
      two measurements increases.

6.   A decrease in temperature from $25^{\circ}C$ to $15^{\circ}C$ markedly
      delays the initiation of ammonia volatilization and decreased
      total losses from urea treated soil.

7.   Soils with a pH of 8.0 are subject to greater losses
      of ammonia from urea treatments than soils with a pH of
      6.0 to 7.6.

VIII   BIBLIOGRAPHY

1.   Atkinson, H. J., Giles, G. R., Maclean, A. J., and
       Wright, J. R. 1958. Chemical Methods of Soil
       Analysis Contribution No. 169 C.D.A. p.29-31

2.   Bates, R. G. and Pinching, G. D. 1950. Dissociation
       constant of agueous ammonia at 0 to 50° from
       emf studies of the ammonium salt of a weak acid.
       J. Amer. chem. Soc. 72:1393-6

3.   Black, C. A., Editor 1965. Methods of Soil Analysis,
       Part 2. Monograph 9. American Society of Agronomy.,
       Madison, Wisconsin, U.S.A.

4.   Brage, B. L., Zich, W. R. and Fine, L. 0. 1960. Germin-
       ation of small grain and corn as influenced by urea
       and other nitrogenous fertilizers. Soil Sci. Soc.
       Amer. Proc. 24:294-296.

5.   Bremner, J. M. and Keeney, D. R., 1966. Determination
       and isotope-ratio analysis of different forms of
       nitrogen in soils. 3. Exchangeable ammonium,
       nitrate, and nitrite by extraction-distillation
       methods. Soil Sci. Soc. Amer. Proc. 26:577-582.

6.   Broadbent, F. E., Hill, G. N. and Tyler, K. B. 1958
       Transformation and movement of urea in soils.
       Soil Sci. Soc. Amer. Proc. 22:303-307.

7.   Broadbent, F. E. and Nakashima, T. 1965. Plant recovery
       of immobilized nitrogen in greenhouse experiments.
       Soil Sci. Soc. Amer. Proc. 29:55-60.

8.   Broadbent, F. E. and Nakashima, T. 1968. Plant uptake
       and residual values of six tagged nitrogen fertil-
       izers. Soil Sci. Soc. Amer. Proc. 32:388-393.

9.   Broadbent, F. E. and Tyler, K. B. 1962. Laboratory and
       greenhouse investigations on nitrogen immobiliz-
       ation. Soil Sci. Soc. Amer. Proc. 26:459-462.

10. Broadbent, F. E. and Tyler, K. B. 1965. Effect of pH
       on nitrogen immobilization in two California soils.
       Plant and Soil 23:314-322.

11. Carnie, A. 1966. Exchangeable ammonium and its avail-
       ability to plants. M. Sc. thesis Univ. of Manitoba

12. Chapman, H. D. and Liebig, G. F. 1952. Field and laboratory studies of nitrite accumulation in soils. Soil Sci. Soc. Amer. Proc. 16: 267-282.

13. Chin, W. T. and Kroontje, W. 1963. Urea hydrolysis and subsequent loss of ammonia. Soil Sci. Soc. Amer. Proc. 27: 316-318.

14. Conrad, J. P. 1941. Catalytic activity causing the hydrolysis of urea in soils as influenced by several agronomia factors. Soil Sci. Soc. Amer. Proc. 5: 238-241.

15. Cooke I. J. 1962. Damage to plant roots caused by urea and anhydrous ammonia. Nature Lond. 194: 1262-63.

16. Cotton and Wilkinson 1962. Advanced Inorganic Chemistry A Comprensive Text. Interscience Publishers pp 247-248.

17. Court, M. N., Stephen, R. C. and Waid, J. S. 1962. Nitrite toxicity arising from the use of urea as a fertilizer. Nature Lond. 194: 1263-1265.

18. Court, M. N., Stephen, R. C. and Waid, J. S. 1964. Toxicity as the cause of the inefficiency of urea as a fertilizer. I. Review J. Soil Sci. 15: 41-48.

19. Court, M. N., Stephen, R. C. and Waid, J. S. 1964. Toxicity as a cause of the inefficiency of urea as a fertilizer. II Experimental J. Soil Sci. 15:49-65.

20. Devine, J. R. and Holmes, M. R. J. 1963. Field experiments comparing ammonium sulfate, ammonium nitrate, calcium nitrate and urea combined-drilled with spring barley. J. Agric. Sci. 61:381-390.

21. Doak, B. W. 1952. Some chemical changes in the nitrogenous constituents of urine when voided on pasture. J. Agric. Sci. 42:162-171.

22. Duisberg, P. C. and Beuhrer, T. F. 1954. Effect of ammonia and its oxidation products on rate of nitrification and plant growth. Soil Sci. 78:37-49

23. Ehrlich, W. A., Poyser, E. A., Pratt, L. E. and Ellis, J. H. 1953. Report of Reconnaissance Soil Survey of Winnipeg and Morris Map Sheet Areas. No. 5 Man. Dept. of Agric. Winnipeg

24. Ehrlich, W. A., Poyser, E. A. and Pratt, L. E. 1957. Report of Reconnaissance Soil Survey of Caherry Map Sheet Area. No. 7 Man. Dept. of Agric and Immigration. Winnipeg

25. Ellis, J. H. and Shafer, W. H. 1943. Report of
         Reconnaissance Soil Survey of South-Central
         Manitoba No. 4 Man. Dept. of Agric. Winnipeg

26. Ernst, J. W. and Massey, H. F. 1960. The effects of
         several factors on volatilization of urea in soils.
         Soil Sci. Soc. Amer. Proc. 24: 87-90.

27. Fehr, P. I. 1969. Technique for Measurement of non-
         symbiotic nitrogen fixation in some Manitoba soils
         using ^{15}N. M. Sc. thesis University of Manitoba
         pp 17-24.

28. Finar, I. L. 1956 Organic Chemistry
         1. The fundamental principles. Longmans London
         pp 383-388.

29. Fischer, W. B. Jr. and Parks, W. L. 1958. Influence of
         soil temperature on urea hydrolysis and subsequent
         nitrification. Soil Sci. Soc. Amer. Proc. 22:247-
         248.

30. Gasser, J. R. R. 1964. Some factors affecting losses of
         ammonia from urea and ammonium sulfate applied to
         soils. J. Soil Sci. 15:258-272.

31. Gasser, J. K. R. 1964. Urea as a Fertilizer. Soils and
         Ferts. 27:175-180.

32. Gibson, T. 1930. The decomposition of urea in soils
         J. Agric. S ci. 20:549-558.

33. Harding, R. B., et al. 1963. Leaching and gaseous losses
         of nitrogen from some non tilled California soils.
         Agron. J. 55: 515-518.

34. Hunter, A. S. and Rosenau, W. A. 1966. The effects of
         urea, biuret, and ammonia on germination and early
         growth of corn. Soil Sci. Soc. Amer. Proc. 30:77-81.

35. Jackson, M. L. 1958. Soil Chemical Analysis. Prentice
         Hall Inc. Englewood Cliffs, N. J. U.S.A. pp 45-46.

36. Jansson, S. L. 1963. Balance sheet and residual effects
         of fertilizer nitrogen in a six year study with
         ^{15}N. Soil Sci. 95: 31-37.

37. Jansson, S. L., Hallam, M. J. and Bartholomew, W. V.
         1955. Preferential utilization of ammonium over
         nitrate by micro-organisms in the decomposition of
         straw. Plant and Soil 6:382-390.

38. Jewitt, T. N. 1942. Loss of ammonia from ammonium sulfate
         applied to alkaline soils. Soil Sci. 54: 401-409.

39. Jones, H. W. 1932. Some transformations of urea and their resultant effects on the soil. Soil Sci. 34: 281-299.

40. Jones, R. W. 1968. Laboratory studies on the behaviour of mineral N on three Manitoba soil materials M. Sc. thesis Univ. of Manitoba.

41. Jones, D. W. and Harvard, M. E. 1964. Competition of ammonia and water for adsorption sites on clay minerals Soil Sci. Soc. Amer. Proc. 28: 636-640.

42. Kondrat'e V, I. G. and Podkolziua, G. U. Effect of urea in Field experiments (from results of the geographical series of the N I V I F in 1958-64) Agrokhimiya No. 2 3-15.

43. Kresbe, C. B. and Satchell, D. P. 1960. Gaseous losses of ammonia from nitrogen fertilizers applied to soils. Agron. J. 52: 104-107.

44. Laidler, K. J. and Hoave, J. P. 1949. The molecular Kinetics of the urea-urease system. I. The Kinetic laws. J. Amer. Chem. Soc. 7:2699-2702.

45. Martin, J. P. and Chapman, H. D. 1951. Volatilization of ammonia from surface-fertilized soils. Soil Sci. 71: 25-34.

46. McGarity, J. W. and Myers, M. G. 1967. A survey of urease activity in soils of Northern New South Wales. Plant and Soil 27:217-238.

47. Mees, G. C. and Tomlinson T. E. 1964. Urea as a Fertilizer. Ammonia evolution and brairding of wheat. J. Agric. Sci. 62: 199-205.

48. Meyer, R. D., Olson R. A. and Rhoades, H. F. 1961. Ammonia losses from fertilized Nebraska soils. Agron. J. 53:241-244.

49. Moe, P. G. 1967. Nitrogen losses from urea as affected by altering soil urease activity. Soil Sci. Soc. Amer. Proc. 31:380-382.

50. Mortland, M. M. and Wolcott, A. R. 1965. Sorbtion of Inorganic Compounds by Soil Materials. Soil Nitrogen, Monograph 10 Editors, W. V. Bartholomew and F. E. Clark. American Society of Agronomy Inc., Madison Wisconsin, U.S.A.

51. Nommik, H. 1965. Ammonium Fixation and Other Reactions Involving a Nonenzymatic Immobilization of Mineral

Nitrogen in Soil. Soil Nitrogen, Monograph 10. Editors, W. V. Bartholomew and F. E. Clark. American Society of Agonomy Inc., Madison, Wisonsin, U.S.A.

52. Olson, S. R. et al. 1954. Estimation of available phosphorous in soils by extraction with sodium bicarbonate U.S. D. A. Cir. No. 939.

53. Overrein, L. N. 1967. Immobilization of tracer nitrogen in forest raw humus.
I. Effect of temperature on the interchange of nitrogen ofter addition of urea, ammonium and nitrate ^{15}N. Plant and Soil 27: 1-19.

54. Overrein, L. N. and Moe, P. G. 1967. Factors affecting urea hydrolysis and ammonia volatization in soil. Soil Sci. Soc. Amer. Proc. 31: 57-61.

55. Paech, K. and Tracey, M. V. 1956. Modern Methods of Plant Analysis Vol. 1 Springer-Verlag. Berlin.

56. Parr, J. F. and Papendick, R. I. 1966. Retention of anhydrous ammonia by soil. II Effect of ammonia concentration and soil moisture. Soil Sci. 101: 109-119.

57. Pinck, L. A. and Allison, F. E. 1961. Adsorption and release of urease by and from clay minerals. Soil Sci. 91: 183-182.

58. Pratt, L. A., Allison, F. E. and Gaddy, V. L. 1946. Nitrogen requirements in the utilization of carbon - aceous residues in soil. J. Amer. Soc. Agron. 38: 410-420.

59. Pratt, L. E. et al. 1961. Report of Detailed Reconna- issance Soil Survey of Fisher and Teulon Map Sheet Areas No. 12., Man. Dept. of Agric. and Cons.Winnipeg.

60. Richards, E. H. and Norman, A. G. 1931. The biological decomposition of plant materials V. Some factors determining the quantity of nitrogen immobilized during decomposition. Biochem. J. 25: 1769-1778.

61. Richards, E. H. and Shickhande, J. G. 1935. The preferential utilization of different forms of inorganic nitrogen in the decomposition of plant materials. Soil Sci. 39:1-8.

62. Roberge, M. R. and Knowles, R. K. 1968. Urease activity in a Black Spruce Humus sterilized by gamma radiation. Soil Sci. Soc. Amer. Proc. 32:518-521.

63. Simpson, D. M. H. and Melstad, S. W. 1963. Urea
        hydrolysis and transformation in some Illinois
        soils. Soil Sci. Soc. Amer. Proc. 27: 48-50.

64. Smith, J. H. 1963, Relationships between soil cation
        exchange capacity and the toxicity of ammonia
        to the nitrification process. Soil Sci. Soc.
        Amer. Proc. 28: 640-648.

65. Soulides, D. A. and Clark, F. E. 1958. Nitrification
        in grassland soils. Soil Sci. Soc. Amer. Proc.
        22: 308-311.

66. Stanier, R. Y., Doudoroff, M. and Adelberg, E. A. 1965.
        The Microbial World 2nd Ed. Prentice Hall Engle-
        wood Cliffs, N. J. p. 446-447.

67. Stephen, R. C. and Waid, J. S. 1963. Pot experiments
        on urea as a fertilizer.
        I. A comparison of responses by various plants,
        Plant and Soil 18: 309-316.

68. Stephen, R. C. and Waid, J. S. 1963. Pot experiments
        on urea as a fertilizer. II The influence of other
        fertilizer constituents on the response of maize
        to urea. Plant and Soil 19: 97-105.

69. Stephen, R. C. and Waid, J. S. 1963. Pot experiments
        on urea as a fertilizer. III. The influence of
        rate, form, time and placement. Plant and Soil
        19: 184-191.

70. Stojanovic, B. J. and Broadbent, F. E. 1956. Immob-
        ilization and mineralization of nitrogen during
        decomposition of plant residues in soil. Soil
        Sci. Soc. Amer. Proc. 20:213-218.

71. Terman, G. L. and Brown, U. A. 1968. Crop recovery of
        applied fertilizer nitrogen. Plant and Soil
        29: 48-65.

72. Wagner, G. H. and Smith, G. E. 1958. Nitrogen losses
        from soils fertilized with different nitrogen
        carriers. Soil Sci. 85:125-129.

73. Wahhab, A., Khan, M. and Ishag, M. 1960. Nitrification
        of urea and its loss through volatilization of
        ammonia under different soil conditions J. Agric.
        Sci. 55:42-51.

74. Walkley, A. and Black J. M. 1934. An examination of
        the Deglariff method for determining soil organic
        matter and a proposed modification of the chromic
        acid titration method. Soil Sci. 37: 29-38.

75. Warren, K. S. 1962. Ammonia toxicity and pH. Nature Lond. 195: 47-49.

76. Widdowson, F. U., Penny, H. and Williams, R. J. B. 1964. Side placing urea and other nitrogen fertilizers for spring barley. J. Agric. Sci. 62: 73-82.

77. Wolcott, A. R. et al. 1965. Nitrogen carriers: I. Soil effects. Soil Sci. Soc. Amer. Proc. 29: 405-410.

78. Volk, G. M. 1959. Volatile loss of ammonia following surface application of urea to turf or bare soils. Agron. J. 51: 746-749.

79. Volk, G. M. 1961. Gaseous losses of ammonia from surface applied nitrogenous fertilizers. J. Agric. Food Chem. 9: 280-283.

80. Volk, G. M. 1966. Efficiency of fertilizer urea as affected by method of application, soil moisture, and lime. Agron. J. 58: 249-252.

81. Volk, G. M. 1966. Transformations and mobility of band-placed urea. Proc. Soil Crop Sci. Soc. Fla. 25: 202-211.

82. Volk, G. M., Kelley, W. H. and Blue, W. G. 1959. Recovery of nitrogen from several sources by oats and millet. Proc. Soil Crop Sci. Soc. Fla. 19: 379-385.

IX   APPENDIX

TABLE 1A — EFFECT OF DRILLED NITROGEN CARRIER AND RATE OF APPLICATION ON EMERGENCE OF BARLEY SEEDLINGS ON EIGHT SOILS (%)

Carrier	N lb/Ac	P_2O_5 lb/Ac	Almasippi	Stockton (1968)	Plum Ridge*	Altona	Stockton (1969)	New dale	Lake land	Red River
$NH_4H_2PO_4$	7	30	100.0	100.0	–	100.0	100.0	100.0	100.0	100.0
Urea Phosphate (23-23-0)	20	20	91.5	95.8	95.9	109.0	74.0	79.0	89.3	99.0
" "	30	30	69.5	89.1	86.8	100.0	65.5	63.6	92.3	85.5
Urea Phosphate (27-27-0)	20	20	88.8	95.1	98.7	98.1	89.4	83.8	98.5	98.0
" "	30	30	66.9	86.6	92.0	96.3	91.0	81.1	95.4	98.0
$NH_4H_2PO_4 + NH_4NO_3$	20	20	95.0	103.3	99.3	91.3	99.3	90.0	98.5	104.0
" "	20	30	87.9	100.0	101.7	85.1	95.3	99.6	99.0	97.5
" "	30	30	85.8	101.4	100.0	94.0	99.5	88.7	100.0	106.5
" "	40	30	88.2	106.8	120.9	90.7	97.5	92.8	107.6	95.5
" "	60	30	77.5	94.8	97.2	84.5	97.1	86.4	100.5	97.0
" "	90	30	–	–	–		89.4	82.1	92.9	97.5
" + Urea	20	20	76.8	96.0	93.7	98.1	–	–	–	
" "	20	30	80.5	99.1	91.3	92.6	88.4	89.7	95.9	100.0
" "	30	30	68.8	88.9	84.7	91.6	85.2	87.5	93.4	93.5
" "	40	30	52.0	68.2	80.4	85.9	76.8	80.3	93.9	88.5
" "	60	30	30.5	45.2	56.7	75.1	59.3	60.5	87.2	87.5
" "	30S	30					97.4	99.2	103.6	99.5
" "	40S	30					100.4	100.2	102.6	101.5
" "	60S	30					102.0	99.6	96.9	105.0

S = Banded 1" to side of seed

* % emergence based on 20, 40, 60 and 90 lb N/Ac rate of ammonium nitrate broadcast since emergence data from $NH_4H_2PO_4$ treatment was considered unreliable.

TABLE 2A EFFECT OF NITROGEN CARRIER AND RATE OF APPLICATION ON NITROGEN UPTAKE (lb/Ac)

SOIL TYPE / Fertilizer Carrier	N/P$_2$O$_5$ lb/Ac	STOCKTON Grain	Straw	Total	NEWDALE Grain	Straw	Total	LAKELAND Grain	Straw	Total	RED RIVER Grain	Straw	Total
Urea Phosphate (23-23-0)	20/20 D	30.6	6.7	37.3	23.0	3.8	26.8	20.5	6.3	26.8	44.5	8.3	52.8
Urea Phosphate (27-27-0)	20/20 D	28.2	5.8	34.0	18.4	3.3	21.7	13.8	6.9	20.7	41.3	8.2	49.5
NH$_4$NO$_3$+NH$_4$H$_2$PO$_4$	20/20 D	32.6	5.9	38.5	26.1	3.1	24.2	16.7	5.1	21.8	44.9	10.1	55.0
NH$_4$NO$_3$+NH$_4$H$_2$PO$_4$	20/30 D	35.1	6.7	41.8	21.4	4.1	25.5	14.5	4.1	18.6	41.7	9.6	51.3
Urea + "	20/30 D	33.4	7.9	41.3	19.8	3.6	23.4	13.8	4.6	18.4	37.5	8.1	45.6
NH$_4$NO$_3$+ "	20/30 B	37.3	5.3	42.6	18.7	3.7	22.4	13.4	6.0	19.4	34.8	7.2	42.0
Urea + "	20/30 B	34.6	7.0	41.6	20.1	4.0	24.1	12.2	4.1	16.3	40.4	8.9	49.3
Urea Phosphate (23-23-0)	30/30 D	43.6	11.0	54.6	29.3	5.5	34.8	28.1	8.9	37.0	51.1	11.0	62.1
Urea Phosphate (27-27-0)	30/30 D	40.2	7.6	47.8	20.6	3.3	23.9	–	6.0	–	45.9	9.2	59.1
NH$_4$NO$_3$+ NH$_4$H$_2$PO$_4$	30/30 D	41.4	7.1	48.5	27.3	5.2	32.5	21.7	6.0	27.7	50.9	9.5	60.4
Urea + "	30/30 D	37.1	8.1	45.2	26.8	4.8	31.6	19.4	4.0	23.4	47.9	9.2	57.1
Urea + "	30/30 S	37.9	8.1	46.0	28.4	9.7	33.1	21.0	5.0	26.0	51.9	11.7	63.6
NH$_4$NO$_3$+ NH$_4$H$_2$PO$_4$	40/30 D	48.0	9.1	57.1	34.1	5.9	40.0	26.5	6.4	32.9	57.3	10.8	68.1
Urea + "	40/30 D	42.5	8.8	51.3	29.7	5.2	34.9	25.9	6.5	32.4	50.9	10.3	61.2
NH$_4$NO$_3$+ "	40/30 B	41.2	7.9	49.1	32.6	5.3	37.9	22.4	6.3	28.7	58.4	11.9	70.3
Urea + "	40/30 B	39.9	7.9	47.8	30.9	4.2	35.1	25.8	6.1	31.9	53.1	16.5	69.6
Urea + "	40/30 S	44.5	9.6	54.1	36.4	7.5	43.9	24.4	6.2	30.6	56.9	–	–
NH$_4$NO$_3$+NH$_4$H$_2$PO$_4$	60/30 D	59.7	12.3	72.0	42.7	7.6	50.3	34.8	10.6	45.4	65.7	15.4	81.1
Urea + "	60/30 D	37.2	10.4	47.6	36.5	6.4	42.9	32.3	9.3	41.6	53.6	13.3	66.9
NH$_4$NO$_3$+ "	60/30 B	52.5	10.3	62.8	42.5	5.8	48.3	33.8	9.7	43.5	66.8	14.8	81.6
Urea + "	60/30 B	53.9	12.9	66.8	44.2	7.2	51.4	28.4	6.2	34.6	66.6	17.4	84.0
Urea + "	60/30 S	63.1	13.2	76.3	45.7	8.9	54.1	33.7	8.3	42.0	68.6	16.1	84.7
NH$_4$NO$_3$+ "	60/30 S	57.6	11.9	69.5	43.0	7.9	50.9	33.1	8.8	41.9	65.3	12.6	77.9

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Fertilizer	Carrier	N/P$_2$O$_5$ lb/Ac		STOCKTON Grain	Straw	Total	NEWDALE Grain	Straw	Total	LAKELAND Grain	Straw	Total	RED RIVER Grain	Straw	Total
NH_4NO_3+$NH_4H_2PO_4$		90/30	D	75.5	16.1	91.6	57.3	9.7	67.0	49.5	11.7	56.2	82.9	20.7	103.6
NH_4NO_3+ "		90/30	B	66.7	18.1	84.8	61.0	12.3	73.3	44.7	13.2	57.9	85.2	30.9	116.1
Urea + "		90/30	B	68.1	14.0	86.1	56.5	9.9	66.4	48.7	15.4	64.1	80.6	30.2	110.8
NH_4NO_3+ "		90/30	S$_{p2}$	71.9	16.8	88.7	59.0	9.7	68.7	51.2	16.2	67.4	79.8	23.8	103.6
NH_4NO_3+ "		90/30	S$_{p3}$	74.5	14.6	89.1	55.0	10.0	65.0	46.3	13.5	59.8	80.1	25.1	105.2
NH_4NO_3+ $NH_4H_2PO_4$		120/30	B	71.5	22.4	93.9	71.4	14.4	85.8	57.1	17.7	74.8	81.4	31.5	112.9
Urea + "		120/30	B	75.7	27.7	103.4	65.9	14.5	80.4	56.5	16.8	73.3	83.7	39.5	123.2
NH_4NO_3+ "		120/30	S$_{p4}$	80.0	22.7	102.7	67.0	14.4	81.4	53.5	13.3	66.8	78.8	30.2	109.0
NH_4NO_3+ $NH_4H_2PO_4$		7/30	D	26.4	6.6	33.0	14.5	2.3	16.8	10.5	4.2	14.7	42.3	7.0	49.3
NH_4NO_3+ "		90/30/30	B	62.0	13.9	75.9	53.9	9.1	63.0	48.0	–	–	82.9	24.0	106.9
NH_4NO_3+ "		90/0	B	21.8	18.7	40.5	40.1	7.8	47.9	45.9	11.3	57.2	58.0	26.8	84.8
NH_4NO_3+ "		180/30	B	72.1	35.6	107.7	89.8	26.0	115.8	72.6	32.8	105.4	82.2	54.0	136.2
NH_4NO_3+ "		240/30	B	84.4	42.8	127.2	94.5	35.6	130.1	67.8	42.0	109.8	88.9	62.7	151.6

D = Nitrogen drilled with seed
B = Broadcast and incorporated with surface 2½" of soil
S = Banded 1" to side of seed
S$_p$ = Split application S$_{p1}$ = 40D + 20B, S$_{p2}$ = 40D + 50B, S$_{p3}$ = 60D + 30B, S$_{p4}$ = 60D + 60B

TABLE 3A   STATISTICAL ANALYSIS OF PLANT YIELD DATA (Greenhouse)

Statistical Analysis

Source of Variance	(Early Harvest) Variance	F	(Late Harvest) Variance	F
Replications	0.084	2.18	0.49	0.68
N Rate	0.104	2.70	99.31	138.13**
N Source	0.134	3.49*	6.77	9.42**
Soil Type	3.034	78.91**	243.19	338.26**
Rate x Source	0.027	0.71	2.54	3.53*
Rate x Soil	0.045	1.17	12.18	16.94**
Source x Soil	0.085	2.20	1.05	1.45
Rate x Source x Soil	0.089	2.32	0.76	1.06
Error	0.038		0.72	

    *   Significant at   5% level

  **   Significant at   1% level

TABLE 4A   STATISTICAL ANALYSIS OF PLANT NITROGEN UPTAKE (Greenhouse)

Source of Variance	(Early Harvest)		(Late Harvest)	
	Variance	F	Variance	F
Replications	272.69	2.21	559.5	2.84
N Rates	588.88	4.77*	152,938.0	775.44**
N Source	491.34	3.98*	2,465.5	12.50**
Soil Type	12,491.81	101.24**	429,335.0	2,176.85**
Rate x Source	96.41	0.78	900.5	4.56*
Rate x Soil Type	160.31	1.30	3,588.0	18.20**
Source x Soil Type	260.69	2.11	2,352.5	11.93**
Rate x Source x Soil Type	334.60	2.71	862.0	4.37*
Error	123.38		197.3	

*   Significant at 5% level

**   Significant at 1% level

TABLE 5A STATISTICAL ANALYSIS OF % ^{15}N UTILIZATION (Greenhouse)

Source of Variance	Early Harvest Variance	F	Late Harvest Variance	F
N rates	102.67	20.74**	89.68	4.26
Soil type	4.94	1.00	681.04	32.32**
N Source	58.35	11.79*	406.22	19.28**
Soils x source	8.29	1.67	13.54	0.64
Error	4.95		21.07	

* Significant at 5% level

** Significant at 1% level