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TITLE OF THESIS/*TITRE DE LA THÈSE* Losses of Mineral Nitrogen Over the Winter in Chernozemic and Luvisolic Soils

UNIVERSITY/*UNIVERSITÉ* The University of Alberta, Edmonton, Alberta T6G 2E3

DEGREE FOR WHICH THESIS WAS PRESENTED/*GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE* Ph.D. (Doctor of Philosophy)

YEAR THIS DEGREE CONFERRED/*ANNÉE D'OBTENTION DE CE GRADE* Spring, 1978

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THE UNIVERSITY OF ALBERTA

LOSSES OF MINERAL NITROGEN OVER THE WINTER IN CHERNOZEMIC AND LUVISOLIC SOILS

by

SUKHDEV SINGH MALHI

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

in

SOIL FERTILITY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA
SPRING, 1978

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "Losses of Mineral Nitrogen Over the Winter in Chernozemic and Luvisolic Soils" submitted by Sukhdev Singh Malhi in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Soil Fertility.

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Date Feb. 20/78

This thesis is dedicated to the memory of
my grandparents whose help and encouragement
have made my education possible.

ABSTRACT

Fall application of commercial N fertilizers has caused some concern about over-winter losses of mineral N (NH_4-N + NO_3-N) from the soil. The study was carried out to determine the magnitude of over-winter losses of mineral N, and to determine the mechanisms by which fall-applied N was lost. Another facet of the work was to find some practical means to reduce the over-winter losses of mineral N. The work consisted of incubation and field experiments.

The results of field experiments at 10 locations over two years (1973-74 and 1974-75) indicated that 38% of fall-applied urea N (applied at 56 kg N/ha) disappeared over the winter from the mineral N pool. Fall-applied urea gave about 10 quintals/ha (1 quintal = 100 kg) lower yield and one half as much N (kg/ha) in barley grain as did spring-applied urea. The losses were greater from fall-applied calcium nitrate. On the average of six field experiments, 50% of fall-applied calcium nitrate (applied at 56 kg N/ha) disappeared over the winter. Nitrogen was generally not lost until early March, regardless of whether it was applied as calcium nitrate or urea. By early May, the NO_3 either applied in the fall or produced through nitrification of urea during the winter was partially lost.

Like fall-applied fertilizer N, soil mineral N was not lost from the soil until March and was partially lost in early spring after thawing. Ammonification and nitrification of soil N occurred in non-fallowed and fallowed fields throughout the winter and as a consequence soils accumulated between 15 and 240 kg/ha of mineral N before the spring thaw. On the average, approximately 60 kg of soil mineral N/ha was lost over the winter in three fallowed soils.

No leaching losses of labelled N applied in the fall, at a rate of 112 kg N/ha, were observed over the winter. The highest over-winter losses, through denitrification, were from KNO_3 mixed into the soil (39%), followed by urea mixed into the soil (29%). The lowest losses (16%) were from $(NH_4)_2SO_4$ banded. Approximately one-fifth of the fall-applied N was immobilized.

Five inhibitors were used in incubation experiments. Of these, thiourea suppressed nitrification the most and only one-third of the added urea N was found as NO_3-N after six weeks. Pelleting with urea increased the efficiency of thiourea as a nitrification inhibitor. Placing urea in bands rather than mixing it into the soil slowed nitrification in the field. Application of pelleted urea + thiourea (2:1) in bands resulted in almost complete inhibition of nitrification of urea for four weeks.

Slowing nitrification of fall-applied urea, reduced the over-winter losses. Higher yield and N uptake of barley grain with fall-applied urea + thiourea (2:1) than with urea were associated with higher mineral N content of the soil in early May, before seeding. Urea + thiourea (2:1) banded in the fall gave 6.4 quintals/ha higher yield of barley grain and 1.5 times more N/ha in barley grain than with urea banded alone in the fall. The N uptake (kg N/ha) by barley grain obtained with urea + thiourea (2:1) banded in the fall was about 90% of the N uptake obtained with urea banded in the spring. The method of applying urea alone had some effect on yield of barley grain. Band placement of urea

in the fall resulted in an increase of 1.7 quintals/ha [illegible] barley grain over mixed application.

ACKNOWLEDGEMENTS

I take this opportunity to express my deep sense of gratitude to Dr. M. Nyborg, Professor of Soils, Department of Soil Science, for his untiring guidance and supervision, healthy criticism and keen interest evidenced throughout the course of this investigation; and for his assistance in preparation of the Thesis in the final form.

Thanks are also extended to the following: Dr. F.D. Cook, Dr. W.B. McGill and Dr. J.A. Robertson, all of the Soil Science Department, for valuable discussions at different phases of the investigation, for reviewing the manuscript and for serving on the Thesis Committee.

Dr. J.M. Mayo, Department of Botany, who served on the Thesis Committee and reviewed the manuscript.

Dr. J. Bole, Canada Department of Agriculture Research Station, Lethbridge, Alberta, for serving as External Examiner and for reviewing the manuscript.

Dr. J.A. Toogood, former Chairman of the Soil Science Department, and Dr. S. Pawluk, Chairman of the Soil Science Department, for providing me the necessary facilities.

My parents, brother and sister for their encouragement and concern in my studies.

Mr. G.W. Oborn for his technical assistance especially taking soil samples during winter.

Anita Moore for her excellent typing.

Mr. Gurchand Singh and Miss Daisy Thomas for their help in proof reading.

My friend Mr. H.S. Khosa for his concern in my studies.

Miss Fay Farris, Mr. Dennis Lay, Mr. Tom Kelling and Mr. John Timmermans for their help in field work.

Fellow graduate students and members of the Soil Science Department who offered their time and advice in this study.

I also take the opportunity to extend my profound thanks to Western Co-operative Fertilizers Limited, the Alberta Agricultural Research Trust and the National Research Council of Canada for their financial assistance.

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1. INTRODUCTION

In the Prairie Provinces, for spring-sown grain crops, N fertilizers are sometimes applied in fall rather than in spring. Fall application has several benefits. These include improved efficiency in the use of production and distribution facilities for the manufacturers; lower prices and a certain supply of fertilizers for farmers. Based on research conducted prior to 1968, in the Canadian Prairies, it was generally concluded that fall-applied fertilizers were as effective as spring-applied. However, research conducted in the 1970's in Alberta and Manitoba has shown that fall-applied N is often inferior to N applied in the spring.

Nitrogen loss, where it occurs, is mainly a consequence of nitrification. The NO_3 is subject to loss through leaching, runoff and denitrification. Unlike NO_3, NH_4 is held on the exchange complex of the soil and therefore is not readily lost by leaching.

Several approaches have been used to minimize losses and to increase crop recovery of N added as fertilizer. In addition to management practices involving split applications and band placement, efforts to reduce the rate of release of N from fertilizers have been made. A degree of success has been achieved in this respect through development of low or limited solubility N sources, coated or encapsulated N sources and chemicals designed to inhibit nitrification. All these practices share a common attempt to reduce the accumulation of NO_3 before N is taken up by plants. The use of nitrification inhibitors represents a promising recent method to conserve applied fertilizer N. Most of the work on this problem has been performed either in greenhouse or under climatic conditions different from those under which the present investigation was conducted.

In the Prairie Provinces, recent shifts in the type of N fertilizers and in their time of application may make the use of nitrification inhibitors important. The use of N fertilizers which contain no NO_3 has increased, as has the amount of fertilizer N applied in the fall. The increased use of urea is due to its high content of N and less bulk which reduces transport costs. Ammonium-based N fertilizers, however, under favorable conditions are rapidly transformed through the activities of nitrifying bacteria, to NO_3 which may then be lost by leaching and denitrification.

On the basis of rather limited results, the practice of fall application of N fertilizers was begun in the Prairie Provinces. The practice is increasing and eventually perhaps half of the N fertilizers used for grain crops will be applied in the fall. However, before fall fertilization could be recommended, the potential for over-winter losses under the climatic conditions prevailing in the Prairie Provinces required study. Therefore, the present study has the following objectives:

1. To determine the magnitude of over-winter losses of mineral N either from fall-applied fertilizer N or from soil N.

2. To determine the mechanism by which the fall-applied N is lost.

To evaluate the effectiveness of thiourea, and other nitrification inhibitors, in the over-winter conservation of mineral N.

2. LITERATURE REVIEW

Nitrogen in the soil occurs in two major forms: (1) the organic fraction which comprises about 90% of the total soil N in the Ap horizon of cultivated chernozemic soils, and (2) the inorganic fraction which comprises the remainder is non-exchangeable and exchangeable NH_4 and water soluble NO_3. The rate at which the organic fraction is mineralized is generally slower than the rate at which crops can remove mineral N. Therefore, addition of fertilizer N increases yield unless substantial biological N_2 fixation occurs in a crop rotation. Most N fertilizers contain inorganic forms of N (NH_4 or NO_3) which are readily available to plants. When urea is added to soil it is rapidly hydrolyzed to NH_4. The enzymatic conversion of urea to ammonium (urea hydrolysis) has been reviewed in detail by Gould (1970 and 1976). Therefore, this review will not include urea hydrolysis, although urea is the main fertilizer used in the present study. The NH_4 produced from the hydrolysis of urea is converted to NO_3. The NO_3 whether issued from the fertilizer N or from the soil N, may be subject to losses by leaching and denitrification.

The present investigation has been undertaken to determine the extent to which over-winter losses of N occur, to find the mechanism by which losses take place, and to find some practical means to reduce these losses. Consequently, this review considers soil processes and management practices pertinent to this problem.

2.1 Nitrification

According to McLaren (1971) the rates of nitrification may be taken as proportional to the growth of nitrifiers which is related to substrate concentration when the concentration is less than that needed to achieve the maximum growth rates and provided the population size is much smaller than the maximum attainable population. At low NH_4-N concentrations in soil, nitrification is rapid and complete within a few weeks (Broadbent et al., 1957), but it appears to be inhibited at higher concentrations (McIntosh and Frederick, 1958; Stojanovic and Alexander, 1958; Justice and Smith, 1962; and Anderson and Boswell, 1964). The inhibition has generally been attributed to ammonia toxicity. Acidification of soil by $(NH_4)_2SO_4$ (Justice and Smith, 1962) may also be a factor. The maximum tolerable NH_4-N concentration in soil appears to vary between 400 ppm (McIntosh and Frederick, 1958; and Anderson and Boswell, 1964) and 800 ppm (Broadbent et al., 1957). The critical concentration varies with the initial pH (as pH affects $NH_4^+ \rightleftharpoons NH_3$ equilibrium), and the NH_4 source (Broadbent et al., 1957). Jones and Hedlin (1970) reported that with 50 ppm N as ammonium sulphate and urea, nitrification for both fertilizers was complete in 12 days. At high N concentrations (200, 400 and 800 ppm N), however, urea led to high nitrite concentrations in the neutral Wellwood soil. Pang et al. (1975) reported accumulation of large quantities of nitrite when urea was banded at a rate of 800 kg N/ha, but no nitrite accumulated when 100 kg N/ha was applied. They attributed this nitrite accumulation to lower activity of Nitrobacter at higher concentration of ammonia produced by rapid hydrolysis of urea.

If nitrification were inhibited sufficiently by low temperatures, NH_4 bearing fertilizers applied in late fall could conceivably remain without nitrification, and without appreciable less until spring. In general below 35°C, the lower the temperature the slower the rate of nitrification. Some studies have shown that nitrification of applied NH_4 occurs in some soils at temperatures considerably lower than were previously thought (Anderson and Purvis, 1955; Frederick, 1956; Stojanovic and Broadbent, 1956; Broadbent et al., 1957; Sabey et al., 1956 and 1959; and Justice and Smith, 1962). Nitrification has been reported to occur at 1° to 2°C (Frederick, 1956; and Sabey et al., 1956). The optimum temperature for nitrification varies and has been reported as 30° to 32°C (Fisher and Parks, 1958; Anderson and Powell, 1964), 25° to 27°C (Waksman and Madhock, 1937; Justice and Smith, 1962; Thiagalingam and Kanehiro, 1973; and Kowalenko and Cameron, 1976) and for a tropical soil 35°C (Myers, 1974). Anderson and Purvis (1955), Frederick (1957), and Sabey et al. (1959) concluded that variations among soils in regard to the temperature range, over which NO_3 formation from NH_4 occurs, appear to be due to differences in size of the initial populations of nitrifiers.

Although numerous workers have reported the effect of soil moisture on nitrification, in only a few investigations have moisture levels been reported in terms of soil moisture tension. Early in the century workers such as Greaves and Carter (1920), Panganiban (~~1925~~), and Russell et al. (1925) determined the generally accepted optimum range of moisture (50% to 60% of water holding capacity) for nitrification. Although

Dubey (1968) reported [illegible] maximum rate of nitrification occurred [illegible] and 0.5 bar (Miller and Johnson, 1964) and [illegible] nitrification could be detected at 15 bars [illegible] (Miller and Johnson, 1964; Dubey, 1968).

It has been pointed out that nitrification takes place at the colloidal surfaces (Lees and Quastel, 1946; [illegible] and [illegible], [illegible]; Meiklejohn, 1953). Therefore, small films of water [illegible] particles at moisture tensions greater than 15 bars should be [illegible] to allow this process to proceed.

The optimum pH for nitrification is near neutrality and the rate drops quickly below a pH of 6.2 to 6.5 (Frederick, 1957; Dancer et al., 1973). Lack of nitrification at low pH values has been shown to be due to low nitrifier populations (Pang et al., 197[illegible]).

In summary, the review concerning nitrification shows that the optimum range of NH_4-N concentration for nitrification varies between 400 ppm and 800 ppm NH_4-N, and nitrification appears to be inhibited at higher concentrations. A temperature range of 25° to 35°C seems to be optimum for nitrification and the rate of nitrification decreases beyond this. Nitrification also occurs at temperatures as low as 1° to 2°C. The rate of nitrification increases 5 to 11 fold with an increase in moisture content from near permanent wilting point to near field capacity. The optimum pH for nitrification ranges between 6.8 and 7.7.

2.2 Denitrification

The term denitrification applies to the microbial process whereby NO_3 is reduced to gaseous nitrogen compounds such as N_2O, NO and N_2. Denitrification differs from assimilatory reduction of NO_3 in that denitrification leads to gaseous loss of N to the atmosphere. Despite the long historic awareness of denitrification (Gayon and Dupetit, 1886), the kinetics of denitrification in soils are not clear. For the most part, denitrification rates have been thought to be independent of NO_3 concentration (zero order kinetics) over a fairly wide range of 40 to 500 ppm NO_3-N (Broadbent, 1951; Wijler and Delwiche, 1954; Nommik, 1956; Bremner and Shaw, 1958; and Cooper and Smith, 1963). However, Bowman and Focht (1974) found denitrification rates to be substrate-dependent at lower concentrations approximating first order kinetics and gradually diminished at higher concentrations (1000 μg NO_3-N/ml) to become zero order. The maximum rate in a soil suspension obtained was 150 μg N/ml/day.

The rate of denitrification is closely associated with temperature. The lower temperature limit of denitrification has been set at 2°C (Bremner and Shaw, 1958), at 3°C (Nommik, 1956), and 5°C (Bailey and Beauchamp, 1973). The upper temperature limit ranges from 70°C (Bremner and Shaw, 1958) to 85°C (Nommik, 1956). The optimum temperature varies between 60°C (Bremner and Shaw, 1958) and 65°C (Nommik, 1956). The ratio between N_2O and N_2 in denitrification gas varied with incubation temperatures, and N_2O dominated at lower temperatures (Nommik, 1956). Similarly Bailey (1976) reported that decrease in temperature resulted in an increase of NO production which was the principal gas produced at 6° to 8°C. No research, to the knowledge of the writer, has been reported on denitrification at temperatures below 0°C.

Most research workers (Meiklejohn, 1940; Broadbent, 1951; Jones, 1951; Greenland, 1962; Jansson and Clark, 1952; Hauck and Melsted, 1956; Allison et al., 1960; and Pilot and Patrick, 1971) apparently have accepted the concept that the effect of moisture in saturated soils is primarily that of reducing the volume of air-filled pores with a concomitant reduction in O_2. Bremner and Shaw (1958), and Greenwood (1962) observed that the rate of denitrification as measured by NO_3 disappearance in soils, increased as the moisture level was increased even beyond the saturation level. They concluded that this was due to the slower diffusion of O_2 into the soil mass with increasing moisture. Greenwood (1961), and Greenwood and Berry (1962) showed that the changeover from aerobic to anaerobic metabolism takes place at an O_2 concentration less than about 5×10^{-6} M. Even under apparently aerobic conditions, microsites having anaerobic conditions at the centres of crumbs larger than 3 mm in diameter (Greenwood, 1961; Greenwood and Berry, 1962) may permit denitrification to occur (Broadbent and Clark, 1965). Since crumbs of this size are present in most soils, it would mean that anaerobic conditions can be found in soils even when they are not wet; and perhaps denitrification can take place, at least slowly, in soils that are not saturated. Denitrification has been reported to occur at or near 15 bars moisture tension (McGarity, 1961; and Ekpete and Cornfield, 1964).

Nommik (1956) pointed out that at lower moisture contents, the denitrification gas consisted chiefly of N_2O. This indicates that the degree of anaerobiosis is one of the factors which determine the composition of denitrification gas.

In addition to NO_3 concentration, O_2 supply, and temperature, the effect of energy supply on the denitrification rate has been discussed (Bremner and Shaw, 1958; and Bowman and Focht, 1974). Bowman and Focht (1974) found that glucose addition at a rate of 1000 µg/ml increased the rate of denitrification by 58%. Denitrification rates in soils under saturated conditions are correlated with the amount of total organic carbon (Bremner and Shaw, 1958; Dawson and Murphy, 1972; Stanford et al., 1975; and Smid and Beauchamp, 1976) and very closely associated with the supply of readily decomposable organic carbon (Burford and Bremner, 1975; and Kohl et al., 1976).

The rate of denitrification increases with increases in pH from 5.0 to 7.0 or 8.0; further increases in pH lead to a suppression of denitrification, until it ceases altogether at pH 10.5 (Jansson and Clark, 1952; and Nommik, 1956). Nommik (1956) also showed that at lower pH values, denitrification products consisted chiefly of N_2O.

Moisture, temperature, supply of available carbon, amount of NO_3, and pH are all important to the rate of denitrification. This review regarding denitrification shows that rate of NO_3 losses in gaseous forms increases 8 to 20 fold when tem[illegible] is raised from 10^o to the optimum range. The rate of denitrification at 100% moisture saturation is approximately nine times greater than at 80% saturation. The rate of denitrification depends upon the amount of available carbon. The rate of denitrification under optimum conditions increases with increase in NO_3-N concentrations up to 1000 µg N/ml and becomes constant beyond this level.

2.3 Leaching Losses

Leaching losses from agricultural soils are of importance as these can reduce the availability of essential plant nutrients, and may result in NO_3 pollution of ground and surface water (Ray et al., 1957; Harmsen and Kolenbrander, 1965; and Viets, 1965). The NO_3 due to its extreme solubility and anionic form which prevents its adsorption onto the soil colloids (except under strongly acidic conditions), is more susceptible to leaching than NH_4 (Parker, 1972). Substantial movement of NO_3 in coarse textured soils has been recorded (Scholefield, 1945; and Wetselaar, 1962). Leaching losses of soil NO_3 under field conditions have been measured in lysimeter experiments, or in controlled field drainage plots by measuring the NO_3 content in the effluent (Bizzel, 1944; Chapman et al., 1949; Allison, 1955; and Owens, 1960). On the basis of the results of 156 lysimeter experiments conducted at experimental stations in the United States, Allison (1955) attributed 25% to 60% of NO_3 loss due to leaching. Studies using pure iron and aluminum oxides and hydroxides (Hingston et al., 1972), and kaolinite (Scholefield and Samson, 1953; Quirk, 1960; and Wada and Harward, 1974) have shown that under acid conditions, these minerals possess the ability to adsorb anions such as NO_3 and Cl and may reduce leaching losses in soils containing large amounts of these minerals. Moshi et al. (1974) showed that organic matter prevented Cl adsorption in the surface soil, so that it might be expected that adsorption would occur only in the sub-soil where the levels of organic matter are low. Leaching column experiments have shown that adsorption results in slow movement of anions relative to water (Corey and Fenimore, 1968; Kinjo et al., 1971; and Black and Waring, 1976). Singh and Kanehiro (1969), and Black and Waring (1976) reported that the rate of NO_3 leaching decreased with depth because of higher adsorption of NO_3 in the sub-soil than in the surface soil which has a high net negative charge due to the presence of organic matter.

In the Prairie Provinces, summerfallowing has resulted in much deeper penetration of precipitation and subsequently NO_3 than was possible prior to cultivation. The results of studies conducted in Manitoba by Michalyna (1959) have shown that the amount of NO_3 in the sub-soil increased as the frequency of fallow increased, and little or no NO_3 was found in the sub-soil under continuous cropping. Rennie et al. (1976) have found very substantial amounts of NO_3 below the rooting zone at University Farm in Saskatchewan. The total NO_3-N to a depth of 4 m averaged approximately 500 kg N/ha (a two-year rotation of fallow-wheat has been followed on these soils for 40 years). They suggested that leaching losses may account for approximately 10% to 15% of N released from the soil organic matter since cultivation began in Saskatchewan. High concentrations of NO_3 have been reported at groundwater level in Alberta (*Alberta Environment, 1975), but the origin of this NO_3 is not known.

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*Nitrates in Shallow Groundwater Near Lethbridge. 1975. Published by Alberta Environment.

2.4 Effect of Placement Method and Inhibitors on Nitrification

In areas of intensive agriculture, it is becoming common ~~to~~ place N fertilizers in bands. This results in high local concentrations of ammonia and soluble salts which reduce the rates of nitrification of fertilizers. Gasser (1965) and Leitch (1973) found that band placement of $(NH_4)_2SO_4$ reduced nitrification, and this effect was enhanced by addition of a nitrification inhibitor to banded $(NH_4)_2SO_4$. Total amount of NO_3 formed per unit area decreased with increased local concentration of NH_4 in the band (Wetselaar et al., 1972). Maximum rate of nitrification in fertilizer materials (urea, ammonium sulphate and ammonium hydroxide) took place not at the middle of the fertilizer band, but near the edges of the diffused zone (Pang et al., 1973). The progress in nitrification was characterized by a decrease in pH in the diffused zone.

Nitrification inhibitors may be of practical value in the production of crops for a number of reasons. The use of inhibitors with ammonium-based fertilizers may reduce the losses of fertilizer N by leaching and denitrification because NH_4 is less subject to losses than NO_3 (Wagner and Smith, 1958; Parker, 1972). It permits the use of fall-applied NH_4-N, where otherwise such practice may not be economical. Slowing nitrification of ammonium-based N fertilizers may also be beneficial because it provides more uniform release of NO_3 which eliminates NO_3 accumulation (Goring, 1962), and may reduce the severity of plant diseases (Huber and Watson, 1972).

Several inhibitors of nitrification have been studied, but N-Serve

(2-chloro, 6-trichloromethyl-pyridine) is considered the most promising (Ansorge et al., 1967; Hoflich, 1968; Bundy and Bremner, 1973, 1974; and Reddy and Prasad, 1975). The amount of N-Serve required for maximum inhibition of nitrification in the field experiments varied from 0.28 kg to 2.24 kg/ha. Treating soils with 1 ppm of N-Serve or 3 ppm 2-amino, 4-chloro, 6-methyl-pyrimidine (AM) suppressed nitrification of soils incubated in plastic bags in the field during autumn, winter and spring (Sabey, 1968). Ten ppm N-Serve applied with aqueous NH_3 and $(NH_4)_2SO_4$ to a sandy loam soil in October retarded nitrification for more than 2 weeks (Jauert et al., 1968). Nitrosomonas europea was greatly inhibited by 1 ppm of N-Serve, Nitrobacter agilis was also inhibited, but much less than Nitrosomonas europea (Shattuck and Alexander, 1963). Growth of Nitrosomonas was inhibited by 0.2 ppm N-Serve, and 1.0 ppm completely inhibited the oxidation of NH_4 by fresh cell suspensions (Campbell and Aleem, 1965). They further reported that cytochrome-oxidase activity (involved in NH_4 oxidation) inhibited by N-Serve was partly restored by adding cupric ions and inhibition of NH_4 oxidation by allylthiourea was not reversed by cupric ions.

Smaller NO_3 losses and improved crop recovery of N have been obtained on using nitrification inhibitors such as N-Serve. However, these inhibitors are expensive and are not economical to use in commercial agriculture. Carbon disulphide (CS_2) is very inexpensive and has been recognized as an effective nitrification inhibitor in a closed system in the laboratory (Gainey, 1914; Powlson and Jenkinson, 1971; and Bremner and Bundy, 1974). Nitrification of aqueous NH_3 was completely inhibited by CS_2 for three weeks at 25°C (Ashworth and Flint, 1974). At Rothamsted, 15 kg CS_2/ha was able to completely inhibit nitrification of aqueous NH_3, applied at a rate of 260 kg N/ha, for 50 days in a field experiment (Ashworth et al., 1975).

Thiourea, a sulphur-containing N compound, is one of the earliest reported nitrification inhibitors. Quastel and Scholefield (1949) found a concentration of 25 ppm thiourea in a perfusion liquid inhibited nitrification for a period of 16 days Subsequently (1951) they reported that nitrification was completely inhibited for 21 days with 380 ppm thiourea. Complete inhibition of nitrification has been observed in a pure culture of <u>Nitrosomonas</u> <u>sp</u> in the presence of 10^{-3} to 10^{-6} M thiourea (Jensen and Sorensen, 1952). Exponential growth of <u>Nitrosomonas</u> <u>sp</u> and active nitrification were suppressed by a concentration of 50 ppm thiourea in the perfusion liquid (McBeath, 1962). In a soil system, Jaques et al. (1959) reported that 1.5×10^{-3} moles of thiourea/kg soil (120 ppm thiourea) inhibited nitrification for 20 days. Leitch (1973) found thiourea to be an effective nitrification inhibitor under field conditions, when applied at the rate of 56 kg/ha with banded $(NH_4)_2SO_4$. Application of thiourea modified the growth and N uptake pattern of a rapeseed crop and decreased the midseason accumulation of NO_3 in rape and oats.

The possible biological importance of copper ion in enzymes has been stressed by Baudisch (1945). As <u>Nitrosomonas</u> contains cytochromes in its oxidase enzyme system (Aleem and Lees, 1963), it is reasonable to expect that these are involved in NH_4 oxidation. Therefore, one would expect the inhibition of NH_4 oxidation by immobilization of copper ions by adding copper-enzyme poisons. However, Lees (1946), Campbell and Aleem (1965), and Quastel (1965) reported that the inhibitory effect of allylthiourea was not caused by the immobilization of copper ions.

Thiourea has also been studied as a source of N for plant growth. After incubating 540 ppm of thiourea (containing 200 ppm N) in soil for 90 days, Fuller et al. (1950) recovered 154 ppm of NH_4-N, but no NO_3-N or NO_2-N, showing that NH_4 released from thiourea had not nitrified. Hamlyn and Gasser (1967) while studying the possible use of thiourea as a N fertilizer, observed that high rates of thiourea mixed into the soil (1523 kg thiourea/ha) inhibited nitrification of the NH_4 produced for up to 24 weeks.

2.5 Fall Application versus Spring Application of Fertilizer N

Even though NH_4 is more stable in soils than NO_3, there is a question of whether crops can make use of NH_4 as well as of NO_3. Generally, NO_3 is the form taken up by plants, not necessarily because plants prefer it, but because NH_4 applied is rapidly nitrified in most soils. Under conditions where plants take up NH_4-N, reduction in growth may be expected, particularly in dicotyledenous species (Kirby, 1968). Rapeseed when grown in the greenhouse on soils, gave poor growth when fertilized with NH_4-N and a nitrification inhibitor (Nyborg et al., 1977). On the other hand, field experiments showed that most soils in the field have enough NO_3 so that application of NH_4-N with a nitrification inhibitor for rapeseed gave nearly as much yield as did NO_3 fertilizer. Work at Rothamsted showed that wheat yielded slightly more with NO_3-N than with NH_4-N plus inhibitor when water was adequate, but the NH_4-N plus inhibitor yielded more when soil water was limited (Spratt and Gasser, 1970).

The unsettled question of whether NH_4 can be used as the sole source of N for various crops with success equal to NO_3 is intertwined with the subjects of time of application of N fertilizers, and the use of nitrification inhibitors. However, the matter of physiological preference of plants for NH_4 or NO_3 is beyond the scope of this review.

Autumn applications of N have been found inferior to equivalent spring application at Rothamsted (Widdowson et al., 1961; Devine and Holmes, 1964), and in north and north-central Georgia (Olson et al., 1964). Pearson et al. (1961) found fall-applied N about half as effective in producing corn as spring-applied N at seven locations in Alabama, Georgia and Mississippi. The results of field studies conducted in Illinois for 3 years by Welch et al. (1966) suggested that 1 kg of spring-applied N as ammonium nitrate produced the same yield of wheat grain as 1.5 kg of N applied in the fall. The average of four field experiments conducted in Ontario showed that spring applications of ammonium nitrate, urea and anhydrous ammonia produced about 18% more corn grain than fall application of these fertilizers (Stevenson and Baldwin, 1969). In Kentucky, spring-applied N produced greater yield of corn than fall application (Frye and Hutcheson, 1971; Miller et al., 1975; Frye, 1977).

There are some reports available in the literature where fall application of N has been found to be as effective in increasing yield as spring-applied N. Larsen and Kohnke (1946) reported that two of three Indiana soils showed no differences in corn yields between fall- and spring-applied N. In Georgia, Boswell (1971) and Boswell et al. (1974) observed no statistical difference in corn yields between fall- and spring-applied N at a rate of 156 kg N/ha. The field work conducted in Wisconsin by Chalk et al. (1975) showed that there were no differences between grain yields of corn with fall and spring application of anhydrous ammonia. In these studies, either the responses to applied N were small or the rates of N application were high.

In a summary of 22 field trials conducted in the Prairie Provinces from 1950 to 1968, McAllister (1969) reported that at 15 of the 22 locations there were no differences in the yields of cereal grains between fall and spring application, at 3 locations fall application was better than spring application, and at 4 locations spring-applied N was better than fall-applied N. In most of the tests, there were generally small responses to applied N, suggesting that these tests were not suitable to compare fall- and spring-applied N fertilizers. In one of the tests, however, conducted in Peace River region, where there was a very large response to N, the spring-applied N was much superior to fall-applied N. Under the Prairie Provinces' climatic conditions, where the soils remain frozen for most of the winter, one would not expect losses of mineral N over the winter. However, the results of research in the early 1970's showed crop yields and N uptake to be favored by spring application. In Alberta, Leitch and Nyborg (1972) found that N uptake with spring application was about two times greater than with fall-applied N. Spring application of urea, ammonium nitrate and calcium nitrate at four locations in Alberta, on the average gave 5.3 quintals/ha (1 quintal = 100 kg) more barley grain than the fall application of these fertilizers (Malhi and Nyborg, 1974). For the Manitoba lowlands, on imperfectly drained soils, spring application on the average of nine sites was 56% better than fall application (Partridge and Ridley, 1974). In the uplands, where the soils were well drained, the difference in the yield of barley grain on the average of 13 sites was 15%. Field studies conducted in Saskatchewan by Paul and Rennie (1977) suggested that fall-applied N was inferior to spring application.

Nitrification inhibitors have been found to reduce over-winter losses of fall-applied NH_4-N in England (Gasser, 1965) and in the United States (Huber et al., 1969). Gasser and Hamlyn (1968) reported that autumn applied ammonium sulphate + N-Serve resulted in greater early season growth and N uptake by winter-wheat than ammonium sulphate alone. In the United States, Huber and Watson (1972) found that N-Serve with fall-applied NH_4-N suppressed nitrification, and therefore prevented N loss and reduced the severity of *Cercosporella* foot rot of winter-wheat. In Georgia, a three year average of corn grain yield from fall-applied N plus the nitrification inhibitor (N-Serve) was almost 250 kg/ha greater than from the same amount of N applied in the fall without inhibitor (Boswell et al., 1974). Field studies conducted at Cookeville in Tennessee, using corn fertilized with 112 kg N/ha, showed that the relative efficiency of fall compared to spring application, was only 0.49 for uncoated urea, but 0.80 for coated urea (Frye, 1977).

2.6 Summary of Literature Revi

When ammonium-based fertilizers are added to soil, these are converted to NO_3 by nitrifying bacteria. Under certain conditions, the NO_3 produced from NH_4, or added directly, may be subject to losses by denitrification.

The rates of nitrification and denitrification are influenced by several factors. The temperature range of 25° to $35^\circ C$ for nitrification appears to be optimum and the nitrification rate decreases above $35^\circ C$. Nitrification has been reported to occur at temperatures as low as 1° to $2^\circ C$. The rate of nitrification has been found to be maximum at 0.3 bar soil moisture tension and decreases beyond this moisture content. A measurable rate of nitrification occurs at 15 bar soil moisture tension. The rate of nitrification increases with increases in NH_4 concentration up to a maximum tolerable concentration between 400 to 800 ppm NH_4-N.

The rate of denitrification increases markedly with increases in temperature up to $65^\circ C$ and decreases with further increases in temperature until it ceases at $85^\circ C$. The lower temperature limit of denitrification has been set at 2° to $5^\circ C$. The rate of denitrification is a maximum under saturated conditions (0 bar soil moisture tension). The rate of denitrification also increases with increases in NO_3 concentration and amount of readily available carbon present in the soil.

Losses due to the formation of NO_3 can be reduced by preventing the formation of NO_3 from NH_4 by placing ammonium-based N fertilizers in bands, using slow release N fertilizers (sulphur-coated urea), or by use of chemicals which inhibit the growth of nitrifying bacteria. Placement of N fertilizers in bands, rather than mixing throughout the soil, reduces the rate of nitrification of ammonium-based fertilizers by increasing the local NH_4 concentration.

The reduction of nitrification by band placement can be enhanced by addition of a nitrification inhibitor to ammonium-based fertilizers. Nitrification inhibition may be of practical value in the production of crops for a number of reasons. The use of a nitrification inhibitor may reduce leaching and denitrification losses of fertilizer N. Slow oxidation of ammonium-based N fertilizers may be beneficial because it might provide more uniform release of NO_3 and eliminate possible NO_3 accumulation. The use of inhibitors which inhibit urea hydrolysis, and subsequent nitrification, may prevent nitrite accumulation to the levels which are toxic to the seedlings and stop gaseous N losses which could occur in soils. The use of inhibitors may reduce the severity of some crop diseases (such as foot rot of wheat by Cercosporella) which are associated with luxury consumption of NO_3, by suppressing the formation of NO_3 from added fertilizer.

Fall-applied fertilizer N is usually inferior to spring application in the eastern United States, in England, and in Ontario. Apparently, the losses from fall-applied N can occur as well in the Prairie Provinces. Inhibition of nitrification through either the use of chemical inhibitors or placement methods may permit application of N fertilizers in fall without over-winter losses of N.

3. MATERIALS AND METHODS

3.1 Incubation Experiments

Incubation experiments with different soils (Malmo SiCL from Ellerslie, Falun L from Egremont, and Cooking Lake SL from Smoky Lake), which had been cropped to barley, were conducted under controlled conditions of temperature and moisture in the absence of light to prevent the growth of algae. A brief summary of the characteristics of the soils appears in Appendix A, Table 1. Appropriate amounts of air-dried Ap horizon (0-15 cm), ground and passed through 5.0 mm sieve, were weighed into pots (11.0 cm diameter x 8.5 cm high) which had no drainage holes. The soils were incubated for one week at experimental moisture levels and temperatures before treating them with fertilizers. After adding fertilizers, the pots were closed with plastic having holes, 3 mm in diameter, to allow aeration, and incubated at required temperatures for different periods of time. All the containers were randomized, and moisture levels were maintained for the duration of each experiment. Soil samples were taken at various times, and analyzed for the content of NH_4-N, NO_3-N and/or urea according to the nature of the experiment. Experimental design for each of the incubation experiments is in the Results section.

3.2 Field Experiments

Field experiments were conducted at various locations in 1973-74 and 1974-75. The description of the soils used is in Appendix A, Table 1. The general purpose of these experiments was to assess fall and spring applications of N fertilizers in their effect on yield and N uptake of barley, and also to find the effect of placement of N fertilizers, or treatment with thiourea (a nitrification inhibitor) on nitrification and on yield and N uptake of barley. Specific objectives and experimental design for each experiment appear in the Results section.

In all the experiments, N was applied at a rate of 56 kg N/ha, with the exception of two field experiments, where N was applied at a rate of 100 kg N/ha. Nitrogen present in thiourea or in other inhibitors was taken into consideration. In "mixed" application the fertilizers were spread on the soil surface and then mixed into the soil 10 cm deep with a "rototiller", while in the "band placement" the fertilizers were placed 5 cm deep in rows 23 cm apart. In spring, the fertilizers were placed in bands approximately 5 cm to the side and 2.5 cm below the seed row at the time of seeding. All treatments received a blanket application of P, K and S at a rate of 41 kg P, 41 kg K and 17 kg S/ha. Fertilizers used were treble superphosphate and potassium sulphate. At the time of seeding, the fall banded N fertilizers were no longer in bands because all the treatments were rototilled in order to prepare the seed bed. Individual plots were 6.8 m x 1.8 m and were replicated four times in a randomized complete block design or split-plot design. At all sites, the banded treatments contained 8 rows, 23 cm apart and 6.8 m long.

To determine the fate of fall-applied N, a small field experiment was set out in the late fall, 1974 at Ellerslie (Malmo SiCL) using N^{15}. The plots consisted of 30 cm diameter, 17.5 cm high galvanized steel cylinders driven 15 cm into the soil. The cylinders represented three N^{15} enriched (11.0% N^{15} excess) N fertilizers (urea, KNO_3 and ammonium sulphate) and the fertilizers were applied at a rate of 112 kg N/ha. Treatments were duplicated. The fertilizer needed for each cylinder was dissolved in 25 ml of distilled water, and the solutions of KNO_3 and urea were mixed into the top 10 cm of soil while the solution of ammonium sulphate was placed in a band 4 cm long at a depth of 4.5 cm.

Soil samples were taken in late May 1975 from the 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm, and 90-120 cm depths. For the 0-15 cm soil sample, the whole of the soil from the cylinder was taken out, mixed well and a representative soil sample was taken. For other depths soil samples were taken with a 2.4 cm diameter coring tube. The soil samples were also taken at 15 cm, 30 cm, and 60 cm lateral distances from the cylinders, with a 4.3 cm diameter coring tube to a depth of 120 cm. The soil samples were dried at 20°C, ground and passed through a 10-mesh sieve for N^{15} analyses in mineral N (NH_4-N + NO_3-N) and sieved through 100-mesh for total N content of soil.

3.3 Soil Sampling

In October, 1973 and in October, 1974, all the field experiments were sampled in 15 cm increments to a depth of 30 cm, and in 30 cm increments below to a depth of 90 cm prior to the application of N fertilizers. Each soil sample was taken by combining 10 cores for the 0-15 cm depth taken with a 3.8 cm diameter coring tube (step sampler), and by combining 10 cores for each depth below 15 cm taken with a 2 cm diameter coring tube (Oakfield sampler). The fall-applied N and the control plots were sampled to a depth of 0-15 cm at various times throughout the winter from November, 1974 to March, 1975. All the plots, except those which received band placement, were sampled with a coring tube (3.6 cm diameter) made up of hard steel, taking eight cores from each treatment. The plots which received N fertilizers in fall as band placement were sampled with a different technique. A volume of soil 46 cm (long) x 15 cm (wide) x 15 cm (deep) was dug with a chisel across the bands, thawed for a very short time, passed through 5 mm sieve and a representative soil sample was taken. The rest of the soil was returned to the appropriate hole. In early May, 1974, all the plots were "rototilled" to a depth of 10 cm prior to soil sampling and soil samples were taken the same way as in October, 1973 or October, 1974. The plots were sampled differently in May, 1975. In plots which received mixed application, or no fertilizer in the fall, soil samples were taken by combining 10 cores for the 0-15 cm depth taken with a 3.8 cm diameter coring tube, and by combining 10 cores for the 15-30 cm depth taken with a 2 cm diameter coring tube. Below the

30 cm depth, 5 cores (2.4 cm diameter) taken with a hydraulic, truck-mounted sampler, were combined. The plots which received band applications were sampled to the 0-15 cm depth by the same method as used in winter 1974-75. Below 15 cm, soil samples were taken the same way as in the plots that received mixed application. Soil samples were air dried, ground to pass a 2 mm sieve, and analyzed for NH_4-N and NO_3-N content.

3.4 Grain and Straw Sampling

The samples of mature barley were taken (usually in late August) and consisted of 5.0 m from each of the center two rows of each treatment. The samples were placed in cloth sacks, dried at 65°C, weighed and threshed to determine the grain yield. Representative grain and straw samples were collected, ground to 40-mesh and analyzed for total N.

3.5 Analytical Procedures

Ammonium and nitrate were extracted from soil samples by shaking with a 1:5 ratio of soil:2NKCl for one hour. Ammonium and nitrate in the extract were determined, using the steam distillation method of Bremner and Keeney (1966). This method measures nitrite and nitrate together. The amounts of nitrite were insignificant in the soils. Therefore, nitrite was not determined separately.

Soil reaction was measured with a pH meter using a glass electrode in a 1:2.5 soil water suspension.

Organic carbon was estimated by the modified Walkley-Black method as outlined by Allison (1965).

Total N was estimated by the semimicro-Kjeldahl method (Bremner, 1965) without modification to include NO_3-N with the exception of soil samples having N^{15} where samples were treated to include NO_3-N in total soil N.

The particle size analysis of soil samples was carried out by the hydrometer method (Bouyoucos, 1962).

The moisture contents of soils at 0 bar and 1/3 bar soil moisture tension were determined using a saturation paste and by the porous plate method respectively. The moisture contents of soils at 7 bar and 15 bar soil moisture tension were determined using the pressure membrane method (U.S.D.A. Handbook 60, 1954).

Bulk density was estimated by taking cores from the 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm, and 90-120 cm depths, in the field. The soil samples were dried at 105°C, weighed and bulk density was calculated from the ratio of weight of soil (grams) to volume of the core (cm^3).

Urea was estimated using the colorimetric procedure as outlined by Watt and Chrisp (1954).

The N^{15} analyses were carried out using a CEC 21-614 cycloidal mass spectrophotometer at the Department of Chemistry, University of Alberta. Sample preparation and conversion of ammonium to N_2 gas was performed according to the method outlined in Tracer Manual on Crops and Soils by International Atomic Energy Agency, Vienna (1976).

(i) Sample Preparation

The N in the samples ($\simeq 3$ mg N/sample) was converted to ammonia, which was distilled into H_2SO_4. These samples were evaporated to a final volume of about 3 ml. The concentrated samples were transferred to glass vials and stored in the deep freezer until analyzed.

(ii) Conversion of NH_4 to N_2 Gas

The conversion of NH_4-N to N_2 gas for mass spectrometer analysis was accomplished by treatment of the sample in Rittenburg tubes with 4 ml of alkaline sodium hypobromite solution after evacuating to 10^{-8} Torr. The N_2 gas was evolved as described by the following reaction:

$$2\ NH_3 + 3\ NaOBr \longrightarrow 3\ NaBr + 3\ H_2O + N_2$$

The evolved N_2 was collected in break-seal tubes.

(iii) Determination of Isotopic Composition of Nitrogen

The break-seal tubes were connected by a high vaccuum O-ring system to the gas inlet system of the mass spectrometer and the gas was then introduced into the ionization chamber at a regulated pressure predetermined to give effective ionization of gas molecules.

(iv) Calculation of Results

The mass spectrometer measured the intensities of the currents produced by mass 28 and mass 29 ionic beams separately. The ratio (R) is that of the ion currents corresponding to mass 28($N^{14}N^{14}$) and mass 29 ($N^{14}N^{15}$), i.e.:

$$R = \frac{N^{14}N^{14}}{N^{14}N^{15}}$$

Isotopic abundances were expressed in terms of atom % of the isotope under investigation. To calculate atom % of N^{15}, the following relationship was used (Bremner, 1965)*:

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

Further calculations for atom % N^{15} excess and labelled N recovered in the soil were made as follows:

$$\text{Percent fertilizer N in the soil}$$

$$= \frac{\text{mg } N^{15} \text{ in the soil}}{\text{mg } N^{15} \text{ applied}} \times 100$$

$$= \frac{\text{Atom \% } N^{15} \text{ excess of soil N x Wt of Soil (mg/cylinder)}}{\text{Atom \% } N^{15} \text{ excess of applied N x Wt of applied N(mg/cylinder)}} \times 100$$

The data was analyzed by analysis of variance and Duncan's multiple range test was applied.

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*Bremner, J.M. 1965. Isotope-ratio analysis of nitrogen in nitrogen-15 tracer investigations. <u>In</u> Methods of Soil Analysis. pp. 1, 256-1, 286. Black, C.A. Ed. Am. Soc. Agron. Monograph, No. 9, part 2.

4. RESULTS

4.1 Over-Winter Losses of Fertilizer N Applied in Fall, 1973, in Field Experiments

Until 1969, the results of 22 field experiments (unpublished data summarized by McAllister, 1969) conducted by researchers in the Prairie Provinces showed on the average no differences in the grain yields of cereal crops with fall and spring application of N fertilizers. In all the field trials, only the grain yields of crops with fall and spring application were measured, and not N uptake by the crops. In addition, no attempts were made to determine any over-winter loss of mineral N applied in the fall.

Due to the reasons mentioned above, in October, 1973, four field experiments were set out at four locations on farm fields: at Calmar (Demay L), at Ell lie (Malmo SiCL), at Smoky Lake (Cooking Lake SL), and at Warspite (Falun L). All the experiments were located on non-fallowed fields with the aim of obtaining low mineral N levels to get large responses to fertilizer N. On the Demay L soil and the Malmo SiCL soil, the fields previously had a barley crop and on the other two soils, the fields had been previously seeded to rapeseed. The purpose of these experiments was to determine the quantity of fall-applied N lost over the winter, and to find whether these over-winter losses were great enough to reduce the yield and N uptake of barley grain with fall-applied N as compared to spring application. For this purpose, soil samples taken to a depth of 90 cm in May, 1974, were analyzed for mineral N, and the yield and N uptake of Galt barley (*Hordeum vulgare*) grain, obtained with fall and spring application of various N fertilizers (e.g. urea, ammonium nitrate and calcium nitrate) were compared. In all treatments except the control, N fertilizers were applied at a rate of 56 kg N/ha and were mixed into the top 10 cm of soil with a rototiller. Individual plots were 6.8 m by 1.8 m and were replicated four times in a split-plot design. In one set of the plots, the N fertilizers were applied in October, 1973, while in the other set of the plots, the fertilizers were applied just before seeding in May, 1974.

4.1.1 Mineral N (NH_4-N + NO_3-N) content of soil in May, 1974

Only 40% of the fall-applied urea N was recovered as mineral N in the top 90 cm on the Demav L soil (Table 1). The over-winter losses of fall-applied N in plots which received ammonium nitrate or calcium nitrate were significantly greater than in plots receiving urea. For these two fertilizers, about 75% of the applied N disappeared from the mineral N pool by early May, 1974. Apparently, 19% of calcium nitrate N had leached down to the 15-60 cm layer, with very small amounts leached into the 60-90 cm layer. Similar patterns of downward movement of mineral N were observed in urea or ammonium nitrate plots.

The over-winter losses of mineral N on the Malmo SiCL soil, the Cooking Lake SL soil and the Falun L soil were somewhat smaller than in the previous soil (Table 1). As with the Demay L soil, the lowest mineral N recovery in the top 90 cm was from calcium nitrate, but there were no significant differences between urea and

Table 1. The recovery of mineral N(NH_4-N + NO_3-N) in May, 1974, with N fertilizers applied *in October, 1973, at a rate of 56 kg N/ha to four soils in Alberta.*

Location†	Fertilizer*	Apparent % recovery of applied N as mineral N(NH_4-N + NO_3-N)**			
		0-15 cm	0-30 cm	0-60 cm	0-90 cm
1	Urea	21 a	32 a	39 a	40 a
	Ammonium nitrate	10 b	18 b	27 b	26 b
	Calcium nitrate	5 c	15 b	24 b	25 b
2	Urea	43 a	52 a	56 a	58 a
	Ammonium nitrate	42 a	50 a	58 a	60 a
	Calcium nitrate	24 b	34 b	49 b	50 b
3	Urea	47 a	53 a	64 a	66 a
	Ammonium nitrate	38 b	48 a	60 a	63 a
	Calcium nitrate	11 c	24 c	47 b	51 b
4	Urea	39 a	50 a	57 a	59 a
	Ammonium nitrate	37 a	51 a	58 a	60 a
	Calcium nitrate	21 b	37 b	45 b	47 b
Average	Urea	38	47	54	56
	Ammonium nitrate	31	41	50	52
	Calcium nitrate	15	27	41	43

†Location 1 - Demay L at Calmar
Location 2 - Malmo SiCL at Ellerslie
Location 3 - Cooking Lake SL at Smoky Lake
Location 4 - Falun L at Warspite

*The fertilizers were mixed into the soil, 10 cm deep with a rototiller.

**The values were calculated as = $\dfrac{\begin{pmatrix}\text{Mineral N recovered in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{Mineral N recovered in}\\ \text{control treatment}\end{pmatrix}}{\text{N applied}} \times 100$

In lumn, the values for each depth at each location are significantly different (9 level of ity) when not followed by the same letter.

ammonium nitrate. The lowest mineral N recovery from fall-applied N which took place on the Demay L soil was probably because of the longer wet period which occurred in spring before sampling. This prolonged wet period might have resulted in more denitrification on this soil than the other soils.

Based on the average of mineral N recovery from these soils in the top 90 cm, apparently half of the fall-applied N disappeared from the mineral N pool by early spring, 1974 (Table 1). Mineral N losses from the top 90 cm were greater in plots which received calcium nitrate than in those which received urea or ammonium nitrate. Between 16% and 26% of the applied N was recovered in the 15-60 cm layer, and only small amounts of fertilizer N seemed to have moved below the 60 cm layer.

4.1.2 Yields and N uptake of barley grain

On the Demay L soil, yield and N uptake of barley grain were significantly greater with spring application than with fall application of calcium nitrate, ammonium nitrate, and urea (Table 2). Among the fall-applied N fertilizers, the lowest yield was obtained with calcium nitrate. Fall application of calcium nitrate produced only one-half the yield of barley grain (7.7 quintals/ha) as did spring application of the same fertilizer. The N uptake by barley grain from fall-applied calcium nitrate was only 5%, which was about one-fifth of the amount of N recovered in barley grain with spring-applied calcium nitrate. Similar trends of yield and N uptake of barley grain with fall and spring application of fertilizer N were

Table 2. Yield and N uptake of barley grain with fall and spring application of N fertilizers to four soils in Alberta in 1973-74.

Location†	Fertilizer*	Rate of application (kg N/ha)	Yield of barley grain (100 kg/ha)**		Apparent % of applied N in grain**	
			Fall	Spring	Fall	Spring
1	Control	0	6.2 a	6.5 a		
	Urea	56	8.7 b	16.1 a	8 b	29 a
	Ammonium nitrate	56	9.0 b	15.6 a	9 b	27 a
	Calcium nitrate	56	7.7 b	14.1 a	5 b	23 a
2	Control	0	14.3 a	13.9 a		
	Urea	56	20.9 b	27.4 a	21 b	45 a
	Ammonium nitrate	56	19.9 b	26.5 a	18 b	39 a
	Calcium nitrate	56	17.4 b	23.8 a	10 b	31 a
3	Control	0	4.6 a	4.8 a		
	Urea	56	12.5 a	15.1 a	23 b	32 a
	Ammonium nitrate	56	13.0 b	16.9 a	25 b	39 a
	Calcium nitrate	56	9.2 b	14.3 a	13 b	30 a
	Control	0	18.4 a	19.0 a		
	Urea	56	35.6 a	36.6 a	54 a	58 a
	Ammonium nitrate	56	31.9 b	38.5 a	46 b	66 a
	Calcium nitrate	56	31.6 b	38.1 a	42 b	65 a
Average	Control	0	10.8	11.0		
	Urea	56	19.4	23.8	26	41
	Ammonium nitrate	56	18.4	24.3	24	43
	Calcium nitrate	56	16.4	22.5	18	37

†Location 1 - Demay L at Calmar
Location 2 - Malmo SiCL at Ellerslie

Table 2. Continued.

Location 3 - Cooking Lake SL at Smoky Lake
Location 4 - Falun L at Warspite
*The fertilizers were mixed into the soil.

**The values for N uptake were calculated as = $\dfrac{\left(\begin{array}{l}\text{N uptake in}\\\text{fertilized treatment}\end{array}\right)-\left(\begin{array}{l}\text{N uptake in}\\\text{the control}\end{array}\right)}{\text{N applied}}$ X 100

In each row, the values separately for yield and N uptake of barley grain at each location are significantly different (95% level of probability) when not followed by the same letter.

observed on the Malmo SiCL soil (Table 2), but the yield and N uptake of barley grain from the fall- and spring-applied N fertilizers were higher on this soil than on the Demay L soil.

On the Cooking Lake SL soil, the yields of barley grain with fall and spring application of urea were not significantly different (Table 2), but the N uptake by barley grain with spring-applied urea was significantly greater than with fall application. The N uptake by barley grain with calcium nitrate applied in the fall was only 13%, which was less than one-half as much as with spring-applied calcium nitrate. On the Falur L soil, unlike the previous soils, both yield and N uptake of barley grain with urea applied in fall and in spring were not significantly different.

The average yield and N uptake of barley grain obtained with calcium nitrate, ammonium nitrate and urea applied at four locations during 1973-74 were lower with fall application than spring application of these fertilizers. Spring applications of urea, ammonium nitrate and calcium nitrate on the average gave 5.5 quintals/ha greater yield of barley grain than did fall applications. Among the fall-applied N fertilizers, the lowest N uptake by barley grain (18% of the N applied) was from calcium nitrate, which was less than one-half the N recovered in barley grain with spring application of the same fertilizer.

4.2 Over-Winter Losses of Fertilizer N Applied in Fall, 1974, in Field Experiments

The results of field experiments conducted in 1973-74 demonstrated that there were substantial over-winter losses of fall-applied N which reduced the yields and N uptake by barley grain grown in the following spring. During 1973-74, the time of losses was not determined. Therefore, to determine whether the fall-applied fertilizer N was nitrified during the winter, and to find approximately when over-winter losses occurred, field experiments were set out in October, 1974, at six locations in farm fields: Blue Sky (Albright CL), Calmar (Demay L), Canwood (Whitewood L), Egremont (Falun L), Bon Accord (Angus Ridge CL), and Ellerslie (Malmo SiCL). All the fields had previously been cropped to barley. The following commercial fertilizers were used: urea, ammonium sulphate, ammonium nitrate and calcium nitrate. The fertilizers were applied at a rate of 56 kg N/ha and were mixed into the top 10 cm soil with a rototiller. Each plot was 6.8 m by 1.8 m and was replicated four times in a split-plot design. Each treatment was further divided into two sub-treatments (i.e. fall and spring). Fall treatments received N fertilizers in October, 1974; and in spring treatments, the N fertilizers were applied in May just before seeding. All the plots were seeded to Galt barley (Hordeum vulgare) in the spring. Soil samples were taken throughout the winter to find the rate of nitrification of urea, and in May, 1975, to determine the apparent loss of fall-applied N over the winter. The yield and N uptake of barley grain were measured at the six locations to asses the relative efficiency of fall application compared to spring application of N fertilizers.

The dates on which the soils were permanently frozen for the winter (Table 3) were estimated from the soil temperature (at a depth of 10 or 15 cm) either from the measurements taken at the location, or from the records of the nearest meteorological station. The soils remained frozen until after the last soil sampling (except Delacour where soil periodically thawed and froze throughout the winter). Light temporary snowfalls occurred in November, and the dates of the first permanent snow cover are shown in Table 3.

4.2.1 Nitrification of fall-applied urea during the winter

The percent nitrification varied from location to location ranging from 76% to 14% by late winter (Table 4). The soil moisture tension varied with soil and with time, but after the second sampling on the Angus Ridge CL soil, the Cooking Lake SL soil, the Falun L soil, and the Demay L soil, the soil moisture tension was well below 1/3 bar and the Airdrie CL soil was above 15 bars (Table 3). In general, the percent nitrification increased with lower moisture tension. The amount of nitrification of urea, two weeks after application on the Angus Ridge CL soil, the Cooking Lake SL soil, the Falun L soil, the Demay L soil, the Malmo SiCL soil and the Airdrie CL soil varied from 14% to 31% on October 20 to 23. The amount nitrified increased further after October 20 to 23 to values of about 75% by late winter on the Angus Ridge CL soil, the Cooking Lake SL soil and the Falun L soil and to about 45% on the Demay L soil and the Malmo SiCL soil. The average soil temperature for the locations

Table 3. Moisture tension of soils used for experiments.

Location†	Estimated date of permanently frozen soil	Approximate date of permanent snow cover	Soil moisture tension (bars) at different dates					
			Date	Tension	Date	Tension	Date	Tension
1	Nov. 11	Dec. 22	Oct. 7	0.4	Oct. 27	<0.1	Feb. 28	<0.1
2	Nov. 12	Dec. 22	Oct. 7	0.1	Dec. 6	0.2	Feb. 27	0.3
3	Nov. 11	Dec. 22	Oct. 7	8.9	Oct. 27	0.1	Mar. 11	0.2
4	Nov. 8	Dec. 22	Oct. 6	7.9	Oct. 29	0.3	Mar. 8	0.2
5	Nov. 8	Dec. 22	Oct. 6	15.9	Oct. 29	8.9	Mar. 11	11.7
6	*	*	Oct. 8	>>15	Oct. 25	>>15	Feb. 26	>>15
7	Nov. 15	Dec. 17	Oct. 16	1.6	*	*	Mar. 15	0.9
8	Nov. 11	Nov. 18	Oct. 30	1.6	*	*	Mar. 1	0.5

†Location 1 - Angus Ridge CL at Bon Accord
Location 2 - Cooking Lake SL at Smoky Lake
Location 3 - Falun L at Egremont
Location 4 - Demay L at Calmar
Location 5 - Malmo SiCL at Ellerslie
Location 6 - Airdrie CL at Delacour
Location 7 - Whitewood L at Canwood (Sask.)
Location 8 - Albright CL at Blue Sky
*Not determined.

Table 4. The amount of nitrification of urea during winter, applied at a rate of 56 kg N/ha in October, 1974, in field experiments.

Location*	Date of application	Apparent % recovery of applied urea N as NO_3-N (in 0-15 cm depth) at different dates**			
1	Oct. 7	Oct. 21 31 c		Dec. 6 65 b	Feb. 28 76 a
2	Oct. 7	Oct. 21 28 c		Dec. 6 42 b	Feb. 27 73 a
3	Oct. 7	Oct. 21 18 d	Nov. 7 39 c	Dec. 6 60 b	Mar. 9 74 a
4	Oct. 6	Oct. 21 30 b		Dec. 10 38 b	Mar. 8 49 a
5	Oct. 6	Oct. 20 14 c		Dec. 4 31 b	Mar. 11 42 a
6	Oct. 8	Oct. 23 18 b		Dec. 10 24 ab	Mar. 8 27 a
7	Oct. 16			Dec. 27 10 a	Mar. 15 15 a
8	Oct. 30			Dec. 26 6 a	Mar. 1 14 a

*Location 1 - Angus Ridge CL at Bon Accord
Location 2 - Cooking Lake SL at Smoky Lake
Location 3 - Falun L at Egremont
Location 4 - Demay L at Calmar
Location 5 - Malmo SiCL at Ellerslie
Location 6 - Airdrie CL at Delacour
Location 7 - Whitewood L at Canwood (Sask.)
Location 8 - Albright CL at Blue Sky

**The values were calculated as = $\frac{\left(\text{NO}_3\text{-N recovered in fertilized treatment}\right) - \left(\text{NO}_3\text{-N recovered in the control}\right)}{\text{N applied}} \times 100$

In each row, the values are significantly different (95% level of probability) when not followed by the same letter.

was calculated at 3.7^{o}C during October 23 to 31, and 1.6^{o}C during November 1 to 8. On the Falun L soil from November 7, only four days before "freeze up" (Table 3), until December 6, the amount nitrified increased from 39% to 60%. The other soils such as the Angus Ridge CL soil, the Demay L soil, the Malmo SiCL soil and the Airdrie CL soil also showed nitrification at below 0^{o}C, but not to the same extent. On the Whitewood L soil and the Albright CL soil, the treatments were set out later (October 16 and October 30, respectively) and nitrification was only 15% and 14%, respectively by late winter (Table 4).

There was a question of whether these results are typical for only urea. At two of the locations, the plots were set out with $(NH_4)_2SO_4$ and results were similar to urea. On the Malmo SiCL soil, the percent nitrification in late winter was 42% and 45% for urea and $(NH_4)_2SO_4$, respectively. Corresponding values were 27% and 29% on the Airdrie CL soil.

The fall and winter of 1974-75 was normal. Discounting the Airdrie CL soil, average soil temperatures taken from the nearest meteorological stations were 6.0, -0.4, -3.1, -4.7, -5.3 and -3.4^{o}C for the months October to March in 1974-75, as compared to the previous 10-year averages of 4.9, -0.6, -4.5, -5.7, -4.9 and -3.8^{o}C, respectively.

4.2.2 Mineral N (NH_4-N + NO_3-N) content of soil in March, and in May, 1975

The results in Table 5 showed that there was almost complete recovery of fertilizer N as mineral N in the top 15 cm of soil in late winter when the ground was frozen. The apparent

Table 5. The mineral N(NH_4-N + NO_3-N) recovered with fall-applied N fertilizers† at a rate of 56 kg N/ha in 1974-75.

Fertilizer†	Apparent % recovery of applied N as mineral N(NH_4-N + NO_3-N) in 0-15 cm depth**											
	Albright CL		Demay L		Whitewood L		Falun L		Angus Ridge CL		Malmo SiCL	
	Mar.1	May18	Mar.3	May 5	Mar.5	May 7	Mar.9	May 4	Feb.28	May 1	Mar.11	May 3
Urea	99 a	65 b	90 a	37 b	93 a	61 b	97 a	60 b	92 a	52 b	94 a	72 b
Ammonium sulphate	*	*	*	*	*	*	*	*	91 a	53 b	93 a	81 a
Calcium nitrate	*	*	*	*	*	*	*	*	96 a	48 b	94 a	50 b

†Fertilizers were mixed into the soil

*Ammonium sulphate and calcium nitrate were not applied at these locations

$$\text{**The values were calculated as} = \frac{\begin{pmatrix}\text{Mineral N recovered in}\\ \text{fertilizer treatment}\end{pmatrix} - \begin{pmatrix}\text{Mineral N recovered}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100$$

The values at each location for each fertilizer are significantly different (95% level of probability) when not followed by the same letter.

recovery of fall-applied urea in early March or late February averaged 94% (range from 90% to 99%). In early spring it was only with the snow thaw and prolonged wetness of the soil that mineral N losses occurred (Table 5). There was much lower recovery of mineral N by early May in the top 15 cm of the soil (average recovery of urea was 57% with a range from 37% to 72%). Essentially the applied mineral N was not lost until at least early March, whether the fertilizers were [illegible] NH_4 or NO_3.

Apparently, only 44% and 68% of fall-applied urea N was recovered in the top 90 cm (as NH_4-N + NO_3-N) on the Demay L soil and the Falun L soil (Table 6), respectively. Approximately 8% of the fall-applied urea N was recovered in the 15-60 cm layer. The results of mineral N recovery in the 60-90 cm depth indicated no further downward movement of mineral N below 60 cm depth. Similar trends were shown on the Albright CL soil and the Whitewood L soil. Likewise on the Angus Ridge CL soil which received ammonium sulphate, ammonium nitrate and calcium nitrate in addition to urea, the mineral N recovery from different fertilizers in the top 90 cm averaged only 57% (range 55% to 60%). However, on the Malmo SiCL soil, apparently, more than 80% of the fall-applied urea or ammonium sulphate N was recovered in the top 90 cm in early May. The lowest recovery of mineral N (70%) was with calcium nitrate. Very little or no movement of mineral N below 60 cm was observed, regardless of the fertilizer applied.

In summary, soil sampling in May for the determination of

Table 6. The recovery of mineral N (NH_4-N + NO_3-N) in May, 1975, with N fertilizers applied in October, 1974, at a rate of 56 kg N/ha to six soils.

Location†	Fertilizer*	Apparent % recovery of applied N as NH_4-N + NO_3-N**			
		0-15 cm	0-30 cm	0-60 cm	0-90 cm
1	Urea	65	69	75	75
2	Urea	37	39	44	44
3	Urea	61	66	70	70
4	Urea	60	64	69	68
5	Urea	52 a	55 a	61 a	60 a
	Ammonium sulphate	50 a	53 b	57 ab	57 a
	Ammonium nitrate	40 b	49 b	54 b	55 a
	Calcium nitrate	35 c	48 b	54 b	56 a
6	Urea	72 a	81 a	84 a	83 a
	Ammonium sulphate	73 a	81 a	82 a	84 a
	Ammonium nitrate	52 b	65 b	74 b	75 b
	Calcium nitrate	18 c	50 c	68 b	70 b

†Location 1 - Albright CL at Blue Sky
Location 2 - Demay L at Calmar
Location 3 - Whitewood L at Canwood
Location 4 - Falun L at Egremont
Location 5 - Angus Ridge CL at Bon Accord
Location 6 - Malmo SiCL at Ellerslie

*Fertilizers were mixed into the soil.

**The values were calculated as

$$= \frac{\left(\text{Mineral N recovered in fertilized treatments}\right) - \left(\text{Mineral N recovered in the control}\right)}{\text{N applied}} \times 100.$$

In each column, the values for each depth at each of the locations No. 5 and 6 are significantly different (95% level of probability) when not followed by the same letter.

mineral N recovery in the 0-90 cm depth for plots which received fall-applied N fertilizers, indicated that substantial over-winter losses of mineral N occurred in the six field experiments. About 33% of the fall-applied urea mixed into the soil was lost from the mineral N pool by early May. In plots which received urea or ammonium sulphate, most of the recovered mineral N in May was present in the top 15 cm layer while in calcium nitrate plots, more than half of the recovered mineral N in May was present in the 15 to 60 cm layer..

4.2.3 Yields and N uptake of barley grain

Yields and N uptake of barley grain were significantly greater with spring application than with fall application for urea mixed into the soil at all the six locations (Table 7). Spring-applied urea on the Demay L soil gave 20.7 quintals/ha more yield of barley grain than the fall application. On the Angus Ridge CL soil spring-applied urea produced 21.8 quintals/ha greater yield of barley grain than fall-applied urea. On this soil the fertilizer N uptake by barley grain* was 86% with spring-applied urea N as compared to 20% with fall application. A similar trend was found on other soils. Ammonium sulphate, ammonium nitrate and calcium nitrate, which were applied only to the Angus Ridge CL soil and the Malmo SiCL soil showed a trend similar to urea.

Based on the average of six field experiments, spring

$$*\%\ \text{fertilizer N uptake} = \frac{\begin{pmatrix}\text{N in grain in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{N in grain}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100$$

Table 7. Yield and N uptake of barley grain with fall- and spring-applied N fertilizers to six soils in 1974-75.

Location†	Fertilizer*	Rate of application (kg N/ha)	Yield of barley grain (100 kg/ha)**		Apparent % of applied N in grain**	
			Fall	Spring	Fall	Spring
1	Control	0	13.3 a	13.0 a		
	Urea	56	29.2 b	36.5 a	47 b	79 a
2	Control	0	16.6 a	16.2 a		
	Urea	56	27.4 b	48.1 a	28 b	97 a
3	Control	0	6.9 a	7.3 a		
	Urea	56	16.9 b	25.2 a	28 b	51 a
4	Control	0	7.0 a	6.8 a		
	Urea	56	18.2 b	28.0 a	31 b	60 a
5	Control	0	8.2 a	8.5 a		
	Urea	56	15.6 b	37.4 a	20 b	86 a
	Ammonium sulphate	56	19.2 b	37.5 a	31 b	84 a
	Ammonium nitrate	56	19.2 b	36.5 a	30 b	81 a
	Calcium nitrate	56	15.0 b	32.6 a	19 b	73 a
6	Control	0	21.6 a	21.2 a		
	Urea	56	38.6 b	46.8 a	50 b	87 a
	Ammonium sulphate	56	44.0 b	49.4 a	72 b	96 a
	Ammonium nitrate	56	42.8 b	47.2 a	59 b	98 a
	Calcium nitrate	56	40.5 b	47.2 a	54 b	95 a

Table 7. Continued.

Location†	Fertilizer*	Rate of application (kg N/ha)	Yield of barley grain (100 kg/ha)**		Apparent % of applied N in grain**	
			Fall	Spring	Fall	Spring
Average	Control	0	12.3	12.2		
	Urea		24.2	37.0	34	77

†Location 1 - Albright CL at Blue Sky
Location 2 - Demay L at Calmar
Location 3 - Whitewood L at Canwood
Location 4 - Falun L at Egremont
Location 5 - Angus Ridge CL at Bon Accord
Location 6 - Malmo SiCL at Ellerslie

*Fertilizers were mixed into the soil.

**The values for N were calculated as

$$= \frac{\left(\begin{array}{l}\text{N uptake in}\\ \text{Fertilized treatment}\end{array}\right) - \left(\begin{array}{l}\text{N uptake in}\\ \text{the control}\end{array}\right)}{\text{N applied}} \text{ X } 100$$

In each row, the values separately for yield and N in grain are significantly different (95% level of probability) when not followed by the same letter.

application of urea produced about 13 quintals [illegible] more barley grain than did fall application. The N uptake with spring-applied urea was 2.3 times greater than with fall applied urea.

4.3 Effect of Date of Application in October on the Relative Efficiency of Fall vs Spring Application of N

The nitrification of NH_4 added to soil is closely related to soil temperature which is higher during early fall than late fall. Therefore, one would expect more over-winter losses of mineral N, and subsequently lower yields of crops, with ammonium-based fertilizers applied in early fall than when applied in the late fall. To find the effect of date of application in October, of urea and calcium nitrate, on the relative efficiency of fall vs spring application in increasing the N uptake by barley grain, the relative efficiencies* were plotted against the dates of application in October (Fig. 1,2). The results of N uptake by barley grain were taken from field tests conducted for four years (1971-72, 1973-74, 1974-75 and 1975-76). For urea 19 field experiments and for calcium nitrate 11 field experiments including 2 field experiments reported by Leitch (1973) were used. The description for each abbreviation in Fig. 1 and 2 is shown in Appendix A Table 1.

The efficiency of fall-applied fertilizer N, relative to the efficiency of spring-applied fertilizer N, increased from 41% with urea N applied during the first week of October to 82% with urea N applied on October 31, as calculated from the regression equation shwon in Fig. 1. There was a close correlation (r = 0.73**) between the dates of application of urea in the fall and the relative efficiency of fall vs spring application. However, with calcium nitrate, the date of appli-

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$$\text{*Relative efficiency} = \frac{\begin{pmatrix}\text{N uptake with}\\ \text{fall-applied N}\end{pmatrix} - \begin{pmatrix}\text{N uptake}\\ \text{of control}\end{pmatrix}}{\begin{pmatrix}\text{N uptake with}\\ \text{spring-applied N}\end{pmatrix} - \begin{pmatrix}\text{N uptake}\\ \text{of control}\end{pmatrix}} \times 100$$

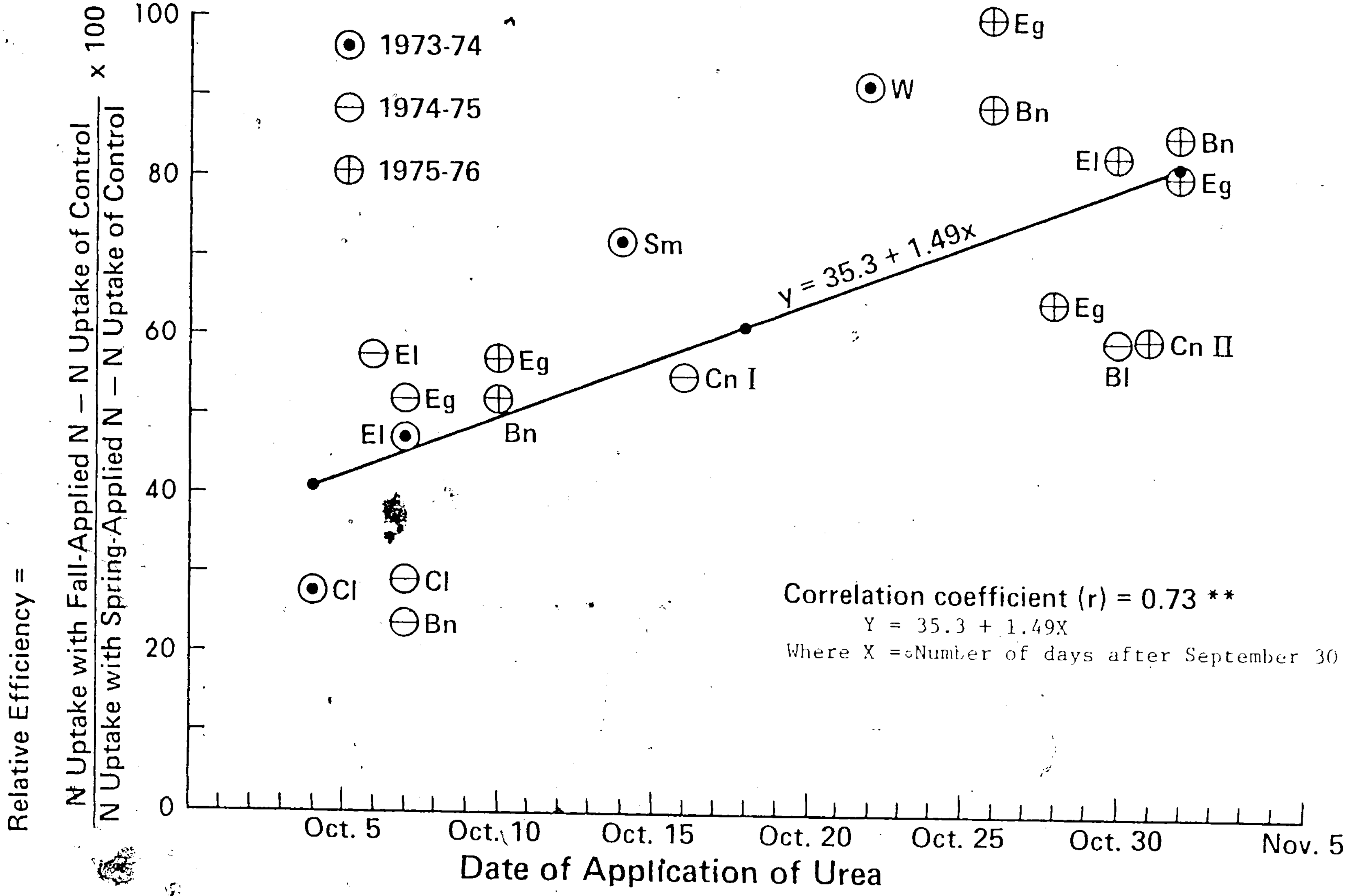

Figure 1. Effect of date of application on the relative efficiency of fall vs spring application of urea at a rate of 56 kg N/ha in increasing the N uptake of barley grain.

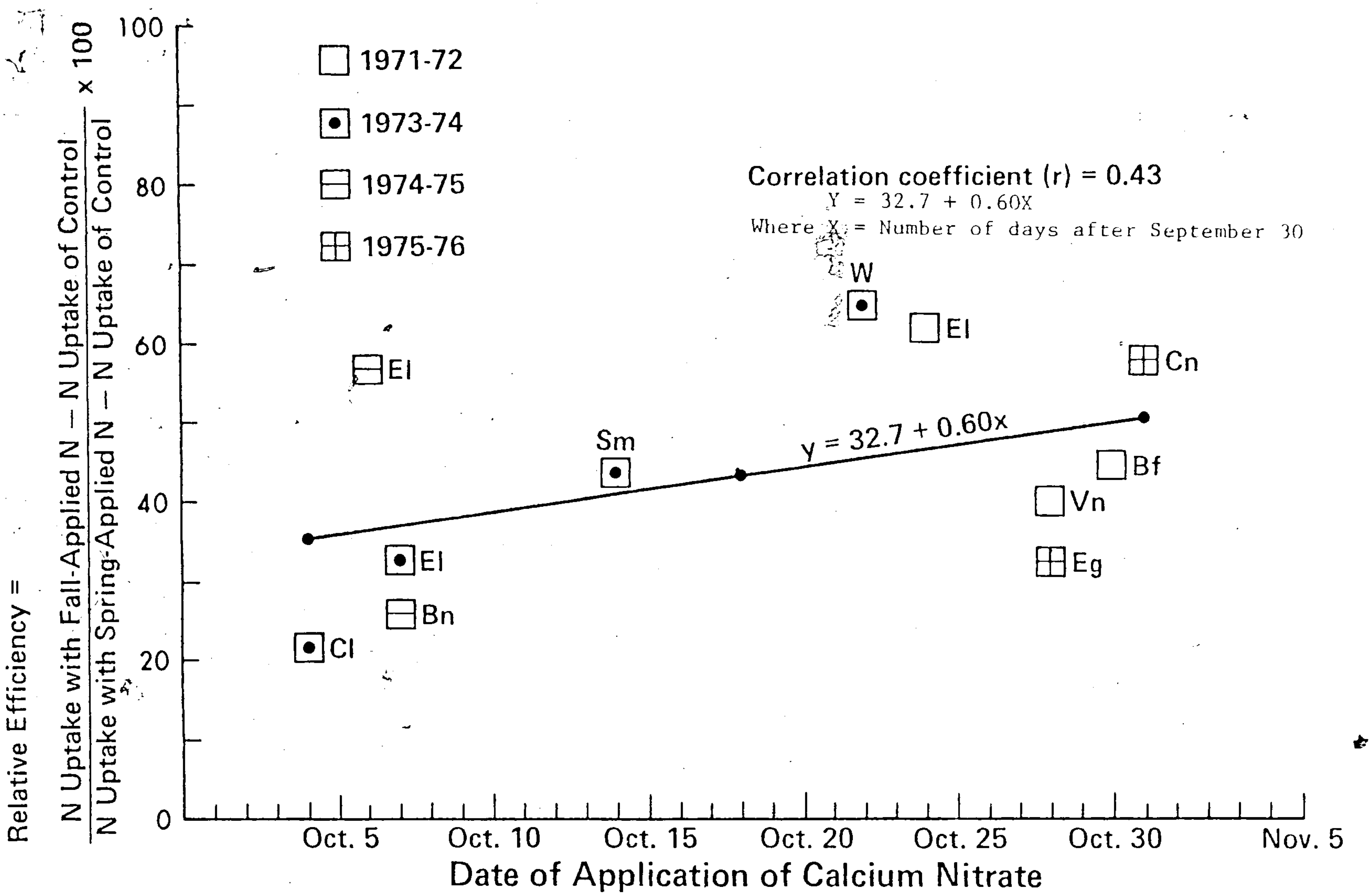

Figure 2. Effect of date of application on the relative efficiency of fall vs spring application of calcium nitrate at a rate of 56 kg N/ha in increasing the N uptake of barley grain.

cation in the fall (from October 4 to October 31) had almost no effect on the efficiency of fall relative to spring application (Fig. 2). The relative efficiency of fall vs spring application of calcium nitrate ranged only from 35% in the first week of October to 51% in the end of October. The correlation coefficient (r) between the dates of application of calcium nitrate and the relative efficiencies was only 0.43. This r value (0.43) was not significant at 5% level of confidence.

4.4 Losses of Soil Mineral Nitrogen (NH_4-N + NO_3-N) from Non-Fallowed and Fallowed Soils Over the Winter

Considerable losses of N from the soils of the Prairie Provinces have occurred since they have been brought under cultivation (Shutt, 1925; Newton et al., 1945; Doughty et al., 1954), and losses are much larger than can be explained by crop removal (Campbell et al., 1976; Rennie et al., 1976). For example, Rennie et al. (1976) reported that only 35% of the N mineralized from Saskatchewan soils was removed by crops. Leaching, volatilization, denitrification and erosion have been suggested as the mechanisms responsible for these losses of soil N. Until recently it was not known that soils in Alberta might mineralize substantial amounts of N from fall to late winter, and that as the soils thawed, considerable amounts of mineral N might be lost; and these observations which came from the results presented in this section, might have a role in explaining the N losses from the soils of the Prairie Provinces.

The results of the field experiments conducted during 1973-74 and 1974-75 with fertilizers, showed that over-winter losses of mineral N occurred from fall-applied fertilizer N. One might assume that soil mineral N would behave the same way as fertilizer N. The present study was carried out to obtain quantitative information about over-winter soil mineral N changes in non-fallowed and fallowed soils.

The soils used in 10 field experiments in this investigation were sampled in fall through winter to early spring. The soil samples, in October and in May, were taken with a sampling corer (2.0 cm diameter), and for winter sampling, a hard steel corer (3.6 cm diameter) was used in frozen soils. Soil samples were analyzed for NH_4-N and NO_3-N.

Table 8 displays the results of soil mineral N content (0-15 cm depth) in soil samples taken from October, 1974, through winter to May, 1975, of seven field experiments. All these fields were non-fallowed and low in mineral N content. The average mineral N in soil samples taken in October was 7 kg N/ha and by early December, it increased to an average of 17 kg N/ha. By early March, the soil mineral N content increased further to 24 kg N/ha. On the Falun L soil, the mineral N content increased from 5 kg N to 20 kg N/ha from November 7, only four days before the soil was frozen until December 6. The soil temperature at 7.5 cm depth ranged from 3.3 to $-1.7^{o}C$ during this period. Similarly, on the Demay L soil, the mineral N content in frozen soil increased from 26 kg N/ha in early December, to 41 kg N/ha in early March, 1975. The last sampling, in early May, gave surprising results. One would expect mineralization of organic N to occur at an accelerated rate during late April or early May, however, all the locations showed a net loss of mineral N in the top 15 cm soil. On the average of the seven locations, the soil mineral N decreased from 24 kg N/ha in early March, 1975, to 13 kg N/ha in early May, 1975.

By early March, there was a significant build up of NH_4-N in all the seven soils. On the average, the NH_4-N content increased from 3 kg N/ha in late fall, 1974, to 10 kg N/ha in early March, or late February, 1975 (Table 9). During this period, the NO_3 content on the average, increased by 10 kg N/ha.

Table 8. The content of mineral N(NH_4-N + NO_3-N) in non-fallowed soils (0-15 cm) in October, 1974, in late February or early March, 1975, and in early May, 1975.

Location†	The soil content of mineral N (kg N/ha)* Oct. 1974	Dec. 1974	Mar. 1975	May 1975
1	6 c	11 b	23 a	10 b
2	8 d	16 b	20 a	12 c
3	4 d	26 b	41 a	17 c
4	6 c	12 b	15 a	7 c
5	4 c	8 b	15 a	8 b
6	5 c	20 a	23 a	15 b
7	17 c	28 b	33 a	19 c
Average	7	17	24	13

†Location 1 - Albright CL at Blue Sky
Location 2 - Angus Ridge CL at Bon Accord
Location 3 - Demay L at Calmar
Location 4 - Whitewood L at Canwood
Location 5 - Airdrie CL at Delacour
Location 6 - Falun L at Egremont
Location 7 - Cooking Lake SL at Smoky Lake

*In each row, the N values are significantly different (95% level of probability) when not followed by the same letter.

The soils were sampled to a depth of 60 cm only in October, 1974, and in early May, 1975. The mineral N content in the top 60 cm, on the average of seven locations, increased from 12 kg N/ha in October, 1974, to 27 kg N/ha in early May, 1975 (Table 10). Since samples were not taken in late winter just prior to thawing, one is left to wonder about the mineral N content in the soil profile (0-60 cm) in early March.

To confirm the results of over-winter soil mineral N changes in non-fallowed soils obtained in 1974-75, three plots were set out in the fall of 1975, in farm fields. Table 11 shows the mineral N

Table 9. The NH_4-N and NO_3-N content of seven non-fallowed soils in the 0-15 cm depth in fall, 1974, and in late February or early March, 1975.

Location†	Date	NH_4-N* (kg/ha)	Date	NH_4-N* (kg/ha)	Date	NO_3-N* (kg/ha)	Date	NO_3-N* (kg/ha)
1	Oct. 8	3 b	Mar. 1	9 a	Oct. 8	3 b	Mar. 1	14 a
2	Oct. 4	3 b	Feb. 28	7 a	Oct. 4	5 b	Feb. 28	13 a
3	Oct. 1	2 b	Mar. 8	19 a	Oct. 1	2 b	Mar. 8	22 a
4	Oct. 16	2 b	Mar. 16	7 a	Oct. 16	4 b	Mar. 16	8 a
5	Oct. 8	2 b	Feb. 26	8 a	Oct. 8	2 b	Feb. 26	7 a
6	Oct. 3	3 b	Mar. 9	11 a	Oct. 3	2 b	Mar. 9	12 a
7	Oct. 2	5 b	Feb. 27	10 a	Oct. 2	12 b	Feb. 27	23 a
Average		3		10		4		14

†Location 1 - Albright CL at Blue Sky
Location 2 - Angus Ridge CL at Bon Accord
Location 3 - Demay L at Calmar
Location 4 - Whitewood L at Canwood
Location 5 - Airdrie CL at Delacour
Location 6 - Falun L at Egremont
Location 7 - Cooking Lake SL at Smoky Lake

*In each row, the values separately for NH_4-N and NO_3-N contents are significantly different (95% level of probability) when not followed by the same letter.

Table 10. The mineral N (NH_4-N + NO_3-N) content of stubble soils in fall, 1974, and in early spring, 1975, sampled to a depth of 60 cm.

Location†	Mineral N content (kg N/ha)* in the 0-60 cm depth	
	Oct. 1974	May, 1975
1	10 b	17 a
2	12 b	22 a
3	10 b	34 a
4	9 b	19 a
5	7 b	22 a
6	11 b	30 a
7	27 b	43 a
Average	12	27

†Location 1 - Albright CL at Blue Sky
Location 2 - Angus Ridge CL at Bon Accord
Location 3 - Demay L at Calmar
Location 4 - Whitewood L at Canwood
Location 5 - Airdrie CL at Delacour
Location 6 - Falun L at Egremont
Location 7 - Cooking Lake SL at Smoky Lake

*In each row, the N values are significantly different (95% level of probability) when not followed by the same letter.

contents of soil samples taken from the 0-15 cm depth, four times from October, 1975, to May, 1976. The soil was frozen by the end of the third week of November and remained so until the end of the first week of April. In the Angus Ridge CL soil, the mineral N content increased from 19 kg N/ha on November 15, 1975, to 40 kg N/ha on March 20, 1976, and by April 6, the mineral N content reached to 72 kg N/ha. It is noteworthy that between the sampling dates, from November 15, 1975, to April 6, 1976, the soil was frozen for most of the time, and yet 53 kg

Table 11. The changes in mineral N(NH_4-N + NO_3-N) content of non-fallowed soils from November, 1975 to May, 1976, sampled to a depth 15 cm.

Location†	The mineral N content (kg N/ha)* in 0-15 cm depth at different dates during 1975-76			
1	Nov. 2 17 d	Mar. 24 37 a	Apr. 16 22 c	May 11 31 b
2	Nov. 15 19 c	Mar. 16 40 b	Apr. 6 72 a	May 1 40 b
3	Nov. 16 17 d	Mar. 6 36 c	Apr. 6 50 a	May 9 44 b

†Location 1 - Demay L at Calmar
Location 2 - Angus Ridge CL at Bon Accord
Location 3 - Falun L at F[illegible]mont
*In each row, the N values [illegible] significantly different (95% level of probability) when [illegible] followed by the same letter.

of N/ha was mineralized. On the other hand, from April 6, to May 1, the mineral N content decreased by 32 kg N/ha. By contrast, on the Falun L soil, the mineral N content increased by 33 kg N/ha from November 16, 1975, to April 6, 1976, but in this soil, apparently, the loss of soil mineral N in the 0-15 cm depth, from early April to early May, was only 6 kg N/ha. In this soil, either there was little loss of mineral N or the mineralization prior to soil sampling might have occurred cancelling any loss.

On the Demay L soil, there was an increase in mineral N content from 17 kg N/ha in early November, 1975, to 37 kg N/ha by late March, 1976 (Table 11), but the mineral N content decreased by 15 kg N/ha on A 16, 1976, sampling. It was observed that the soil remained satura for about a week just before April sampling. By May, the soil mineral N

Table 12. The changes in NH_4-N and NO_3-N contents in the 0-15 cm depth of three non-fallowed soils sampled in November, 1975, and in late March or early April, 1976.

Location†	Date	NH_4-N* (kg/ha)	Date	NH_4-N* (kg/ha)	Date	NO_3-N* (kg/ha)	Date	NO_3-N* (kg/ha)
1	Nov. 2	14 b	Mar. 24	23 a	Nov. 2	3 b	Mar. 24	14 a
2	Nov. 15	8 b	Apr. 6	41 a	Nov. 15	11 b	Apr. 6	31 a
3	Nov. 16	6 b	Apr. 6	28 a	Nov. 16	11 b	Apr. 6	22 a
Average		9		31		8		22

†Location 1 - Demay L at Calmar
Location 2 - Angus Ridge CL at Bon Accord
Location 3 - *Falun L at Egremont*

*In each row, the N values separately for NH_4-N and NO_3-N content are significantly different (95% level of probability) when not followed by the same letter.

content increased to 32 kg N/ha.

At ll the locations, there was a build-up of [illegible] by late March or early April (Table 12). On the average of three l[illegible]ns, the NH_4-N content in the top 15 cm layer increased from 9 kg N/ha in November, 1975, to 31 kg NH_4-N/ha by late March or early April. During this period, the NO_3-N content on the average increased by 14 kg N/ha (Table 12).

To find the amount of loss of soil mineral N in fallowed soils, two field plots, one at Canwood (Whitewood L) in Saskatchewan and the other at Ellerslie (Malmo SiCL) in Alberta, were set out in late October, 1975. The data on the dates of permanent freeze up and permanent snow cover, and soil temperature are shown in Table 15. The soils were sampled to a depth of 60 cm in late October, 1975, and in early May, 1976. The soil samples were analyzed for NH_4-N and NO_3-N.

The average amount of mineral N in the 0-60 cm depth in the fall in the two soils was 127 kg N/ha (Table 13), but in early May, the mineral N content had decreased to 83 kg N/ha. Therefore, apparently, the average over-winter loss of [illegible]ral N was 44 kg/ha. It would be expected that the mineral N would have increased considerably from October to just before thawing in these soils. Considering that mineralization likely occurred during the winter, the actual losses of mineral N might have been even larger than the observed losses.

Table 14 displays the mineral N content of a fallowed soil at Ellerslie (Malmo SiCL), sampled four times from November 8, 1976, to April 18, 1977, to a depth of 120 cm. The mineral N content in the soil sampled to a depth of 120 cm, increased from 174 kg N/ha in early November, 1976, to 239 kg N/ha in early March, 1977, when the soil was near-frozen or frozen during this period (Table 15), and by mid-April approximately 90 kg N/ha disappeared from the soil. There was a small increase in the content of NH_4-N in the top 30 cm layer from late fall, 1976, to early March, 1977, but by mid-April the NH_4-N content decreased by 23 kg N/ha. There was a considerable increase in the NO_3-N in the top 30 cm from early November, 1976, to early March, 1977, and almost half of NO_3-N present in early March sampling was lost by mid-April. The mineral N content from early November, 1976, to mid-April, 1977, increased considerably (59 kg N/ha) in the 0-30 cm layer, but the 30-60 cm layer showed little increase (6 kg N/ha) and the mineral N content at depths below 60 cm remained essentially constant. In mid-April, when the soil was very wet for many days, one would expect leaching losses of mineral N to the lower [illegible] but results here show [illegible] apparent downward movement of mineral N to the lower depths.

The results given, so far, clearly point out that mineral N, whether derived from fertilizer or from the soil, can be lost over the winter, particularly around the time of the thaw. The results reported in this section indicate that soil N was mineralized from fall until just before the time of spring thaw. When over-winter changes in soil mineral N are evaluated by making measurement in the fall and another one in the spring, the result is a net effect of these mineralization and loss processes. It is therefore quite possible that a relatively large accumulation of mineralized N is partly, if not wholly, hidden by

Table 13 The content of mineral N(NH_4-N + NO_3-N) of two fallowed soils in late fall, 1975, and spring, 1976.

		Soil content of NH_4-N and NO_3-N (kg N/ha)					
		*Late fall,1975			*Spring,1976		
Location†	Depth (cm)	NH_4-N	NO_3-N	(NH_4-N + NO_3-N)**	NH_4-N	NO_3-N	(NH_4-N + NO_3-N)**
1	0-15	15	68	83	5	43	48
	15-30	13	17	30	4	21	25
	30-60	5	16	21	5	11	16
	0-60	33	101	134 a	14	75	89 b
2	0-15	20	65	85	4	53	57
	15-30	10	9	19	3	9	12
	30-60	6	9	15	4	4	8
	0-60	36	83	119 a	11	66	77 b

†Location 1 - Whitewood L at Canwood
Location 2 - Malmo SiCL at Ellerslie

*Soil sample were taken on October 29 at Canwood and on November 2 at Ellerslie in late fall, 1975 and the soil samples in early spring, 1976 were taken on May 14 at Canwood and on May 9 at Ellerslie.

**In 0-60 cm depth; the values for NH_4-N + NO_3-N are significantly different (95% level of probability) when not followed by the same letter.

a subsequent loss during the thaw period. Such "hidden losses" can be detected by sampling just before and soon after the thaw period. Probably many studies of over-winter mineral N changes have overlooked this possibility.

Table 14. Soil content of mineral N (NH_4-N + NO_3-N) over the winter in a fallowed field at Ellerslie (Malmo SiCL) in 1976-77.

Depth (cm)	NH_4-N (kg/ha)*				NO_3-N (kg/ha)*				Mineral N (kg/ha)*			
	Nov.8	Jan.8	Mar.4	Apr.18	Nov.8	Jan.8	Mar.4	Apr.18	Nov.8	Jan.8	Mar.4	Apr.18
0-15	17	19	25	8	52	67	84	42	69	86	109	50
15-30	11	10	13	7	12	18	29	16	23	28	42	23
30-60	23	21	24	20	9	12	13	10	32	33	37	30
60-90	22	23	24	21	6	5	4	5	28	28	28	26
90-120	19	18	20	21	3	3	3	3	22	21	23	24
0-30	28 b	29 b	38 a	15 c	64 c	85 b	113 a	58 c	92 c	114 b	151 a	73 d
0-120	92 b	91 b	106 a	77 c	82 c	105 b	133 a	76 c	174 c	196 b	239 a	153 d

*In each of the rows for 0-30 cm and 0-120 cm depth, the values separately for NH_4-N, NO_3-N and mineral N contents are significantly different (95% level of probability) when not followed by the same letter.

Table 15. Soil temperature data during 1975-76 and 1976-77.

Location and year in brackets	Approximate date of permanent frozen soil	Approximate date of permanent snow cover	Approximate date of thawing	Monthly average soil temperature (°C) at a depth of 10 cm from Oct,1975 to April,1976						
				Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.
Canwood (1975-76)	Nov. 18	Nov. 26	Apr. 1	5.6	-1.3	[illegible]	-6.6	-3.9	-4.2	6.5
Ellerslie (1975-76)	Nov. 12	Nov. 22	Apr. 4	5.7	-0.3	-3.4	-3.4	-3.6	-2.9	3.3
Ellerslie (1976-77)	Nov. 11	Dec. 5	Apr. 7	5.6	0.1	-1.9	-0.9	-1.6	-0.7	2.6

4.5 Incubation Studies on Nitrification

Nitrate N content of soil samples taken in plots which received N fertilizers in fall showed that urea was nitrified throughout the winter and more than half of the fall-applied urea N was found as NO_3-N by March on the average for 8 locations. Since the NO_3 is subject to losses by leaching and denitrification, there was a need to obtain information about nitrification over a range of different temperatures and moisture levels encountered in the field. Three incubation experiments were conducted, each with three different soils (Malmo SiCL, Falun L, and Cooking Lake SL). The details of the experiments are in Table 16.

4.5.1 Effect of different temperatures on the rates of nitrification of added $(NH_4)_2SO_4$

The maximum nitrification rate occurred at 20°C (Table 17). Beyond 20°C, the rate dropped off rapidly and was 10 to 15% of the maximum rate at 30°C. No NO_3 was produced at 40°C. The rate [illegible]itrification increased rapidly from 4° to 10°C with the greatest temperature response occurring between 10° and 20°C (Fig. 3). Nitrification was measurable at 4°C but the rate of nitrification at -4°C was not significantly greater than 0.

4.5.2 The rates of nitrification of added $(NH_4)_2SO_4$ at four moisture levels

There was an increase in the relative rate of nitrification with increased soil moisture from 15 bar to 1/3 bar soil moisture tension, with the greatest response occurring between 7 bar and 1/3 bar soil moisture tension (Fig. 4). Nitrification ceased at 0 bar soil

Table 16. Experimental design of incubation experiments on the rates of nitrification of added $(NH_4)_2SO_4$.

Experiment*	Purpose	Rate of NH_4-N addition (µg/g)	Temperature (°C)	Soil moisture tension (bars)
1	Effect of different temperatures on nitrification.	0 100	-4 4 10 20 30 40	1/3
2	Rate of nitrification at different moisture levels.	0 100	20	0 1/3 7 15
3	Influence of NH_4-N concentration on nitrification.	0 50 100 200 300	20	1/3

*In all the experiments, each treatment was duplicated.

Table 17. The rates of nitrification of $(NH_4)_2\ SO_4$ applied at [illegible] of 100 μg N/g to three soils in an incubation experiment at six different temperatures and 1/3 bar soil moisture tension.

Temperature (°C)	Rate of nitrification (μg N/g/day)**		
	*Soil I	*Soil II	*Soil III
-4	0.02 e	0.02 e	0.02 e
4	0.15 d	0.14 d	0.14 d
10	0.85 b	0.82 b	0.81 b
20	3.72 a	3.20 a	3.02 a
30	0.44 c	0.49 c	0.34 c
40	0.00 e	0.00 e	0.00 e

*Soil I - Cooking Lake SL from Smoky Lake
Soil II - Falun L from Egremont
Soil III - Malmo SiCL from Ellerslie
**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

moisture tension in all of the three soils (Table 18). The rate of nitrification at 1/3 bar moisture tension was about 2.8 times greater than at 15 bar, and about 1.7 times greater than at 7 bar moisture tension. These data indicated that an appreciable amount of nitrification could be expected at permanent wilting point.

4.5.3 Effect of NH_4-N concentrations on the rates of nitrification

The nitrification rate increased with increasing NH_4-N concentration from 50 μg/g to 200 μg/g, but decreased with further increase in NH_4-N concentration (Table 19). The rate of nitrification at a concentration of 200 μg NH_4-N/g was about 2.5 times greater than at 50

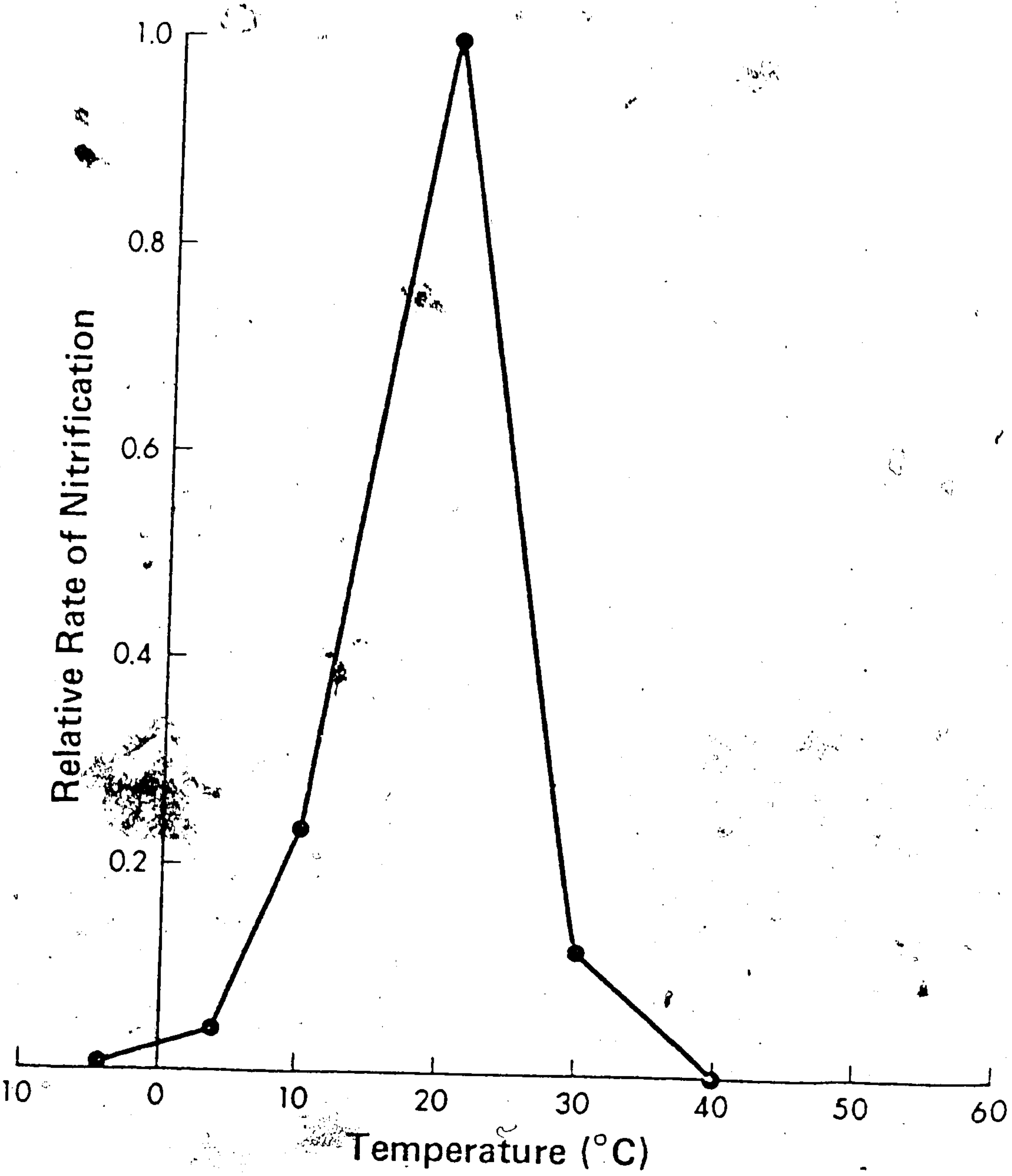

Figure 3. Influence of various temperatures on the rates of nitrification of $(NH_4)_2SO_4$ added at a rate of 100 μg N/g to a Cooking Lake SL soil incubated at 1/3 bar soil moisture tension.

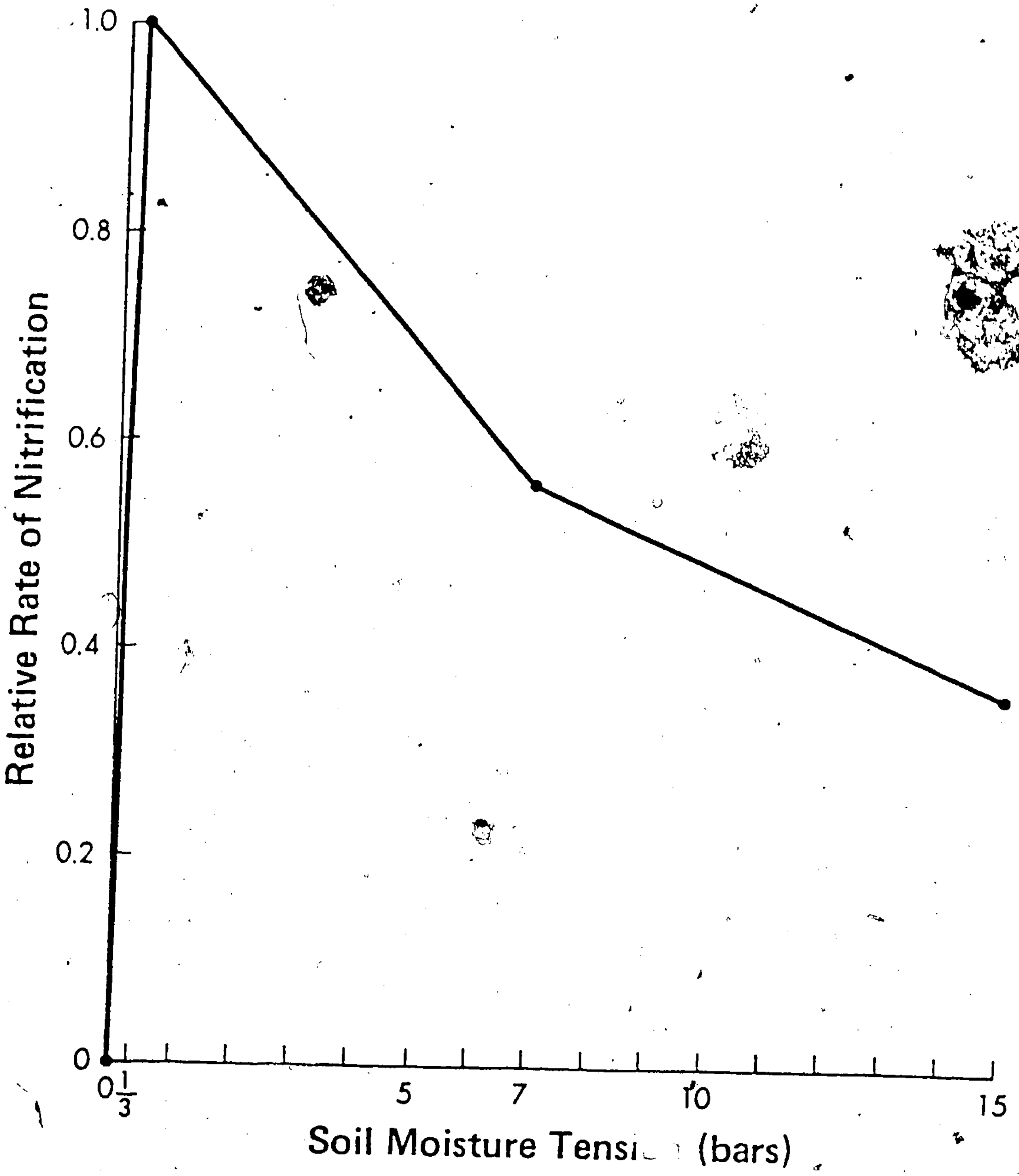

Figure 4.1 Effect of different soil moisture levels on the rates of nitrification of $(NH_4)_2SO_4$ added at a rate of 100 μg N/g to a Cooking Lake SL soil in an incubation experiment at 20°C.

Table 18. The rates of nitrification of 100 µg NH_4-N/g added to three soils incubated at four soil moisture tensions and 20°C.

Soil moisture tension (bars)	Rate of nitrification (µg N/g/day)**		
	*Soil I	*Soil II	*Soil III
0	0.0 d	0.0 d	0.0 d
1/3	3.6 a	3.4 a	3.2 a
7	2.0 b	2.1 b	2.0 b
15	1.3 c	1.3 c	1.2 c

*Soil I - Cooking Lake SL from Smoky Lake
Soil II - Falun L from Egremont
Soil III - Malmo SiCL from Ellerslie
**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

µg NH_4-N/g. In general, the rate of nitrification was higher in the Cooking Lake SL soil, although the differences among soils were small. The rates of nitrification could be represented by Michaelis-Menten kinetics (Fig. 5). Vmax varied from 9.1 to 9.9 µg/g soil/day and Km varied between 154 and 186 µg N/g soil (Table 20). Among the three soils the Cooking Lake SL had the highest value of Vmax and the lowest value of Km.

Table 19. The rates of nitrate formation in three soils incubated with different concentrations of NH_4-N at 20°C and 1/3 bar soil moisture tension.

Concentration of NH_4-N (μg/g)	Rate of NO_3-N formation (μg/g/day)**		
	*Soil I	*Soil II	*Soil III
50	2.5 d	2.0 d	1.9 d
100	3.8 c	3.3 c	3.4 c
200	5.9 a	5.1 a	4.9 a
300	4.5 b	4.1 b	4.1 b

*Soil I - Cooking Lake SL from Smoky Lake
Soil II - Falun L from Egremont
Soil III - Malmo SiCL from Ellerslie
**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

Table 20. The values of Vmax and Km for nitrification in three Alberta soils.

Soil type	Vmax (μg/g/day)	Km (μg/g)
Cooking Lake SL	[illegible]	15[illegible]
Falun L	9.1	175
Malmo SiCL	9.0	186

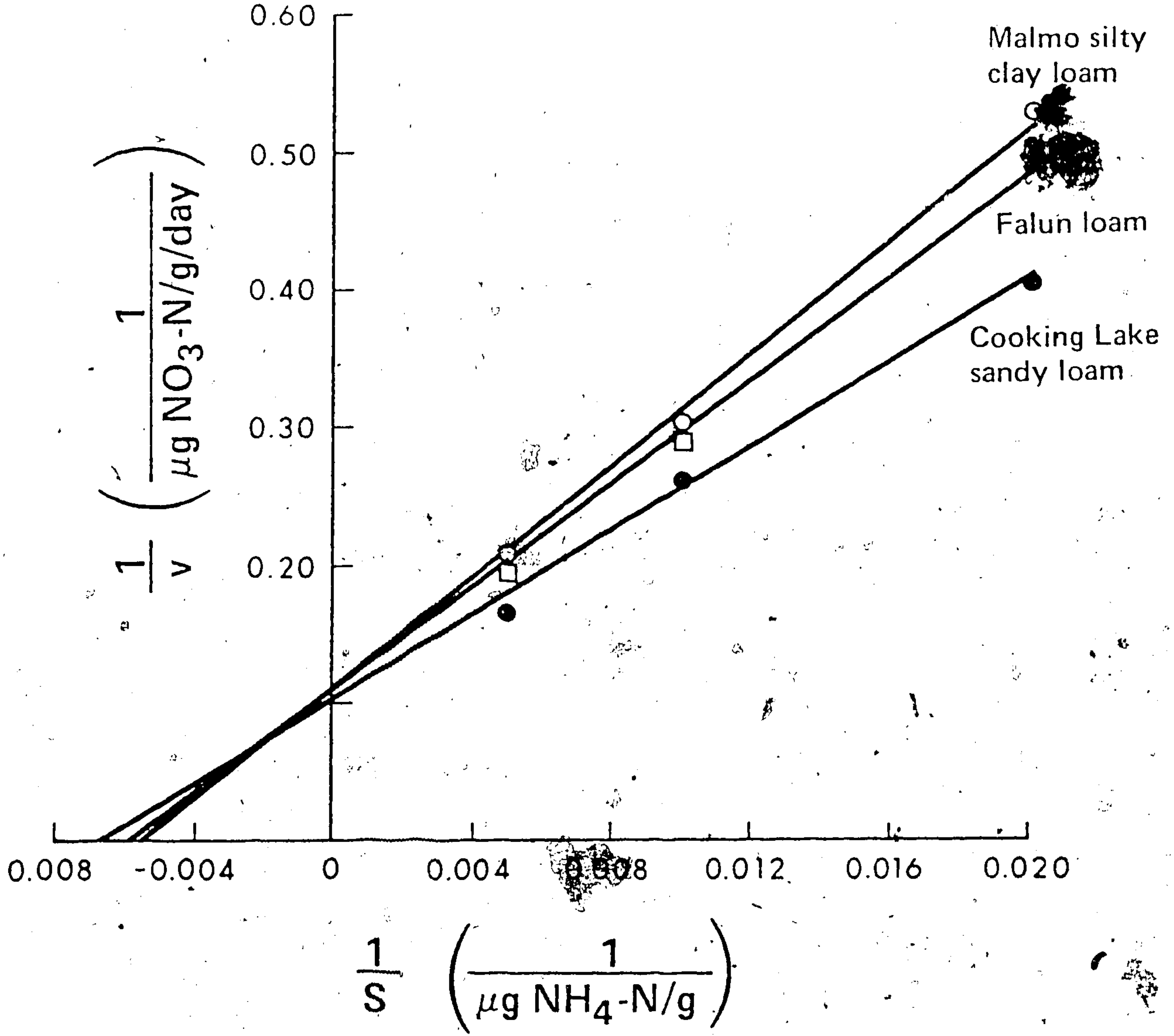

Figure 5. Lineweaver-Burke plot of nitrification rates in three Alberta soils at 1/3 bar moisture tension and 20°C.

4.6 Incubation Studies on NO_3-N Losses

The nitrate produced during winter, or applied in fall, may be subject to losses in early spring. Therefore, three incubation experiments with three soils (Malmo SiCL, Falun L, and Cooking Lake SL) were conducted to obtain detailed information regarding the effect of different levels of temperatures and moistures on NO_3 losses. The description for these experiments is given in Table 21.

4.6.1 Influence of various temperatures on NO_3-N losses at 0 bar soil moisture tension

The rate of loss of NO_3-N increased with temperature between 4° and $40^\circ C$ (Table 22). Raising the temperature to $60^\circ C$, decreased the rate of NO_3-N loss. Loss of NO_3-N was observed at temperature below freezing ($-4^\circ C$). The rate of NO_3-N loss at $40^\circ C$ was 3.5 times greater than at $10^\circ C$ and 13.5 times greater than at $4^\circ C$. The greatest response of NO_3-N losses to temperature was between 4° and $10^\circ C$ (Fig. 6).

4.6.2 The rate of loss of NO_3-N at different moisture levels

Although the highest rate of NO_3-N loss was under flooded conditions, a detectable loss at 15 bar moisture tension occurred (Table 23). At higher moisture levels, the rate of loss was greater in the Malmo SiCL than other two soils. The rate of NO_3-N loss at 0 bar was 16 times greater than at 7 bar and about six times than at 1/3 bar moisture tension. The response of NO_3-N loss to the soil moisture level was the highest when soil moisture tension decreased from 1/3 bar to 0 bar (Fig. 7).

Table 21. Experimental design for incubation experiments on NO_3-N losses.

Experiment**	Purpose	Rate of NO_3-N addition (μg/g)	Temperature (°C)	Soil moisture tension (bars)
1	Rate of NO_3-N loss at different temperatures.	0 400	-4 4 10 20 40 60	0
2	Influence of moisture levels on NO_3-N loss.	0 400	20	Flooded* 0 1/3 7 15
3	Effect of NO_3-N concentration on the rates of NO_3-N loss.	0 50 75 125 250 500	20	0

*Flooded means about 1 cm of water above soil surface.

**In all the experiments, each treatment was duplicated.

Table 22. The rates of NO_3-N losses in three soils incubated at six temperatures with 400 µg NO_3-N at 0 bar soil moisture tension.

Temperature (°C)	Rate of NO_3-N loss (µg/g/day)**		
	*Soil I	*Soil II	*Soil III
-4	2.1 f	2.2 f	2.5 f
4	4.8 e	4.7 e	5.0 e
10	14.2 d	20.2 d	22.8 d
20	27.4 c	29.4 c	31.6 c
40	60.1 a	65.5 a	71.2 a
60	59.1 b	63.2 b	65.3 b

*Soil I - Cooking Lake SL from Smoky Lake
Soil II - Falun L from Egremont
Soil III - Malmo SiCL from Ellerslie
**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

Table 23. The rates of loss of NO_3-N added to three soils incubated at five different moisture levels and 20°C with 400 µg NO_3-N/g of soil.

Soil moisture tension (bars)	Rate of loss of NO_3-N (µg/g/day)**		
	*Soil I	*Soil II	*Soil III
Flooded†	49.9 a	45.4 a	51.6 a
0	30.2 b	32.7 b	38.6 b
1/3	5.8 c	7.8 c	9.9 c
7	1.8 d	2.0 d	3.2 d
15	0.8 e	0.3 e	0.7 e

†Flooded means 1.0 cm of water above soil surface.
*Soil I - Cooking Lake SL from Smoky Lake
Soil II - Falun L from Egremont
Soil III - Malmo SiCL from Ellerslie
**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

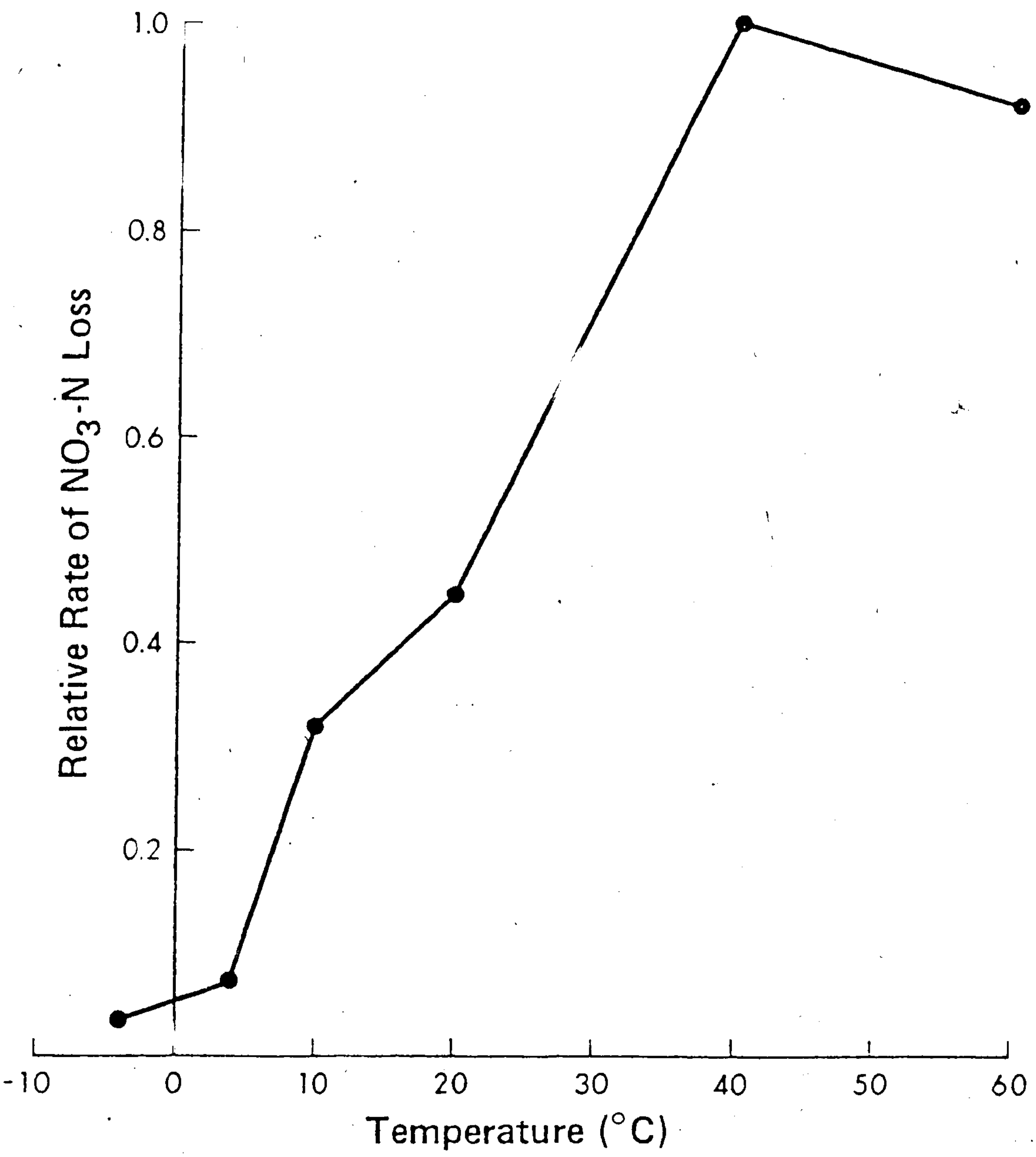

Figure 6. Influence of different temperatures on the rate of loss of NO_3-N added to a Malmo SiCL soil at a rate of 400 μg N/g in an incubation experiment at 0 bar soil moisture tension.

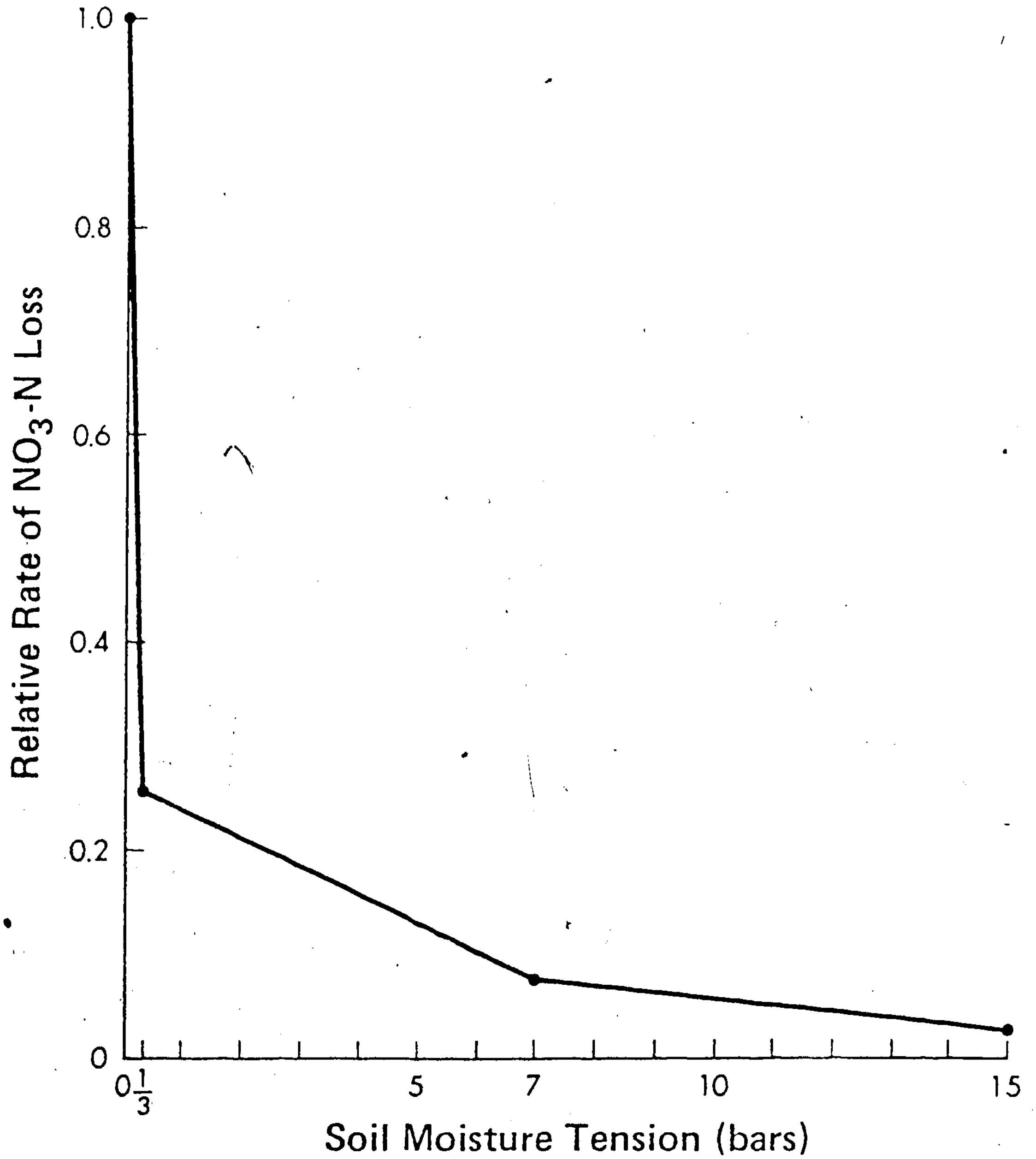

Figure 7. Effect of different moisture levels on the rate of loss of NO_3-N added at a rate of 400 µg N/g to a Malmo SiCL soil in an incubation experiment at 20°C.

Table 24. The rates of NO_3-N losses in three soils incubated with different concentrations of NO_3-N at 0 bar soil moisture tension and 20°C.

Concentration of NO_3-N (µg/g)	Rate of loss of NO_3-N (µg/g/day)**		
	*Soil I	*Soil II	*Soil III
50	9.8 e	11.3 e	12.1 e
75	12.9 d	14.5 d	16.5 d
125	16.7 c	17.4 c	20.0 c
250	24.4 b	26.5 b	29.1 b
500	29.0 a	31.8 a	34.2 a

*Soil I - Cooking Lake SL from Smoky Lake
Soil II - Falun L from Egremont
Soil III - Malmo SiCL from Ellerslie
**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

Table 25. The values of Vmax and Km for NO_3-N losses in three Alberta soils.

Soil type	Vmax (µg/g/day)	Km (µg/g)
Cooking Lake SL	37.4	143
Falun L	38.5	126
Malmo SiCL	42.8	126

4.6.3 Relationship between the rates of NO_3-N losses and the NO_3-N concentrations

The rate of loss of NO_3-N increased with the increasing levels of NO_3-N from 50 to 500 µg/g (Table 24). The rate was higher in the Malmo SiCL soil than the other two soils. The maximum rates of nitrate loss were about 4 to 6 fold greater than those of nitrification. The rate of NO_3 loss at 500 µg NO_3-N/g was about 2.8 times greater than at 50 µg/NO_3-N/g level. Nitrate losses in all three soils, could be represented by Michaelis-Menten kinetics (Fig. 8). Vmax varied from 37.4 to 42.8 µg/g/day and the Km ranged between 126 and 143 µg N/g soil (Table 25).

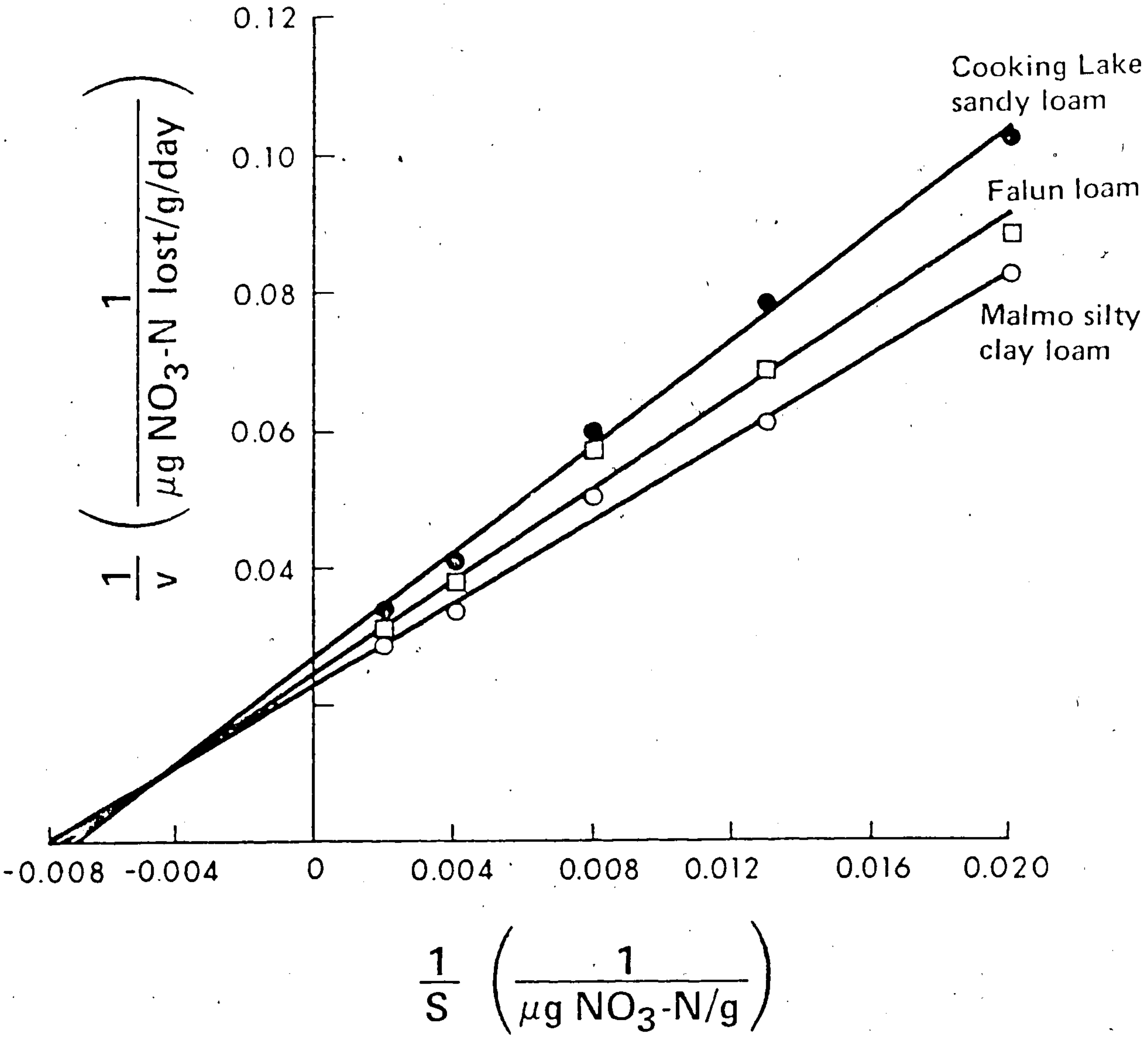

Figure 8. Lineweaver-Burke plot of denitrification rates in three Alberta soils at 0 bar moisture tension and 20°C.

4.7 Fate of Fall-Applied N as Determined by Using N^{15} Labelled Fertilizers

From the field work with commercial fertilizers, it was found that essentially the fertilizer N was not lost until early in March, whether the fertilizers had been applied as NO_3 or NH_4 in the fall. By May, the NO_3 either applied in fall or produced from the oxidation of ammonium-based N fertilizers was partially lost, and also moved downwards into the soil. The N loss was apparently by denitrification and by immobilization, but it was not possible to find the proportion of losses by denitrification as opposed to immobilization. Therefore, to study the fate of fertilizer N applied in fall, tracer N^{15} was used in a field experiment, set out in October, 1974, at Ellerslie (Malmo SiCL). Urea, KNO_3 and $(NH_4)_2SO_4$ fertilizers tagged with N^{15} were added to cylinders (30 cm diameter x 17.5 cm high) driven 15 cm deep into the soil. The plots were sampled in May, 1975, to a depth of 120 cm, taking samples from each of the 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm, and 90-120 cm depths. The soil samples were analyzed for N^{14} to N^{15} concentrations in total soil N content and in mineral N content with a mass spectrometer.

Table 26 shows the percent recoveries of fall-applied N fertilizers labelled with N^{15}, in the total N of the soil, in May, 1975. Considerable losses were observed from fall-applied N fertilizers, particularly from KNO_3. In the top 120 cm, the highest recovery (83.9%) of fall-applied fertilizers was with banded $(NH_4)_2SO_4$, followed by urea mixed into the soil (70.3%). The lowest recovery (58.7%) of N^{15} in total N of soil was with the KNO_3. No leaching was observed below 60 cm and 90 cm in $(NH_4)_2SO_4$ and urea treatments, respectively. In the treatment which received KNO_3, mixed in the soil, 27.2% of the fall-applied N leached down to the 15-30 cm depth, but only a very small amount of tagged nitrate (0.4% of applied) was detected in the 90-120 cm depth. There was more downward movement, however, with KNO_3 than with urea. The least leaching below 15 cm was with $(NH_4)_2SO_4$, and almost all of the recovered N^{15} was in the 0-15 cm depth.

The recovery of tagged N fertilizers in the mineral N content of the soil are shown in Table 27. The labelled KNO_3 gave lower recoveries (36.0%) in mineral N than similarly applied urea (53.6%) in the 0-120 cm depth, and the differences between KNO_3 and urea were statistically significant. About one-half of the recovered KNO_3 as mineral N was found in the 15-30 cm layer. There was only 8.2% of fall-applied urea in the 15-30 cm layer. Almost negligible leaching was observed below 15 cm in treatments which received $(NH_4)_2SO_4$.

To determine the amount of N^{15} labelled fertilizer N immobilized into organic N, calculations were made of the differences between the recovery of labelled fertilizer N in the total N of the soil and in the mineral N of the soil. (It was assumed that there was no fixed N from the applied fertilizers, but if there was any, it was included in the immobilized N.) Approximately one-fifth (ranging from 16.8% for $(NH_4)_2SO_4$ to 22.7% for KNO_3) of the fall-applied N was found to be immobilized (Table 28). The amount of immobilized N was higher (22.7%) with KNO_3 than with urea (16.8%).

Table 26. The percent of N applied in the fall at a rate of 112 kg N/ha recovered in late May, 1975, in the total N in a field experiment using $*N^{15}$ labelled fertilizers on a Malmo SiCL, Ellerslie.

	% of fall-applied N recovered in total N* in May,1975		
Depth (cm)	KNO_3-Mixed	Urea-Mixed	$(NH_4)_2\ SO_4$-Banded
0-15	28.2	54.3	80.6
15-30	27.4	14.2	3.2
30-60	2.2	1.5	0.1
60-90	0.5	0.3	0.0
90-120	0.4	0.0	0.0
0-120	58.7 c	70.3 b	83.9 a

*Atom % N^{15} excess of N fertilizers was 11.0 percent.
**For each row, the values are significantly different (95% level of probability) when not followed by the same letter.

Soil samples were taken in three concentric areas outside the cylinders, to find whether there was any horizontal movement of fall-applied N fertilizers. The first area extended from the edge of the cylinder out for a distance of 23 cm, the second for another 23 cm, and the third still another 23 cm. There was no evidence of horizontal movement of N^{15} at a distance of 23 cm or 46 cm in the treatment which received $(NH_4)_2SO_4$ (Table 29). Only 2.0 % of applied N from KNO_3 and 0.6% of applied N from urea were recovered in an area between the edge of the cylinder and a distance of 23 cm from it, in the 15-60 cm layer; and no N^{15} was detected beyond this distance (Table 29).

At this location, at least, there was no leaching loss of any consequence below the 60 cm soil depth from the N fertilizers, urea,

Table 27. The percent of fall-applied N at a rate of 112 kg N/ha, recovered in late May, 1975, in the soil mineral N (NH_4-N + NO_3-N) in a field experiment using *N^{15} labelled fertilizers on a Malmo SiCL at Ellerslie.

Depth (cm)	% of fall-applied N recovered in soil mineral N** in May, 1975		
	KNO_3-Mixed	Urea-mixed	$(NH_4)_2$ SO_4-Banded
0-15	17.2	44.2	65.6
15-30	16.2	8.2	0.3
30-60	1.7	0.8	0.1
60-90	0.5	0.4	0.0
90-120	0.4	0.0	0.0
0-120	36.0 b	53.6 a	66.0 a

*Atom % N^{15} excess of N fertilizers was 11.0 percent.

**In 0-120 cm depth, the values are significantly different (95% level of probability) when not followed by the same letter.

$(NH_4)_2SO_4$ and KNO_3. This means that the amount of tagged fertilizer N, not recovered in the total N of the soil in the 0-120 cm depth, was lost from the soil system essentially by denitrification. The estimated amounts of denitrification were 39.3% for KNO_3, 29.1% for urea, and 16.1% for $(NH_4)_2SO_4$, while the amounts of immobilization were 22.7%, 16.8%, and 17.9%, respectively. These results demonstrated that the greatest over-winter losses occurred in the field with the N fertilizers which contained NO_3, or which produced NO_3 most quickly.

Table 28. The percent of fall-applied N^{15} immobilized (% of the fall-applied N^{15} in the total N of the soil minus % of the fall-applied N^{15} in the mineral N (NH_4-N + NO_3-N) of the soil) by late May, 1975, in a field experiment using $*N^{15}$ labelled fertilizers on a Malmo SiCL at Ellerslie.

Depth (cm)	% of fall-applied labelled N immobilized**		
	KNO_3-Mixed	Urea-Mixed*	$(NH_4)_2SO_4$-Banded
0-15	11.0	10.1	15.0
15-30	11.2	6.0	2.9
30-60	0.5	0.7	0.0
60-90	0.0	0.0	0.0
90-120	0.0	0.0	0.0
0-120	22.7 a	16.8 a	17.9 a

*Atom % N^{15} excess of N fertilizers was 11.0 percent.

**In 0-120 cm depth, the values were significantly different (95% level of probability) when not followed by the same letter.

Table 29. The percent of N applied in the fall at a rate of 112 kg N/ha recovered in late May, 1975, in the total N of the soil in an area between cylinder and a point 23 cm from cylinder in a field experiment using $*N^{15}$ labelled fertilizers on a Malmo SiCL at Ellerslie.

Depth (cm)	% of fall-applied N in total N in late May, 1975		
	KNO_3-Mixed	Urea-Mixed	$(NH_4)_2SO_4$-Banded
0-15	0.0	0.0	0.0
15-30	1.8	0.6	0.0
30-60	0.2	0.0	0.0
60-90	.0	0.0	0.0
90-120	.0	0.0	0.0
0-120	2.0	0.6	0.0

*Atom % N^{15} excess of N fertilizers was 11.0 percent.

4.8 Inhibition of Nitrification in Incubation Experiments

4.8.1 Rates of nitrification of various N fertilizers

The incubation experiments were conducted to compare the rates of nitrification of various N fertilizers, and specifically to determine if thiourea would inhibit nitrification of urea. The experiments were carried out with two soils (Malmo SiCL and Falun L). One thousand grams of air-dried Ap horizon (0-15 cm), ground and passed through 5.0 mm sieve, were weighed into 14 cm diameter plastic pots. The pots were incubated at 20°C and 1/3 bar soil moisture tension. The fertilizers were banded at a depth of 4.5 cm below the soil surface, in a groove 6.2 cm long and 0.5 cm wide in the center of the pot. There were four treatments: (1) control, (2) urea, (3) urea + thiourea (2:1) pelleted together, and (4) ammonium sulphate. All the treatments were replicated four times. Nitrogen was applied at a rate of 50 μg N/g soil. The addition of thiourea had a considerable effect on inhibiting nitrification for at least 6 weeks in both soils (Table 30). On the average for the two soils, about 85% of the urea N was nitrified, while approximately 30% of the urea + thiourea (2:1) was nitrified. The data for 3 weeks showed that urea + thiourea (2:1) was a slow nitrifying fertilizer (about 12% nitrification) as compared to other N fertilizers which nitrified quickly (i.e. 62% to 76% of urea N and 42% to 44% of ammonium sulphate N was nitrified after 3 weeks of incubation). Even after 9 weeks, there was some inhibition of nitrification from the addition of thiourea to urea.

Table 30. Rate of nitrification of various N fertilizers added at a rate of 50 µg N/g to two soils in an incubation experiment at 20°C and 1/3 bar soil moisture tension.

Fertilizerϕ	Apparent % recovery of applied N as NO_3-N**					
	3 weeks		6 weeks		9 weeks	
	Soil I*	Soil II*	Soil I*	Soil II*	Soil I*	Soil II*
Urea	62 a	76 a	81 a	89 a	92 a	[illegible] a
Urea + thiourea (2:1)†	13 c	11 c	22 c	33 c	45 c	61 c
Ammonium sulphate	42 b	44 b	64 b	74 b	75 b	[illegible] b

*Soil I - Malmo SiCL from Ellerslie
Soil II - Falun L from Warspite

**The values were calculated as =

$$\frac{\begin{pmatrix}\text{NO}_3\text{-N recovered in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{NO}_3\text{-N recovered}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100$$

In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

†Two parts of urea and one part of thiourea were *pelleted* together and the pellets were applied considering the N in thiourea as well as in urea.

ϕAll the fertilizers were banded.

4.8.2 Comparison of nitrification inhibitors

This incubation experiment was conducted with two soils (Malmo SiCL and Cooking Lake SL) to select a nitrification inhibitor which could be used in the field experiments in this investigation. Urea + inhibitors were not pelleted in this experiment. Urea alone and urea + inhibitors were banded at a depth of 4.5 cm below the soil surface in a groove 6.2 cm long and 0.5 cm wide in the center of the pot containing 1000 g air-dried soil (Ap horizon). The pots were incubated at 1/3 bar soil moisture tension and 20°C. There were six treatments: (1) control, (2) urea, (3) urea + thiourea (2:1), (4) urea + thioacetamide (2:1), (5) urea + calcium sulphide (2:1), and (6) urea + phosphorus pentasulphide (2:1). All the treatments were replicated four times. Nitrogen was applied at a rate of 50 μg N/g soil.

When urea alone was applied in bands, more than 90% of applied N was nitrified in both soils after 5 weeks incubation (Table 31). The addition of inhibitors suppressed nitrification significantly. The greatest inhibition was in treatments which received urea + thiourea (2:1), followed by urea + thioacetamide (2:1). Calcium sulphide and phosphorus pentasulphide were found not very effectve in suppressing nitrification.

Table 31. Effect of thiourea and other sulphur compounds on nitrification of urea applied at a rate of 50 µg N/g to two soils in an incubation experiment at 20°C and 1/3 bar soil moisture tension.

Treatment$^{\phi}$	Apparent % recovery of applied urea N as NO_3-N after 5 weeks**	
	Soil I*	Soil II*
Urea	92 a	97 a
Urea + †thiourea (2:1)	43 c	48 c
Urea + †thioacetamide (2:1)	48 c	70 b
Urea + †calcium sulphide (2:1)	71 b	91 a
Urea + †phosphorus pentasulphide (2:1)	70 b	91 a

*Soil I - Malmo SiCL from Ellerslie
Soil II - Cooking Lake SL from Smoky Lake

**The values were calculated as

$$= \frac{\left(\begin{array}{c}NO_3\text{-N recovered in}\\ \text{fertilized treatment}\end{array}\right) - \left(\begin{array}{c}NO_3\text{-N recovered}\\ \text{in the control}\end{array}\right)}{\text{N applied}} \times 100$$

†Inhibitors were not pelleted with urea.

ϕFertilizers were banded in all the treatments.

4.9 Inhibition of Nitrification in Field Experiments

4.9.1 Effect of band placement and addition of thiourea on nitrification of urea

To study the effect of the method of application and the addition of thiourea on the rate of nitrification of urea under field conditions, experiments were set out in September, 1973, one at Ellerslie (Malmo SiCL), and another at Breton (Breton L). There were five treatments: (1) control, (2) urea - mixed, (3) urea - banded, (4) urea + thiourea (2:1) - mixed, and (5) urea + thiourea (2:1) - banded. Individual plots were 6.8 m x 1.8 m and each plot was replicated four times in a randomized complete block design. Nitrogen was applied at a rate of 100 kg N/ha.

At both sites, four weeks after fertilizer application, nitrification was slightly (5%) lower when urea was banded rather than mixed into the soil (Table 32). The addition of thiourea to urea inhibited nitrification of urea almost completely, and the nitrification of urea + thiourea (2:1) was significantly lower with band placement than with mixing it into the soil. Incidentally, at the two-week sampling, urea + thiourea (2:1) placed in bands, inhibited nitrification of soil N, as evidenced by the lower amount of NO_3-N in this treatment than in the control. The results of these field experiments showed that thiourea was very effective in inhibiting the nitrification of urea. The results of this experiment demonstrated that the band placement of pelleted urea + thiourea would serve as a technique for the field experiments in this project to attain inhibition of nitrification while

Table 32. Effect of band placement and addition of thiourea on nitrification of urea applied on September 19, 1973 at a rate of 112 kg N/ha on two soils in field experiments.

Fertilizer	Method of application	Apparent % of applied N recovered as NO_3-N (0-15 cm)**			
		Malmo SiCL		Breton L	
		2 weeks	4 weeks	2 weeks	4 weeks
Urea	Mixed	12 a	26 a	13 a	25 a
	Banded	11 a	21 b	11 a	20 b
Urea + thiourea (2:1)*	Mixed	4 b	6 c	5 b	8 c
	Banded	-3 c	3 d	-3 c	5 d

*Two parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

**The values were calculated as = $\dfrac{\begin{pmatrix}\text{NO}_3\text{-N recovered in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{NO}_3\text{-N recovered}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100.$

In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

comparing fall and spring application of N fertilizers. At the same time, this technique might be of practical importance in agriculture.

4.9.2 Effect of different amounts of thiourea on the rates of nitrification of urea

Field experiments were conducted to determine the nitrification rates of different mixtures of urea and thiourea. The experiments were laid out in the first week of June, 1975, at two locations: one at Ellerslie (Malmo SiCL) and the other at Canwood (Whitewood L). There were eight treatments: (1) control, (2) urea, (3) urea + thiourea (10:1), (4) urea + thiourea (5:1), (5) urea + thiourea (2:1), (6) urea + thiourea (1:1), (7) urea + thiourea (1:2), and (8) thiourea. Individual plots were 6.8 m x 1.8 m. Each plot was replicated four times in a randomized complete block design. In all treatments except the control, N was banded at a rate of 56 kg N/ha. The various mixtures of urea and thiourea were prepared on a weight basis. Soil samples were taken from the 0-15 cm depth.

On the Malmo SiCL soil, 38% of applied urea was nitrified at 4 weeks after application (Table 33), and the addition of thiourea reduced the amount of nitrification. At 4 weeks, urea + thiourea (2:1) inhibited nitrification almost completely. It was also observed that the addition of thiourea at high rates (i.e. urea + thiourea in a ratio of 1:2) inhibited nitrification of soil N as evidenced by less NO_3-N in fertilized plots than in the control (Table 33). At 4 weeks, about 90% of applied N was recovered as NH_4-N + NO_3-N (Appendix A Table 16) in plots which received urea alone, or received urea +

Table 33. Effect of different amounts of thiourea on the amounts of nitrification of urea applied at a rate of 56 kg N/ha on two soils under field conditions.

Treatment*	Apparent % of applied N recovered as NO_3-N (0-15 cm)**			
	At 4 weeks		At 8 weeks	
	Malmo SiCL	Whitewood L	Malmo SiCL	Whitewood L
Urea	38 a	67 a	77 a	89 a
Urea + thiourea (10:1)	29 b	47 b	73 b	82 b
Urea + thiourea (5:1)	21 c	36 c	61 c	72 c
Urea + thiourea (2:1)	5 d	10 d	38 d	52 d
Urea + thiourea (1:1)	2 e	1 e	29 e	33 e
Urea + thiourea (1:2)	-2 f	-2 f	13 f	25 f
Thiourea	-7 f	-5 f	5 f	12 g

*Fertilizers were placed in bands.

**The values were calculated as = $\dfrac{\begin{pmatrix}NO_3\text{-N recovered in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}NO_3\text{-N recovered}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100$

In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

thiourea (10:1). However, the higher rates of thiourea (i.e. urea + thiourea in a ratio of 2:1 and 1:2) resulted in considerable reduction in the recovery of mineral N. The lower recoveries of mineral N in these plots were probably due to the inhibition of urea hydrolysis by thiourea. At 8 weeks, almost all the N in urea + thiourea (2:1 and 1:1) was recovered as NH_4-N + NO_3-N, however, with urea + thiourea (1:2) and thiourea alone where the mineral N (NH_4-N + NO_3-N) recovery was 73% and 37%, respectively. The amounts of nitrification for urea + thiourea (2:1) and (1:1) were low (38% and 29%, respectively) as compared to urea alone (77%). Almost no NO_3 was found in plots which received only thiourea.

A similar pattern existed between the extent of nitrification inhibition and the amount of thiourea on Whitewood L soil (Table 33). At 4 weeks, 67% of the urea applied was found as NO_3-N compared to 10% and 1% with urea + thiourea, (2:1) and (1:1), respectively. Higher rates of thiourea also inhibited nitrification of soil N.

These experiments showed that urea and thiourea in a ratio of 2:1, or narrower, can inhibit nitrification and consequently may prevent over-winter losses of fall-applied N.

4.10 Effect of Thiourea on Increasing the Efficiency of Fall-Applied Urea During 1973-74

The results of incubation and preliminary field experiments with urea, including the use of nitrification inhibitors, suggested that thiourea when pelleted with urea in a ratio of two parts urea and one part thiourea and placed in bands, was effective in inhibiting nitrification of urea. In October, 1973, four field experiments were set out with the purpose of comparing fall and spring application of N fertilizers and assessing the effect of thiourea as an inhibitor of nitrification over the winter. The four experiments were located at Calmar (Demay L), Ellerslie (Malmo SiCL), Smoky Lake (Cooking Lake SL), and Waispite (Falun L). There were two fertilizers (urea and urea + thiourea - 2:1), and two methods of application (mixing into the soil and band placement). Individual plots were 6.8 m x 1.8 m. All the plots were replicated four times in a split-plot design, and each plot was further divided into two sub-plots (i.e. fall and spring). The plots were sampled to a depth of 90 cm in May, 1974, and analyzed for NH_4-N and NO_3-N contents.

4.10.1 Ammonium N content of soil in May, 1974

The results of the NH_4-N contents in the 0-90 cm depth of the soils (Table 34) showed that when urea was applied by itself in the fall, and mixed into the soil, it was almost completely nitrified by the following spring. (The nitrification was calculated as percent of applied N, not recovered as KCl extractable NH_4-N.) With band placement of urea, there was a slightly lower nitrification. For

Table 34. Effect of band placement and addition of thiourea on the amounts of nitrate production from urea applied in October, 1973, at a rate of 56 kg N/ha on four soils.

Fertilizer	Method of application	Apparent % recovery of applied N as NH_4-N** in the top 90 cm of soil in late May, 1974			
		*Site I	*Site II	*Site III	*Site IV
Urea	Mixed	5 c	8 d	12 d	6 d
	Banded	7 c	16 c	28 c	16 c
Urea + thiourea (2:1)†	Mixed	11 b	36 b	56 b	38 b
	Banded	33 a	57 a	76 a	50 a

*Site I - Demay L at Calmar
Site II - Malmo SiCL at Ellerslie
Site III - Cooking Lake SL at Smoky Lake
Site IV - Falun L at Warspite

$$\text{**The values were calculated as} = \frac{\left(\begin{array}{l}NH_4\text{-N content in}\\ \text{fertilized treatment}\end{array}\right) - \left(\begin{array}{l}NH_4\text{-N content}\\ \text{in the control}\end{array}\right)}{\text{N applied}} \text{ X } 100$$

In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

†Two parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

example, on the average of four experiments, the NH_4-N content was approximately 1.8 times greater with the urea banded than with the urea mixed into the soil. With the addition of thiourea to urea, and especially when applied in bands, nitrification was greatly suppressed. On the average of four field tests, the NH_4-N content was approximately three times greater with the urea + thiourea banded than with the urea banded by itself. Approximately 54% of fall-applied N was recovered as NH_4-N in plots which received urea + thiourea (2:1), as compared to 17% where urea alone was banded.

4.10.2 Mineral N (NH_4-N + NO_3-N) content of soil in May, 1974

In May, about 40% of fall-applied urea N was recovered* as mineral N in the top 90 cm depth on the Demay L soil (Table 35). The band placement of thiourea to urea in a ratio of 1:2 increased the mineral N recovery in this plot by 24%. Cooking Lake SL soil was the only soil on which band placement of urea alone influenced mineral N recovery from the 0-90 cm layer. However, mineral N recovery from only the 0-15 cm depth was significantly greater with band placement of urea, than mixing it into the soil, at three of four field tests. Band application of urea + thiourea (2:1) gave significantly higher mineral N recovery in the 0-90 cm depth, than mixed application of the same fertilizer, on all the soils except the Falun L soil.

On the average of four locations, the application of urea

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*Recovery was calculated as =

$$\frac{\begin{pmatrix}\text{Soil content of KCl}\\ \text{extractable } NH_4\text{-N} + NO_3\text{-N}\\ \text{in fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{Soil content of KCl}\\ \text{extractable } NH_4\text{-N} + NO_3\text{-N}\\ \text{in control treatment}\end{pmatrix}}{\text{Applied N}} \times 100$$

Table 35. The recovery of mineral N(NH_4-N + NO_3-N) in May, 1974, with the application of urea and U + T (2:1)* in October, 1973, at a rate of 56 kg N/ha at four locations.

Location†	Fertilizer	Method of application	Apparent % recovery of applied N as NH_4-N + NO_3-N** 0-15 cm	0-30 cm	0-60 cm	0-90 cm
1	Urea	Mixed	21 c	32 c	39 c	40 c
		Banded	24 c	33 c	41 c	39 c
	U + T (2:1)*	Mixed	32 b	43 b	47 b	47 b
		Banded	56 a	63 a	65 a	64 a
2	Urea	Mixed	43 d	52 d	56 d	58 c
		Banded	48 c	58 c	62 c	61 c
	U + T (2:1)*	Mixed	66 b	69 b	71 b	70 b
		Banded	77 a	80 a	81 a	80 a
3	Urea	Mixed	47 d	53 d	64 d	66 d
		Banded	57 c	63 c	71 c	73 c
	U + T (2:1)*	Mixed	77 b	81 b	87 b	88 b
		Banded	89 a	92 a	94 a	94 a
4	Urea	Mixed	39 d	50 c	57 b	59 b
		Banded	45 c	51 c	58 b	58 b

Table 35. Continued.

Location†	Fertilizer	Method of application	Apparent % recovery of applied N as NH_4-N + NO_3-N** 0-15 cm	0-30 cm	0-60 cm	0-90 cm
	U + T (2:1)*	Mixed	60 b	62 b	64 a	65 a
		Banded	65 a	67 a	68 a	67 a
Average	Urea	Mixed	38	47	54	56
		Banded	44	51	58	58
	U + T (2:1)*	Mixed	59	64	67	68
		Banded	72	76	77	76

†Location 1 - Demay L at Calmar
Location 2 - Malmo SiCL at Ellerslie
Location 3 - Cooking Lake SL at Smoky Lake
Location 4 - Falun L at Warspite

*U + T (2:1) - Urea + thiourea (2:1). Urea + thiourea was applied at a rate of 89.2 kg of urea and 44.6 kg of thiourea per hectare. Urea and thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

**The values were calculated as = $\dfrac{\begin{pmatrix}\text{Mineral N content in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{Mineral N content}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100$

In each column, the values for each depth at each location are significantly different (95% level of probability) when not followed by the same letter.

+ thiourea (2:1) pellets in bands gave 18% greater mineral N recovery than when urea alone was applied. In plots which received urea + thiourea (2:1), the mineral N recovery was higher and almost all of the mineral N was recovered in the surface layer (0-15 cm), whereas with the urea alone the mineral N recovery was less and some of mineral N had moved to the 30-60 cm layer.

4.10.3 Yield and N uptake of barley grain with urea and urea + thiourea (2:1)

Fall-applied urea at a rate of 56 kg N/ha when mixed into the soil produced only 8.7 quintals (1 quintal = 100 kg) of barley grain/ha on Demay L soil, as compared to 16.1 quintals when applied in the spring (Table 36). Band placement of urea in the fall gave 3.2 quintals more barley grain than urea mixed into the soil. Application of urea + thiourea (2:1) pellets increased the yield of barley grain further. Among the fall applications, the highest yields and N uptake of barley grain (16.9 quintals/ha and 40%, respectively) were obtained with urea + thiourea (2:1) pellets banded in the fall. Also the banded urea + thiourea (2:1) applied in the fall produced almost as high yields of barley grain as did spring-applied urea. Spring-banded urea + thiourea (2:1) showed some toxicity symptoms on the barley leaves, depressed the growth of barley in the early growing season, and eventually lowered the yields of grain slightly. No toxic symptoms were observed with fall-applied urea + thiourea (2:1).

At the other three locations, the addition of thiourea to urea improved the efficiency of fall-applied urea by increasing the

Table 36. Yield and N uptake of barley grain with fall and spring application of urea and U + T* (2:1) on four soils in 1973-74.

Location‡	Treatment	Rate of application (kg N/ha)	Time of application*	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
1	Control	0		6.4 f	
	Urea-Mixed	56	Fall	8.7 e	8 f
	Urea-Banded	56	Fall	11.9 d	17 e
	U + T (2:1)†-Mixed	56	Fall	13.1 d	26 d
	U + T (2:1)†-Banded	56	Fall	16.9 bc	40 ab
	Urea-Mixed	56	Spring	16.1 c	29 cd
	Urea-Banded	56	Spring	18.6 bc	33 bcd
	U + T (2:1)†-Mixed	56	Spring	19.6 ab	42 a
	U + T (2:1)†-Banded	56	Spring	17.4 bc	36 abc
2	Control	0		14.1 c	
	Urea-Mixed	56	Fall	20.9 b	21 b
	Urea-Banded	56	Fall	21.4 b	24 b
	U + T (2:1)†-Mixed	56	Fall	22.5 b	28 b
	U + T (2:1)†-Banded	56	Fall	26.9 a	43 a
	Urea-Mixed	56	Spring	27.4 a	45 a
	Urea-Banded	56	Spring	27.2 a	43 a
	U + T (2:1)†-Mixed	56	Spring	26.5 a	45 a
	U + T (2:1)†-Banded	56	Spring	27.5 a	46 a
3	Control	0		4.7 e	
	Urea-Mixed	56	Fall	12.5 d	23 f
	Urea-Banded	56	Fall	13.6 cd	27 def
	U + T (2:1)†-Mixed	56	Fall	16.9 ab	36 ab
	U + T (2:1)†-Banded	56	Fall	18.7 a	42 a

Table 36. Continued.

Location Φ	Treatment	Rate of application (kg N/ha)	Time of application*	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
	Urea-Mixed	56	Spring	15.1 bcd	32 bcd
	Urea-Banded	56	Spring	15.8 bc	34 abc
	U + T (2:1)†-Mixed	56	Spring	15.4 bc	36 ab
	U + T (2:1)†-Banded	56	Spring	14.4 bcd	31 bcde
4	Control	0		18.7 d	
	Urea-Mixed	56	Fall	35.6 c	54 c
	Urea-Banded	56	Fall	37.6 abc	62 b
	U + T (2:1)†-Mixed	56	Fall	37.1 abc	61 bc
	U + T (2:1)†-Banded	56	Fall	39.3 a	75 a
	Urea-Mixed	56	Spring	36.6 bc	58 bc
	Urea-Banded	56	Spring	39.2 a	75 a
	U + T (2:1)†-Mixed	56	Spring	38.3 ab	71 a
	U + T (2:1)†-Banded	56	Spring	37.5 abc	66 ab
Average	Control	0		11.0	
	Urea-Mixed	56	Fall	19.4	26
	Urea-Banded	56	Fall	21.1	33
	U + T (2:1)†-Mixed	56	Fall	22.2	38
	U + T (2:1)†-Banded	56	Fall	25.5	50

Table 36. Continued.

LocationΦ	Treatment	Rate of application (kg N/ha)	Time of application*	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
	Urea-Mixed	56	Spring	23.8	41
	Urea-Banded	56	Spring	25.2	46
	U + T (2:1)†-Mixed	56	Spring	25.0	49
	U + T (2:1)†-Banded	56	Spring	24.2	44

ΦLocation 1 - Demay L at Calmar
Location 2 - Malmo SiCL at Ellerslie
Location 3 - Cooking Lake SL at Smoky Lake
Location 4 - Falun L at Warspite

†U + T (2:1) - Urea + thiourea (2:1)
Urea + thiourea was applied at a rate of 89.2 kg of urea and 44.6 kg of thiourea per hectare. Urea and thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

*For fall application the fertilizers were applied in October and for spring application the fertilizers were applied in May at the time of seeding.

**The values for N uptake by grain were calculated as $\frac{\left(\text{N uptake in fertilized treatment}\right) - \left(\text{N uptake in the control}\right)}{\text{N applied}} \times 100$

In each column, values separately for yield and N uptake of barley grain at each location are significantly different (95% level of probability) when not followed by the same letter.

yields and N uptake of barley grain (Table 36). The highest N uptake with fall banded urea + thiourea (2:1) was associated with the highest mineral N (NH_4-N + NO_3-N) recovered in this plot in early May soil sampling (Table 34). Also, at these locations, urea + thiourea when banded in the spring was found slightly toxic to barley and resulted in reduction of yield of barley grain. Although, urea + thiourea (2:1) mixed into the soil did not produce any toxicity symptoms when applied in the spring, it gave no increase in yield and N uptake of barley grain over urea alone applied in the spring.

These field experiments demonstrated that band placement and use of thiourea improved over-winter conservation of fall-applied urea N, and increased the yield and N uptake of barley seeded in the following spring. Urea + thiourea (2:1) banded in the fall produced as much yield (25.5 quintals/ha) and N uptake (50%) of barley grain as did spring-applied urea alone (25.2 quintals and 46%, respectively).

2

4.11 Influence of Thiourea and Band Placement in Improving the Over-Winter Conservation of Fall-Applied Urea During 1974-75

To confirm the results obtained in the field experiments conducted during 1973-74 concerned with over-winter conservation of fall-applied urea N, six experiments were set out in October, 1974, on stubble fields. These experiments were located at Blue Sky (Albright CL), Calmar (Demay L), Canwood (Whitewood L), Egremont (Falun L), Bon Accord (Angus Ridge CL), and Ellerslie (Malmo SiCL). The following fertilizers were used: urea, and urea + thiourea (2:1) pelleted. The fertilizers were applied by two methods (mixing into the soil, and band placement), and at two times (fall application and spring application). Nitrogen was applied at a rate of 56 kg N/ha. Individual plots were 6.8 m x 1.8 m. Each plot was replicated four times in a split-plot design. Soil samples were taken to a depth of 90 cm in early spring, 1975, and were analyzed for the contents of NH_4-N and NO_3-N.

4.11.1 Effect of thiourea and band placement on the inhibition of nitrification of fall-applied urea over the winter

The NH_4-N content (Table 37) of soils sampled to a depth of 90 cm in May, 1975, from six fields experiments set out in October, 1974, showed that by early May, only 9% of the urea mixed into the soil remained as NH_4-N. There was slight inhibition of nitrification from band placement (nitrification was calculated as % of the fall-applied N not recovered as NH_4-N), with 14% of the applied urea recovered as NH_4-N. The addition of thiourea to urea increased the

Table 37. Effect of band placement and addition of thiourea on the inhibition of nitrification of urea applied in October, 1974, at a rate of 56 kg N/ha at six locations in field experiments.

Fertilizer		Apparent % recovery of applied N as NH_4-N** in the top 90 cm of soil in May, 1975					
		*Site I	*Site II	*Site III	*Site IV	*Site V	*Site VI
Urea	Mixed	20 d	3 d	10 c	1 d	1 d	16 d
	Banded	34 c	6 c	12 c	9 c	4 c	21 c
Urea + thiourea (2:1)†	Mixed	50 b	16 b	35 b	12 b	16 b	27 b
	Banded	70 a	28 a	51 a	23 a	20 a	47 a

*Site I - Albright CL at Blue Sky
Site II - Demay L at Calmar
Site III - Whitewood L at Canwood
Site IV - Falun L at Egremont
Site V - Angus Ridge CL at Bon Accord
Site VI - Malmo SiCL at Ellerslie

**The values were calculated as $= \dfrac{\left(\begin{array}{l}\text{NH}_4\text{-N content in}\\ \text{fertilized treatment}\end{array}\right) - \left(\begin{array}{l}\text{NH}_4\text{-N content}\\ \text{in the control}\end{array}\right)}{\text{N applied}} \text{ X } 100$

In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

†Two parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the nitrogen in thiourea as well as in urea.

inhibition effect greatly and about 40% of the fall-banded urea + thiourea (2:1) remained as NH_4-N.

4.11.2 Mineral N (NH_4-N + NO_3-N) content of soil in May, 1975

Apparently, 44%, 68% and 60% of the fall-applied urea N mixed into the soil was recovered in May in the top 90 cm layer on the Demay L soil, the Falun L soil and the Angus Ridge CL soil, respectively (Table 38). The band placement of fall-applied urea resulted in significantly greater mineral N recovery than did mixing into the soil. On the Demay L soil, the mineral N recovered was 16% greater with banded urea than when it was mixed into the soil. The addition of thiourea to urea improved the over-winter conservation of fall-applied urea N, and band placement of urea + thiourea (2:1) pellets enhanced this effect. Thus, the highest mineral N recovery (87%) was with urea + thiourea (2:1) banded, and that was two times greater than urea alone mixed into the soil.

On the three other soils, although banded urea gave higher mineral N recovery than mixing of urea into the soil, the differences were not significant. However, the addition of thiourea had a significant effect in increasing the mineral recovery of fall-applied N. The mineral N recovery in May, at various depths revealed that fall-applied urea was partially moved downwards. In general, the downward movement was the highest in plots where urea was mixed into the soil and was the lowest in urea + thiourea (2:1) banded plots. Apparently, there was little or no leaching below the 60 cm depth.

Thus, in the six field experiments, the over-winter losses

Table 38. The recovery of mineral N(NH_4-N + NO_3-N) in May, 1975, with the application of urea and U + T (2:1)* in October, 1974, at a rate of 56 kg N/ha at six locations.

Location†	Fertilizer	Method of application	Apparent % recovery of applied N as NH_4-N + NO_3-N**			
			0-15 cm	0-30 cm	0-60 cm	0-90 cm
1	Urea	Mixed	65 c	69 c	75 c	75 c
		Banded	75 b	77 b	80 b	79 bc
	U + T (2:1)*	Mixed	78 b	81 b	83 b	82 b
		Banded	87 a	89 a	90 a	90 a
2	Urea	Mixed	37 d	39 d	44 d	44 d
		Banded	51 c	56 c	59 c	60 c
	U + T (2:1)*	Mixed	66 b	71 b	75 b	76 b
		Banded	79 a	85 a	87 a	87 a
3	Urea	Mixed	61 c	66 c	70 c	70 c
		Banded	66 c	69 c	72 c	73 bc
	U + T (2:1)*	Mixed	72 b	75 b	78 b	77 b
		Banded	82 a	83 a	83 a	83 a
4	Urea	Mixed	60 d	64 d	69 d	68 d
		Banded	70 c	72 c	75 c	76 c
	U + T (2:1)*	Mixed	76 b	78 b	81 b	82 b
		Banded	85 a	86 a	88 a	86 a
5	Urea	Mixed	52 d	55 c	61 c	60 c
		Banded	64 c	67 b	72 b	72 b

Table 38. Continued.

Location†	Fertilizer	Method of application	Apparent % recovery of applied N as NH_4-N + NO_3-N** 0-15 cm	0-30 cm	0-60 cm	0-90 cm
	U + T (2:1)*	Mixed	70 b	74 a	80 a	78 a
		Banded	74 a	76 a	82 a	81 a
6	Urea	Mixed	72 c	81 b	84 b	83 b
		Banded	80 b	84 b	86 b	86 b
	U + T (2:1)*	Mixed	80 b	82 b	83 b	83 b
		Banded	92 a	93 a	93 a	91 a
Average	Urea	Mixed	58	62	67	67
		Banded	68	71	74	74
	U + T (2:1)*	Mixed	74	78	80	80
		Banded	83	85	87	86

†Location 1 - Albright CL at Blue Sky
Location 2 - Demay L at Calmar
Location 3 - Whitewood L at Canwood
Location 4 - Falun L at Egremont
Location 5 - Angus Ridge CL at Bon Accord
Location 6 - Malmo SiCL at Ellerslie

*U + T (2:1) - Urea + thiourea (2:1). Two parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

**The values were calculated as = $\frac{\begin{pmatrix}\text{Mineral N recovered in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{Mineral N recovered}\\ \text{in the control}\end{pmatrix}}{\text{N applied}}$ X 100

In each column, the values for each depth at each location are significantly different (95% level of probability) when not followed by the same letter.

of mineral N from fall-applied urea were reduced by the addition of thiourea to urea, especially when placed in bands (Table 38).

4.11.3 Yields and N uptake of barley grain with urea and urea + thiourea (2:1)

On the Demay L soil, fall-applied urea when mixed into the soil produced 20.7 quintals/ha (1 quintal = 100 kg) lower yield of barley grain than the spring-applied urea (Table 39). Band application of urea increased the yield and the N uptake of barley grain by 4.2 quintals/ha and 14%, respectively, as compared to urea mixed into the soil. The addition of thiourea to urea produced [illegible] quintals/ha more barley grain than urea banded in the fall, while the [illegible] placement of urea + thiourea gave an increase of 6.6 quintals/ha of barley grain. Among the fall applications, banded urea + thiourea (2:1) gave the highest N uptake by barley grain (65% of applied N), and this N uptake was approximately two-thirds of the N uptake with urea banded in the spring. However, when urea + thiourea (2:1) was banded beside the seed in the spring it produced toxicity symptoms, and caused slowing of emergence. This resulted in reduction of the number of plants and ultimately depressed the yield and N uptake of barley grain in this treatment. Even when urea + thiourea was applied in the spring but mixed into the soil, there were no visual toxicity symptoms, but on ~~the~~ average there was depression in the yield as compared to urea applied in the spring.

On the Albright CL soil, the Whitewood L soil and the Falun L soil, similar to the previous location, urea + thiourea (2:1)

Table 39. Yield and N uptake of barley grain with fall and spring application of urea and U + T (2:1)* on six soils in 1974-75.

Location Φ	Treatment	Rate of application (kg N/ha)	Time of application*	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
1	Control	0		13.2 e	
	Urea-Mixed	56	Fall	29.2 cd	47 c
	Urea-Banded	56	Fall	29.9 cd	51 c
	U + T (2:1)†-Mixed	56	Fall	29.6 cd	52 bc
	U + T (2:1)†-Banded	56	Fall	32.4 bc	72 ab
	Urea-Mixed	56	Spring	36.5 ab	79 a
	Urea-Banded	56	Spring	36.8 ab	75 a
	U + T (2:1)†-Mixed	56	Spring	37.4 a	81 a
	U + T (2:1)†-Banded	56	Spring	26.6 d	50 c
2	Control	0		16.4 e	
	Urea-Mixed	56	Fall	27.4 d	28 c
	Urea-Banded	56	Fall	31.6 cd	42 bc
	U + T (2:1)†-Mixed	56	Fall	33.7 cd	50 bc
	U + T (2:1)†-Banded	56	Fall	38.2 bc	65 b
	Urea-Mixed	56	Spring	48.1 a	97 a
	Urea-Banded	56	Spring	48.8 a	96 a
	U + T (2:1)†-Mixed	56	Spring	43.9 ab	90 a
	U + T (2:1)†-Banded	56	Spring	34.7 cd	61 b
3	Control	0		7.1 f	
	Urea-Mixed	56	Fall	16.9 e	28 e
	Urea-Banded	56	Fall	18.6 de	33 de
	U + T (2:1)†-Mixed	56	Fall	20.4 bcd	36 cde
	U + T (2:1)†-Banded	56	Fall	23.6 bc	47 bc

Table 39. Continued.

LocationΦ	Treatment	Rate of application (kg N/ha)	Time of application*	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
	Urea-Mixed	56	Spring	25.2 ab	51 b
	Urea-Banded	56	Spring	28.0 a	63 a
	U + T (2:1)†-Mixed	56	Spring	23.7 bc	51 b
	U + T (2:1)†-Banded	56	Spring	21.5 bcd	44 bc
4	Control	0		6.9 e	
	Urea-Mixed	56	Fall	18.2 d	31 e
	Urea-Banded	56	Fall	19.2 d	35 de
	U + T (2:1)†-Mixed	56	Fall	22.7 cd	47 bcd
	U + T (2:1)†-Banded	56	Fall	24.8 bc	56 abc
	Urea-Mixed	56	Spring	28.0 ab	60 ab
	Urea-Banded	56	Spring	29.6 a	68 a
	U + T (2:1)†-Mixed	56	Spring	29.6 a	66 a
	U + T (2:1)†-Banded	56	Spring	22.7 cd	48 bcd
5	Control	0		8.3 h	
	Urea-Mixed	56	Fall	15.6 g	20 d
	Urea-Banded	56	Fall	17.4 efg	25 d
	U + T (2:1)†-Mixed	56	Fall	20.6 def	35 cd
	U + T (2:1)†-Banded	56	Fall	24.0 cd	47 bc
	Urea-Mixed	56	Spring	37.4 a	86 a
	Urea-Banded	56	Spring	36.5 a	87 a
	U + T (2:1)†-Mixed	56	Spring	31.6 ab	71 a
	U + T (2:1)†-Banded	56	Spring	24.6 cd	51 b

Table 39. Continued.

LocationΦ	Treatment	Rate of application (kg N/ha)	Time of application*	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
6	Control	0		21.4 e	
	Urea-Mixed	56	Fall	38.6 d	50 d
	Urea-Banded	56	Fall	40.8 d	54 cd
	U + T (2:1)†-Mixed	56	Fall	44.4 c	70 bc
	U + T (2:1)†-Banded	56	Fall	45.8 bc	82 ab
	Urea-Mixed	56	Spring	46.8 abc	87 a
	Urea-Banded	56	Spring	46.0 abc	92 a
	U + T (2:1)†-Mixed	56	Spring	48.0 ab	95 a
	U + T (2:1)†-Banded	56	Spring	39.4 d	71 c
Average	Control	0		12.2	
	Urea-Mixed	56	Fall	24.2	34
	Urea-Banded	56	Fall	26.2	40
	U + T (2:1)†-Mixed	56	Fall	28.6	48
	U + T (2:1)†-Banded	56	Fall	31.4	61
	Urea-Mixed	56	Spring	37.0	77
	Urea-Banded	56	Spring	37.6	80
	U + T (2:1)†-Mixed	56	Spring	35.7	76
	U + T (2:1)†-Banded	56	Spring	28.0	54

ΦLocation 1 - Albright CL at Blue Sky
Location 2 - Demay L at Calmar
Location 3 - Whitewood L at Canwood
Location 4 - Falun L at Egremont
Location 5 - Angus Ridge CL at Bon Accord
Location 6 - Malmo SiCL at Ellerslie

Table 39. Continued.

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†U + T (2:1) - Urea + thiourea (2:1)
Urea + thiourea was applied at a rate of 89.2 kg of urea and 44.6 kg of thiourea per hectare.
Urea + thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

*For fall application the fertilizers were applied in October and for spring application the fertilizers were applied at the time of seeding.

**The values for N uptake in grain were calculated as $= \frac{\left(\text{N uptake in fertilized treatment}\right) - \left(\text{N uptake in the control}\right)}{\textit{N applied}} \times 100$

In each row, the values for *yield* and N *uptake of barley grain at* each *location are significantly* different (95% level of probability) when not followed by the same letter.

was the best fertilizer for increasing the yield and N uptake of barley grain among the fall-applied N fertilizers. Although N uptake of barley grain with urea banded was greater than with urea mixed into the soil on these three soils, the difference was not statistically significant (Table 39). Similar results were obtained on the Angus Ridge CL soil and the Malmo SiCL soil (Table 39).

On the average of six field experiments, the fall application of urea produced 15 quintals/ha less barley grain than the spring application (Table 39). The band placement of urea + thiourea (2:1) overcame much of the over-winter losses and gave 8.2 quintals/ha more yield of barley grain than fall banded urea alone. Band placement of urea in the fall produced 1.7 quintals/ha more yield of barley grain than mixing of urea into the soil, but when the urea was applied in the spring there was no difference between band placement and mixing into the soil.

The application of urea + thiourea in bands in the spring showed severe toxicity symptoms in all the experiments and gave a decrease in yield of barley grain as compared to urea applied in the spring. Although there was no visual toxicity symptoms with urea + thiourea (2:1) mixed into the soil in the spring, there was some depression in the yield of barley grain. The depression in the yield due to the toxicity of thiourea was much more pronounced during 1974-75 than during 1973-74, and the reason for this difference between the years could not be ascertained.

The N uptake by barley grain with fall-banded urea was about one-half as much as with spring banded urea (Table 39). The addition of thiourea to urea when placed in bands increased the N uptake by barley grain by 21%. The N uptake by barley grain with urea + thiourea (2:1) banded in the fall was about three-fourth of the N uptake with spring banded urea.

The combined data of 10 field experiments conducted during 1973-74 and 1974-75 showed that the yield and N uptake of barley grain with fall-applied urea were considerably lower than spring application (Table 40). Fall application of urea, when mixed into the soil, gave 10.0 quintals lower yield of barley grain than similarly applied urea in the spring. Band placement of urea in the fall resulted in an increase of 1.7 quintals of barley grain over mixed application. The use of thiourea with urea was much more effective and the band placement of urea + thiourea (2:1) produced 8.1 quintals more barley grain than with urea mixed into the soil. The N uptake by barley grain obtained with urea + thiourea (2:1) banded in the fall was about 90% of the N uptake obtained with spring-applied urea.

These 10 field experiments have shown that at least under experimental conditions of this study, most of the over-winter losses of urea can be avoided by its treatment with thiourea and its application in bands.

Table 40. Yield and N uptake of barley grain with fall and spring application of urea and *U + T - 2:1 (average of 10 field experiments of which four experiments in 1973-74 and six experiments in 1974-75 were conducted).

Treatment	Rate of application (kg N/ha)	Time of application**	Yield of barley grain (100 kg/ha)	Apparent % of applied N in grain
Control	0		11.6	-
Urea - Mixed	56	Fall	20.4	31
Urea - Banded	56	Fall	22.1	36
*U + T (2:1) - Mixed	56	Fall	25.4	43
*U + T (2:1) - Banded	56	Fall	28.5	56
Urea - Mixed	56	Spring	30.4	59
Urea - Banded	56	Spring	31.4	63
*U + T (2:1) - Mixed	56	Spring	30.4	63
*U + T (2:1) - Banded	56	Spring	26.1	49

*U + T (2:1) - Urea + thiourea (2:1). Two parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

**The values for N uptake by grain were calculated as $= \dfrac{\left(\text{N uptake in fertilized treatment}\right) - \left(\text{N uptake in the control}\right)}{\text{N applied}} \times 100$

For fall application the fertilizers were applied in October and for spring application the fertilizers were applied at the time of seeding.

4.12 Over-Winter Conservation of Soil N by Using Inhibitors

The results of various field experiments conducted from 1973 to 1977 demonstrated that the mineral N from fall-applied fertilizers, as well as from soil N, was lost over the winter. The over-winter losses from fall-applied fertilizer N were reduced by using thiourea (a nitrification inhibitor) with urea. Assuming that mineral N arising from the soil behaves in a manner similar to the mineral N arising from fertilizer, one might expect that inhibitors, which suppress both ammonification and nitrification, to reduce the over-winter losses of soil mineral N. Consequently, incubation and field experiments were carried out on this subject.

Two preliminary incubation experiments with Malmo SiCL soil from Ellerslie were conducted to determine the effect of inhibitors on the rate of ammonification and subsequently nitrification of soil N. Nine hundred grams of air-dried Ap horizon (0-15 cm), were ground and passed through a 5 mm sieve, and were weighed into 11 cm diameter plastic pots. The pots were incubated at 20°C and 1/3 bar soil moisture tension. In all the treatments, except the control, inhibitors were injected at a depth of 10 cm below the soil surface in the center of the pot. Each treatment was duplicated in the first experiment and was triplicated in the second experiment. The soil samples taken at appropriate times, were analyzed for NH_4-N and NO_3-N contents. The description of the soil used for these experiments is given in Appendix A Table 1.

The soil contents of NH_4-N and NO_3-N (Table 41) after 10 days of

Table 41. The rates of release of NH_4-N and NO_3-N as influenced by the addition of inhibitors to a Malmo SiCL soil from Ellerslie in an incubation experiment at 20°C and 1/3 bar soil moisture tension.

Treatment†	Soil content of NH_4-N and NO_3-N (μg/g)		
	NH_4-N	NO_3-N	Total
0 day incubation	9 ± 0.6	10 ± 0.5	19 ± 1.1
10 days incubation:			
Control	7 ± 0.6	54 ± 2.1	61 ± 2.7
N-Serve* (20 μg/g)	30 ± 2.8	25 ± 0.9	55 ± 3.7
CS_2 (20 μg/g)	36 ± 4.3	12 ± 0.8	48 ± 5.1
CCl_3COCCl_3 (6 μg/g)**	37 ± 4.7	16 ± 1.8	53 ± 6.5
20 days incubation:			
Control	5 ± 0.7	68 ± 1.5	73 ± 2.2
N-Serve* (20 μg/g)	8 ± 1.4	66 ± 1.1	74 ± 2.5
CS_2 (20 μg/g)	35 ± 1.8	31 ± 1.4	66 ± 3.2
CCl_3COCCl_3 (6 μg/g)**	42 ± 3.5	22 ± 3.0	64 ± 6.5

†In all treatments, except the control, the inhibitors were injected at a depth of 10 cm.

*N-Serve: 2-chloro-6-trichloromethyl pyridine

**Chloroacetone (CCl_3COCCl_3)

incubation indicated that the addition of inhibitors to the soil slowed the amount of ammonification, but the differences were statistically significant only with CS_2 injected at a rate of 20 µg/g soil. The amount of NO_3 produced after 10 days of incubation was decreased significantly with all the inhibitors. After 20 days of incubation, N-Serve was not effective in suppressing nitrification, while CS_2 and CCl_3COCCl_3 injected at a rate of 20 µg/g, and 6 µg/g, respectively, were very effective in inhibiting nitrification.

In the other incubation experiment, the addition of inhibitors, such as ATC and CS_2 injected at a rate of 2 µg/g, to the soil significantly slowed the production of mineral N (Table 42). Although N-Serve tended to inhibit the formation of mineral N, the results were not statistically significant. All the inhibitors used in this experiment, suppressed the amount of NO_3 significantly. Among the inhibitors used, ATC was very effective, and was closely followed by CS_2.

The results of the very preliminary incubation experiments (Tables 41 and 42) indicated that the addition of inhibitors at reasonably low rates (20 µg/g, or less) may reduce the amount of ammonification of soil N, while substantially reducing nitrification. In one of the incubation experiments (Table 42) where ATC, CS_2, and N-Serve were compared, the maximum inhibition of ammonification of soil N and subsequent nitrification was with ATC. To find if ATC was an effective inhibitors of mineralization of soil N in the field, and was also effective in reducing winter losses of soil mineral N, two field experiments (one at Ellerslie-Malmo SiCL and the other at Westlock-

Table 42. The effect of inhibitors on the release of mineral N (NH_4-N + NO_3-N) in a Malmo SiCL from Ellerslie incubated at 20°C and 1/3 bar soil moisture tension.

Treatment†	Soil content of NH_4-N and NO_3-N (µg/g) NH_4-N	 NO_3-N	 Total
0 day incubation	6 ± 0.3	7 ± 0.6	13 ± 0.9
14 days incubation:			
Control	5 ± 0.3	62 ± 2.1	67 ± 2.4
ATC* (2 µg/g)	32 ± 2.5	17 ± 1.3	49 ± 3.3
N-Serve** (2 µg/g)	20 ± 1.8	42 ± 1.3	62 ± 3.1
CS_2 (2 µg/g)	22 ± 1.5	30 ± 0.9	52 ± 2.4
CS_2 (6 µg/g)	27 ± 1.2	18 ± 1.7	45 ± 2.9

†In all treatments, except the control, the inhibitors were injected at a depth of 10 cm.

*ATC: 4-amino-1,2,4-triazole hydrochloride.

**N-Serve: 2-chloro-6-trichloromethyl pyridine.

Falun CL) were set out in October, 1976. The description of soils used for the experiments is in Appendix A Table 1. ATC was mixed into the soil to a depth of 10 cm at a rate of 22 kg/ha. The individual plots were 6.8 m x 1.8 m. Each plot was replicated three times in a randomized complete block design. Soil samples were taken from the 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm and 90-120 cm depths, four times from October, 1976, to June, 1977 (the exact dates of sampling for each site are in Table 43). The soil samples were analvzed for NH_4-N and NO_3-N content.

On the Malmo SiCL soil, in plots which did not receive ATC, the mineral N increased from 53 kg N/ha on October 10, 1976, to 176 kg N/ha on March 20, 1977, while in plots where ATC was added, the mineral N increased to only 122 kg N/ha during the same period. In late April, after the snow melted, the mineral N in the control plots decreased to 79 kg N/ha, while in ATC plots, the mineral N decreased to 88 kg N/ha. That is, the calculation shows that the control plots mineralized 123 kg N/ha by late March but 97 kg mineral N/ha was lost by late April, while during the same period the ATC plots mineralized only 69 kg N/ha followed by the mineral N loss of 34 kg N/ha.

Apparently, the changes in mineral N content during winter took place only in the top 60 cm. From early October, 1976, to late March, 1977, the mineral N in the top 60 cm of the control plot increased by 124 kg N/ha while the mineral N content changed by 123 kg N/ha in the 0-120 cm depth. Similar results were obtained in plots which received ATC in the fall. On June 14, the mineral N contents in the control and

Table 43. Effect of ATC* on the release of mineral N (NH_4-N + NO_3-N) over the winter in stubble fields at Ellerslie (Malmo SiCL), and at Westlock (Falun CL) in 1976-77.

Treatment	Depth (cm)	Soil content of mineral N (kg/ha)**							
		Malmo SiCL (Ellerslie)				Falun L (Westlock)			
		Oct.10	Mar.20	Apr.25	June 14	Oct.24	Mar.9	May 5	June 15
Control	0-15	16	74	40	36	22	101	51	55
	15-30	7	50	18	21	11	32	16	21
	30-60	12	35	11	17	9	19	19	20
	60-90	10	11	6	10	9	11	11	11
	90-120	8	6	4	7	7	7	7	7
	0-60	35 c	159 a	69 b	74 b	42 d	152 a	86 c	96 b
	0-120	53 d (a)	176 a (a)	79 c (a)	91 b (a)	58 d (a)	170 a (a)	104 c (a)	114 b (b)
ATC*	0-15	16	46	45	43	22	42	63	74
	15-30	7	27	19	16	11	20	15	17
	30-60	12	32	13	15	9	17	14	19
	60-90	10	10	7	10	9	10	14	13
	90-120	8	7	4	8	7	6	7	7
	0-60	35 c	105 a	77 b	74 b	42 d	79 c	92 b	110aa
	0-120	53 c (a)	122 a (b)	88 b (a)	92 b (a)	58 d (a)	95 c (b)	113 b (a)	130 a (a)

*ATC: 4 - amino - 1,2,4 - triazole hydrochloride. ATC was applied at a rate of 22 kg/ha by mixing throughout the soil.

**In each of the rows for the 0-60 cm and the 0-120 cm depth, separately for Malmo SiCL and Falun L, the values for mineral N contents are significantly different (95% level of probability) when not followed by the same letter; and in each row, the values are significantly different (95% level of probability) when followed by bracketted letter which is not the same.

the ATC plots were almost the same, showing that there was no flush of mineral N from the use of ATC which we had expected to occur.

On the Falun CL soil, as on the previous soil, the apparent over-winter losses of mineral N in the control in the top 120 cm were considerable from March 9 to May 5 (Table 43). However, in the ATC plots on Falun CL soil, the mineral N content increased during the same period. From March 9 to May 5 the mineral N content in the control decreased by 66 kg N/ha, while in the ATC plot the mineral N increased by 18 kg N/ha. At this location, the soil content of mineral N in soil samples (0-120 cm depth) taken on June 15 was greater by 16 kg N/ha in plots with ATC than in the control.

On the average of the two locations, the apparent loss of soil mineral N in the control over the winter was 82 kg N/ha, whereas the loss of mineral N during the same period in ATC treatme[illegible]s only 8 kg N/ha. These field experiments demonstrate that th[illegible]-winter losses of soil-mineral N were reduced by using an inhibitor which suppressed ammonification as well as nitrification.

5. DISCUSSION

The present investigation was carried out to determine the extent of mineral N (NH_4-N + NO_3-N) losses over the winter, to determine the mechanisms by which the fall-applied N was lost, and to find some practical means of reducing these losses. Incubation and field experiments were conducted to meet the objectives of this study.

Fall and spring application of various N fertilizers were compared at 10 locations. The results for mineral N recovered in May (Tables 1 and 6), from these field plots sampled to a depth of 90 cm, showed that 38% of fall-applied urea N disappeared over the winter from the mineral N. The yields and N uptake of barley grain obtained in these field experiments supported this observation of fall-applied urea being less effective than spring-applied urea in increasing the yield and N uptake of barley grain (Tables 2 and 7). These results were in agreement with the findings of Widdowson et al., 1961; Devine and Holmes, 1964; Olson et al., 1964; Partridge and Ridley, 1974; Frye, 1977; and Paul and Rennie, 1977. The mineral N recovered (Table 5) in soil samples taken through the winter suggested that essentially, the applied N was not lost until early March, but by May, the fertilizer N was partially lost.

Thus the results of field experiments with N fertilizers established that substantial losses of fall-applied N occurred over the winter and it was reasonable to think that the mineral N arising from soil organic N, or issuing from fertilizers, would go through the same reactions, particularly those reactions related to their losses from the soil. Field experiments were set out to determine the over-winter losses of soil mineral N in non-fallowed and fallowed soils.

The mineral N contents (Table 8) of soil samples taken in late fall and during winter, from plots where no N was applied, showed that soil N was mineralized over the winter when the soil temperatures were near or below freezing. While the average amounts of mineral N in the 0-15 cm depth, of non-fallowed soils at the seven locations in the late fall was 7 kg N/ha, by December it increased to an average of 17 kg N/ha, and by early March the soil content of mineral N was 24 kg N/ha. The soil was frozen from December to March. The continual increase in the mineral N content in the frozen soil had not been reported previously for soils in the Prairie Provinces. Like fall-applied urea N, the soil mineral N present in March, was partially lost (average loss was 11 kg N/ha) by early May. As in the non-fallowed soils, there was a build up of mineral N during winter and loss of mineral N in early May after thawing in the fallowed soil (Table 14), but the magnitude was greater in the fallowed soil than in non-fallowed soils. On the average of three fallowed fields, the soil content of mineral N in early spring decreased by approximately 60 kg N/ha (Tables 13 and 14). These greater losses of mineral N in fallowed soils were due to the presence of larger amounts of NO_3 in the fallowed soils in the fall than in the non-fallowed soils.

It is known that under saturated conditions NO_3, if present in the soil, can be lost by leaching and denitrification while NH_4 does not. Therefore, one might conclude that the over-winter losses of mineral resulted from the formation of NO_3 during the winter from fall-applied urea. Therefore, the amount of nitrification of urea over the winter was determined. On the average of eight field experiments, approximately one-half of the urea applied the previous fall by mixing into the soil was found as NO_3 (Table 4) by early March. This occurred with cold soil temperatures (6.0, -0.4, -3.1, -4.7, -5.3 and -3.4°C for the months October to March, respectively, at 10 cm depth). The results of NO_3 formation in near-frozen or frozen soils under field conditions were confirmed by incubation experiments (Table 17) in the present investigation. Similarly, Frederick (1956) suggested that in some soils, the rate of nitrification at temperatures 0^{o} to $2^{o}C$ was great enough to oxidize 55 kg of NH_4-N/ha in two months.

The NO_3 of the mineral N pool can be lost by leaching, immobilization, and denitrification (note, however, that only leaching and denitrification are responsible for NO_3 losses from the soil system). The movement of NO_3 in soil is affected by mass flow, diffusion, and dispersion. Being soluble in water and not held on the soil exchange complex (except under strongly acidic soil conditions), NO_3 will generally move as far as the water moves. Mathematical equations have been developed to calculate the rate of movement of NO_3 in the soil. According to Gardner (1965), the concentration of NO_3 at any given depth (X) down a profile, when leaching of a narrow band from the surface occurs in the absence of plant uptake or denitrification is represented by:

$$CX = Co\ Xo\ (4\pi kt)^{-\frac{1}{2}} e\ \frac{-(X-vt)^2}{4kt}$$

where

CX = Concentration of NO_3 in the soil water (μg N/ml) at depth X (cm)
Co = Original concentration of NO_3 in the soil water (μg N/ml)
Xo = Original depth of soil (cm) in which the band of NO_3 was located
k = dispersion coefficient ($cm^2 day^{-1}$)
v = flow rate (cm day^{-1})
t = time (days)

The parameter k varies with flow rate. The parameter β which is the characteristic of the system was introduced by Day and Forsythe (1957). Since $k/v = \beta/2$, k in the above equation can be replaced by β (McGill, 1977) and then the formulation becomes

$$CX = Co\ Xo\ (2\pi\beta vt)^{-\frac{1}{2}} e\ \frac{-(X-vt)^2}{2\beta vt}$$

where all units are as previously defined. The important observation results from this equation is that the depth of NO_3 movement (X) exceeds the depth of water movement (vt) because of dispersion and diffusion.

However, these equations are not practical to calculate the movement of NO_3 over the winter down the soil profile under Alberta conditions where the soils freeze in winter to a depth of very approximately 100 cm (although it varies greatly from year to year). "Monitoring of soil moisture changes during the melt period showed that very little infiltration occurred until the soil had thawed (Granger et al., 1977)". In early spring, when snow melts, the soil underneath remains frozen and restricts the free movement of water down the profile by sealing soil pores with ice formed at the interface of thawed and frozen soil. This process of thawing and ice formation repeats many times before the whole frozen soil profile thaws. The thawing front moves very slowly (say 7 to 10 days for complete thawing of the frozen soil profile). Under these conditions, the relation between the depth of movement of NO_3 and the depth of water movement, will not follow the presently available water-solute movement models. Work conducted in Manitoba by Chang and Cho (1974), and Field-Ridley (1975) showed that the downward movement of applied NO_3 was due to mass flow.

Making the assumption that water movement is by mass flow, then the depth to which water moved after thawing in the present study was calculated from the data presented in Table 44 according to the following logic:

Moisture content of 0-14 cm soil on April 22 when the soil below was frozen = 70.4%
Moisture content while the soil was frozen = 25.3%
Total amount of precipitation from November, 1974, to April, 1975 = 8.0 cm
Actual amount of precipitation retained by the soil was calculated from the formula, $d = \frac{Pw \times D \times Db}{100}$

Where d = Depth of precipitation (cm) retained by the soil
D = Depth of soil (14 cm)
Db = $0.99 g/cm^3$
Pw = Water as % of soil weight retained by the soil (70.4 - 25.3 = 45.1)

$$d = \frac{45.1 \times 14 \times 0.99}{100} = 6.2 \text{ cm}$$

The 6.2 cm of winter precipitation which was retained by soil, will, after thawing, bring 41 cm depth of soil upto 1/3 bar moisture tension and this is the approximate depth to which the

Table 44. Depth of water needed to bring the various depths of a Malmo SiCL, to 1/3 bar soil moisture tension in April, 1975.

Depth (cm)	Db (g/cm^3)	Pw (%)	d(cm)*
0-15	0.99	15.7	2.3
15-30	1.03	14.6	2.3
30-60	1.21	12.3	4.5
60-90	1.35	10.9	4.4

*Depth of Water (d) needed to bring the various depths to 1/3 bar moisture tension was calculated by using the formula:

$$d = \frac{Pw \times D \times Db}{100}$$

Where Pw = (% of water at 1/3 bar soil moisture tension) - (% of water present in the soil at freeze up)
D = depth of soil (cm)
Db = bulk density of soil (gm/cm^3)

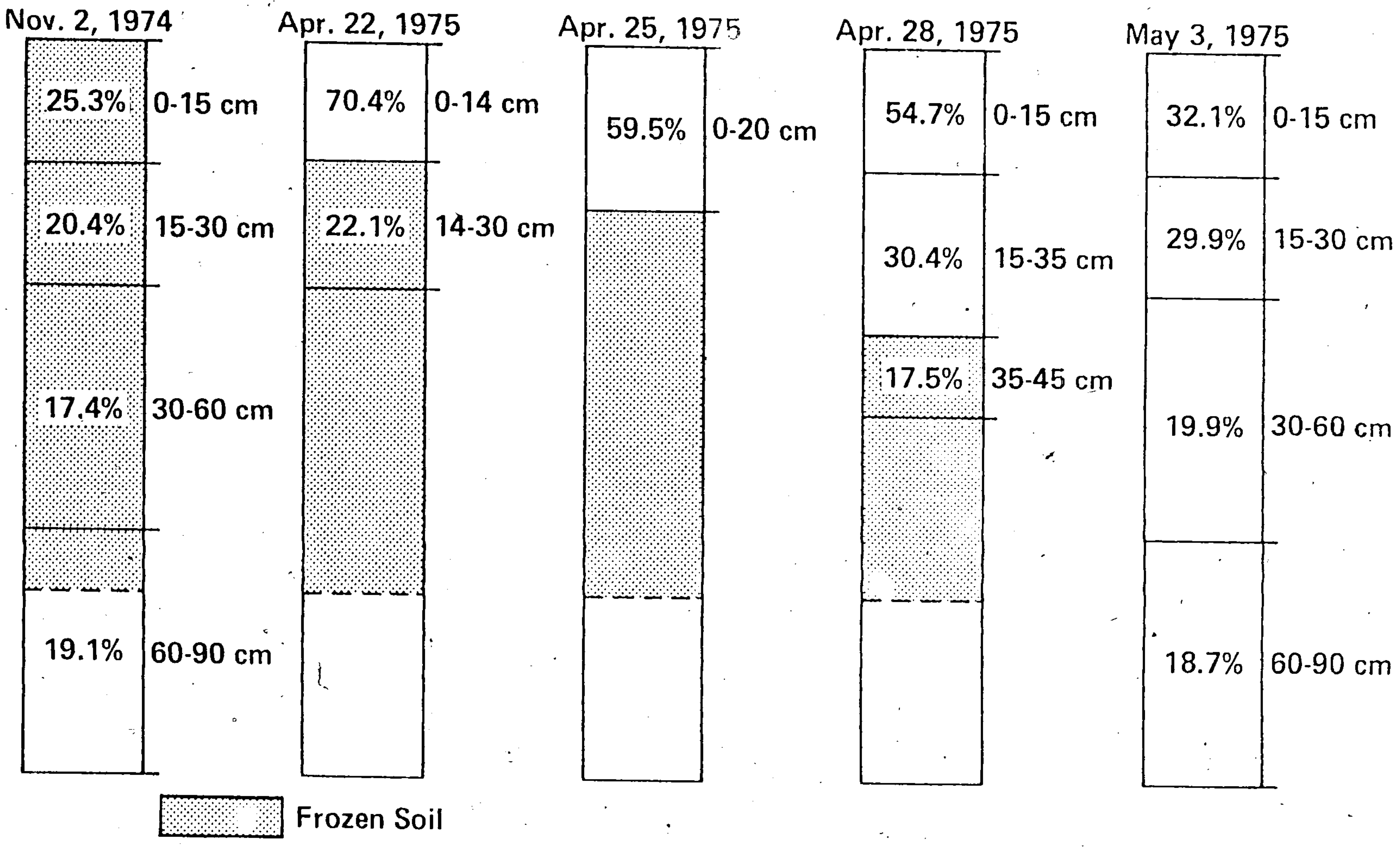

Figure 9. The % moisture content of a Malmo SiCL soil at Ellerslie at different times over the winter during 1974-75.

water will move soon after thawing.
Percent of total precipitation retained by the soil = $\frac{6.2}{8.0} \times 100$
= 78%
This means that 22% of the total precipitation was lost by runoff and evaporation.

These calculated results of water movement coincide with the field observations (Table 26). The soil moisture content in the 0-15 cm and in the 15-30 cm layers was considerably higher on May 3, 1975, than at freezing time (Nov. 2, 1974). There was very little increase in moisture content in the 30-60 cm layer on May 3 and no increase in moisture content below 60 cm depth (Fig. 9). A similar pattern of water movement was observed in another field at the same location in the same year (Table 45). Similar calculations for 1976-77 showed that snow water retained would wet 42 cm of soil to 1/3 bar soil moisture tension. Based on these calculations, it would appear unlikely that NO_3 leached below 42 cm during snow melt in 1977 (Table 46).

Table 45. Soil moisture content of a Malmo SiCL on November 2, 1974 (at the freeze up), and on May 3, 1975 (after the thaw).

Depth (cm)	Soil moisture (%)	
	Nov. 2	May 3
0-15	24.9	34.5
15-30	18.8	30.1
30-60	15.7	18.8
60-90	19.4	19.8

Table 46. Depth of water needed to bring the various depths of a Malmo SiCL, to 1/3 bar soil moisture tension in April, 1977.

Depth (cm)	Db (gm/cm^3)	Pw (%)	d(cm)*
0-15	0.98	21	3.1
15-30	1.06	17	2.7
30-60	1.26	13	4.9
60-90	1.33	10	4.0
90-120	1.39	10	4.2

*Depth of water (d) needed to bring the various depths to 1/3 bar soil moisture tension was calculated by using the formula:

$$d = \frac{Pw \times D \times Db}{100}$$

Where Pw = (% of water at 1/3 bar soil moisture tension) - (% of water present in the soil at freeze up)
D = Depth of soil (cm)
Db = bulk density of soil (gm/cm^3)

Total amount of precipitation from November, 1976 to April, 1977 was 10 cm.

The soil content of NO_3-N recovered from various depths upto 150 cm (Fig. 10) on March 4, 1977, in frozen soil and on April 18, 1977, after thawing to a depth of 55 cm showed that there was no change in NO_3-N content below the 60 cm depth and there was a decrease in NO_3-N in the surface layer down to a depth of 60 cm as shown by April sampling. On April 18, the soil thawed to a depth of 55 cm and there was no increase in the soil content of NO_3-N in the frozen soil showing that NO_3 did not diffuse through the frozen soil. The data on calculated depth of water movement, field observations on water movement, and NO_3 movement in the fallowed soil demonstrated that NO_3 probably did not leach below 60 cm. Similarly, the results of field experiments with commercial fertilizers (Tables 1 and 6) and the use of N^{15} labelled NO_3 (Table 26) under field conditions showed that leaching was not the mechanism responsible for the over-winter losses of fall-applied N. The results of the present investigation are in agreement with the findings of the study conducted on the movement of NO_3 in Manitoba by Field-Ridley (1975), which showed that applied NO_3-N at a rate of 550 kg N/ha as calcium nitrate, was retained primarily in the surface 25 or 30 cm of soil after two years of application.

Thus far it has been established that leaching does not seem to be the mechanism of over-winter losses of mineral N. Therefore, the apparent losses must be due to immobilization and denitrification. This conclusion was supported by field studies conducted in Manitoba by Field-Ridley (1975), in which low recoveries of applied NO_3 have

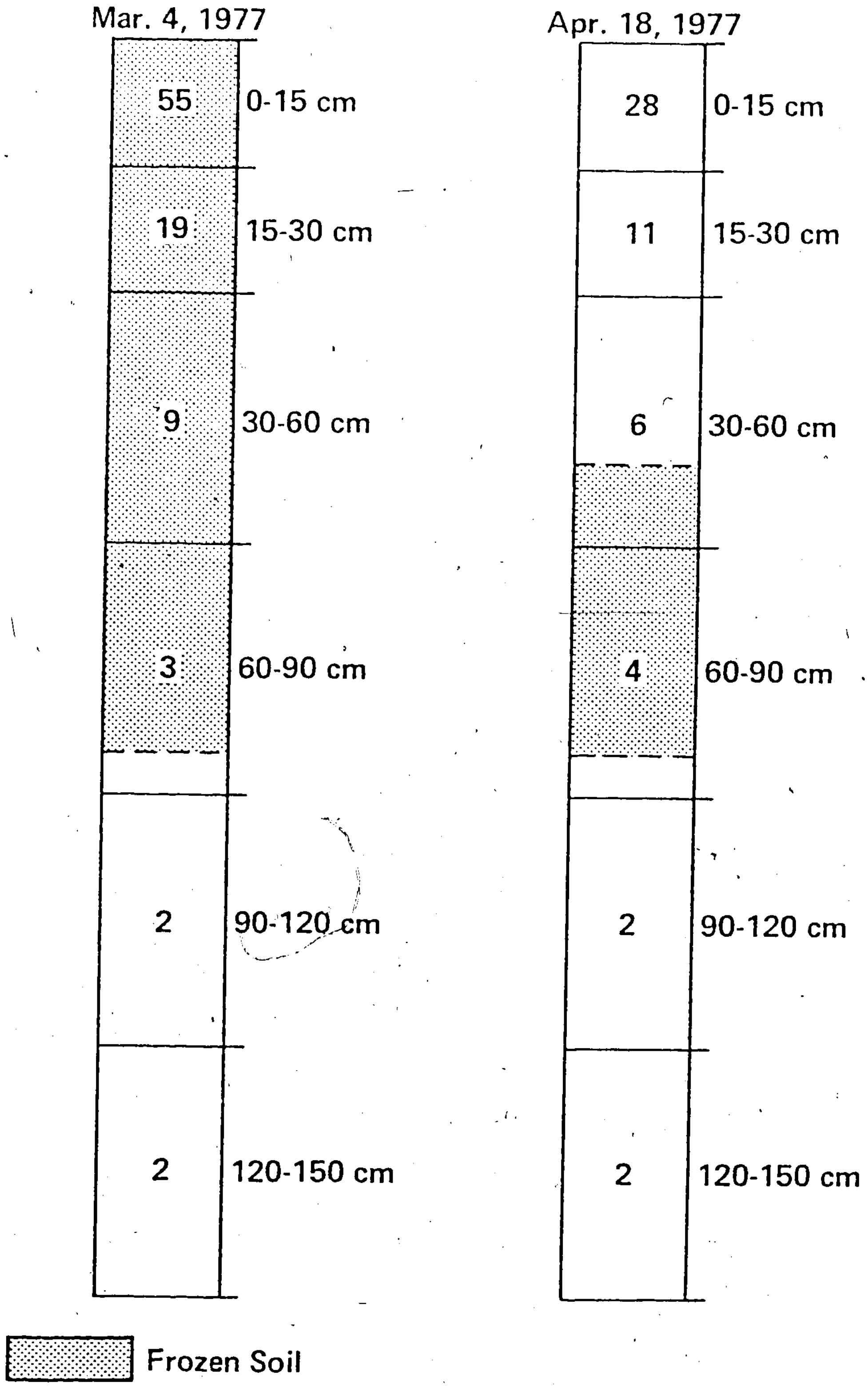

Figure 10. Soil content of NO_3-N (ppm) of a fallowed field at Ellerslie (Malmo SiCL) in March, and in April, 1977.

been attributed to both immobilization and denitrification. It was not possible from the results of field experiments with commercial fertilizers to establish how much of the missing mineral N was immobilized and how much denitrified. Therefore, to determine the fate of fall-applied N, one field experiment was carried out using N^{15} enrichment. The results of N^{15} labelled NO_3 showed that approximately one-third of the missing fall-applied N from the mineral N pool was recovered in the organic fraction of the soil.

Therefore, the rest of the losses of applied N from the mineral N pool must be due to denitrification. Laboratory incubation studies had indicated that potential losses could amount to 44 μg N/g soil during the period April 20 to 29 (Table 47). The potential losses through denitrification exceeded the actual losses as measured by N^{15} technique. Results of incubation studies on denitrification (Sacks and Barker, 1952; Nommik, 1956; and Bailey, 1976) conducted under saturated soil conditions with NO_3 suggested that almost all of the NO_3 lost from the soil could have been in the gaseous form.

Research work of Bremner et al. (1965), Wellman et al. (1968), Delwiche and Steyn (1970), Blackmer and Bremner (1976), and Chien et al. (1977), has demonstrated that a significant discrimination occurred between N^{14} and N^{15} during denitrification of NO_3. They suggested that in general isotopic fractionation results from the fact that N^{15} bearing molecules react more slowly than N^{14} bearing molecules during denitrification so that the substrate is enriched and the product is depleted in N^{15}. Therefore, the actual losses by denitrification

Table 47. The expected amount of NO_3-N loss in early spring, 1975, under field conditions (calculated on the basis of equations developed from the results of incubation experiments) from KNO_3 applied at a rate of 112 kg N/ha (or 75 µg N/g) to a Malmo SiCL at Ellerslie in fall, 1974.

Date	Soil temperature (°C) at 7.5 cm depth	Soil moisture tension (bars)	Expected NO_3-N loss (µg/g/day)*
April 20	1.7	Very wet	2.1
21	1.7	Very wet	2.0
22	2.2	0.002	2.2
23			2.1
24	3.8		2.2
25	5.4	0.009	4.2
26	6.1		4.9
27	8.3		7.3
28	11.7	0.01	8.9
29	13.2		8.1
			Total 44.0

*Expected NO_3-N loss (µg/g/day) = $\frac{Vm\ [S]}{Km + [S]}$ x RRNLFM x RRNLFT

Where Vm = Maximum rate of NO_3-N loss (µg/g/day)

S = Concentration of NO_3-N (µg/g)

(Km) = Michaelis Menten constant (µg/g)

RRNLFM = Relative rate of NO_3-N loss for soil moisture

RRNLFT = Relative rate of NO_3-N loss for soil temperature

Observed loss of NO_3-N in May, 1975, from KNO_3 applied in fall, 1974, at a rate of 112 kg N/ha (approximately 75 µg NO_3-N/g), as determined by using N^{15} technique was = 31.6 µg N/g.

would be more than the losses observed by using N^{15} tracer. In the present investigation, the actual over-winter losses of fall-applied N by denitrification could have been more than the observed losses as determined by N^{15} technique.

Since under water saturated soil conditions NO_3 is subject to losses by denitrification while NH_4 is not, therefore one would expect more losses from NO_3-N than from NH_4-N after spring thaw. In the present study, the apparent loss of fall-applied commercial fertilizers over the winter was greater in plots which received calcium nitrate (50% loss) than urea-treated plots (38% loss). Similarly, in the N^{15} experiment, the losses of fall-applied N by denitrification were 1.3 times greater in KNO_3-treated plots than in urea-treated plots. The lower apparent recovery of fall-applied NO_3-N than urea in the soil samples taken the following spring corresponded with the yield and N uptake of barley grain in the present study where fall-applied calcium nitrate was inferior to fall-applied urea (Table 2). This supported the suggestion that NO_3 is lost over the winter more than NH_4. Similarly the field work reported by Devine and Holmes (1964) has shown that autumn-applied ammonium sulphate resulted in higher average yield of winter-wheat than did calcium nitrate.

The N uptake data plotted in Fig. 1 showed that the relative efficiency of fall versus spring application of urea was increased by delaying the application in October. This higher efficiency of urea applied in late October as opposed to early October could be due to conversion of lower amounts of urea to NO_3. Following this observation, one would suggest that over-winter losses of mineral N could be prevented by inhibiting the formation of NO_3 from ammonium-based fertilizers. Therefore, incubation and field experiments were conducted to find some practical means to reduce the rate of nitrification of urea and subsequent conservation of fall-applied N.

The incubation experiments showed that thiourea (a nitrification inhibitor), at a rate of 40 μg/g of soil, was effective in inhibiting nitrification of urea for at least six weeks when pelleted with urea (two parts of urea and one part of thiourea) and placed in bands (Table 30). The particular interest of these experiments was to find methods of maximizing the effect of thiourea in inhibiting nitrification of urea applied in fall so that most of the fall-applied urea would remain as NH_4 which is much less subject to losses than NO_3 (Wagner and Smith, 1958; and Parker, 1972). The amounts of thiourea found effective in inhibiting nitrification of urea in the present study were much lower than the levels which have previously been reported necessary to control nitrification (Fuller et al., 1950).

The results of the field experiments (Tables 32, 34 and 37) showed that the amount of nitrification was lower in plots where urea alone was placed in bands than where it was mixed into the soil. The lower rate of nitrification of band placement than mixed application of NH_4-N has also been reported (Larson and Kohnke, 1946; Gasser, 1965; and Leitch, 1973). The lower rates of nitrification of banded urea were probably due to higher concentrations of NH_4, produced by hydrolysis of urea (in its vicinity), which probably inhibited the activity of nitrifying bacteria. Higher concentrations of NH_4 in the bands, than in the area between the bands, has been reported (Leitch, 1973). Similarly, in incubation studies, the addition of $(NH_4)_2SO_4$ to soil at a rate of 300 μg N/g depressed the rate of nitrification (Table 27). The addition of thiourea to urea increased the inhibition effect greatly when placed in bands. A similar trend in inhibition of nitrification of $(NH_4)_2SO_4$ placed in bands by the use of thiourea has been obtained [illegible] (1973).

In [illegible] study, the field experiments set out in October, 1973, [illegible] 1974, showed that 45 kg thiourea pelleted with 90 kg urea/ha [illegible] placed in bands inhibited nitrification of urea substantially over the winter (Tables 34 and 37) and prevented the losses of fall-applied N (Tables 35 and 38). A very large amount of thiourea (1523 kg of thiourea/ha) was required to inhibit nitrification of NH_4 for upto 24 weeks when mixed into the soil (Hamlyn and Gasser, 1967). The field experiments demonstrated that the problem of very large amounts of thiourea necessary for inhibiting nitrification of NH_4 under field conditions can be overcome in part by pelleting thiourea with urea and placing the pellets in bands.

The use of inhibitors has been reported to increase the yield and N uptake of crops. N-Serve (2 - chloro, 6 - trichloromethyl pyridine) when used with ammonium sulphate increased the N uptake of winter-wheat more than autumn-applied ammonium sulphate alone (Gasser and Hamlyn, 1968; and Huber et al., 1969). Huber and Watson (1972) found that N-Serve prevented N loss when used with fall-applied ammonium sulphate. This treatment prevented the NO_3 formation from fall-applied NH_4 and consequently reduced the severity of foot rot of winter-wheat caused by Cercosporella. Similarly in the present study, the pelleting of thiourea with urea and placement of this fertilizer in bands in the fall increased the yield of barley grain by 6.4 quintals/ha over the fall-applied urea alone (Table 40). Higher yield and N uptake of barley grain with urea + thiourea (2:1) as compared to urea alone were not due to pathological differences because no evidence of any disease to barley plants was observed in this study. The increase in yield of barley grain by urea + thiourea (2:1) banded in fall was about 85% of the increase in yield from urea alone banded in the spring at the time of seeding.

These field experiments demonstrated that thiourea applied in the fall inhibited nitrification and therefore reduced the over-winter losses of fall-applied urea. If soil mineral N and the fertilizer mineral N react in a similar manner, then the inhibitors which suppress both ammonification and nitrification, may reduce the over-winter losses of soil mineral N.

In incubation experiments, the addition of inhibitors (ATC (4 - amino - 1,2,4 - triazole hydrochloride), N-Serve, CS_2, and CCl_3COCCL_3) to soil lessened the amount of ammonification and nitrification of soil N (Tables 41 and 42). Of the four inhibitors used, ATC was the most effective. To determine the effectiveness of ATC under field conditions, ATC was mixed into the soil at a rate of 22 kg/ha in two farm fields in fall, 1976. The application of ATC in the fall slowed the release of soil mineral N from fall through winter, and substantially reduced the amount of soil mineral N lost over the winter (Table 43). It was expected that a flush of mineral N could be found, but it was not detected. By way of speculation, the use of some of the inhibitors that slow both ammonification and nitrification, might be a practical way of reducing over-winter losses of soil N under farm conditions in the Prairie Provinces. This is especially true for fallowed fields, which normally accumulate large amounts of mineral N and then lose much of it over the winter.

In summary, the results showed that there were substantial over-winter losses of mineral N from fall-applied fertilizers as well as from soil mineral N. These mineral N losses were mainly by denitrification. Approximately one-fifth of the fall-applied N was recovered in the organic fraction of soil N. The over-winter losses of fall-applied urea were prevented by pelleting thiourea (a nitrification inhibitor) with urea and placing this fertilizer in bands. Losses of soil mineral N were reduced by the application of an inhibitor (ATC) to soil. Some of the other practical implications resulted from this study will be discussed in the following paragraphs.

The efficiency of fall-applied ammonium-based fertilizers depended on when conditions favorable for nitrification occurred relative to conditions favoring N loss. If conditions favorable for N loss occurred before nitrification, one would expect lower N loss than if such conditions occurred after NH_4 was nitrified. The N uptake data plotted in Fig. 1 indicated that the efficiency of fall relative to spring application was considerably lower with urea applied in early October than with urea applied in late October. For example the relative efficiency of fall vs spring application decreased from 82% with urea applied on October 31 to 41% with urea applied on October 4. The linear regression equation, $Y = 35.3 + 1.49 X$ (where X is the date of application in October) could be used to predict the relative efficiency of fall vs spring application of urea in October and may be useful to producers for choosing the date of urea application in fall.

If the main reason for over-winter N losses is denitrification at spring thawing time or leaching of NO_3, it would be expected that the date of fall application would have little effect on the relative efficiency of a NO_3 fertilizer. The experimental data supported this hypothesis, since the relative efficiency of $Ca(NO_3)_2$ increased from 35% on October 4 to only 51% on October 31 (Fig. 2).

In three fallowed fields, apparently 57 kg of soil mineral N per hectare disappeared over the winter. In the N^{15} experiment with fall-applied N, approximately one-third of the missing mineral N applied was immobilized. Therefore, the rest of the missing mineral N (i.e., 67% of 60 kg N = 40 kg N/ha) from the soil mineral N in the 0-120 cm depth appeared to be lost by denitrification. If losses of 40 kg mineral N per hectare (average of only three fallowed fields) occurred in most of the fallowed soils, then the annual over-winter losses of soil N would be approximately 440,000 tons in the Prairie Provinces from fallowed soils alone. These calculations were based on the assumption that approximately 11 million hectares of cultivated land were fallowed each year in the Prairie Provinces. The soil mineral N losses over the winter in the top 15 cm layer on stubble soils would amount to 200,000 tons of mineral N. These large overwinter losses of soil mineral N may be of some concern to soil testing programs for available N, inasmuch as the soil samples are generally taken in the fall.

The presence of NO_3 at thawing time is a prerequisite for any losses of fall-applied N. Therefore, some part of the study was devoted to determining the rates of NO_3 formation from NH_4 and the rate of NO_3 losses in the laboratory at different levels of temperature and moisture.

Nitrification was sensitive to high temperature as evidenced by the increased rate of nitrification with increasing incubation temperature from 4° to 20°C, and decreased with further increase in temperature (Table 17). There was no NO_3 formation at 40°C which agrees with the findings of Meiklejohn (1954). Tyler et al. (1959) have reported that nitrification of added NH_4 occurs at temperatures as low as 3°C. Results of a similar nature were obtained in the present study. The rapid nitrification in all the three soils at 20°C, and very slow nitrification at 30°C, suggested that the optimum temperature close to 35°C reported by Myers (1974) is higher than for soils used in the present study. The variation in optimum temperature for nitrification for soils from different climatic regions probably exists because the nitrifying bacteria in soils may vary in their adaptabilities to temperatures (Thiagalingam and Kanehiro, 1973).

The measurable rates of nitrification (Table 18) at 15 bar soil moisture tension are in agreement with the results of Miller and Johnson (1964), and Dubey (1968). The maximum rate of nitrification at 1/3 bar soil moisture tension is in agreement with the findings of Justice and Smith (1962). The absence of nitrification at 0 bar soil moisture tension probably was due to the shortage of free O_2 in the soil, caused by excess water. Similar results have been reported by Miller and Johnson (1964), and Alexander (1965). The absence of nitrification at 0 bar is contrary, however, to the findings of Dubey (1968) who reported appreciable nitrification at 0 bar soil moisture tension, but he did not offer any reason for this behaviour.

The rate of NO_3-N loss (Table 22) at 4°C in the present study was higher than the NO_3-N loss which has been reported to be quite insignificant at 3°C (Nommik, 1956). This could be due to the difference in the type of micro-organisms present in soils from two different climatic regions because the micro-organisms in soils developed under different climates would probably be different in their adaptation to temperature. The optimum temperature of 65° and 60°C for NO_3 disappearance reported by Nommik (1956), and Bremner and Shaw (1958), respectively, may be much higher than for soils used in this study where the maximum rate of NO_3 loss was at 40°C (Table 22).

The high rate of NO_3 loss under flooded conditions (Table 23) is in agreement with the findings of Bremner and Shaw (1958), and

Greenwood (1962). At the same time, NO_3 loss can occur at moisture content near permanent wilting point, probably due to creation of micro-anaerobic sites within the aggregates (Greenwood, 1961; and Greenwood and Berry, 1962). On the basis of the results of the incubation experiments one can expect considerable losses of NO_3 in early spring after thawing, when the soil is saturated and soil temperature is sufficiently high (5°C). From the results of incubation experiments, it seems that the soil moisture and temperature in late fall and during winter under snow cover are high enough to result in NO_3 formation from ammonium-based N fertilizers applied in late fall.

In conclusion, the results of incubation experiments for nitrification and for NO_3-N losses can be used to predict the rate of NO_3 production from NH_4 and NO_3 losses over a range of soil moisture levels and temperatures encountered in the field.

6. CONCLUSIONS

This thesis has touched upon several topics concerning soil N and fertilizer N: the over-winter losses of mineral N issuing from fertilizer as well as from soil N; the mechanisms of over-winter losses of mineral N; and the ways of preventing the losses of mineral N. The following conclusions were drawn:

In 10 field experiments, 38% of urea N applied in the previous fall at a rate of 56 kg N/ha was lost from the mineral N pool over the winter. Fall-applied urea resulted in about 10 quintals/ha (1 quintal $\approx$ 100 kg) lower yield and one-half as much N uptake by barley grain as did spring-applied urea. Considerable over-winter losses of soil-derived mineral N were observed. For example, in three fallowed soils, approximately 60 kg of soil mineral N disappeared over the winter.

The N^{15} study, deep profile sampling and calculation of spring water movement showed that the losses could not be accounted for by leaching. Further the N^{15} experiment showed that only 22% of the applied N as KNO_3 was immobilized. Hence it was concluded that 39% of this fertilizer was lost by denitrification. It is suggested, and laboratory data support the suggestion, that ammonification and nitrification occur throughout the winter leading to large amounts of NO_3^- just prior to spring thaw. At the time of spring thaw, the water saturated conditions of the soil above the frozen layer lead to relatively rapid denitrification of the accumulated NO_3.

Nitrification was slowed by placing urea in bands and the effect was much greater when pelleted urea + thiourea (2:1) was in the bands. Slowing nitrification of fall-applied urea, by applying thiourea with urea, reduced the over-winter losses. Hence this increased the yield of barley grain by 6.4 quintals over urea banded alone in the fall in 10 field experiments. The N uptake by barley grain with urea + thiourea (2:1) banded in the fall was 1.5 times greater than with urea banded alone in the fall. Similarly, the losses of soil mineral N were reduced by the application of the inhibitor ATC.

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8. APPENDICES

APPENDIX A

MISCELLANEOUS DATA TABLES

Table 1. Description of the soils (0-15 cm) used in experiments.

Location	Designation	Soil Classification	Soil Series	Texture	pH (1:2.5)	% O.M. (O.c. x 1.72)
Blue Sky	Bl	Dark Gray Chernozemic	Albright	CL	6.7	4.7
Bon Accord	Bn	Black Chernozemic (Eluviated)	Angus Ridge	CL	6.6	6.9
Breton	Br	Gray Luvisol	Breton	L	6.2	2.2
Buford	Bu	Gleysol	Navarre Meadow	CL	6.4	11.3
Calmar	Cl	Eluviated Gleysol	Demay	L	8.2	4.3
Canwood I	CnI	Gray Luvisol	Whitewood	L	7.1	3.5
Canwood II	CnII	Gleysol	Meadow	CL	8.0	7.0
Delacour	Dl	Black Chernozemic	Airdrie	CL	6.9	6.3
Egremont	Eg	Dark Gray Chernozemic	Falun	L	7.3	5.0
Ellerslie	El	Black Chernozemic	Malmo	SiCL	6.0	10.5
Smoky Lake	Sm	Gray Luvisol	Cooking Lake	SL	6.5	2.5
Vilna	Vn	Gray Luvisol	La Corey	SL	6.1	5.0
Warspite	Wr	Dark Gray Chernozemic	Falun	CL	6.6	6.6
Westlock	Wt	Dark Gray Chernozemic	Falun	CL	6.4	5.2

Table 2. pH of soils used in experiments.

Location	0-15 cm	15-30 cm	30-60 cm	60-90 cm
Blue Sky	6.7	7.0	7.1	7.7
Bon Accord	5.6	6.1	5.8	7.6
Breton	6.[illegible]	6.3	6.6	n.d.*
Calmar	8.2	8.6	8.7	8.7
Canwood	7.1	7.2	7.7	n.d.*
Delacour	5.9	6.1	6.4	n.d.*
Egremont	7.3	7.8	8.0	8.3
Ellerslie	6.0	6.1	6.2	6.0
Smoky Lake	6.5	7.2	7.2	7.3
Warspite	6.6	7.0	7.4	n.d.*

*Not done

Table 3. Soil moisture characteristics of soils (0-15 cm)

Location	Percent moisture				
	Air dry	Saturation	1/3 bar	7 bars	15 bars
Blue Sky	2.8	55.9	29.7	21.3	8.6
Bon Accord	5.1	58.5	30.3	20.5	13.5
Breton	1.9	46.9	24.9	15.7	8.6
Calmar	4.0	48.4	26.3	18.9	10.9
Canwood	3.7	46.3	23.2	15.3	7.0
Delacour	4.1	59.4	31.2	23.5	16.9
Egremont	3.6	40.2	20.7	13.8	9.8
Ellerslie	5.6	76.1	39.7	28.9	18.1
Smoky Lake	1.3	30.4	15.5	10.9	6.2
Warspite	3.5	55.2	29.2	20.8	12.3

Table 4. Bulk density (Db) of soils.

Location	0-15 cm	15-30 cm	30-60 cm	60-90 cm	90-120 cm
Blue Sky	1.36	1.39	1.59	1.64	1.70
Bon Accord	1.32	1.30	1.66	1.70	1.81
Breton	1.31	1.41	1.74	n.d.*	n.d.*
Calmar	1.61	1.89	2.01	1.98	1.94
Canwood	1.39	1.47	1.54	1.61	1.64
Delacour	1.14	1.23	1.42	1.53	n.d.*
Egremont	1.30	1.50	1.69	1.71	1.77
Ellerslie	0.99	1.03	1.21	1.45	1.59
Smoky Lake	1.44	1.50	1.49	1.51	n.d.*
Warspite	1.23	1.40	1.43	1.47	n.d.*

*Not done

Table 5. Mechanical analysis of soils used in experiments.

Location	Depth (cm)	%Sand	%Silt	%Clay	Textural Class
Blue Sky	0-15	36	32	32	CL
	15-30	30	32	38	CL
	30-60	22	18	60	C
Bon Accord	0-15	24	40	36	CL
	15-30	32	38	30	CL
	30-60	38	32	30	CL
	60-90	12	38	50	C
Breton	0-15	44	32	24	L
	15-30	32	36	32	CL
	30-60	34	26	40	CL
Calmar	0-15	43	30	27	L
	15-30	38	23	39	CL
	30-60	36	28	36	CL
	60-90	38	26	36	CL
Canwood	0-15	38	41	21	L
	15-30	24	46	30	CL
	30-60	44	30	26	L
Delacour	0-15	34	37	29	CL
	15-30	26	38	36	CL
	30-60	[illegible]	36	38	CL
Egremont	0-15	50	28	22	L
	15-30	40	26	34	CL
	30-60	42	20	38	CL
Ellerslie	0-15	20	42	38	SiCL
	15-30	22	40	38	SiCL
	30-60	22	38	40	CL
Smoky Lake	0-15	69	21	10	SL
	15-30	56	20	24	SCL
	30-60	58	18	24	SCL
	60-90	40	24	36	CL
Warspite	0-15	34	36	30	CL
	15-30	28	38	34	CL
	30-60	32	32	36	CL

Table 6. The content of NH_4-N and NO_3-N of soils in late September, 1973 used for field experiments.

Location	The soil content of NH_4-N and NO_3-N (kg/ha) in 0-15 cm depth		
	NH_4-N	NO_3-N	Total
Calmar	4.6	7.3	11.9
Ellerslie	7.1	24.8	31.9
Smoky Lake	4.2	4.3	8.5
Warspite	3.3	9.5	12.8

Table 7. The content of NH_4-N and NO_3-N of soils in May, 1974

Location	The soil content of NH_4-N and NO_3-N (kg/ha)											
	0-15 cm			15-30 cm			30-60 cm			60-90 cm		
	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total
Calmar	7.1	10.4	17.5	3.4	5.0	8.4	4.0	4.1	8.1	2.1	3.2	5.3
Ellerslie	6.4	20.0	26.4	6.0	5.1	11.1	5.6	5.7	11.3	4.8	3.8	8.6
Smoky Lake	6.4	8.1	14.5	4.6	5.6	10.2	4.0	4.7	8.7	2.9	4.9	7.8
Warspite	8.6	6.1	14.7	5.2	3.6	8.8	5.0	3.2	8.2	3.1	2.8	5.9

Table 8. The content of NH_4-N and NO_3-N in the 0-15 cm, 15-30 cm and 30-60 cm depth in soils used for field experiments in late fall, 1974.

Location	The soil content of NH_4-N and NO_3-N (kg/ha)								
	0-15 cm			15-30 cm			30-60 cm		
	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total
Blue Sky	2.6	3.4	6.0	1.0	1.2	2.2	0.9	0.6	1.5
Bon Accord	3.4	4.1	7.5	2.4	1.1	3.5	0.4	0.6	1.0
Calmar	2.1	2.4	4.5	3.2	1.8	4.0	0.6	0.4	1.0
Canwood	2.4	3.9	6.3	1.3	1.6	2.9	0.4	0.2	0.6
Delacour	1.9	2.1	4.0	1.2	1.0	2.2	0.6	0.2	0.8
Egremont	2.9	2.1	5.0	[illegible].4	1.2	3.6	0.8	0.6	1.4
Ellerslie	2.4	4.1	6.5	2.4	1.3	3.7	1.3	1.0	2.3

Table 9. The content of NH_4-N and NO_3-N in the 0-15 cm, 15-30 cm, 30-60 cm, and 60-90 cm depth in soils in early May, 1975.

Location	The soil content of NH_4-N and NO_3-N (kg/ha)											
	0-15 cm			15-30 cm			30-60 cm			60-90 cm		
	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total	NH_4-N	NO_3-N	Total
Blue Sky	5.4	4.7	10.1	1.3	1.3	2.6	2.6	2.0	4.6	1.4	3.4	4.8
Bon Accord	2.9	8.6	11.5	2.1	2.4	4.5	3.4	2.6	6.0	1.8	2.8	4.6
Calmar	5.2	11.8	17.0	2.6	4.4	7.0	5.4	4.2	9.6	1.1	2.2	3.3
Canwood	2.2	5.2	7.4	2.2	2.4	4.6	2.4	5.0	7.4	1.7	2.6	4.3
Delacour	3.9	4.4	8.3	2.9	2.9	5.8	2.8	4.9	7.7	n.d.*	n.d.*	n.d.*
Egremont	4.4	13.0	17.4	1.6	5.6	7.2	1.8	3.1	4.9	1.8	3.2	5.0
Ellerslie	9.5	21.5	31.0	8.5	15.9	24.4	4.4	19.3	23.7	1.7	6.0	7.7

*Not done

Table 10. N uptake of barley straw from four field experiments in 1973-74 with fall and spring applications of N fertilizers.

Fertilizers	Method of application	N uptake of barley straw (kg/ha)							
		*Site I		*Site II		*Site III		*Site IV	
		Fall	Spring	Fall	Spring	Spring	Fall	Fall	Spring
Control		6.0	6.1	3.7	3.7	4.8	4.6	2.6	2.6
Ammonium nitrate	Mixed	9.1	9.1	5.5	10.7	12.5	9.3	5.4	5.6
	Banded	9.5	10.0	5.7	11.4	12.2	10.4	5.8	5.5
Urea	Mixed	9.8	8.2	5.9	8.5	9.1	7.8	5.2	4.8
	Banded	9.0	8.0	6.3	9.0	9.6	8.6	5.1	5.2
Urea + thiourea (2:1)	Mixed	8.4	8.6	6.8	9.4	8.1	9.2	4.8	5.4
	Banded	8.5	7.8	7.9	9.6	8.7	8.7	4.6	5.5
Calcium nitrate	Mixed	10.1	10.4	5.2	10.1	7.7	6.4	4.2	5.2

*Site I	- Falun CL	(at Warspite, Alberta).
Site II	- Demay L	(at Calmar, Alberta).
Site III	- Malmo SiCL	(at Ellerslie, Alberta).
Site IV	- Cooking Lake SL	(at Smoky Lake, Alberta).

Table 11. N uptake of barley straw from four field experiments in 1974-75 with fall and spring application of N fertilizers.

Fertilizers	Method of application	N uptake of barley straw (kg/ha)							
		*Site I		*Site II		*Site III		*Site IV	
		Fall	Spring	Fall	Spring	Spring	Fall	Fall	Spring
Control		3.4	3.6	2.6	2.5	2.4	2.6	2.9	3.0
Urea	Mixed	5.2	11.2	4.7	7.0	6.1	8.1	5.4	8.2
	Banded	6.9	10.9	6.0	8.1	5.2	7.9	6.3	9.6
Urea + thiourea (2:1)	Mixed	8.7	8.3	5.9	6.9	6.0	7.0	6.4	8.6
	Banded	10.1	6.7	6.1	6.8	5.9	6.8	6.1	7.5

*Site I - Demay L (at Calmar, Alberta).
Site II - Whitewood L (at Canwood, Saskatchewan).
Site III - Albright CL (at Blue Sky, Alberta).
Site IV - Falun L (at Egremont, Alberta).

Table 12. N uptake of barley straw from two field experiments in 197 -75 from fall and spring application of N fertilizers.

Fertilizers	Method of application	N uptake of barley straw (kg/ha)			
		*Site I		*Site II	
		Fall	Spring	Fall	Spring
Control		2.1	2.1	6.4	6.6
Urea	Mixed	3.2	9.8	10.3	10.2
	Banded	2.9	11.9	9.6	11.9
Urea + thiourea (2:1)	Mixed	3.1	8.3	9.2	12.3
	Banded	5.7	3.9	10.9	7.4
Ammonium nitrate	Mixed	3.7	9.2	10.1	13.7
	Banded	3.7	8.1	10.0	12.9
Calcium nitrate	Mixed	3.6	6.8	9.3	12.6
	Banded	4.1	8.4	9.7	12.8
Ammonium sulfate	Mixed	4.2	11.7	11.1	12.0

*Site I - Angus Ridge CL (Bon Accord, Alberta).
Site II - Malmo SiCL (Ellerslie, Alberta).

Table 13. Soil moisture content of various soils at different times in 1974-75.

Location	Date	Soil moisture (%) 0-15 cm	15-30 cm	30-60 cm	60-90 cm
Blue Sky	Oct. 30, 1974	25.3	26.3	21.3	
	Dec. 6, 1974	26.5			
	March 1, 1975	27.7			
	May 18, 1975	29.1	28.3	22.0	
Bon Accord	Oct. 7, 1974	29.8			
	Oct. 21, 1974	38.7			
	Oct. 27, 1974	40.3	34.8	27.8	29.4
	Dec. 6, 1974	38.1			
	Feb. 28, 1975	42.8			
	April 18, 1975	63.1	(Free water on soil surface and frozen ground below 20 cm)		
	April 24, 1975	42.8	38.9	(The ground was frozen below 35 cm)	
	May 2, 1975	31.4	37.0	28.4	30.1
Calmar	Oct. 6, 1974	17.6			
	Oct. 22, 1974	25.8			
	Oct. 29, 1974	27.0	17.2	16.7	29.9
	Dec. 10, 1974	25.9			
	March 8, 1975	28.1			
	April 20, 1975	41.7	29.1	(The ground was frozen below 28 cm)	
	May 5, 1975	28.8	24.4	23.1	31.1
Canwood	Oct. 16, 1974	18.7	18.6	12.0	16.9
	Dec. 27, 1974	17.8			
	March 15, 1975	19.9			
	May 7, 1975	20.4	18.1	14.3	17.2
Delacour	Oct. 8, 1974	9.9			
	Oct. 25, 1974	11.3	14.2	11.3	
	Dec. 8, 1974	10.0			
	Feb. 26, 1975	10.9			
	April 11, 1975	10.5			
	April 26, 1975	9.1			
	May 9, 1975	16.4	19.3	10.9	
Egremont	Oct. 7, 1974	12.6			
	Oct. 20, 1974	10.0			
	Oct. 27, 1974	22.9	15.2	11.5	
	Nov. 7, 1974	21.7	17.8	10.1	16.1
	Dec. 6, 1974	20.6			
	March 11, 1975	21.7			
	April 16, 1975	46.2			

Table 13. (Continued)

Location	Date	Soil moisture (%)			
		0-15 cm	15-30 cm	30-60 cm	60-90 cm
	April 24, 1975	39.8	26.4	16.8 (The ground was frozen below 40 cm)	
	May 11, 1975	24.9	21.5	14.9	17.0
Ellerslie (Field I)	Oct. 6, 1974	18.1			
	Oct. 20, 1974	24.4			
	Oct. 29, 1974	25.9	19.7	14.1	
	Nov. 17, 1974	24.9	18.8	14.7	19.4
	Dec. 4, 1974	26.6			
	March 11, 1975	23.1			
	April 21, 1975	73.2	(The ground was frozen below 14 cm)		
	April 28, 1975	59.4	34.9		
	May 3, 1975	34.5	30.1	18.9	19.8
Ellerslie (Field II)	Oct. 27, 1974	22.2	18.9	16.1	19.6
	Nov. 2, 1974	24.2	20.4	18.4	19.1
	Dec. 4, 1974	24.9			
	March 11, 1975	25.3			
	April 21, 1975	70.4	(The ground was frozen below 12 cm)		
	April 28, 1975	54.7	30.4 (The ground was frozen below 35 cm)		
	May 3, 1975	29.1	29.9	18.9	18.7

Table 14. Nitrogen fertilizers and other chemical compounds used in experiments.

Chemical Name	Chemical formula	%N	Solubility in water (g/100 ml)
Ammonium nitrate	NH_4NO_3	34	118.3 @ 0°C
Ammonium sulphate	$(NH_4)_2SO_4$	21	70.6 @ 0°C
Calcium nitrate	$Ca(NO_3)_2$	15.5	50.5 @ 0°C
Calcium sulphide	CaS	---	0.021 @ 15°C
Phosphorus penta-sulphide	P_2S_5	---	Insoluble
Thioacetamide	$NH_2CS\ CH_3$	18.7	---
Thiourea	$NH_2CS\ NH_2$	36.8	9.18 @ 13°C
Urea	$NH_2CO\ NH_2$	46	78.0 @ 0°C

Table 15. The pH of three Alberta soils after incubation with various levels of NH_4-N as $(NH_4)_2SO_4$.

Treatment	Soil pH(1:2.5)		
	Soil I*	Soil II**	Soil III***
Control	6.4	7.2	5.9
50 μg NH_4-N/g	5.8	6.8	5.7
100 μg NH_4-N/g	5.7	6.6	5.5
200 μg NH_4-N/g	5.3	6.6	5.4
300 μg NH_4-N/g	5.3	6.5	5.4

*Soil I - Cooking Lake (from Smoky Lake, Alberta).
**Soil II - Falun L (from Egremont, Alberta).
***Soil III - Malmo SiCL . (from Ellerslie, Alberta).

Table 16. Effect of different amounts of thiourea on the mineral N(NH_4-N + NO_3-N) recovery from urea applied at a rate of 56 kg N/ha on two soils in field experiments.

	Apparent % recovery of applied N as NH_4-N + NO_3-N (0-15 cm)*			
	At 4 weeks		At 8 weeks	
Treatment†	Malmo SiCL	Whitewood L	Malmo SiCL	Whitewood L
Urea	93a	94a	88a	91a
Urea + thiourea (10:1)	96a	83b	86a	89a
Urea + thiourea (5:1)	80b	85b	86a	88a
Urea + thiourea (2:1)	55c	84b	89a	93a
Urea + thiourea (1:1)	45d	58c	91a	89a
Urea + thiourea (1:2)	35e	48d	73b	78b
Thiourea	26f	22e	37c	65c

†Fertilizers were placed in bands in all the treatments.

*The values were calculated as

$$= \frac{\begin{pmatrix}\text{Mineral N recovered in}\\ \text{fertilized treatment}\end{pmatrix} - \begin{pmatrix}\text{Mineral N recovered}\\ \text{in the control}\end{pmatrix}}{\text{N applied}} \times 100$$

In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

Table 17. Equations for the rates of nitrification and NO_3-N losses at different temperatures and soil moisture levels.

Rate of nitrification and incubation temperature

Between -4° and $4^\circ C$
Relative rate of nitrification = 0.004(temperature, $^\circ C$) + 0.021

Between 10° and $20^\circ C$
Relative rate of nitrification = 0.031(temperature, $^\circ C$) - 0.084

Between 20° and $30^\circ C$
Relative rate of nitrification = -0.088(temperature, $^\circ C$) + 2.760

Between 30° and $40^\circ C$
Relative rate of nitrification = -0.012(temperature, $^\circ C$) + 0.478

Rate of nitrification and soil moisture

Between 0 bar and 1/3 bar soil moisture tension
Relative rate of nitrification = 3.030(soil moisture tension, bar)

Between 1/3 bar and 7 bar soil moisture tension
Relative rate of nitrification = -0.067(soil moisture tension, bar) + 1.022

Between 7 bar and 15 bar soil moisture tension
Relative rate of nitrification = -0.024(soil moisture tension, bar) + 0.724

Rate of NO_3-N loss and incubation temperature

Between -4° and $4^\circ C$
Relative rate of NO_3-N loss = 0.004(temperature, $^\circ C$) + 0.051

Between 4° and $10^\circ C$
Relative rate of NO_3-N loss = 0.042(temperature, $^\circ C$) - 0.098

Between 10° and $20^\circ C$
Relative rate of NO_3-N loss = 0.012(temperature, $^\circ C$) + 0.200

Between 20° and $40^\circ C$
Relative rate of NO_3-N loss = 0.028(temperature, $^\circ C$) - 0.116

Between 40° and $60^\circ C$
Relative rate of NO_3-N loss = 0.004(temperature, $^\circ C$) + 1.160

Table 17. (Continued)

Rate of NO_3-N loss and soil moisture

Between 0 bar and 1/3 bar soil moisture tension
Relative rate of NO_3-N loss = -2.255(soil moisture tension, bar)
\+ 1.000

Between 1/3 bar and 7 bar soil moisture tension
Relative rate of NO_3-N loss = -0.026(soil moisture tension, bar)
\+ 0.265

Between 7 bar and 15 bar soil moisture tension
Relative rate of NO_3-N loss = -0.008(soil moisture tension, bar)
\+ 0.139

Table 18. Effect of ATC* on the release of soil content of mineral N(NH_4-N + NO_3-N) over the winter in a stubble field at Ellerslie (Malmo SiCL) in 1976-77.

Treatment	Depth (cm)	NH_4-N (kg/ha)** Oct. 10	Mar. 20	Apr. 25	June 14	NO_3-N (kg/ha)** Oct. 10	Mar. 20	Apr. 25	June 14	Mineral N (kg/ha)** Oct. 10	Mar. 20	Apr. 25	June 14
Control	0-15	7	25	8	7	9	49	32	29	16	74	40	36
	15-30	5	22	5	5	2	28	13	16	7	50	18	21
	30-60	10	24	8	8	2	11	3	9	12	35	11	17
	60-90	8	8	4	4	2	3	2	6	10	11	6	10
	90-120	7	5	2	3	1	1	2	4	8	6	4	7
	0-60	22	71	21	20	13	88	48	54	35	159	69	74
	0-120	37	84	27	27	16	92	52	64	53	176	79	91
ATC*	0-15	7	16	14	17	9	30	31	26	16	46	45	43
	15-30	5	11	6	5	2	16	13	11	7	27	19	16
	30-60	10	22	8	6	2	10	5	9	12	32	13	15
	60-90	8	8	4	4	2	2	3	6	10	10	7	10
	90-120	7	6	2	3	1	1	2	5	8	7	4	8
	0-60	22	49	28	28	13	56	49	46	35	105	77	74
	0-120	37	63	34	35	16	59	54	57	53	122	88	92

*ATC: 4 - amino - 1,2,4 - triazole hydrochloride. ATC was applied at a rate of 22 kg/ha by mixing throughout the soil.

**In each of the rows for 0-60 cm and 0-120 cm depth, the values for NH_4-N, NO_3-N, and mineral N contents are significantly different (95% level of probability) when not followed by the same letter.

Table 19. Effect of ATC* on the release of soil content of mineral N(NH_4-N + NO_3-N) over the winter in a stubble field at Westlock (Falun CL) in 1976-77.

Treatment	Depth (cm)	NH_4-N (kg/ha)**				NO_3-N (kg/ha)**				Mineral N (kg/ha)**			
		Oct. 24	Mar. 9	May 5	June 15	Oct. 24	Mar. 9	May 5	June 15	Oct. 24	Mar. 9	May 5	June 15
Control	0-15	15	68	6	11	7	33	45	44	22	101	51	55
	15-30	8	11	4	8	3	21	12	13	11	32	16	21
	30-60	6	8	9	13	3	11	10	7	9	19	19	20
	60-90	3	4	5	7	6	7	6	4	9	11	11	11
	90-120	4	4	5	4	3	3	2	3	7	7	7	7
	0-60	29	87	19	32	13	65	67	64	42	152	86	96
	0-120	36	95	29	43	22	75	75	71	58	170	104	114
ATC*	0-15	15	20	42	42	7	22	21	32	22	42	63	74
	15-30	8	8	5	7	3	12	10	10	11	20	15	17
	30-60	6	9	6	13	3	8	8	6	9	17	14	19
	60-90	3	4	6	9	6	6	8	4	9	10	14	13
	90-120	4	4	3	4	3	2	4	3	7	6	7	7
	0-60	29	37	53	62	13	42	39	48	42	79	92	110
	0-120	36	45	62	75	22	50	51	55	58	95	113	130

*ATC: 4 - amino - 1,2,4 - triazole hydrochloride. ATC was applied at a rate of 22 kg/ha by mixing throughout the soil.

**In each of the rows for 0-60 cm and 0-120 cm depth, the values for NH_4-N, NO_3-N, and mineral N contents are significantly different (95% level of probability) when not followed by the same letter.

Table 20. Nitrogen content of barley grain from fall- and spring-applied N fertilizers applied at a rate of 56 kg N/ha in field experiments.

Year	Location	Soil type	Fertilizer	N content of barley grain (%)*	
				Fall	Spring
1973-74	Calmar	Demay L	Calcium nitrate	1.33 b	1.47 a
			Ammonium nitrate	1.41 b	1.49 a
			Urea	1.40 b	1.51 a
	Ellerslie	Malmo SiCL	Calcium nitrate	1.50 a	1.55 a
			Ammonium nitrate	1.52 a	1.5[illegible] a
			Urea	1.64 a	1.64 a
	Smoky Lake	Cooking Lake SL	Calcium nitrate	1.62 b	1.74 a
			Ammonium nitrate	1.64 b	1.76 a
			Urea	1.62 b	1.70 a
	Warspite	Falun L	Calcium nitrate	1.68 b	1.76 a
			Ammonium nitrate	1.73 a	1.76 a
			Urea	1.68 b	[illegible] a
1974-75	Blue Sky	Albright CL	Urea	1.64 a	1.69 a
	Bon Accord	Angus Ridge CL	Urea	1.50 b	1.63 a
	Calmar	Demay L	Urea	1.62 b	1.72 a
	Canwood	Whitewood L	Urea	1.57 a	1.59 a
	Egremont	Falun L	Urea	1.60 a	1.62 a
	Ellerslie	Malmo SiCL	Urea	1.68 b	1.80 a

*In each row, the values are significantly different (95% level of probability) when not followed by the same letter.

APPENDIX B

RATE OF HYDROLYSIS OF UREA AS INFLUENCED BY THIOUREA AND PELLET SIZE

ABSTRACT

Two incubation experiments and a number of field experiments were conducted to determine the effect of soil moisture tension, pellet size and addition of thiourea to urea on the rate of urea hydrolysis. In the incubation experiments at 20°C, the rate of hydrolysis of urea increased from 15 bar to 1/3 bar soil moisture tension, with the largest change (doubling) occurring from 15 bar to 7 bar soil moisture tension. Increasing pellet size retarded the rate of urea hydrolysis by about 22% with urea pellets weighing 0.21 g as compared to 0.01 g urea pellets after 114 h. When thiourea (a metabolic inhibitor) was pelleted with urea in a ratio of two parts urea and one part thiourea, the inhibition effect was doubled.

In a field experiment, the addition of thiourea to urea and increasing pellet size suppressed the rate of urea hydrolysis considerably for 8 days. The amount of urea hydrolyzed with urea + thiourea (2:1) pellets weighing 2.51 g was one-fourth of the amount of urea hydrolyzed with 0.01 g pellets of urea alone. In the other six field experiments which were set out in October, only 22% to 33% of urea + thiourea (2:1) was hydrolyzed in two weeks after application, while almost all of the urea was hydrolyzed when it was mixed into the soil without an inhibitor.

Under our field conditions, the hydrolysis of urea can be inhibited

for at least one week. The inhibition of urea hydrolysis appears to be great enough that the problems encountered from the rapid hydrolysis of urea, wherever these occur, may be reduced by combined use of thiourea and either increased pellet size or band placement.

INTRODUCTION

In most soils, urea is rapidly hydrolyzed to ammonium through soil urease activity. The resulting accumulation of ammonium and concomitant rise in pH which can lead to several problems such as damage to seedlings, nitrite toxicity, and gaseous loss of urea N as ammonia, has been reported by Martin and Chapman (1951), Volk (1959), Wahhab et al. (1960), Court et al. (1964a, 1964b), Gasser (1964), and Overrein and Moe (1967). The effect of inhibitors on the reduction of hydrolysis of urea in soils has been demonstrated in incubation studies by Kistiakowsky and Shaw (1953), Moe (1967), Bremner and Douglas (1971, 1973), and Gould (1976). The volatilization loss of ammonia from urea applied to a forest soil was substantially retarded by increasing the pellet size in a field study by Nommik (1956). He further suggested that the retardation effect was probably due to decreased rate of urea hydrolysis.

The present study was carried out to inhibit the rate of hydrolysis through the use of thiourea (a metabolic inhibitor) with urea and by increasing the pellet size.

MATERIALS AND METHODS

Two incubation experiments with two different soils (Malmo silty clay loam and Falun loam) were conducted to determine the rate of hydrolysis of urea as influenced by moistire levels, method of application, pellet size, addition of thiourea (an inhibitor of hydrolysis). The description of the soil used for the experiments is given in Table 1. One thousand grams of air-dried Ap horizon (0-15 cm), ground and passed through 5.0 mm diameter sieve, were weighed into pots (11.0 cm diameter x 12.0 cm high). The soils were incubated at experimental moisture levels and temperature of 20°C for a week before treating them with fertilizers. Urea and urea + thiourea pellets were spread uniformly over the soil surface. The pots were closed with plastic having holes, 3 mm in diameter, to allow aeration and incubated for different periods of time. All the containers were randomized and moisture levels were maintained for the duration of the experiments. Soil samples were taken at various times, and analyzed for their content of urea with colorimetric procedure as outlined by Watt and Chrisp (1954). The experimental design for these experiments is given in Table 2.

The field experiments were conducted in central and northern Alberta. The climate of this area has an average annual precipitation of 350 mm to 475 mm and an average annual temperature of 2.5°C.

One field experiment was conducted with different sulphur compounds as inhibitors in August, 1974 on a Malmo silty clay loam soil. There were six treatments: (1) control, (2) urea, (3) urea + thiourea, (4) urea + thioacetamide, (5) urea + calcium sulphide, and (6) urea + phosphorus pentasulphide. Except for the control, all the treatments received nitrogen at a rate of 112 kg N/ha and the fertilizers were banded at a depth of 5 cm. Each treatment was replicated four times in a randomized complete block design. Individual plots were 6.8 m x 1.8 m. Soil samples were taken to a depth of 15 cm with a coring tube, 2.0 cm in diameter, and were analyzed for only NH_4-N and NO_3-N content using the steam distillation method described by Bremner and Keeney (1966).

Six field experiments were set out in the fall of 1974 to find the effect of thiourea and method of application on the rates of hydrolysis of urea. The description of soils used in the experiments is given in Table 1. There were five treatments: (1) control, (2) urea-mixed, (3) urea-banded, (4) urea + thiourea (2:1)-mixed, and (5) urea + thiourea (2:1)-banded. All the treatments were replicated four times in a randomized complete block design. Individual plots were 6.8 m x 1.8 m. The plots which received band placement contained 8 rows, 23 cm apart, and the fertilizers were banded at a depth of 5 cm. The mixed application consisted of spreading the fertilizer on the soil surface and then mixing it into the soil 10 cm deep with a "rototiller". The soil samples from the plots with fertilizers mixed into the soil were taken to a depth of 15 cm with a coring tube, 2.0 cm in diameter, while the plots which received band placement were sampled by taking a volume (46 cm x 15 cm x 15 cm) of soil across the bands. The soil samples were analyzed for only NH_4-N and NO_3-N content as described previously.

To determine the effect of pellet size and thiourea under field conditions, an experiment was set out on a Malmo silty clay loam soil in late August, 1975. There were seven treatments and each treatment was replicated four times in a randomized complete block design: (1) control, (2) urea (0.01 g each pellet), (3) urea + thiourea--2:1 (0.01 g each pellet), (4) urea (0.21 g each pellet), (5) urea + thiourea--2:1 (0.21 g each pellet), (6) urea (2.26 g each pellet), and (7) urea + thiourea--2:1 (2.51 g each pellet). Nitrogen was applied at a rate of 112 kg N per hectare. In all treatments, except those receiving 2.26 g- or 2.51 g-pellets, the fertilizers were banded 5 cm deep in rows 23 cm apart. The pellets greater than 2 g were applied by hand every 30 cm in a grid pattern, at a depth of 5 cm. Individual plots were 6.8 m x 1.8 m. Soil samples in all the treatments, except those which received greater than 2-g pellets, were obtained by taking a volume of soil (46 cm x 15 cm x 15 cm). In treatments which received greater than 2-g pellets, representative soil sample was taken from a volume of soil obtained by digging a hole (30 cm x 30 cm x 15 cm). The soil samples were air dried, ground to pass through a 2.0 mm diameter sieve and analyzed for the content of NH_4-N and NO_3-N as described previously.

The recoveries of fertilizers were calculated by taking the differences between the contents of NH_4-N + NO_3-N, or urea, in the controls and in the fertilizer treatments. The hydrolysis of urea in the incubation experiments was based on the amounts of urea recovered from the treated soil samples, while the hydrolysis in the field experiments was determined from the contents of NH_4-N + NO_3-N recovered in the treated soil samples. Both of these techniques were found to be in good agreement.

RESULTS

Rate of hydrolysis of urea and urea + thiourea (2:1) in the incubation experiment

The rate of urea hydrolysis increased with soil moisture from 15 bar to 1/3 bar soil moisture tension (Table 3). The rate of hydrolysis at 1/3 bar was 2.6 times greater than at 15 bar and 1.3 times greater than at 7 bar moisture tension after 160 h incubation. From the data it is seen that a considerable amount of hydrolysis can be expected at wilting point moisture content of the soil. At all moisture levels, the hydrolysis of urea was inhibited significantly by addition of thiourea to urea. After 80 h incubation, at 1/3 bar moisture, only 27% of urea was hydrolyzed in urea + thiourea (2:1) treatment as compared to 65% when urea alone was applied.

Effect of pellet size, method of application and thiourea on the rate of urea hydrolysis in the incubation experiment

In all the cases, the amounts of urea hydrolyzed were significantly greater with urea mixed into the soil than with top-dressed urea (Table 4). The rate of hydrolysis decreased with the increased size of pellet, the pellets weighing 0.21 g for urea treatments had about 22% lower hydrolysis than with 0.01 g urea pellets. The inhibition effect of increasing pellet size was enhanced when thiourea pelleted with urea in 2:1 ratio was used. At 114 h incubation, the amount of urea hydrolyzed with 0.01 g urea pellets was about 1.5 times greater than 0.21 g pellets of urea + thiourea (2:1).

Comparison of various sulphur compounds in inhibiting urea hydrolysis in the field experiment

At 35 days after fertilizer application almost all of the urea N was hydrolyzed, but the hydrolysis was delayed by the addition of thiourea to the urea (Table 5). Only about 43% of the N in the urea + thiourea and urea + thioacetamide fertilizers was hydrolyzed after 35 days. The time over which the inhibition continued was longer than the other experiments. This probably was due to low moisture content of soil at the time of fertilizer application and for the next 35 days (greater than 15 bar soil moisture tension). This experiment showed that all four compounds reduced the rate of hydrolysis of urea, but thiourea and thioacetamide were both more effective than phosphorus pentasulphide and calcium sulphide.

Effect of method of application and thiourea on hydrolysis of urea in six field experiments

In the field experiments on Malmo silty clay loam and Angus Ridge clay loam (Table 6), soil sampling at 14 days after fertilizer application showed 88% and 92% hydrolysis of urea mixed into the soil, respectively, and 74% and 78% hydrolysis of urea banded in the soil, respectively. Th[illegible]lysis of urea + thiourea was much lower, with only 37% and [illegible] [illegible]sis with mixed and banded applications, respectively.

In the other four field experiments (Table 5), urea alone mixed or banded in the soil was almost completely hydrolyzed when the soil was sampled 14 days after application. However, with the urea + thiourea fertilizer, hydrolysis was about 50% when the fertilizer was mixed into the soil and only about 30% when the fertilizer was banded.

The average soil temperature in October at a 10 cm depth was 6°C. The soil moisture at the time of fertilizer application at different locations varied from 0.1 bar to 15.9 bar soil moisture tension. A few days after the fertilizer application, some of the soils gained moisture due to a rainfall. However, the amount of hydrolysis did not vary much from location to location.

Effect of thiourea and pellet size on the rate of urea hydrolysis in the field experiment

Soil samples taken at 8 days showed that the hydrolysis of urea was significantly suppressed with the addition of thiourea to urea (Table 7). This effect was further increased by increasing the pellet size. At 8 days, almost all of the urea N applied was hydrolyzed in treatments which received 0.01 g urea pellets which is about 1.5 times greater than 2.26 g urea pellets. The soil was near saturation from rainfall for most of the 8 days period. The amount of urea hydrolyzed in treatments which received urea + thiourea (2.51 g each pellet) was one-half as much as found in urea + thiourea of 0.01 g pellets.

DISCUSSION

The hydrolysis of urea was affected by soil moisture level, method of application, and use of inhibitors. In the incubation study, urea applied to the surface of the soil at a rate of 224 kg N per hectare (approximately 200 ppm of urea N) required almost 160 h for nearly-complete hydrolysis. Gould (1970), and Douglas and Bremner (1971), reported that in incubation studies at 25°C and 37°C, urea added at a rate of 100 μg N/g and 1000 μg N/g to soil hydrolyzed in 8 h and 20 h, respectively. The lower rate of hydrolysis of urea in the present investigation was probably due to the fact that we used urea pellets (0.01 g each pellet, the size of commercial urea used for fertilizer) whereas Gould (1970), and Douglas and Bremner (1971) used urea solutions which were thoroughly mixed into the soil.

Under incubation, the amount of hydrolysis approximately doubled by increasing soil moisture from 15 bar to 7 bar soil moisture tension, but there was only slight increase by increasung soil moisture further to 1/3 bar soil moisture tension. In the field experiments, the amount of hydrolysis of urea changed only slightly from location to location, although there were differences in the soil moisture tension from one location to another.

Thiourea has been shown as urease inhibitor (Kistiakowsky and Shaw, 1953). In the present study, thiourea pelleted with urea suppressed the hydrolysis of urea by about 50% for approximately one week, regardless of the size of the pellet and the method of application.

In a field experiment, while studying the extent of ammonia loss from surface applied urea materials of different sizes to a forest soil, Nommik (1956) reported that the gaseous loss was significantly retarded by increasing the pellet size. He further suggested that the retardation effect was probably because of decreased rate of hydrolysis. In the present work, the rate of hydrolysis of urea in a field experiment was inhibited by one-third with increased pellet size, from 0.01 g (commercial urea) to 2.26 g urea pellets. The addition of thiourea to urea in bigger pellets reduced the hydrolysis to one-fourth as compared to urea + thiourea of 0.01 g pellets.

In six field experiments, the addition of thiourea to urea reduced the amount of hydrolysis of urea to one-half. The band placement of urea + thiourea (2:1) inhibited the hydrolysis to one-third. Therefore, the use of thiourea with urea, and the application of this fertilizer in bands, substantially reduced the amount of hydrolysis of urea in the field. Bundy and Bremner (1974) found that the use of inhibitors, which have little effect on urea hydrolysis, but inhibit nitrification, promoted gaseous loss of urea N as ammonia produced from very rapid hydrolysis of urea. The rapid hydrolysis may result in the accumulation of large amounts of nitrite which are toxic to seedlings, and result in gaseous loss through chemical decomposition of nitrite (Court et al., 1964a and 1964b; Gasser, 1964). Thiourea, an inhibitor of urea hydrolysis and also an effective inhibitor of nitrification, may reduce any problems encountered in the use of urea as a fertilizer.

This study suggested that the use of an inhibitor, which can suppress the hydrolysis and subsequently the nitrification, together with increasing the pellet size, or the band placement, of urea, will reduce the hydrolysis of urea under practical conditions.

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Table 1. Description of soils used for experiments.

Location	Soil type	Soil Great-Group*	pH (1:2.5)	OM(%)
Bon Accord	Angus Ridge clay loam	Black Chernozem	6.6	6.9
Calmar	Demay loam	Gleysol	8.2	4.3
Delacour	Airdrie clay loam	Dark Brown Chernozem	6.9	6.3
Egremont	Falun loam	Dark Gray Chernozem	7.3	5.0
Ellerslie	Malmo silty clay loam	Black Chernozem	6.0	10.5
Smoky Lake	Cooking Lake sandy loam	Gray Luvisol	6.5	2.5

*According to The System of Soil Classification for Canada, 1974

Table 2. Experimental design of incubation experiments for the rates hydrolysis of urea applied at a rate of 224 kg N/ha to soil.

Experiment	Purpose	Treatments*	Temperature (^oC)	Soil moisture tension (bar)
1	Rate of hydrolysis of urea and urea + thiourea (2:1)	(1) Nil		
		(2) Urea	20	1/3
		(3) Urea + thiourea**	20	1/3
		(4) Urea	20	7
		(5) Urea + thiourea**	20	7
		(6) Urea	20	15
		(7) Urea + thiourea**	20	15
			Method of application	Pellet size (g)
2†	Effect of pellet size, method of application and thiourea on urea hydrolysis	(1) Nil		
		(2) Urea	Top-dressed	0.01
		(3) Urea	Mixed	0.01
		(4) Urea + thiourea**	Top-dressed	0.01
		(5) Urea + thiourea**	Mixed	0.01
		(6) Urea	Top-dressed	0.21
		(7) Urea	Mixed	0,21
		(8) Urea + thiourea**	Top-dressed	0.21
		(9) Urea + thiourea**	Mixed	0.21

†Experiment #2 was conducted at 20^oC and 1/3 bar soil moisture tension.
*Each treatment was duplicated.
**Nitrogen in thiourea was not taken into consideration.

Table 3. Hydrolysis of urea + thiourea (2:1)* applied at a rate of 224 kg N/ha to a Falun loam soil in an incubation experiment at 20°C and 1/3, 7 and 15 bar soil moisture tension.

Treatment	Soil moisture tension (bar)	Urea hydrolyzed as percent of applied**			
		20 h	40 h	80 h	160 h
Urea	1/3	18 a	36 a	65 a	96 a
Urea + thiourea (2:1)*	1/3	6 c	13 c	27 c	52 c
Urea	7	11 b	23 b	45 b	75 b
Urea + thiourea (2:1)*	7	3 d	10 d	20 d	27 e
Urea	15	6 c	13 c	26 c	37 d
Urea + thiourea (2:1)*	15	1 d	4 e	11 e	16 f

*Two parts of urea and one part of thiourea were pelleted together and the pellets were top-dressed on the surface.

**For each column values are significantly different (95% level of probability) when not followed by the same letter.

Table 4. Influence of pellet size, method of application and thiourea on hydrolysis of urea applied at a rate of 224 kg N/ha to two soils in an incubation experiment at 20°C and 1/3 bar soil moisture tension for 114 h.

Treatment	Method of application	Pellet size (g)	Urea hydrolyzed as percent of applied**	
			Soil I*	Soil II*
Urea	Top-dressed	0.01	67 b	72 b
	Mixed	0.01	77 a	76 a
Urea + thiourea (2:1)†	Top-dressed	0.01	30 ef	31 c
	Mixed	0.01	38 d	39 d
Urea	Top-dressed	0.21	55 c	57 c
	Mixed	0.21	62 b	69 b
Urea + thiourea (2:1)†	Top-dressed	0.21	27 f	25 f
	Mixed	0.21	35 de	31 e

†Two parts of urea and one part of thiourea were pelleted together and the pellets were top-dressed on the surface.

*Soil I - Målmo silty clay loam
Soil II - Falun loam

**For each column values are significantly different (95% level of probability) when not followed by the same letter.

Table 5. Effect of thiourea and other sulphur compounds on hydrolysis of urea in a field experiment on a Malmo silty clay loam.

Fertilizer*	Apparent % of applied N as urea, hydrolyzed** At 5 weeks	Apparent % of applied N as urea, hydrolyzed** At 10 weeks
Urea	100 a	97 a
Urea + thiourea (2:1)†	42 c	93 a
Urea + thioacetamide (2:1)†	43 c	95 a
Urea + calcium sulphide (2:1)†	71 b	100 a
Urea + phosphorus pentasulphide (2:1)†	68 b	95 a

†Two parts of urea and one part of the compound were mixed together before application and were not pelleted.

*Fertilizers were applied on August 14, 1974 at a rate of 112 kg N/ha.

**For each column the values are significantly different (95% level of probability) when not followed by the same letter.

Table 6. Effect of thiourea on hydrolysis of urea applied at a rate of 56 kg N/ha in six field experiments (fertilizers were applied on October 6 to 8, 1974).

Soil type	Treatment$^{\Phi}$	Apparent % of applied urea N hydrolyzed after 14 days**
Falun loam	Urea-Mixed	95 a
	Urea-Banded	88 b
	U + T (2:1)†-Mixed	46 c
	U + T (2:1)†-Banded	33 d
Airdrie clay loam	Urea-Mixed	95 a
	Urea-Banded	92 a
	U + T (2:1)†-Mixed	51 b
	U + T (2:1)†-Banded	32 c
Demay loam	Urea-Mixed	101 a
	Urea-Banded	91 b
	U + T (2:1)†-Mixed	48 c
	U + T (2:1)†-Banded	27 d
Malmo silty clay loam	Urea-Mixed	88 a
	Urea-Banded	74 b
	U + T (2:1)†-Mixed	37 c
	U + T (2:1)†-Banded	22 d
Angus Ridge clay loam	Urea-Mixed	92 a
	Urea-Banded	78 b
	U + T (2:1)†-Mixed	53 c
	U + T (2:1)†-Banded	39 d
Cooking Lake sandy loam	Urea-Mixed	96 a
	Urea-Banded	94 a
	U + T (2:1)†-Mixed	49 b
	U + T (2:1)†-Banded	32 c

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†U + T (2:1) - Two parts of urea and one part of thiourea were pelleted together.

*Mixed and Banded refer to method of fertilizer application.

**For each location, the values in each column are significantly different (95 level of probability) when not followed by the same letter.

ΦThe average weight of urea pellets was 0.01 g, but that of urea + thiourea pellets was 0.11 g.

Table 7. Effect of pellet size and thiourea on hydrolysis of urea at a rate of 112 kg N/ha in a field experiment on a Malmo silty clay loam on August 20, 1975.

Fertilizer	Pellet size (g)	Apparent % of applied N as urea, hydrolyzed at 8 days (0-15 cm)**
Urea	0.01	98 a
Urea + thiourea (2:1)*	0.01	49 d
Urea	0.21	84 b
Urea + thiourea (2:1)*	0.21	36 e
Urea	2.26	63 c
Urea + thiourea (2:1)*	2.51	25 f

*The urea + thiourea was applied at a rate of 178.4 kg urea plus 89.2 kg of thiourea per hectare. Urea and thiourea were pelleted together and the pellets were applied at a rate of 112 kg N per hectare considering the N in thiourea as well as urea.

**For each column values are significantly different (95% level of probability) when not followed by the same letter.

APPENDIX C

ACIDIFICATION OF SOILS BY NITROGEN FERTILIZERS

ABSTRACT

Incubation and field experiments were conducted to find the rate of soil acidification of typical Alberta soils by ammonium-based fertilizers. On the average of four soils, a depression of soil pH by 0.37 and 0.20 units was observed with ammonium sulphate and urea added at a rate of 50 μg N/g, respectively, after 6 weeks of incubation. The depression in soil pH was lower in plots which received urea pelleted with thiourea (a nitrification inhibitor). The depression in soil pH was related to the amount of nitrification. In three field experiments, the average pH of the soils in May, 1974 was 0.23 units lower than in October, 1973, when urea N was applied by mixing into the soil. Band placement of urea reduced the extent of acidification of soil compared to mixing of urea into the soil. The explanation for this behaviour of placement of urea N was a slowing of nitrification.

INTRODUCTION

The acidification of soils by ammonium-based N fertilizers is a fact that has long been accepted in many parts of the world. The increased soil acidity has been attributed to fertilizers (King, 1972). Soil acidity, when associated with ammonium-based fertilizers, results from the conversion of NH_4 to NO_3 by nitrifying bacteria. The importance of soil acidity in growing crops is well known (Pearson and Adams, 1967). In Alberta, some of the agricultural soils are naturally acid and a small decrease in soil pH may eliminate the production of acidity-sensitive crops (Hoyt et al., 1974). Therefore, incubation and field experiments were carried out to determine the rate at which some of the typical Alberta soils acidify with the application of ammonium-based fertilizers.

MATERIALS AND METHODS

Incubation Experiments

Incubation experiments with four soils (Malmo SiCL from Ellerslie, Falun CL from Warspite, Cooking Lake SL from Smoky Lake, and Falun L from Egremont) were conducted under controlled temperature and moisture to compare various N fertilizers with respect to their effect on pH. Three hundred grams of air-dried Ap horizon (0-15 cm), which had been ground and passed through a 5.0 mm diameter sieve, were weighed into pots (11.0 cm diameter x 10 cm high). The soils were incubated for a week at 20°C and 1/3 bar soil moisture before treating them with fertilizers. There were four treatments: (1) control, (2) urea, (3) urea + thiourea (2:1), and (4) ammonium sulphate. Each treatment was duplicated. Nitrogen was added at a rate of 50 μg N/g. All the fertilizers were banded at a depth of 3.8 cm below the surface in a groove 6.25 cm long and 0.5 cm wide in the center of the pot. The pots were closed with plastic with holes, 3 mm in diameter, to allow aeration. All the containers were randomly arranged and moisture levels were maintained at 1/3 bar soil moisture tension. The experiments were conducted for a period of 6 weeks from the middle of January to about the end of February, 1974. The soil samples were taken at six weeks, air dried, ground to pass through 2.0 mm sieve, and determined pH of 1:2.5 soil water suspension with a pH meter. The samples were also analysed for NH_4-N and NO_3-N using the distillation method described by Bremner and Keeney (1966).

Field Experiments

Three field experiments were conducted to determine the rate of acidification of soils with various nitrogen fertilizers and to see the effect of method of application (mixing into the soil and band placement) of fertilizers on the rate of acidification. Three field experiments: at Ellerslie (Malmo SiCL), Smoky Lake (Cooking Lake SL) and Breton (Breton L) were set out in October, 1973. The description of soils used is given in Table 1. There were five treatments: (1) control, (2) urea-mixed, (3) urea-banded, (4) urea + thiourea (2:1)-mixed, and (5) urea + thiourea (2:1)-banded. Nitrogen was applied at a rate of 100 kg N/ha at Ellerslie and at Breton, and 56 kg N/ha at Smoky Lake. Individual plots were 6.8 m x 1.8 m and each plot was replicated four times in a randomized complete block design. In plots which received mixed applications, the fertilizers were mixed in the top 10 cm soil with a rototiller; while in plots which received band application, the fertilizers were placed 4.5 cm deep in 23 cm apart rows. The soil samples were taken the following spring from the 0-15 cm depth, air dried, ground to pass through 2.0 mm sieve and analysed for pH, NH_4-N and NO_3-N as mentioned previously.

RESULTS

Effect of Nitrification of Ammonium-Based Fertilizers on Soil pH in Incubation Experiments

The rate of acidification is influenced by the proportion of NH_4 that is nitrified. The results of the incubation experiments presented in Table 2 showed that the pH was decreased markedly at six weeks in plots that received urea and ammonium sulphate. In the Falun CL soil, the pH was dropped from 6.68 to 6.33 with ammonium sulphate and to 6.44 with urea at six weeks. Similarly, in the Cooking Lake SL soil, the pH was depressed by 0.47 units with ammonium sulphate and by 0.17 with urea, while depression in soil pH was lower (i.e., 0.07 units) in plots which received thiourea (a nitrification inhibitor) with urea. The results in Table 2 showed that urea alone nitrified faster than did urea + thiourea, and resulted in more depression in pH. The depression in pH was greatest with ammonium sulphate.

Effect of Transformations of Fall-Applied N Fertilizers on Soil pH in Field Experiments

The results of the effect of method of application and the use of thiourea (a nitrification inhibitor) on the acidification of soils by urea, in three field experiments set out in October, 1973, are given in Table 2. There was more reduction in soil acidity when urea was placed in bands than when it was mixed into the soil. On the average in three field experiments, the pH by May, 1974, was depressed by 0.15 units with banded urea as compared to 0.23 units with mixed urea. Almost no depression in soil pH was observed when thiourea was added to urea. This reduced acidification as a result of band placement and addition of thiourea to urea was apparently due to slower nitrification (Table 3).

At Smoky Lake soil samples were taken two times: first in May, 1974, at seeding time and second in September, 1974, after harvesting of barley. The pH results indicated that the pH was depressed further from May, 1974, to September, 1974, during the growing season in all the treatments (Table 3). The greater depression during the summer was in treatments which received urea + thiourea fertilizer mixed in the soil, but urea + thiourea banded still maintained pH higher than other treatments.

DISCUSSION

Since the occurrence of acid soils is related to soil type, much of the soil acidity apparently is inherent, but there are evidences of increased soil acidity resulting from the use of ammonium-based N fertilizers (Webster and McCoy, 1974; Nyborg, 1975). Similarly, in the present study, a depression of soil pH by 0.37 and 0.20 units with incubation of ammonium sulphate and urea, respectively, for six weeks in four soils was observed (Table 2). The highest production of soil acidity by ammonium sulphate as compared to other nitrogen sources has been reported by Andrews (1954). In the field experiments, with urea mixed into the soil in the fall, the soil pH (0-15 cm) was lowered by about 0.20 units in the following spring.

About one-half of the farmed land in Alberta is in the range of pH 5.6 to 6.5. Therefore, a relatively small decrease in the soil pH would cause a large increase in the acreage of acid soils (Penny and Henry, 1976). The long-term use of ammonium-based fertilizers may result in a significant reduction in soil pH and may cause potential problems in the production of crops such as alfalfa (Hoyt et al., 1974; McCoy and Webster, 1977). Therefore, more work should be done to find out the rate of acidification of soils by use of ammonium-based fertilizers and to develop the means to counteract this effect.

During this investigation, a small part of the work was devoted to find some practical means to reduce the rate of acidification by ammonium-based fertilizers. Since the rate of acidification is influenced by the amount of nitrification, therefore the pH of the soil will be depressed more with an ammonium-based fertilizer which nitrifies faster than with a slow-nitrifying fertilizer. The results of the field experiments (Table 3) suggested that there was less depression in soil pH when urea was banded than when it was mixed into the soil. This effect was increased considerably, when thiourea (a nitrification inhibitor) was applied with urea. This lower depression in soil pH, as a result of band placement and addition of thiourea to urea, was apparently due to slower rate of NO_3 formation (Table 3). Therefore, the use of inhibitors with ammonium-based fertilizers may maintain the soil pH at higher level than the fertilizers used without inhibitors, and may possibly eliminate the problem of soil acidification encountered from the use of ammonium-based fertilizers.

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Table 1. Description of soils (0-15 cm) used for field experiments.

Location	Soil classification	Texture	(O.M.%)
Ellerslie	Black Chernozemic	SiCL	10.5
Egremont	Dark Gray Chernozemic	L	5.0
Smoky Lake	Gray Luvisol	SL	2.5
Warspite	Dark Gray Chernozemic	CL	6.6

Table 2. Effect of transformation of various N fertilizers on soil pH in incubation experiments conducted at 20°C and 1/3 bar soil moisture tension after 6 weeks.

Fertilizer†	Soil pH** (6 weeks)				Apparent % of applied N recovered at NO_3-N (6 weeks)	
	Soil I*	Soil II*	Soil III*	Soil IV*	Soil I*	Soil II*
Control	6.00 c	6.68 c	6.54 c	7.52 c		
Urea	5.80 b	6.44 a	6.37 b	7.35 b	81.4 a	89.3 a
Urea + thiourea (2:1)	5.95 c	6.59 c	6.47 bc	7.41 bc	21.8 b	33.1 b
Ammonium sulphate	5.71 a	6.33 a	6.07 a	7.15 a	64.5 c	73.6 c

†In all treatments, except the control, fertilizers were applied at a rate of 50 μg N/g in narrow bands.

*Soil I Malmo SiCL (from Ellerslie, Alberta)
Soil II Falun CL (from Warspite, Alberta)
Soil III Cooking Lake SL (from Smoky Lake, Alberta)
Soil IV Falun L (from Egremont, Alberta)

**In each column, the values are significantly different (95% level of probability) when not followed by the same letter.

Table 3. The change in soil pH by N fertilizers applied in fall, 1973, in field experiments.

	Soil pH**				**Apparent % of applied N recovered as NH_4-N in top 15 cm of soil in May/74		
	Breton	Ellerslie	Smoky Lake				
Treatment†	(May,1974)	(May, 1974)	(May,1974)	(Sept.1974)	Breton	Ellerslie	Smoky Lake
Nil	5.85 c	6.01 c	6.74 c	6.72 d			
Urea - Mixed*	5.64 a	5.81 a	6.46 a	6.34 a	2.8 a	7.8 a	12.5 a
Urea - Banded*	5.72 b	5.86 a	6.58 b	6.39 b	4.1 a	9.7 a	28.0 a
Urea + thiourea (2:1)Φ-Mixed*	5.86 c	5.94 c	6.73 c	6.38 b	21.5 b	44.7 b	56.3 c
Urea + thiourea (2:1)Φ-Banded*	5.93 d	6.13 b	6.79 c	6.56 c	56.3 c	76.7 c	75.8 d

†In all treatments, except the control, fertilizers were applied at a rate of 100 kg N /ha except at Smoky Lake where nitrogen was applied at a rate of 56 kg N/ha. The fertilizers were applied in late September, 1973, and soil samples were taken in late May, 1974, to the depth of 15 cm except Smoky Lake where fertilizers were applied in October, 1973, and the soil samples were taken in early May, 1974, to the depth of 15 cm.

ΦTwo parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the nitrogen in urea as well as thiourea.

*"Mixed" and "Banded" refer to method of fertilizer application.

**For each column, the values are significantly different (95% level of probability) when not followed by the same letter.

APPENDIX D

EFFECT OF THE POSITION OF MINERAL N (NH_4-N + NO_3-N) IN THE SOIL PROFILE ON THE N UPTAKE BY BARLEY GRAIN

The results of the field experiments (Table 1) indicated that one unit of fertilizer mineral N applied to the soil at seeding time, resulted in more N in barley grain than did one unit of mineral N found in the soil at seeding time but originating from urea N applied the previous fall. The amount of fertilizer N at seeding time was 56 kg N/ha for those plots which received urea applied at that rate just before seeding; while for the plots which received urea in the previous fall, the amount of net fertilizer mineral N was determined on soil samples obtained just prior to seeding, to a depth of 90 cm.

The explanation for a lower ratio* of the N in the crop to the fertilizer N found in the soil at seeding time with fall-applied urea N, than with the spring application of urea was probably caused by a distribution of the mineral N from fall-applied fertilizer throughout the top 60 cm or 90 cm depth, whereas the mineral N from the urea applied in the spring remained in the top layer. Given the distribution of mineral N throughout the top 60 cm or 90 cm layer, the mineral N was lost during the growing season (Table 2), be those losses through denitrification, immobilization or leaching.

$$\text{*Ratio (NU:MN)} = \frac{\text{N in barley grain (kg/ha)}}{\text{Fertilizer N at seeding time (kg/ha)}}$$

While not particularly borne out by the results in this study, the following reasons for the lower efficiency of mineral N leached to deeper depths have been cited: (1) greater dilution of mineral by the soil; (2) detrimental effect of poor aeration on nutrient absorption*(Lawton, 1945); and (3) the mineral N being at lower depth may not contribute to increase in yield of crops in the late growing season, even if it becomes available to plants.

In this investigation, higher NU:MN ratios were expected with fall application than with spring application, because it was thought that in most cases the immobilized N from fall-applied N would remineralize during the growing season and increase the N uptake by barley grain, but this did not happen. The results with calcium nitrate were similar to those obtained with urea.

All the experiments did not show this pattern (Table 1). With calcium nitrate five of the six soils, and with urea eight of the 10 soils showed this pattern. On the Falun L soil and the Cooking Lake SL soil, the NU:MN ratios were greater with fall-applied urea than with spring application.

These field experiments demonstrated that one unit of mineral N present at the time of seeding in the top 15 cm layer resulted in more N in the barley grain than when one unit of mineral N recovered in the soil at seeding time was distributed throughout in the top 90 cm depth.

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*Lawton, K. 1945. The influence of soil aeration on the growth and absorption of nutrients by corn plants. Soil Sci. Soc. Am. Proc. 10: 263-268.

Table 1. The ratios of N in barley grain (kg/ha) to mineral N at seeding time (kg/ha) with fall and spring applications of various nitrogen fertilizers in field experiments.

			N in barley grain (kg/ha) / Fertilizer N at seeding time (kg/ha)				
			Urea-Mixed		C.N.*-Mixed		U + T (2:1)†
Year	Location	Soil type	Fall	Spring	Fall	Spring	Banded - Fall
1973-74	Calmar	Demay L	0.21	0.29	0.19	0.23	0.62
	Ellerslie	Malmo SiCL	0.37	0.45	0.21	0.32	0.53
	Smoky Lake	Cooking Lake SL	0.35	0.32	0.26	0.30	0.45
	Warspite	Falun L	0.92	0.59	0.89	0.65	1.13
1974-75	Calmar	Demay L	0.64	0.98	----	----	0.74
	Blue Sky	Albright	0.63	0.79	----	----	0.76
	Canwood	Whitewood L	0.40	0.51	----	----	0.57
	Egremont	Falun L	0.46	0.61	----	----	0.66
	Bon Accord	Angus Ridge CL	0.33	0.86	0.33	0.73	0.58
	Ellerslie	Malmo SiCL	0.60	0.87	0.77	0.96	0.90
	Average		0.49	0.63	----	----	0.69

†U + T - Urea + thiourea (2:1). Two parts of urea and one part of thiourea were pelleted together and the pellets were applied considering the N in thiourea as well as in urea.

*C.N. - Calcium nitrate.

Table 2. The NH_4-N and NO_3-N content of soils in September, 1975 after harvesting.

		NH_4-N and NO_3-N (kg/ha)					
		0-15 cm		15-30 cm		30-60	
Location	Treatment	NH_4-N	NO_3-N	NH_4-N	NO_3-N	NH_4-N	NO_3-N
Bon Accord	Nil	7.4	9.8	4.8	2.8	2.6	3.8
	Urea-Fall	5.6	7.4	4.1	3.1	2.6	3.0
	Urea-Spring	5.9	8.8	4.4	1.4	1.8	2.6
	C.N*-Fall	6.2	8.9	4.7	2.9	2.4	3.5
Calmar	Nil	10.2	4.3	8.0	4.0	2.1	2.1
	Urea-Fall	11.6	2.6	6.5	5.5	3.1	2.1
	Urea-Spring	9.8	3.0	8.5	4.5	3.1	1.0
Canwood	Nil	3.7	8.5	2.7	3.5	2.8	2.4
	Urea-Fall	4.8	7.8	3.1	3.9	2.4	1.6
	Urea-Spring	3.8	7.4	1.9	2.7	1.6	0.8
Egremont	Nil	6.2	3.1	5.6	2.0	5.4	5.4
	Urea-Fall	5.8	4.4	4.0	3.2	5.2	3.6
	Urea-Spring	5.1	3.4	5.2	2.4	3.6	2.6
Ellerslie	Nil	7.8	6.0	4.9	3.5	2.5	4.4
	Urea-Fall	6.8	6.1	4.6	3.0	2.9	3.2
	Urea-Spring	6.2	5.2	3.5	1.9	2.4	1.9
	C.N*-Fall	7.1	5.9	4.6	3.4	2.6	3.8

*C.N. - Calcium nitrate

APPENDIX E

INCREASING EFFICIENCY OF FALL-APPLIED UREA BY "CHUTKI PLACEMENT"

The results of field experiments conducted during 1973-74 and 1974-75 showed that the band placement of 45 kg of thiourea (a nitrification inhibitor) pelleted with 90 kg of urea per hectare gave 6.4 quintals (1 quintal = 100 kg) more barley grain, than did urea applied without an inhibitor. Since thiourea is expensive, its use to reduce the over-winter losses of fall-applied urea N would increase the cost of crop production. Therefore, two experiments in farm fields were carried out at Breton (Breton L) and at Canwood (Whitewood L) during 1976-77 to determine if "chutki placement" (a method of seeding when a number of seeds are placed together at a point, used for seeding chillies in Punjab) is effective in improving the over-winter conservation of fall-applied urea N.

The description of soils is given in Appendix A, Table 1. There were four treatments: (1) control, (2) urea-mixed into the soil in fall, (3) urea-chutki placement in fall, and (4) urea-mixed into the soil in spring at seeding time. Individual plots were 6.0 m (long) x 1.2 m (wide). All the treatments were replicated four times in a randomized complete block design.

Urea was applied at a rate of 84 kg N/ha. In the "mixed" application, urea was spread over the soil surface and then mixed into the top 10 cm with a "rototiller", while in the "chutki placement" the urea was placed at the 5 cm depth in the middle of a 60 cm x 60 cm area. All the plots received a blanket application of 41 kg P, 41 kg K and 17 kg S per hectare. At the time of seeding, urea applied in the fall by chutki placement was no longer intact because all the plots were rototilled before seeding. Galt barley (Hordeum vulgare) was seeded in rows 15 cm apart. At maturity the crop was harvested and threshed to determine grain yield. A representative grain sample was taken for each treatment and analyzed for total N.

The yield of barley grain (Table 1) with spring-applied urea on the Breton L soil was 23 quintals greater than with urea mixed into the soil in the fall. The "chutki placement" increased the yield of barley grain by about 10 quintals over mixed application in the fall. On the Whitewood L soil, like the previous soil, the urea mixed into the soil in the fall was less effective in increasing the yield of barley grain than spring application. However, at this location, "chutki placement" of urea in the fall gave significantly greater yields of barley grain than the spring application. On the average of these two locations, the yield of barley grain with "chutki placement" of urea in the fall was greater by about 11 quintals than urea mixed into the soil in the fall.

Similarly, N in the barley grain as a % of the applied N with "chutki placement" of urea in the fall was significantly greater than with urea mixed into the soil in the fall at both locations. On the average, N in the grain as % of applied N with "chutki placement" of urea in the fall at two locations was greater by 18% than with urea mixed into the soil in the fall.

These experiments demonstrated that fall application of urea by "chutki placement" may eliminate, or reduce, the amount of nitrification inhibitors necessary to improve the over-winter conservation of fall-applied urea.

Table 1. Effect of "chutki placement"* of urea applied in the fall at a rate of 84 kg N/ha, on the yield and N uptake of barley grain during 1976-77.

Location	Soil type	Treatment	Time of application†	Yield of barley grain (100 kg/ha)**	Apparent % of applied N in grain**
Breton	Breton L	Control		7.8 d	
		Urea - Mixed	Fall	14.7 c	9 c
		Urea - Chutki*	Fall	24.4 b	23 b
		Urea - Mixed	Spring	37.5 a	43 a
Canwood	Whitewood L	Control		13.3 d	
		Urea - Mixed	Fall	24.2 c	18 c
		Urea - Chutki*	Fall	36.2 a	40 a
		Urea - Mixed	Spring	29.9 b	29 b

†For fall application urea was applied in mid-October and for spring application urea was applied in May, at the time of seeding.

*"Chutki placement" refers to a method of seeding when a number of seeds are placed together at a point, as used for seeding chillies in Punjab.

**In each column, the values at each location are significantly different (95% level of probability when not followed by the same letter.