

THE UNIVERSITY OF MANITOBA

EFFECT OF NITRIFICATION INHIBITORS ON NITRATE FORMATION FROM UREA
AND RECOVERY OF SPRING-APPLIED UREA-N BY BARLEY

BY

ADENIYI OLU OBI

A THESIS

SUBMITTED TO

THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

DEPARTMENT OF SOIL SCIENCE

WINNIPEG, MANITOBA

SEPTEMBER, 1978



EFFECT OF NITRIFICATION INHIBITORS ON NITRATE FORMATION FROM UREA
AND RECOVERY OF SPRING-APPLIED UREA-N BY BARLEY

BY

ODENIYI OLU OBI

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

MASTER OF SCIENCE

© 1978

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

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

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.....	1
II. LITERATURE REVIEW.....	3
1. Recovery of Applied Nitrogen.....	3
2. Fate of Added Nitrogen in the Soil.....	7
a. Ammonium Fixation.....	7
b. Immobilization.....	8
c. Ammonia volatilization.....	9
d. Leaching Loss of N.....	11
e. Denitrification.....	12
3. Methods of Improving Crop Recovery of Applied N Through Fertilizer Management.....	18
a. Slow-Release Nitrogen Fertilizers.....	20
b. Nitrification Inhibitors.....	21
III. MATERIALS AND METHODS.....	28
IV. RESULTS AND DISCUSSION.....	45
<u>Experiment I.</u> Effect of CS ₂ and 'N-Serve' on inhibiting nitrate formation from urea-N.....	45
<u>Experiment II.</u> Effect of nitrification inhibitors on recovery of urea-N by barley.....	68
V. SUMMARY AND CONCLUSION.....	78
BIBLIOGRAPHY.....	82

LIST OF TABLES

TABLE		PAGE
1	Subgroup designations, physical and chemical characteristics of the soils.....	29
2	Treatments for laboratory experiment.....	34
3	Treatments for field experiment.....	41
4a	Recovery of urea-N as NO_3^- in different zones and at various times during incubation.....	58
4b	Recovery of urea-N as NH_4^+ in different zones and at various times during incubation.....	59
5	Recovery of NH_4^+ -N from urea in 3 soil types after 3 weeks of incubation.....	66
6	Total above ground dry matter yield of barley.....	69
7	Total N in above ground portion of plant.....	71
8	Recovery by barley of spring applied urea-N with or without nitrification inhibitor.....	73
9	Nitrate nitrogen content of soil (0-15 cm).....	75

LIST OF FIGURES

FIGURE		PAGE
1	Diagrammatic representation of container fabricated for banded treatments.....	30
2	Diagrammatic representation of container fabricated for broadcast treatments.....	31
3	Area harvested in each plot for the three sampling dates.....	43
4a	Nitrification rate of banded urea with or without 'N-Serve' or CS ₂	47
4b	Nitrification rate of broadcast urea with or without 'N-Serve' or CS ₂	48
5a	Effect of 'N-Serve' or CS ₂ on inhibition of nitrification of broadcast urea.....	51
5b	Effect of 'N-Serve' or CS ₂ on inhibition of nitrification of banded urea.....	52
6a	Recovery of NH ₄ ⁺ -N from banded urea with or without 'N-Serve' or CS ₂	54
6b	Recovery of NH ₄ ⁺ -N from broadcast urea with or without 'N-Serve' or CS ₂	56
7a	Effect of 'N-Serve' or CS ₂ (broadcast) on accumulation of NO ₃ ⁻ -N in non-fertilized soil.....	63
7b	Effect of 'N-Serve' or CS ₂ (banded) on accumulation of NO ₃ ⁻ -N in non-fertilized soil.....	64
8	Effect of urea and 'N-Serve' or CS ₂ on concentration of NO ₃ ⁻ -N in the soil profile.....	77

ABSTRACT

The effectiveness of some nitrification inhibitors and placement of N-fertilizer on rate of nitrate formation from urea-N was studied on three Manitoba soils of different textures. A laboratory study showed that 'N-Serve' and CS_2 were effective in reducing the nitrification rate of urea-N. Inhibitors showed greater effectiveness when broadcast than when banded, probably due to their presence in lethal concentration over a large volume of soil. 'N-Serve' was more effective and more persistent than CS_2 .

Broadcasting urea-N without inhibitor caused the fertilizer to nitrify faster than when it was banded. The proportion of broadcast urea-N which had been nitrified reached 100 percent within three weeks of application. Such a high proportion of nitrification did not occur from banded urea-N until six weeks after application.

Nitrate-N was well distributed in the soil and considerable movement away from point of fertilizer application occurred. Contrarily, ammonium-N was sparsely distributed and remained close to the point of application. Total recovery of added N was very low after one week, but increased with time with untreated or CS_2 treated urea-N. This suggested that there was a gradual release of nitrogen which was presumably fixed immediately after application. Lowest total inorganic N occurred where 'N-Serve' was applied, indicating that the inhibitor probably reduced the release of the fixed NH_4^+ .

Dry matter yield of barley in field studies showed that there was a highly significant response to spring applied urea-N, but not to the addition of nitrification inhibitors. Total N uptake, crop recovery of added N, and residual NO_3^- -N in the soil profile were

not significantly affected by treating spring-applied urea-N with nitrification inhibitors. There were probably at least three reasons for the failure of the nitrification inhibitors to influence plant N. (1) Nitrogen fertilizer was applied at seeding so that there was little time for N loss to occur. (2) Conditions at seeding and throughout the growing season were moderately dry so that there was little likelihood of NO_3^- -N loss through denitrification or leaching. (3) The barley plants were able to utilize both NH_4^+ and NO_3^- nitrogen.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to:

Professor A.O. Ridley, Department of Soil Science, University of Manitoba, under whose immediate supervision this investigation was conducted, for guidance in the experimental design, for valuable suggestions and constructive criticism in the preparation of this thesis.

Dr. L.J. LaCroix, Professor, Department of Plant Science, and Dr. L.A. Loewen-Rudgers, Assistant Professor, Department of Soil Science, University of Manitoba for serving on the examining committee.

Dr. C.M. Cho for his co-operation and for helping with some complex mathematical calculations.

The University of Ife, Nigeria, for financial support and for granting the study leave.

Technical staff of Soil Survey, Soil Testing and Soil Science Departments, University of Manitoba, for their co-operation during the term of this project.

Mrs. Connie Ashdown, Department of Soil Science, for her excellent work in typing the manuscript.

INTRODUCTION

Recovery of nitrogen (N) by crops is generally less than, or about 50% of the amount applied (Allison 1965). Soper *et al.* (1970) reported that barley in Manitoba recovered 52% of ammonium nitrate-N broadcast after seeding. They noted that some recovery values were very low. Recent work in Manitoba¹ showed that recovery of applied N by barley ranged between 29 and 37 percent for fall and spring applications respectively. The efficiency of recovery also depended on placement of applied N and to the least extent on the form in which the fertilizer was applied.

Loss of N and its temporary tie-up in the soil render the nutrient unavailable to crops, and results in low recovery. This has been attributed to numerous processes, including leaching, immobilization, volatilization, ammonia fixation, and biological and chemical denitrification. Studies of plant uptake of N and residual N in soils conducted in lysimeters using ¹⁵N labelled fertilizers indicated that denitrification was a major cause of low recovery of applied N (Ridley 1976).

Increased cost of N-fertilizer, the utilization of a non-renewable resource (natural gas) in its manufacture, and the potential detrimental effect on the environment following its intensive use, have necessitated better management of nitrogen fertilizer. Such management has been directed towards achieving highest possible efficiency and lowest possible losses. Much of the loss involves the nitrate form, either through leaching or denitrification. Therefore, improved crop utilization of added N may be achieved by application and maintenance of N in the ammonium form.

Nitrification inhibitors have been studied extensively (Goring

1962a,b; Prasad 1968; Bremner and Bundy 1974) to determine their effectiveness in preventing nitrification of ammonium nitrogen (NH_4^+-N), thereby eliminating N loss under wet (reducing) conditions. Some inhibitors, including 'N-Serve' have been found to be effective while others have had variable effects.

This study was conducted to determine the effectiveness of some nitrification inhibitors and placement of N-fertilizers on rate of nitrate formation from urea N and recovery of added N by barley. These two techniques could lead to more convenience of fertilizer handling by farmers, lower production cost and better conservation of energy.

LITERATURE REVIEW

Recovery of Applied Nitrogen

Crops obtain most of their nitrogen (N) from the soil in either the ammonium or nitrate form. Ammonium and nitrate forms of nitrogen occur as a result of mineralization of organic compounds, and through the addition of N-fertilizers. The amount of nitrogen that a plant takes up is a function of several factors, among which are: type of fertilizer added, time and method of application, and type of crop grown. Recoveries of added fertilizer in the crop alone vary widely with growth conditions and cropping systems.

Determination of recovery of added nitrogen has usually been accomplished by one of two methods. The "Difference Method" involves subtracting the amount of nitrogen removed by the crop grown on control soil from that removed by crops grown on fertilized soil. The second and more recent method is by the use of tracer techniques. This method is based on the actual recovery of added ^{15}N in the crop plus the N immobilized in the soil. In this case the experiment is usually conducted on soils where leaching is not expected, otherwise the leachates are collected for analysis. Greater accuracy is achieved by the use of the tracer method because it gives a complete account of the added nitrogen, except that lost in gaseous forms. The difference method is usually preferred by agronomists because of the simplicity of the method and the fact that it is inexpensive, (Allison 1966).

Henzell et al. (1964) noted that recovery of added nitrogen was the same whether obtained by the difference method or ^{15}N analysis, provided allowance was made for immobilized ^{15}N in the soil. In their experiment, they recovered in the crop an average of 82% of added nitrogen,

but only 74% of the ^{15}N . They claimed that the discrepancy was due to retention of ^{15}N in the soil. Other workers have reported similar results (Low and Piper 1957, Cady and Bartholomew 1960a).

Irrespective of the method used for determining the crop recovery of added nitrogen, numerous workers have observed that crop recovery of added nitrogen is generally low (Allison 1955; Bartholomew 1971; Viets and Hageman 1971). Investigations were conducted under various conditions, ranging from greenhouse to field and the results showed a wide variation in the amount of added N recovered, depending on the type of soil on which the experiment was conducted. In greenhouse studies with tagged nitrogen (^{15}N), and using ammonium sulphate as the N-source on sudangrass, MacVicar *et al.* (1951) accounted for 85-97% of added N. They associated the lowest recoveries with a low level of soil organic matter and a high level of N addition. Walker *et al.* (1956) obtained a comparatively low recovery of 70-75% with ammonium sulphate. They attributed this to denitrification, admitting their pots were not well aerated. Lower recovery of 66-71% of the added N with potassium nitrate, in the same experiment, confirmed their conclusion about the occurrence of denitrification in their studies. Cady and Bartholomew (1960a) obtained an average recovery of 80% of the tagged $(^{15}\text{NH}_4)_2\text{SO}_4$ added at different rates to two sandy soils. Addition of 5 tons per acre of corn stover had no appreciable effect on percent total nitrogen recovery in the same experiment of Cady and Bartholomew. Broadbent and Nakashima (1965) obtained an average recovery of 68% of added N, and noted that lower recovery was obtained when straw was added. Gerretsen and de Hoop (1951) recorded one of the lowest recoveries of 26%, with untagged ammonium sulphate added to several acid sandy soils. In their experiment, the low percent recovery obtained was attributed to the formation

of nitrous acid which reacted with ammonium ion to release molecular nitrogen.

Reviews conducted on lysimeter studies in the United States and the United Kingdom (Allison 1955) indicated a N-recovery ranging between 21 and 79% of added N. Loss of 33% of tagged ammonium sulphate added to the soil was reported by Owens (1960) in his two-year lysimeter studies, and he speculated that the loss might have been due to denitrification. Allison et al. (1959) in another lysimeter study in which they claimed there was no evidence for appreciable losses of gaseous nitrogen, accounted for only 80-90 percent of the added untagged nitrogen.

Recovery of applied nitrogen in field experiments was much lower than those reported for both greenhouse and lysimeter studies. Values not greater than 50% recovery of added nitrogen have been reported by various workers in their different field trials (Martin and Skyring 1962; Allison 1965, 1966; Chalk et al. 1974; Hedlin and Cho 1974; Ridley 1975). In field results, consideration is usually given to nitrogen recovered by crops or series of crops in fertilized plots less than in unfertilized plots. Any other gain or loss of added N is not always considered. Pearson et al. 1961 recorded recoveries ranging between 40 and 59% of added nitrogen. They noted that application of fertilizer N in the fall led to recovery of N, only 62% as large as spring application. Data reported by Ridley (1976) showed recovery of fall applied urea to be only 77.3% of spring applied urea. In this report, he concluded that recovery of added N was better with spring than with fall applied nitrogen fertilizer.

Ashley et al. 1965, using split application of ammonium nitrate at rates of 336 and 672 kg N per hectare annually obtained recoveries of 88 and 76% for the low and high rates respectively. They suggested in their report that much of the unrecovered nitrogen probably remained immobilized in the soil since leaching of nitrogen from a grass sod would usually be negligible. Higher recovery of added N was obtained from $(\text{NH}_4)_2\text{SO}_4$ than NaNO_3 and recovery was favoured by presence of a crop (Carter et al. 1966). In this study Carter et al. concluded that percent recovery of ^{15}N was not appreciably affected by soil pH, fertilizer concentration or the addition of an inhibitor.

All factors favouring loss of nitrogen from, or its temporary tie-up in the soil will contribute considerably to low recovery of applied nitrogen. Excess moisture content, that brings about oxygen deficiency in the soil, may lead to low recovery of added N, especially if nitrate fertilizer is used. One of the lowest nitrogen recoveries was obtained with a rice crop planted in a waterlogged soil (Sanchez and de-Calderon 1971). Low recovery of applied N can also occur where the soil is so acid that nitrification of ammonium fertilizer is inhibited. When the rate of application is low, most of the added N may be immobilized, and this can lead to low recovery values. Thus, the percentage of added N recovered by the crops depends upon the various mechanisms of losses and immobilization of applied nitrogen. These losses and immobilization of N, in turn are affected by the soil type, climatic conditions, form of nitrogen fertilizers, rate, time and method of application.

Fate of Added Nitrogen in the Soil

In considering the fate of added N, where a considerable proportion is not recovered by the crop, attention is directed to the amount and means by which nitrogen escapes from the soil. However, not all N left after crop recovery is lost from the soil system. Therefore, consideration is given to the amount of nitrogen that stays in the soil, and its rate of release to subsequent crops.

Ammonium Fixation

Clay minerals with expanding lattices, such as montmorillonite and vermicullite, can absorb ammonia and hold it in such a way that it is not readily available to higher plants or microorganisms. Nommik (1965) noted that fixation of ammonium by clay minerals was quite extensive in some soils. Sowden (1975) reported that about 40% of NH_4^+ -N of manure and fertilizer was fixed by Brunisolic soil containing 20% clay which was largely vermicullite. The fixed NH_4^+ was nitrified very slowly so that the NH_4^+ was protected against rapid nitrification and leaching, and only slowly available to growing crops. Fixation occurs to a much greater extent in subsoils than in topsoils, and this is probably due to the increased clay content in the subsoil.

Ammonia may also react with lignins and certain organic compounds to form complexes that are not readily broken down and thus only very slowly available to plants and soil microflora. Broadbent et al. (1961) and Nommik and Nielsen (1963) studied the effect of soil pH on ammonia fixation, and their respective investigations indicated that ammonia fixation occurs to a large extent only in soils with pH above neutrality. In addition, a linear relationship between pH and ammonia fixation above pH 7 was demonstrated by Broadbent et al. (1967). However, Sohn and

Peech (1958) showed that acid soils containing a large amount of organic matter had the greatest ammonia fixing capacity. Ammonia fixed by soil increases with increased carbon or organic matter content of the soil (Sohn and Peech 1958; Burge and Broadbent 1961; Nommik and Nielsen 1963). Nitrogen thus fixed by both clay minerals and organic matter is slowly released to crops over a period of time.

Immobilization

Immobilization is the conversion of inorganic nitrogen into organic form by soil microorganisms. Immobilization occurs in both cropped and uncropped soil, but it is usually greater in the former. This is probably due to the presence of more energy material and more microorganisms in cropped soils. Walunjkar et al. (1959) observed that immobilization varied directly with the amount of organic matter present and the ease of decomposition of the organic matter. Both ammonium (NH_4^+) and nitrate (NO_3^-) nitrogen can be immobilized, but immobilization is usually greater with NH_4^+-N (Janson et al. 1955; Winsor and Pollard 1956a).

Studies conducted by Myer and Paul (1970) indicated that significant quantities of added nitrogen were immobilized. It was also shown in their studies that immobilization was greater in coarse-textured soil in the presence of straw and at a higher rate of N application. Maximum immobilization of applied nitrogen occurs when large quantities of readily decomposable crop residue of wide carbon to nitrogen (C:N) ratio are added to soils. When C:N ratio is greater than 25 to 30, an external source of N is required for a maximum rate of decomposition and immobilization (Pinck et al. 1946; Allison and Klein 1962). At a C:N ratio less than 20, no external source of N is needed, and N in the form of

NH_3 may be released.

The amount of nitrogen immobilized varies widely with many factors such as temperature, aeration, soil pH and moisture content because of the effects of these factors on microbial population and activity. Agarwal et al. (1972) observed that immobilization was fastest in alkaline soil in the presence of sucrose. Factors such as crop species, rate and amount of growth, stage of growth of plant and environmental conditions of the soil have roles to play in the amount of N immobilized. Inorganic nitrogen thus immobilized is not permanently unavailable to the plants. The lifespan of the microorganisms is comparatively short, and when the microorganisms die, decomposition and mineralization of the organic substrate take place, and the inorganic nitrogen is returned to the soil (Winsor and Pollard 1956b; Allison and Klein 1962; Agarwal et al. 1972).

Ammonia Volatilization

Free ammonia (NH_3) escapes when urea and ammonium yielding fertilizers are applied to the surface of soil that is neutral or alkaline in reaction (Martin and Chapman 1951; Volk 1959; 1961; Gasser 1964; Morrison and Foster 1977). In his detailed review of the reactions of ammonia in soils, Mortland (1958) stated that ammonia may be chemically sorbed by clay minerals or organic matter; it may be physically sorbed by soil colloids or it may just dissolve in the soil moisture. When ammonia is not chemically sorbed by soil, it is free to diffuse slowly through the soil to the atmosphere. The loss of N by ammonia volatilization is due to the reaction: $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$

It has also been shown (Ernst and Massey 1960; Wahab et al. 1960), that ammonia volatilization can occur in slightly acidic soils, especially

after application of a high rate of urea. When urea is applied to a slightly acidic soil, urea hydrolyses to ammonium carbonate which leads to a rise in soil pH to near or above neutrality. Such a situation is favourable for ammonia volatilization. Matocha (1976) reported volatilization loss of nitrogen as high as 18.5% of added N, when urea was applied to a fallowed acid fine sand. On the other hand, application of acidic ammonium salts to acid soils is less prone to induce ammonia volatilization since there is no likelihood of increased soil pH due to the addition of acidic ammonium salts.

Losses of N through ammonia volatilization are inversely related to soil exchange capacity (Gasser 1964; Chai and Hou 1977). Gasser, in his studies, reported that over 20% of added N was lost as ammonia from a soil with a cation exchange capacity of less than 10 meq per 100g soil when 112 kg/ha of urea was broadcast on the soil surface. The magnitude of NH_3 volatilization depends on the type of fertilizer added. Ammonia volatilization is greater with urea than ammonium sulphate when both are added to the same soil (Prasad 1976; Ventura and Yoshida 1977). Hargrove et al. (1977) observed the following ranges of N loss through ammonia volatilization: 3-10% of added N for ammonium nitrate; 36-45% for pelleted ammonium sulphate and 25-55% for liquid ammonia. Condition of the soil prior to application also determines the gravity of ammonia volatilization. When the soil is initially wet at the time of N application, volatilization losses of NH_3 are greater than when the soil is initially dry (Fenn and Escarzaga 1976). Considerable loss of N can occur through NH_3 volatilization, depending on the numbers of favourable factors in attendance at the time of fertilizer application. Losses of urea ranging from 20-70% of added N in brown calcareous Mediterranean soils have been reported

by Gama (1977).

Leaching Loss of N

Loss of added nitrogen through leaching may constitute one of the most important mechanisms of removal of inorganic nitrogen from field soils besides crop absorption. Susceptibility of a nutrient to leaching is directly related to the mobility of the nutrient in the soil. Nitrate nitrogen (NO_3^- -N) is very mobile and is the form of N which is readily moved by water, and thus most susceptible to leaching loss. Irrespective of the chemical form of N-fertilizer added, N was readily converted into nitrate under aerobic conditions (Olson 1972). Nitrate nitrogen is neither adsorbed to the soil nor forms sparingly soluble compounds. Thomas (1970) observed that NO_3^- -N was only weakly adsorbed in soils that have appreciable amounts of ferrous and aluminum oxides, coupled with pH values of 6 or less. Therefore, during a period of heavy rainfall, most of the NO_3^- -N in the topsoil may be moved to the subsoil by water percolating through the soil profile. Wetselaar (1961, 1962) found a high correlation between nitrate movement and amount of rainfall in tropical soils of Australia.

Downward movement of NO_3^- -N does depend also on the water holding capacity of the soil. The higher the water holding capacity of the soil, the less nitrogen will be lost to deeper layers by the same rainfall (Cooke and Cunningham 1957). This, and larger pore size probably explain why NO_3^- -N moves downward more readily in sandy than in clay or peat soils. The NO_3^- -N thus moved can either accumulate in the deeper soil, be lost in the drainage water, or be subject to denitrification.

Urea and other amino compounds are also soluble in water, and because they are only mildly adsorbed by soil particles, move readily with water. However, urea and other amino compounds have only a transient existence in soil since they are readily hydrolysed to ammonium. Ammonium nitrogen ($\text{NH}_4^+\text{-N}$) can be strongly adsorbed on soil colloids, if the adsorption capacity at the site is not saturated. Smith (1952) and Linser et al. (1959) have reported the possibility of a slow leaching of $\text{NH}_4^+\text{-N}$ that depends upon the rate of its exchange with other cations in the soil.

Under the continuous cropping system, leaching loss of N is much less of a problem than when no crop is growing (Allison 1955; Nelson and Uhland 1955). This is because of direct and rapid uptake of $\text{NO}_3^-\text{-N}$ by the growing crop and reduction of water in the soil by evapotranspiration. Such a condition prevents accumulation and downward movement of nitrate in the soil (Wetselaar 1961). Michalyna and Hedlin (1961) have shown that large amounts of nitrate may be located below the rooting zone when summerfallow is included in crop rotations.

Leaching loss of N can be very important in the tropics, even under a continuous cropping system. Leaching losses of N and potassium (K) of 65% and 50% of the amount added respectively, were reported (Gamboa et al. 1971) in Costa Rica when five crops of maize were grown over a period of three years.

Denitrification

Denitrification is the reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to nitrogenous gases, generally nitric oxide (NO); nitrogen dioxide (NO_2); nitrous oxide (N_2O); and molecular nitrogen (N_2). Denitrification is the most important source of loss of soil nitrogen as gaseous products and may be a major cause of low recovery of added

nitrogen in field soils. Losses in excess of 50% of applied nitrogen by denitrification have been reported by various workers (Gerretsen and de Hoop 1957; Wagner and Smith 1958; Soulides and Clark 1958; Broadbent and Clark 1965). Such N-losses are of great importance with respect to fertilizer economy, energy conservation, food production and environmental pollution. It is thought that N_2O may be harmful to the ozone layer in the upper atmosphere which may contribute to harmfully high levels of ultraviolet radiation at the earth's surface since the ozone layer adsorbs ultraviolet radiation. Shapely (1977) gave an estimated prediction of a 12% reduction of the ozone layer in 160 years from the exponentially increasing use of fertilizer.

Two pathways have been found to operate in the process of denitrification. One is the biological reduction of nitrate or nitrite to volatile nitrogenous gases. Biological denitrification is an enzymatic process accomplished mainly under anaerobic conditions. The other pathway is non-biological, achieved under aerobic conditions, purely by chemical processes. This is usually referred to as chemodenitrification (Clark 1962).

Biological Denitrification

Biological denitrification is usually accomplished by facultative anaerobic bacteria, capable of utilizing nitrate in place of oxygen as a hydrogen acceptor. When soils become waterlogged, oxygen is excluded or is present in very low concentrations. Under such situations, and in the presence of nitrate or nitrite, coupled with a readily available source of energy, biological denitrification usually occurs. Nitrate respiration of bacteria in the absence of oxygen may be expressed by the following equation: $C_6H_{12}O_6 + 4NO_3^- \longrightarrow 6CO_2 + 6H_2O + 2N_2 + 4e^-$. Nitrate is first reduced to nitrite and then simultaneously converted

to gaseous products - nitrous oxide and/or molecular nitrogen (Wijler and Delwiche 1954; Nommik 1956; Schwarzbeck et al. 1961; Bollag et al. 1973).

Gaseous loss of N by denitrification may be well pronounced in neutral and alkaline soil, under conditions of poor aeration, and in the presence of active microbial population. Biological denitrification is usually reduced when the soil pH is less than 7.0 (Broadbent and Clark 1965), and the optimum soil pH for biological denitrification has been reported to be between 8.0 and 8.3 (Russell 1973). Decrease in soil pH intensifies NO_2^- toxicity (Tyler and Broadbent 1960), and this appears to inhibit biological denitrification (Broadbent and Clark 1965). Nitrite toxicity can also result from the inability of one strain of denitrifying bacteria to carry NO_3^- reduction beyond the NO_2^- stage. This causes accumulation of NO_2^- which retards the growth of another strain and thus inhibits denitrification (Bollag et al 1970).

When organic matter is added to soil, microbial activity is increased and this may cause oxygen stress which gives a favourable condition for denitrification to occur (Wijler and Delwiche 1954; Myers and McGarity 1972; Stefanson 1972). Biological denitrification is most rapid with easily decomposable carbohydrates such as sugars, and least with lignin and sawdust (Broadbent and Clark 1965). Oxygen concentration in the soil is one of the most important factors influencing biological denitrification since oxygen concentration determines whether anaerobic reduction can proceed or not. In general, all factors which decrease the oxygen status of the soil will promote denitrification. Russell (1973) reported that active reduction of NO_3^- does not occur in a liquid medium until the oxygen concentration is as low as 4×10^{-6} M.

An increase in soil temperature increases biological denitrification. Nommik (1956); Bremner and Shaw (1958b) found the optimum temperature to be as high as 60-65°C, with more N_2O being produced at a lower temperature. The relative proportion of N_2O and N_2 in the denitrification gas varies with temperature. Molecular nitrogen is predominant at a higher temperature.

Soils which are apparently well aerated have been observed to reduce nitrates to nitrous oxide, especially when supplied with readily decomposable organic matter (Allison et al. 1960; Carter and Allison 1960; Cady and Bartholomew 1960, 1961; McGill 1971; Myers and McGarity 1972). This indicates that many moist soils may possess a range of microhabitat containing varying levels of oxygen supply (Russell 1973). Such soils may contain clods that have no free air at field capacity and the soil within the clod will be anaerobic. Nitrification and denitrification can take place simultaneously in such soil when it is at field moisture capacity (Arnold 1954; Greenland 1962). This explains the experimental results in literature showing that denitrification can take place in aerobic soils.

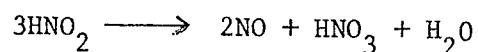
Chemical Denitrification

There has been evidence that considerable gaseous loss of N occurs through chemical decomposition of nitrite formed by nitrification of ammonium fertilizers in the soil (Broadbent and Clark 1965; Allison 1966). Nitrite accumulates in soils as a result of heavy application of urea or ammonium yielding fertilizers (Jones and Hedlin 1970; Pang et al. 1973). Various workers have reported chemical decomposition of nitrite when nitrite is added to, or when it accumulates in soils of acidic or slightly acidic nature. When the soil moisture

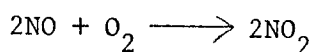
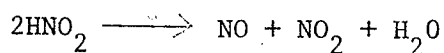
content was low, and in the absence of oxygen, Cady and Bartholomew (1960) and Bollag *et al* (1973) observed evolution of NO when NaNO_2 was added to soils of pH 4.5-5.0.

A review by Broadbent and Clark (1965) summarized the possible pathways for chemical denitrification:

(a) Since nitrous acid is unstable below pH 5.5-6.0 (Allison 1963), it decomposes according to the equation:



Some of the nitrogen dioxide (NO_2) formed may react with water to form nitrous acid and nitric acid. Recent work by Nelson and Bremner (1969) suggested that self decomposition of nitrous acid may be represented by:

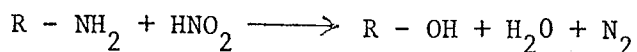


Nitrogen dioxide produced from the reaction can be converted to nitrate. In the absence of oxygen, nitric oxide (NO) and NO_2 are the gaseous products of chemical denitrification.

(b) Reactions of nitrous acid with α -amino acids

(a van Slyke reaction)

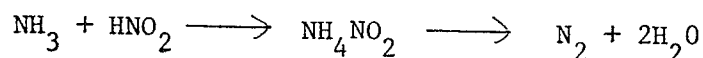
Under an acidic condition (pH 5 or less) nitrous acid reacts with α -amino acids to yield molecular nitrogen according to the reaction:



(c) In a similar reaction to the above, ammonia or ammonia derived from urea may react with nitrous acid to yield molecular nitrogen.



A modification of the van Slyke reaction of ammonia and nitrous acid was proposed by Allison (1963) as:



Investigations conducted on the urea-nitrous acid reaction showed that the concentration of reactants and the low pH required for the evolution of N_2 , made the occurrence of this reaction unlikely in most soils (Sable and Reed 1964). Generally, it is thought that the van Slyke reaction is of little importance in chemical denitrification (Smith and Clark 1960; Clark et al. 1960; Allison 1963; Sable and Reed 1964; Broadbent and Clark 1965). The major objections are that nitrite is not stable in acid conditions and thus will not accumulate. The reaction proceeds slowly and requires greater acidity than is usually found in soils. However, Cho and Sakdinan (1976) obtained a fairly rapid evolution of molecular nitrogen as the major gas produced when soil (pH 6.8) was treated with tagged NaNO_2 in an aerobic atmosphere.

(d) Reactions of nitrous acid with other soil constituents.

Data from Soullides and Clark (1958) and Clark et al. (1960) suggested that the amount of organic matter present in a soil influenced the quantity of gaseous nitrogen lost therefrom. In a further work (Clark and Beard 1960), it was noted that at a given pH value, nitrite showed greater instability in the presence of soil than in its absence. More recent investigations by Nelson and Bremner (1969, 1970a) indicated that gaseous loss of N in nitrite-treated soil was related to organic matter and that the role of soil minerals in nitrite decomposition was insignificant.

Methods of Improving Crop Recovery of Applied N Through Fertilizer Management

Low crop recovery of added N is caused by various forms of loss and temporary tie-up of nitrogen fertilizers. These losses can be reduced by adequate management of N-fertilizers so as to make nitrogen available to the plant in the form, at the time, and in correct amount that is required for optimum crop utilization of added nitrogen. In determining the effective management of N-fertilizers, primary factors which should be considered are: rate, time and method of application, and characteristics of the N carrier.

The amount of N required by a crop varies with many factors such as crop species and expected yield. A meaningful rate evaluation must also take into account the amount of residual N from previous application and/or natural microbial mineralization of the soil organic matter (Olson 1972). When N application is made in excess of what is required for maximum crop production, immobilization of added N can occur. Myer and Paul (1970) concluded in their studies that immobilization of applied nitrogen was greater at higher rates. Recoveries of 88 and 76% of added nitrogen were obtained (Ashley et al. 1965) for low and high rates respectively.

Timely application of N-fertilizer for effective crop utilization is an important factor which has received considerable attention throughout the world. Most of the studies, on timely application of N, have demonstrated the necessity of having an established root system before an effective crop utilization of applied N can be achieved (Olson et al. 1964a; IAEA 1969; Lathwell et al. 1970). When N-applications are made far in advance of the time of crop use, risk of N-loss is increased. Various workers have reported benefit from spring over fall application of N (Pearson et al. 1961; Donald et al. 1963;

Kurtz and Smith 1966; Ridley 1973).

Placement of N-fertilizer has a significant role to play in the availability of added N and its efficient utilization by the crop. It is generally recognised that surface application of ammonia type fertilizer carriers, and of urea, is inefficient because of ammonia volatilization, especially on soils that are calcareous or otherwise have high pH, (Martin and Chapman 1951; Mitsui 1954; Volk 1959; Meyer et al. 1960). Volatilization losses of N as high as 50% of that added on the soil surface, have been reported by many workers (Mitsui 1956; Morrison and Foster 1977; Hargrove et al. 1977). Nitrogen loss through volatilization can be limited by incorporation of the fertilizer with soil to permit adsorption of the ammonium ion on the soils exchange complex where it is fairly secure (Mikkelsen and Finrock 1957; Volk 1959; Meyer et al. 1961; Joint FAO/IAEA Division 1970). Banding of nitrogen fertilizer to the side of, and below the seed, was found to be more effective than when nitrogen was applied by broadcasting and mixing throughout the soil. MacLeod et al. (1975) reported higher grain yield of barley when nitrogen fertilizer was placed 5 cm to the side of, and 5 cm below the seed, than when broadcast on the soil surface. Ridley (1977) observed that banding of nitrogen fertilizers in rows placed at a right angle to the direction of seeding resulted in increased nitrogen uptake and crop yields. Banding reduced loss because of the decreased contact of the fertilizer N with micro-organisms which might have immobilized or nitrified the added N.

Thus, greatest crop use and least loss of applied N is likely to occur when N-fertilizers are adequately managed.

Slow-Release Nitrogen Fertilizers

Considerable interest has developed recently in "controlled" or "slow release" N fertilizers. The purpose of developing these fertilizers is to reduce losses of N, by delaying release of N so that it occurs at the optimum time for plant uptake. Two general ways to achieve this are: (1) synthesizing chemical compounds with inherently slow rates of dissolution and (2) application of coatings or moisture barriers to the surface of water soluble fertilizer particles (Prasad et al. 1971).

Many different slow release N-fertilizers have been investigated to determine their economic feasibility when applied to the agricultural enterprise. Some materials, such as ureaform, crotonylidene diurea (CDU) and isobutylidene diurea (IBDU) have been patented and produced commercially. Ureaform is used mainly on turfs and lawns where the rate of nitrogen consumption is fairly steady and N is required for the entire growing season. Ureaform has not shown any good performance with field crops, especially upland crops (Iswaran et al. 1961; Killian 1964; Scarsbrook 1958). However, an increase in the yield of lowland rice with ureaform, as compared to urea and ammonium sulphate was recorded by Akhundov (1965). In their long term studies on the evaluation of slow release nitrogen sources on turfgrass, Waddington et al. (1976) concluded that proper use of slow release nitrogen fertilizers should be based on their individual release characteristics and factors affecting rate and longevity of release. The greatest response was

obtained with ureaform.

Resins and sulphur have been extensively studied as coatings for restricting release of N from soluble materials. Development of sulphur coated urea (SCU) draws academic interest from the standpoint of cost, technology of preparation, and presence of sulphur which is also an important plant nutrient (Rindt et al. 1968). Sulphur coated urea has been shown (Furura et al. 1968) to be an excellent source of N for ornamental plants in containers, as single application of SCU could supply an adequate amount of N for several month's growth.

Nitrification Inhibitors

Leaching and denitrification losses of fertilizer N constitute the major channels of N-loss in most field soils. These losses occur when nitrogen fertilizer is applied in, or after its conversion to nitrate form. Therefore, adding ammonium or ammonium yielding fertilizers, and preventing nitrate formation may reduce N-losses and thus increase crop utilization of added nitrogen. Goring's investigations (1962a,b) stimulated interest in the prevention of nitrification of ammonium fertilizers, and led to the development of fertilizer blended with chemicals having nitrification inhibitory properties.

A large number of chemical compounds have been tested for their nitrification inhibitory properties. Among the chemicals involved are: thiourea (Fuller et al. 1950; McBeath 1962); mercapto compounds (Brown et al. 1956; Fredrick et al. 1957; Millbank 1959); dicyandiamide, thiourea, isothiocyanates (Harada et al. 1964; Kinoshita et al. 1966); pyridine, pyrimidine, anilines (Andreeva and Shcheglova 1967); potassium azide (Hughes and Welch 1968) and carbon disulphide (Powlson and Jenkinson 1971). Objectives of product development in this area are: to obtain

materials that will supply nitrogen to the crop continuously over an extended time interval; to reduce leaching and runoff losses; to retard gaseous losses of N; to limit biological immobilization reaction in soil; and to minimize luxury consumption of nitrogen. Such chemicals can have a considerable influence on nitrogen nutrition of plants because of their inhibitory effect on nitrification of the ammonium fertilizers applied concurrently (Hauck and Koshino 1970).

Among factors affecting the effectiveness of nitrification inhibitors are: soil type (Goring 1962); soil temperature (Bundy and Bremner 1973; Boswell 1976) and source of nitrifiable nitrogen (Bundy and Bremner 1973). Investigating the effectiveness of 24 compounds proposed as inhibitors, Bundy and Bremner observed that most of the inhibitors were more effective at 15°C than at 30°C. They also noted that the performance of the inhibitors was markedly influenced by soil type, being more effective on light than on heavy textured soils. Bundy and Bremner reported that the average effectiveness of the most potent inhibitors decreased in the order: 2-chloro-6-(trichloromethyl) pyridine ("N-Serve") > 4-amino-1,2,4-triazole (ATC) > sodium or potassium azide > 2,4-diamino-6-trichloromethyl-S-triazine (CL 1580) > dicyandiamide > 3-chloroacetanilide > 1-amidino-2-thiourea > 2,5-dichloroaniline > phenylmercuric acetate > 3-mercapto 1,2,4 triazole or 2-amino-4-chloro-6methyl-pyrimidine (AM) > sulfathiazole (ST) > sodium diethyldithio-carbamate.

Some volatile sulphur compounds like carbon disulphide, dimethyl-disulphide, methylmercaptan, demethyl sulphide and hydrogen sulphide have also been found to retard nitrification of ammonium in soils incubated in closed systems (Bremner and Bundy 1974). Carbon disulphide was found to be the most effective of the volatile sulphur compounds studied.

Bremner and Bundy reported that carbon disulphide was more effective than the patented inhibitors ('N-Serve', AM and ST) for inhibition of nitrification in a closed system.

Very few of the nitrification inhibitors already patented are capable of meeting the desired qualities of specificity, mobility, persistency and economy. Among those nitrification inhibitors that have been subjected to continuous intensive investigation, 'N-Serve' appears to be the most promising in retarding nitrification and thus conserving N, by keeping nitrogen in the reduced form.

'N-Serve'

'N-Serve' is the trade name for 2-chloro-6-(trichloromethyl)pyridine, patented by Dow Chemical Co., Midland, Michigan, U.S.A. 'N-Serve' is toxic to *Nitrosomonas* - the nitrifying bacteria oxidizing ammonium nitrogen to nitrate, but the inhibitor possesses a low order toxicity to enzymes converting urea to ammonia (Shattuk and Alexander 1963). 'N-Serve' is very volatile and can readily be lost from soil or degraded to 6-chloropicolinic acid (Dow Chemical Co., 1962; Alexander 1963). At 20°C, the solubility of 'N-Serve' in water is very low, being 0.004 g/100 ml. Acetone appears to be a good solvent for 'N-Serve' (153 g/100 ml). In anhydrous ammonia at 23°C, the solubility of 'N-Serve' is 38 g/100 ml (Prasad et al. 1971).

Movement of 'N-Serve' in the soil is rather limited; therefore, it stays at a high concentration within the zone of application along the fertilizer band (Ashworth et al. 1975). Thus, application of 'N-Serve' by broadcast method in the soil, was more effective than when 'N-Serve' was banded (Gasser and Penny 1964). This better effectiveness by broadcast method was probably due to the fact that 'N-Serve' was present in a lethal concentration over a larger volume of soil.

Performance of 'N-Serve' as an inhibitor can be affected to a great extent by the reaction of the soil. Hendrickson et al. (1977) (unpublished) observed that 'N-Serve' was less effective in soils with high pH.

When 'N-Serve' is applied at rates varying from 0.2 to 2.0% N, the chemical has been shown to inhibit nitrification of ammonium and ammonium yielding fertilizers, both under laboratory and field conditions (Goring 1962a; McBeath 1962; Turner et al. 1962; Gasser and Penny 1964; Nielsen and Cunningham 1964; Vlassak 1964; Ansorge et al. 1967; Sabey 1968; Prasad 1968; Prasad and Rajale 1972; Bundy and Bremner 1973). A beneficial effect of 'N-Serve' to many crops by increasing crop yield and N recovery both under field and pot conditions has been reported by several workers. Increased yield of upland rice subjected to alternate wetting and drying (Prasad et al. 1966, 1970b; Lakhdive and Prasad 1970; Rajale and Prasad 1970) and higher recovery of applied N (Prasad 1968) were achieved through the use of 'N-Serve' on ammonium fertilizers. Similarly, increased yields of irrigated sugar beet, sweet corn and cotton (Sweezy and Turner 1962) and higher yields of hybrid maize and sugar cane (Das et al., 1965; Prasad and Turkede 1971) have been reported as due to the treatment with 'N-Serve'.

Some workers, however, have not been able to find any consistent crop yield benefit in the use of 'N-Serve' as a nitrification inhibitor (Parish et al. 1965; Jaworski and Morton 1967). It is apparent that the effectiveness of nitrification inhibitors is always well pronounced in soils having potentials for loss of nitrogen through denitrification or leaching. In summarizing the results of a series of experiments involving the use of 'N-Serve' in Nebraska, Olson et al. in 1977

(unpublished) reported that there had not been any consistent yield benefit derived from 'N-Serve' treatment. Hendrickson et al. in 1977 (unpublished) also reported the lack of significant increase in grain yield with 'N-Serve' treatment.

2-Amino-4-Chloro-6-Methylpyrimidine ('AM')

'AM' is a product of Toyo Koatsu Industries, Inc., Tokyo. 'AM', like 'N-Serve' is toxic to ammonium oxidizing autotrophs-Nitrosomonas. 'AM' is less soluble in acetone and anhydrous ammonia than 'N-Serve'. At 25°C, the solubility of 'AM' in acetone is 3.016 g/100 ml and at the same temperature in anhydrous ammonia, the solubility of 'AM' is 4.9 g/100 ml.

A very distinct effectiveness of 'AM' in retarding the nitrification of ammonium sulphate under waterlogged conditions has been reported by various workers (Prasad and Lakhdiva 1969; Mitsui Toatsu Chemicals Inc., 1969; Prasad 1970). 'AM' has an inhibitory effect on nitrification of urea, and the effectiveness of 'AM' increased with increase in concentration (Rajale and Prasad 1970b; Listanka 1972). Like 'N-Serve', 'AM' has been shown from various experiments (Rajale 1970; Prasad and Bains 1968; Weir and Davidson 1968) to increase yield of upland rice. Both 'AM' and 'N-Serve', have been found to be equally effective in preventing nitrification of ammonium fertilizers and in increasing the yield of upland rice grain (Sabey 1968; Prasad et al. 1970).

Carbon disulphide (CS₂)

Recently, carbon disulphide has been recognized as a very potent nitrification inhibitor in a closed system in the laboratory (Powlson and Jenkinson 1971; Bremner and Bundy 1974; Ashworth et al. 1975).

Carbon disulphide is an inexpensive nitrification inhibitor, unlike those inhibitors that are already patented ('N-Serve' and 'AM') and produced commercially. Carbon disulphide is very volatile, highly toxic and is soluble in alcohol.

In their investigation on the effectiveness of some volatile sulphur compounds as nitrification inhibitors of ammonium based nitrogen fertilizers, Bundy and Bremner (1974) found CS_2 to be the most effective compound. Bundy and Bremner (1974); Ashworth *et al.* (1975) reported that CS_2 was more effective than either 'N-Serve' or 'AM' in a closed system. Ashworth *et al.*, in their studies observed that CS_2 diffused further in the soil than 'N-Serve' and that it was detected throughout a 20 x 20 cm cross section, one week after application. 'N-Serve', on the other hand, remained concentrated around the injection point and rate of decomposition was slow (Ashworth *et al.* 1975). Nyborg and Malhi (1977), in their studies of carbon disulphide as a source of sulphur, observed that CS_2 inhibited the nitrification of applied urea for about 4 weeks.

Thiourea [(NH₂)₂CS]

The performance of thiourea as a nitrification inhibitor has been carefully investigated by McBeath (1962) and Fuller and his co-workers (Fuller *et al.* 1950; Fuller 1963). When concentration of thiourea is high in the soil, it inhibits the growth of *Nitrosomonas* and prevents active nitrification of ammonium nitrogen (Hays and Forbes 1974). Hays and Forbes in their work, noted that a concentration of 4-8 mg of thiourea per 100 g of soil retarded nitrification for 3-6 weeks. At Rothamsted Experimental Station, Gasser and Hamlyn (1968) found that thiourea retarded nitrification when mixed with soil in large amounts. Data of Nyborg (1976) indicated that thiourea was more effective when

banded than when mixed with the soil.

Increase in the yield of barley as a result of addition of thiourea at the rate of 56 kg N/ha was reported by Fuller in 1963. Application of thiourea resulted in an increase in crop yield as a result of its inhibitory property. Results of experiments conducted at eight different centres in Japan showed that thiourea treated ammonium sulphate gave an 18% higher yield of rice over untreated ammonium sulphate (International Rice Committee 1966).

4-Amino-1,2,4-triazole (ATC)

ATC is produced and patented by Ishihara Industries, Japan.

ATC is a new type of nitrification inhibitor which is water soluble and does not separate from applied nitrogen. Tests conducted at the Agricultural Technological Research Centre, Agricultural and Forestry Ministry in Japan have shown that ATC has an outstanding nitrification inhibitory property. In a recent comparison of the effectiveness of compounds patented as inhibitors of nitrification in soils, Bundy and Bremner (1973) found ATC to be one of the most effective inhibitors.

Data from the field studies conducted at Nagano Prefectural Agricultural Experiment Station showed that upland rice absorbed more nitrogen and that the availability of nitrogen was high in plots where ATC was applied. It was also noted that ATC contributed to the acceleration of plant growth, and this may well make ATC a very promising agent in the production of farm crops when used in a nitrogen fertilizing program. More investigations are needed on ATC to confirm all the qualities attributed to it as a nitrification inhibitor.

MATERIALS AND METHODS

I. Laboratory Experiment

Soil

Three soils, Wellwood L, Lakeland SiC, and Pine Ridge S were used in the laboratory studies. These soils were collected in the early fall of 1976 from the 0 to 15 cm depths of cultivated fields, air-dried immediately after collection, ground to pass through a 2 mm sieve and stored at 5°C. Subgroup designations and some physical and chemical properties of the soils are shown in Table 1.

Two types of containers were constructed to simulate two methods of fertilizer application: banded and broadcast.

(i) Banded - Containers 204 x 102 mm were made using p.v.c. pipe which was split in half, and polyethylene material for the ends. The internal radius was 102 mm. The ends were fastened with nails (Fig. 1).

(ii) Broadcast - A cylindrical container was cut from acrylic plastic tube with an internal diameter of 102 mm and height of 102 mm. This section of pipe was then cut into four equal sections, which upon completion of the experiment, facilitated separations. They were held together with adhesive tape. The whole unit was placed on a 102 x 102 mm plastic plate and held together with tape (Fig. 2).

Source and Rate of Nitrogen

Nitrogen source was fertilizer grade urea (46-0-0) applied at a rate calculated to provide 100 kg N/ha on an area basis. The urea was in a prilled form.

Table 1. Subgroup Designation, Physical and Chemical Characteristics of the Soils.

Soil Name	Wellwood	Lakeland	Pine Ridge
Subgroup	Black Chernozem	Gleyed Carbonated Rego Black Chernozem	Degraded Eutric Brunisol
Texture	L	SiC	F.S.
pH	6.1	7.9	5.4
C.E.C. (meq/100 g)	29.9	25.3	5.1
Conductivity (mmho)	0.2	1.0	1.2
% Organic Matter	5.9	4.3	1.0
% CaCO ₃ Equivalence	0.2	42.2	0
% Moisture Content at Field Capacity	27.0	22.4	17.3
NaHCO ₃ Extr. P (ppm)	10.6	5.8	15.4

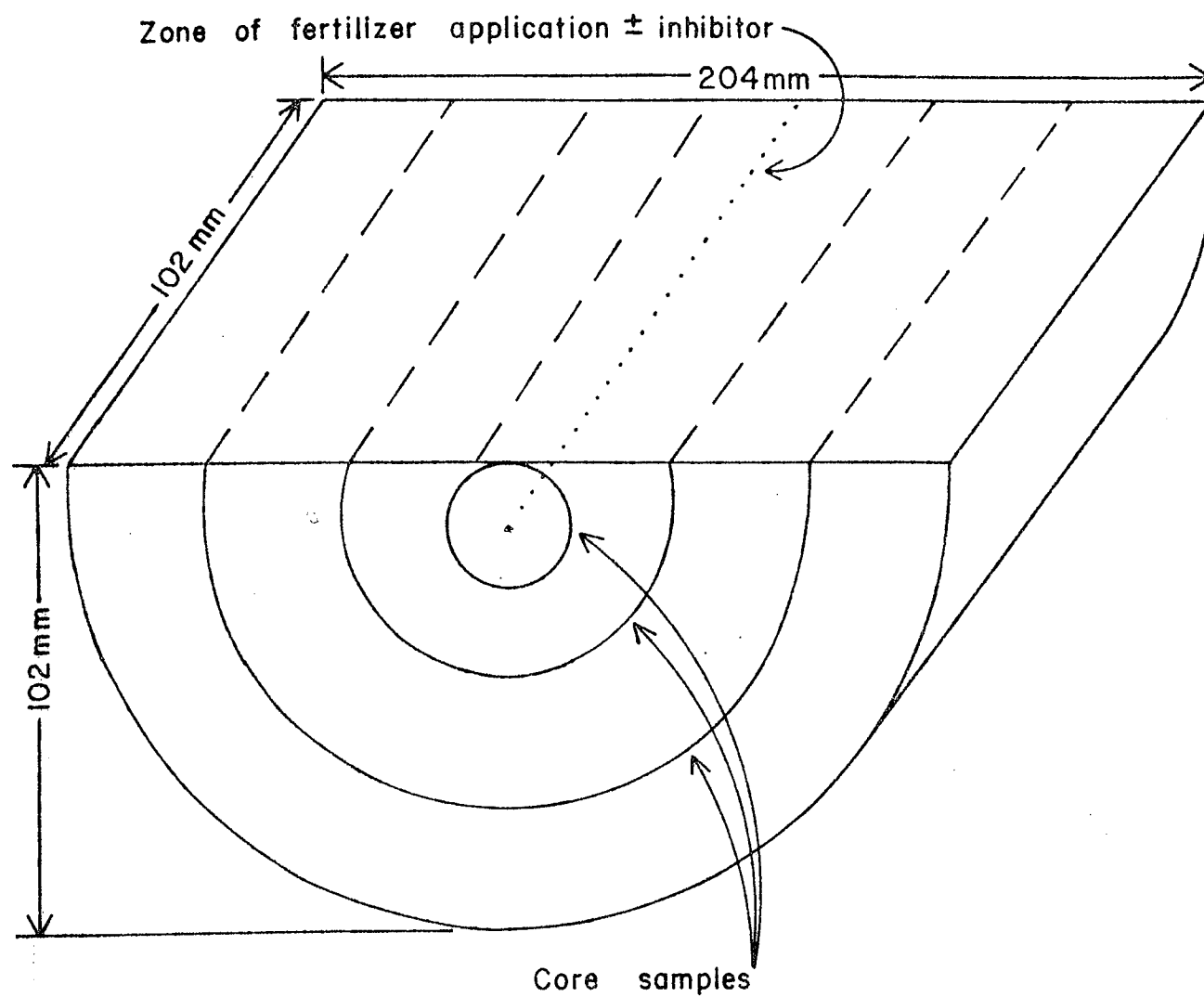


Figure 1. Container fabricated for banded treatments.

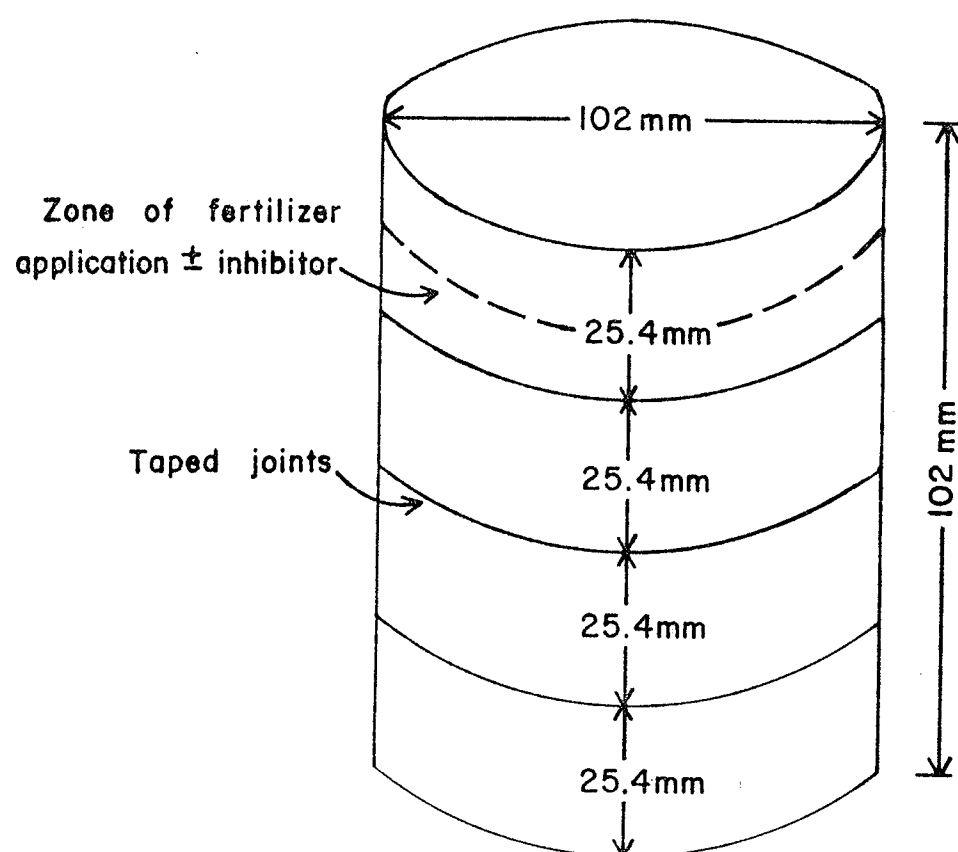


Figure 2 Container fabricated for broadcast treatments.

Nitrification Inhibitors

Nitrification inhibitors used were:

- i. 2-chloro-6-(trichloromethyl)-pyridine, 'N-Serve' of Dow Chemical Company, Midland, Michigan, U.S.A.
- ii. Carbon disulphide (CS_2) manufactured by Thio-Pet Chemicals Ltd., Fort Saskatchewan, Alberta.

i. 'N-Serve' has a long lasting residual effect and is a moderately persistent chemical. The movement of this chemical in soil is very limited (Briggs 1975).

ii. Carbon disulphide is a short persistent chemical with no residual effect (Ashworth et al. 1977). Carbon disulphide diffuses very rapidly in soil.

Inhibitors were applied at equal rates on an area basis for broadcast and banded treatments. The amount applied was 0.2 ml per container for banded and 0.078 ml per container for broadcast treatments. The inhibitors were applied with a syringe to 50 cc of the soil to be used, and mixed thoroughly in a tightly closed plastic bag just before applying fertilizer. This minimized the loss of inhibitor due to volatilization.

The containers were filled with soil and distilled water was added at a rate calculated to bring the soil to field capacity. For the banded container holding 1600 g soil, 449 mg per pot of prilled urea was applied as a band 102 mm in length in the centre and 13 mm below the soil surface. The inhibitor mixed with soil was immediately spread over the fertilizer and covered with soil.

For broadcast treatments, the container, holding 750 g soil, had soil placed within 13 mm of the top and 176 mg per pot of prilled urea was spread uniformly on the surface. Soil mixed with the inhibitor was immediately placed on top of the fertilizer, then additional soil was added to fill containers. Treatments were prepared in plastic bags immediately after treatment. The bags were tightly secured and placed in the laboratory. They were opened daily throughout the period of incubation in order to change the air and prevent reducing conditions. The temperature in the laboratory during the experiment ranged between 15 and 20°C. The longest period of incubation was 12 weeks.

Sampling Technique

Band treatment - Soils were sampled in cores extending along the line of fertilizer placement. This method was necessary because of the possible diffusion of nitrogen in all directions from the fertilizer application point. At the time of sampling the soil was divided into four zones based upon distance from the fertilizer band. Zone A included a core of soil having a radius of 1.27 cm from the fertilizer band. Zones B, C and D were 1.27 to 3.81 cm, 3.81 to 6.35 cm, and 6.35 to 8.89 cm away from the treatment band respectively (Fig. 4). Samples were placed in plastic bags which were immediately sealed and the samples were frozen.

Broadcast treatment - Samples were taken from each depth by removing the tapes from the containers and thus separating the rings. Soil within each ring was thoroughly mixed, and a subsample was placed in a polyethylene bag, sealed and frozen.

Table 2. Treatments for Laboratory Experiment.

	Soil	Fertilizer Applied	Inhibitor Applied	Method of Application	Sampling Periods (weeks)			
					A	B	C	D
1.	Wellwood	Urea	None	Banded	1,	3,	6	& 12
2.	"	Urea	'N-Serve'	Banded	1,	3,	6	& 12
3.	"	Urea	CS ₂	Banded	1,	3,	6	& 12
4.	"	None	None	-	1,	3,	6	& 12
5.	"	None	'N-Serve'	Banded	1,	3,	6	& 12
6.	"	None	CS ₂	Banded	1,	3,	6	& 12
7.	"	Urea	None	Broadcast	1,	3,	6	& 12
8.	"	Urea	'N-Serve'	Broadcast	1,	3,	6	& 12
9.	"	Urea	CS ₂	Broadcast	1,	3,	6	& 12
10.	"	None	None	-	1,	3,	6	& 12
11.	"	None	'N-Serve'	Broadcast	1,	3,	6	& 12
12.	"	None	CS ₂	Broadcast	1,	3,	6	& 12
13.	Lakeland	Urea	None	Banded		3		
14.	"	Urea	'N-Serve'	Banded		3		
15.	"	None	None	-		3		
16.	"	None	'N-Serve'	Banded		3		
17.	"	Urea	None	Broadcast		3		
18.	"	Urea	'N-Serve'	Broadcast		3		
19.	"	None	None	-		3		
20.	"	None	'N-Serve'	Broadcast		3		
21.	Pine Ridge	Urea	None	Banded		3		
22.	"	Urea	'N-Serve'	Banded		3		
23.	Pine Ridge	None	None	-		3		
24.	"	None	'N-Serve'	Banded		3		
25.	"	Urea	None	Broadcast		3		

(Continued)

Table 2 (Continued)

26.	Pine Ridge	Urea	'N-Serve'	Broadcast	3
27.	"	None	None	-	3
28.	"	None	'N-Serve'	Broadcast	3

Sampling was done at four times, i.e., at 1, 3, 6 and 12 weeks after incubation. At each sampling date, samples were immediately frozen. Samples were later analyzed for ammonium nitrogen, nitrate nitrogen, nitrite nitrogen and moisture content.

Analytical Procedures

1. Soil pH: pH was determined electrometrically following the procedure outlined by Schofield and Taylor (1955). A 1:2 ratio of soil to CaCl_2 solution was prepared using 12.5 g of soil and 25 ml of 0.01 M CaCl_2 . A calomel electrode pH meter was used. The suspension was allowed to equilibrate for 30 minutes before determining pH.
2. Soil Organic Matter: Organic matter was determined as described by Walkley and Black (1934). The organic matter was oxidized with excess potassium dichromate. The excess potassium dichromate was back-titrated with ferrous sulphate, using an automatic titrator.
3. Electrical Conductivity: The electrical conductivity of a soil-water saturated paste extract was measured by using a conductivity metre (type CDM 2, Bach-Simpson Ltd.)
4. Inorganic Carbonate Content: A one-gram soil sample was digested in 10% HCl for ten minutes. The CO_2 evolved was drawn through a drying absorption train. It was then absorbed by ascarite in a Nesbitt tube. The weight of CO_2 absorbed was determined and the inorganic carbonate content of the soil was calculated.
5. Moisture Content at Field Capacity: Soil, ground to pass through a 2 mm sieve was placed in a one-litre graduated cylinder. Sufficient water was added to wet the upper half of the soil column. The column was covered with plastic film fastened with a rubber band

and permitted to equilibrate for four days. After downward movement of water had ceased, a soil sample was taken above the wetting front in the cylinder. The sample taken was weighed before and after drying at 105°C for 24 hours. The difference in weights of the sample was determined and the moisture content of the soil was calculated.

6. NaHCO₃ Extractable Phosphorus: NaHCO₃ extractable P was determined as outlined by Olsen *et al.* (1954). Five grams of soil were shaken for 30 minutes with 100 ml of 0.5 N NaHCO₃ extracting solution. The suspension was filtered and 25 ml aliquot of the extract was taken. Five ml of mixed reagent (7.5 g ammonium paramolybdate, 0.14 g antimony potassium tartrate and 88 ml sulphuric acid) were added. After allowing this to stand for 5 minutes, the absorbance was read on Cecil spectrophotometer at 885 nm.

7. Cation exchange capacity: The cation exchange capacity of the soil samples was determined by the ammonium saturation method of Chapman (1965). A 25 g air-dried soil sample was shaken for one hour with 50 ml of 1 N NH₄OAC (pH 7.0) in a 250 ml Erlenmeyer flask. After filtering, the soil was leached 4 times with neutral 1 N NH₄Cl and once with 0.25 N NH₄Cl. The soil was then washed with 200 ml 99% Isopropyl alcohol. The NH₄⁺-saturated soil was leached with 10% acidified NaCl to remove ammonium from the exchange sites. The leachate was distilled into a flask containing 50 ml boric acid (2%) solution. The ammonium in the distillate was determined quantitatively by titrating with 0.1 N H₂SO₄.

8. Ammonium Nitrogen (NH₄⁺-N): Ammonium-N was determined using an ammonium electrode - Orion Model 801A digital pH/mv metre. Soil samples which had been previously frozen were thawed and prepared immediately for analysis. Ammonium-nitrogen was extracted by shaking

10 g of moist soil in 100 ml of 2 N KCl solution for one hour. The suspension was filtered through a Whatman No. 42 filter paper. To a 50 ml aliquot of the filtrate was added 0.5 ml of 10 M NaOH. This was thoroughly mixed by using a magnetic stirrer. Direct reading was taken on the ammonium electrode. Ammonium concentration in ppm was obtained by using the calibration curve prepared from readings of standard solutions. A calibration curve was constructed each time a new set of samples was analysed. The standard solutions consisted of 1.0, 2.5, 5.0, 8.0, 10.0 and 100 ppm of NH_4Cl .

9. Nitrite and Nitrate Nitrogen: Determination of nitrite and nitrate nitrogen was done colorimetrically using a Technicon auto-analyzer as outlined by Kamphake et al. (1967).

A 2.5 g air dried soil sample was weighed into a 125 ml Erlenmeyer flask. One gram of activated charcoal (Darco G-60, CX650 L1026) was added to remove color resulting from organic matter. Extraction was accomplished by shaking the soil with 50 ml 0.5 M NaHCO_3 (pH 8.5) for 30 minutes on the Eberbach reciprocating shaker at medium speed. The soil suspension was filtered through a Whatman No. 40 filter paper into a 125 ml beaker. A portion of the filtrate was transferred to the autoanalyzer sampling cup and analyzed for nitrite nitrogen. Another portion was treated with copper and hydrazine to reduce nitrate to nitrite. This represented combined nitrate and nitrite nitrogen. The concentration of nitrate was calculated by difference. A reagent blank and standard soil sample were included with each set of 48 samples analyzed. Standard solutions and a calibration curve were prepared in order to obtain nitrite and nitrate concentration in ppm.

II. Field Experiment

Materials

A field plot was obtained in the spring of 1977 on a Wellwood L near Carberry (3-11-14W). The site had not been fertilized in recent years. The experimental site occupied an area 36.6 by 24.4 metres. Each plot was 6.1 metres long and 2.13 metres wide. The subgroup designation and some physical and chemical properties of the soil are shown in Table 1.

Urea (46-0-0) was the nitrogen fertilizer used in this experiment. Rate of N applied was 67.2 kg N/ha. The amount required per 6.1 metre row was weighed into paper bags prior to application.

The nitrification inhibitors used were: 'N-Serve' [2-chloro-6-(trichloromethyl)-pyridine]; carbon disulphide (CS_2); and thiourea $[(\text{NH}_2)_2\text{CS}]$.

'N-Serve' at the rate of 0.5 ml per row of 6.1 metre (an amount equivalent to 2.24 l/ha) was mixed with 50 cc of soil taken from the plot area. Carbon disulphide at the rate of 3.85 ml/row (the commercially recommended rate to supply 16.8 kg S/ha¹) was mixed with 50 cc of the soil obtained from the plot site. Thiourea was weighed into bags and mixed with urea fertilizer at a ratio of one part Thiourea to four parts urea. Barley - Hordeum vulgare L. variety Conquest was the test crop used.

Method

Experimental design was a randomized complete block design with seven treatments and six replicates. All plots received P_2O_5 at 44.8

¹W.E. Janke, Research Agronomist and Marketing Co-ordinator, Sherritt Gordon Mines Limited, Edmonton, Alberta (personal communication).

kg per ha using triple super phosphate (0-45-0) applied with the seed. Methods of fertilizer application and the amount applied for each treatment are shown in Table 3.

Fertilizer for banded treatments was placed on the V-belts of the fertilizer applicator. Inhibitors mixed with soil were placed on top of the fertilizer. Thus, both dropped down the spout at the same time and remained in contact. Thiourea and elemental sulphur that were separately mixed with urea were applied on the V-belt of the applicator on plots designated to receive such treatments. Banded treatments consisted of 4 rows spaced at 35 cm. Broadcast treatments received N evenly spread over the entire plot area before seeding.

Planting Procedure

The plot site was prepared and seeded immediately after fertilizer application on May 30, 1977. Barley (Hordeum vulgare L. var. Conquest) was sown at a rate of 119 kg/ha, using an Allis Chalmers nine-run double disc seeder. The seeds were planted at a depth of 7.5 cm in rows which were 17.8 cm apart and perpendicular to the direction of placement of fertilizer bands. Twenty-seven rows were planted in each plot.

Weed Control

The chemical weed control technique was used for routine maintenance of the plots. Herbicides sprayed were: T.C.A. - to control millet; Banvel 3 - to control broad leaf weeds, and Carbyne - to control wild oats. Rates of herbicides sprayed were in accordance with recommended rates¹. The herbicides were sprayed on the experimental plots at a maximum recommended rate on June 20. The second spraying was done

¹1977 Guide to Chemical Weed Control, Publication No. 483, Manitoba Department of Agriculture.

Table 3. Treatments for Field Experiment.

Fertilizer Added	Rate	Inhibitor Applied	Rate	Method of Application
1. Urea	32 g N/row	None	-	Banded
2. Urea	32 g N/row	'N-Serve'	0.5 ml/row	Banded
3. Urea	32 g N/row	CS ₂	3.85 ml/row	Banded
4. Urea	26 g N/row	Thiourea	8 g/row	Banded
5. Urea	195 g N/plot	None	-	Broadcast
6. None	-	None	-	-
7. Urea + Sulphur	32 g N + 3.75 g Sulphur/row	None	-	Banded

on June 24, at which date Banvel and T.C.A. were applied at half the recommended rate, while Carbyne was sprayed at the maximum recommended rate. Good weed control was thus achieved on the experimental plots throughout the growing period.

Sampling technique

Soils: Soil samples were taken from 0 to 15 cm depth in all plots at seeding date using hand trowels. These involved samples taken from a block of soil 18 cm on either side of the fertilizer band, and 18 cm along the band length. In control plots soil samples were taken at intervals to a depth of 90 cm. Subsequent samples were taken from a 0-15 cm depth at every harvest date. At final harvest, samples were also taken at intervals to a depth of 90 cm in three of the replicates. The soil sample obtained from each depth was thoroughly mixed and subsampled. They were frozen to prevent nitrification before analysis.

Plants: Plant samples were taken at three harvest dates to correspond with stages of development of the plants. These were: tillering, heading and maturity. Plant samples consisted of total "above ground" portion of plants at the first and second sampling date. Samples at maturity consisted of grain and crop residue.

A portion of each plot was harvested at each sampling date. The area harvested at each date was 88.9 x 68.6 cm (Fig. 3). The harvested area was thoroughly cleaned of barley plants after each harvesting. The two outside rows on either side of the five middle rows were not harvested in order to guard against border effect. The cotton bags containing the plant samples were hung in a drying room until air-dried. The samples were weighed to determine the



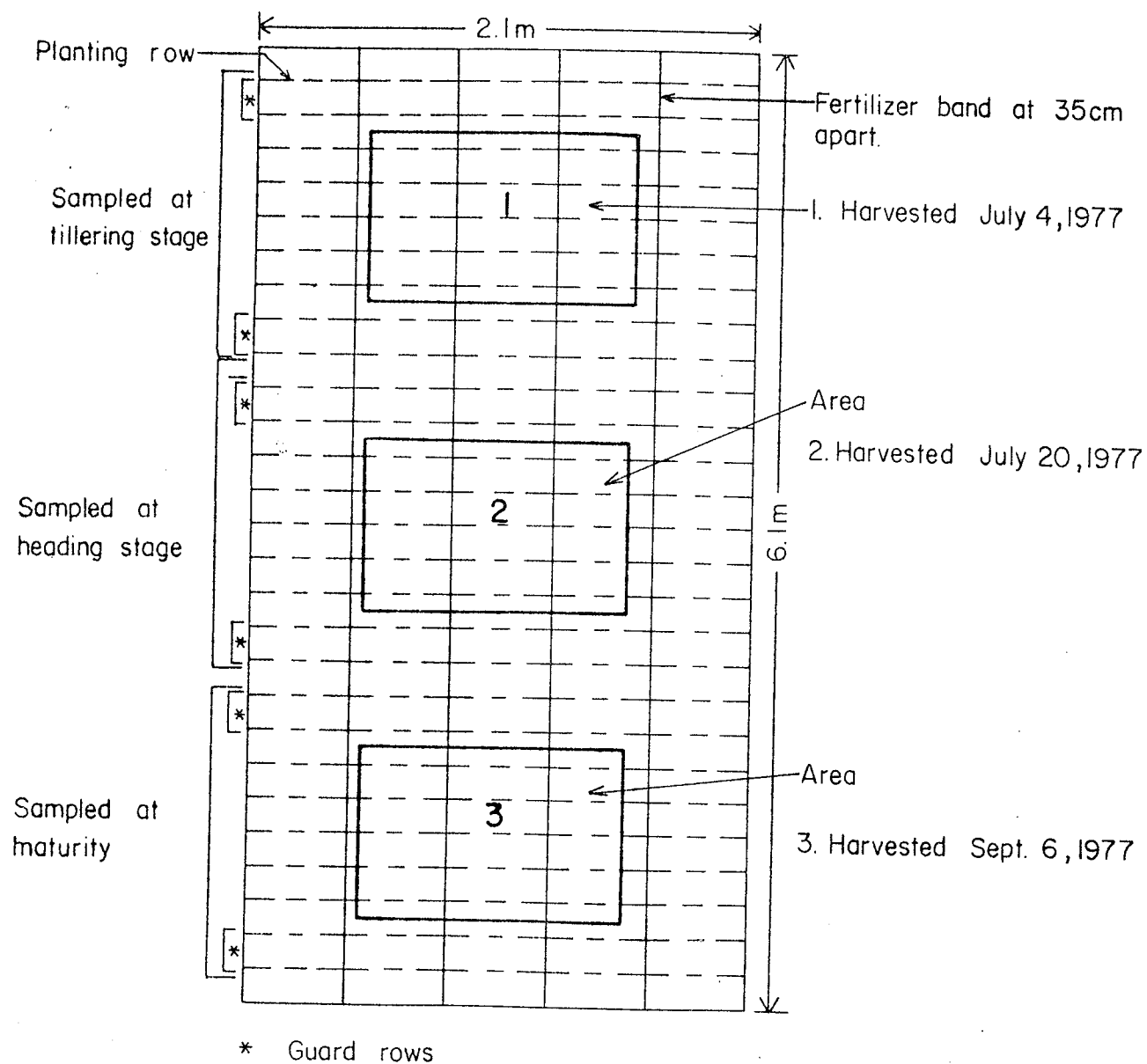


Figure 3. Area harvested in each plot for the three sampling dates.

dry matter yield of barley. Total plant samples for harvest dates one and two, and plant and grain samples for harvest date three were separately ground and analyzed for total nitrogen.

Analytical Procedures

Soil: Soil samples were prepared and analyzed for NH_4^+-N ; NO_3^--N and NO_2^--N as described earlier for the laboratory experiment.

Plant

Total Nitrogen: This was determined according to the Kjeldahl-Gunning method. One gram of plant material was weighed into an 800 ml Kjeldahl flask. A catalyst (Kelpak) containing 0.3 g CuSO_4 and 10 g K_2SO_4 was added with a few pieces of hengar granules to prevent bumping. After adding 25 ml of concentrated H_2SO_4 , the mixture was digested for one hour on Labconco Kjeldahl nitrogen apparatus. The solution was allowed to cool after digestion and 250 ml of tap water were added. Fifty ml of 1:1 NaOH were then added. The mixture was distilled into a 500 ml flask containing 50 ml of 2% boric acid solution. The distillate was titrated with 0.1 NH_2SO_4 . A blank determination accompanied every set of samples analyzed. Percent total nitrogen was then calculated from values obtained.

RESULTS AND DISCUSSION

EXPERIMENT 1: Laboratory incubation study

Urea fertilizer was applied at a rate calculated to supply 100 kg N/ha with or without nitrification inhibitors. The rate of application of the inhibitors was 0.2 ml per container for banded and 0.078 ml per container for broadcast. These rates were equal on an area basis, and higher than those used by researchers and reported in the literature. A high concentration of inhibitors was used because: (i) Only one rate was used and it was necessary to ensure that it was effective. (ii) Containers used in this investigation were not sealed, thus a high concentration was essential to fully demonstrate the effectiveness on added urea fertilizer. Bremner and Bundy (1974) had earlier reported that the inhibitory effects of nitrification inhibitors were more pronounced in sealed than in unsealed containers. (iii) The method adopted for the application of the inhibitors in this study required mixing them with a given volume of soil. Therefore, a higher concentration was considered necessary if the inhibitors were to be present in toxic quantity. It has been noted in an incubation study (Pang *et al.* 1974) that accumulation of nitrite occurred when urea-N was banded in Wellwood soil, at a concentration equal to or greater than 200 ppm N. The amount of nitrite-nitrogen determined in this study was negligibly small. This may have been due to the relatively low rate of urea-N added.

Effect of inhibitors on nitrification rate of urea-N

Percent nitrification rate is defined herein as the amount of nitrate and nitrite nitrogen produced expressed as a percentage of total inorganic nitrogen produced from urea-N.

$$\text{i.e., percent nitrification rate} = \left[\frac{\text{NO}_2^- \text{-N} + \text{NO}_3^- \text{-N}}{\text{NH}_4^+ \text{-N} + \text{NO}_2^- \text{-N} + \text{NO}_3^- \text{-N}} \right] \frac{100}{1}$$

(Prasad and Rajale 1972). Appropriate controls were subtracted to calculate the amount of inorganic nitrogen produced from urea-N. Appropriate control is defined as the relevant control to each treatment.

The nitrification of banded urea-N proceeded rapidly after application (Fig. 4a). After one week, 15 percent of added urea-N had nitrified; and at the end of the third week, the nitrification rate had reached 72 percent. The process was completed in the sixth week. In contrast, after one week of incubation only 3 percent of urea-N was nitrified where CS_2 was applied, but nitrification rate increased rapidly thereafter and was also essentially completed by the sixth week. 'N-Serve' as an inhibitor of nitrification was less effective than CS_2 at one week, but was more effective thereafter. The effectiveness of 'N-Serve' increased with time and by the end of the incubation period, all N recovered was in the NH_4^+ form which indicates complete inhibition. The initial effectiveness of CS_2 as compared to 'N-Serve' may have been due to the rapidity with which CS_2 diffused in the soil. It, however, did not persist or remain as effective as 'N-Serve' after two weeks of incubation.

When urea-N was broadcast without inhibitor, the rate of nitrification was 30 percent after one week of incubation and was essentially completed by the third week (Fig. 4b). Banding of urea-N alone therefore had a delaying effect on nitrification as compared to broadcast urea-N in the early stages of incubation. When broadcast urea-N was treated with CS_2 , the rate of nitrification was decreased by 7 percent after one week of incubation. By the third week, the nitrification rate was 30.

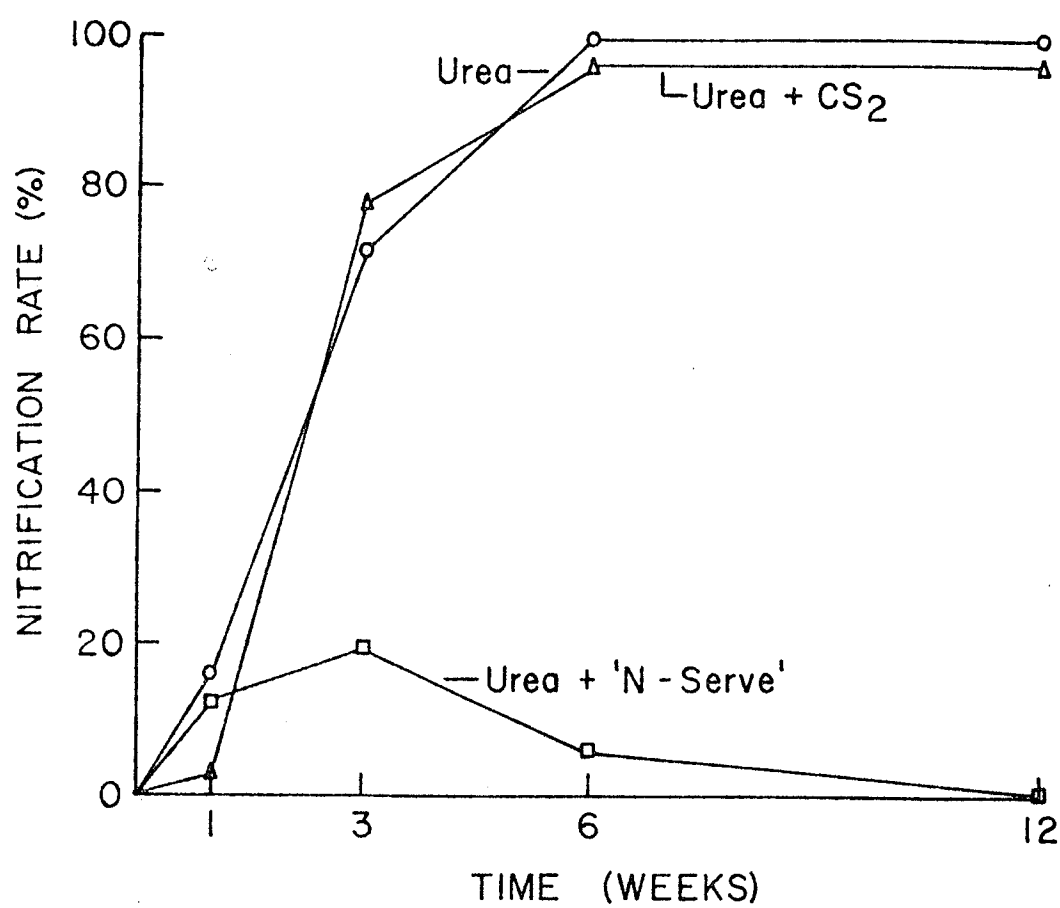


Figure 4A Nitrification rate of banded urea.

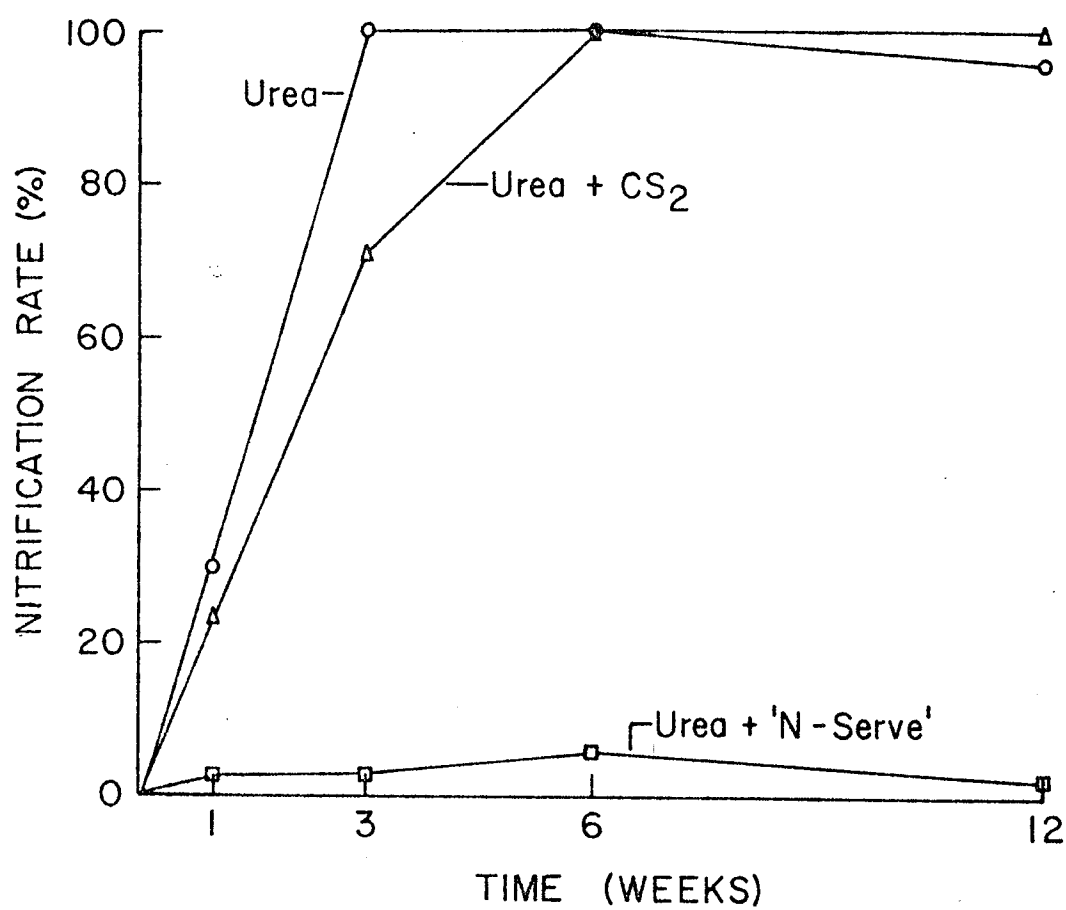


Figure 4B Nitrification rate of broadcast urea.

percent less than where no inhibitor was applied, indicating the effectiveness of CS_2 . By the sixth week, CS_2 was no longer effective in reducing nitrification. When urea-N was treated with 'N-Serve' the nitrification rate was considerably reduced compared to urea-N alone or when treated with CS_2 . The rate was less than 6 percent throughout the period of incubation with 'N-Serve' treated urea-N.

Nitrification rate of urea-N alone proceeded more rapidly than when it was treated with an inhibitor. Both inhibitors were effective in retarding rate of nitrification under the two methods of application, but showed better performances when broadcast than when banded. Carbon disulphide was effective for only one week under banded and for more than three weeks with broadcast application. When banded, the rapid diffusion of CS_2 may have caused its better initial effectiveness compared to 'N-Serve'. However, when both inhibitors were broadcast, each was present in a lethal concentration over a large area.

'N-Serve' showed greater effectiveness and persistency than CS_2 throughout the period of incubation. A more consistent inhibitory property was evident when 'N-Serve' was broadcast than when banded with urea-N.

Broadcasting the fertilizer-N caused it to nitrify faster than when it was banded. Virtually all the added urea-N was nitrified within three weeks of application as compared to six weeks when urea-N alone was banded. Banding urea-N alone was better than broadcast, presumably because of the initially high concentration of NH_4^+ in the band which probably inhibited microbial activity and thereby retarded nitrification.

Inhibition of nitrification of urea-N

Percent inhibition of nitrate formation from urea-N was calculated to directly evaluate the inhibitory properties of the compounds used as nitrification inhibitors. This was calculated from $\left(\frac{C-S}{C}\right) \frac{100}{1}$ (Bundy and Bremner 1972) where S = amount of NO_3^- -N produced in the soil sample containing urea-N treated with the test compound and C = amount of NO_3^- -N produced in the control (urea-N with no test compound added).

When urea-N was broadcast, a higher percentage inhibition of nitrification resulted from treating the fertilizer with 'N-Serve' than with CS_2 (Fig. 5a). Sixty seven percent inhibition was obtained after one week incubation, and within 3 weeks was as high as 85 percent with 'N-Serve'. Higher inhibitory property of 'N-Serve' than CS_2 was evident at all times. After three weeks incubation, only 15% inhibition occurred with CS_2 , whereas 'N-Serve' was 70% higher at the same period. The effect of CS_2 had decreased to 5% six weeks after incubation while 'N-Serve' remained highly effective. At twelve weeks of incubation, 75 percent inhibition occurred with 'N-Serve' while the effectiveness of CS_2 had ceased.

When urea-N was banded with inhibitors, CS_2 was initially more effective than 'N-Serve'. One week after application, 75 percent inhibition occurred with CS_2 as compared to 30 percent with 'N-Serve' (Fig. 5b). Effectiveness of 'N-Serve' may have been confined to the band since it did not diffuse as fast as CS_2 in the soil (Ashworth *et al.* 1975). They reported that CS_2 diffused further in the soil than 'N-Serve'. Three weeks after incubation, percent inhibition from CS_2 had dropped to 33 percent, while that of 'N-Serve' had increased to 77 percent. By six weeks the inhibitory effect of CS_2

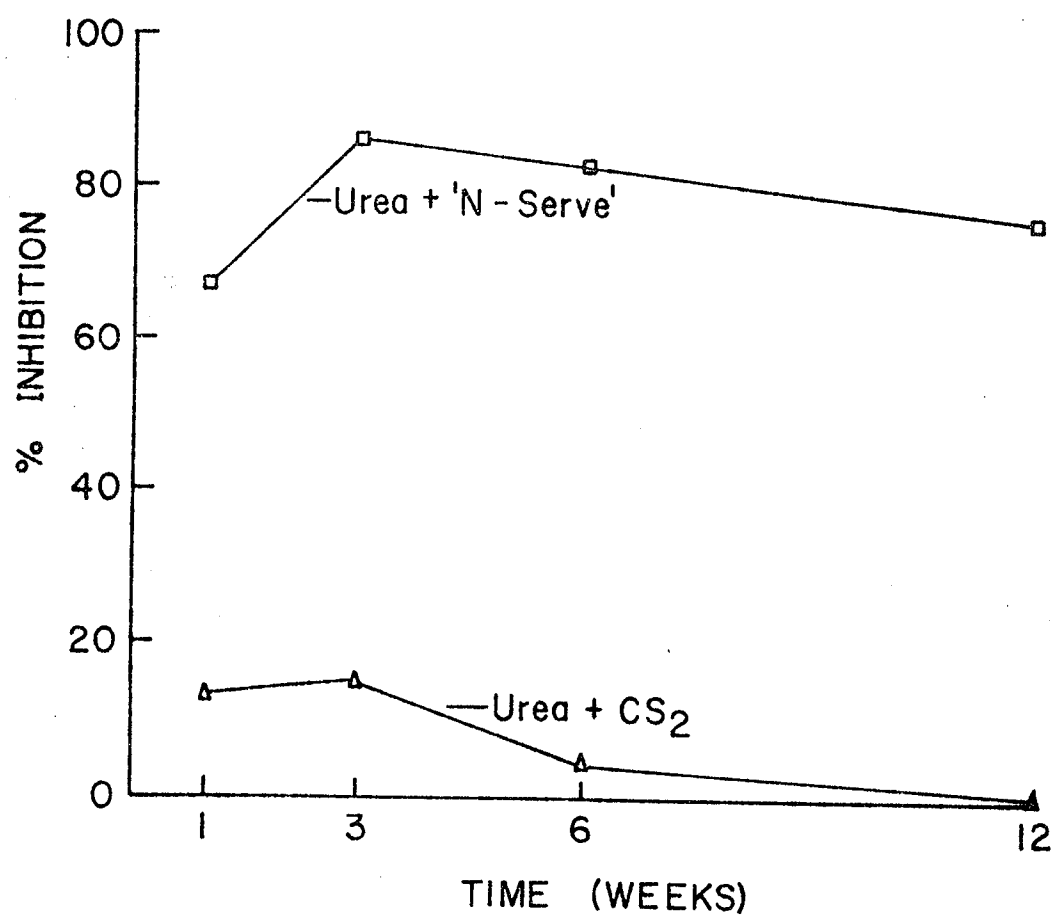


Figure 5A Effect of 'N-Serve' on inhibition of nitrification of broadcast urea.

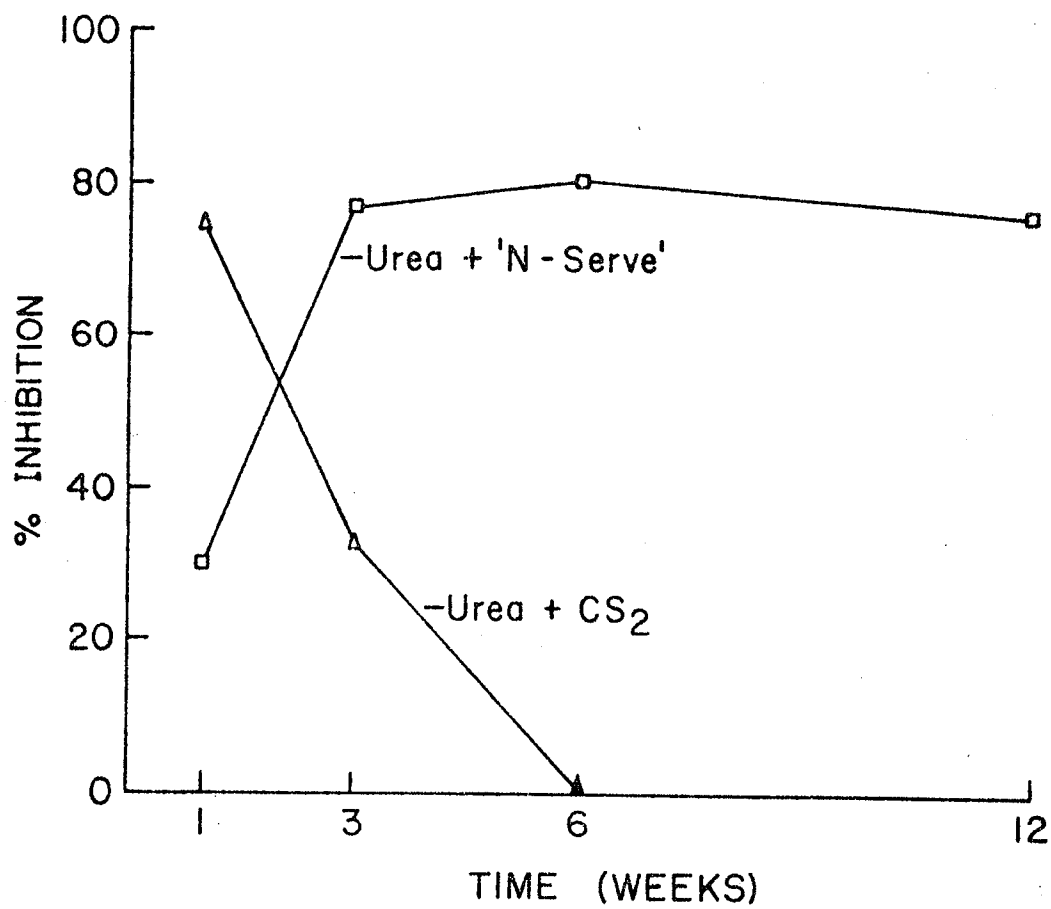


Figure 5B. Effect of 'N-Serve' or CS₂ on inhibition of nitrification of banded urea.

had ceased, whereas 80 percent inhibition still occurred with 'N-Serve'. The inhibitory property of 'N-Serve' was maintained for more than 12 weeks after incubation, thus further confirming its greater effectiveness as compared to CS_2 .

Effectiveness of broadcasting 'N-Serve' instead of banding was more obvious during the initial period of incubation. One week after incubation 67 percent inhibition occurred where 'N-Serve' was broadcast, while only 30 percent occurred where the same inhibitor was banded. However, at six weeks after incubation, the difference due to method of application was negligible.

Recovery of ammonium nitrogen

One week after banded application of urea-N alone and with nitrification inhibitors, recovery of NH_4^+ -N ranged from 38 to 55 percent of added N (Fig. 6a). The lowest value of 38 percent recovery was from treatments where no inhibitor was applied, thus indicating that nitrification was proceeding. After the first week of incubation, recovery of NH_4^+ -N from banded urea-N treated with CS_2 was greater (55%) than when the fertilizer was banded with 'N-Serve' (47%). Three weeks after incubation, recovery of NH_4^+ -N from both urea-N alone, and urea-N treated with CS_2 had declined by about 5 percent. Conversely, recovery from 'N-Serve' treated urea-N had increased to 60 percent within the same period. This indicated that the fertilizer N was being hydrolyzed to NH_4^+ -N, which was not nitrified. No NH_4^+ -N was recovered from urea-N without inhibitor after six weeks of incubation, and this showed that most of the added N had been nitrified before this date. During the same period, recovery of NH_4^+ -N from CS_2 treated urea-N was low. Ammonium nitrogen recovery of 5 percent at this stage indicated

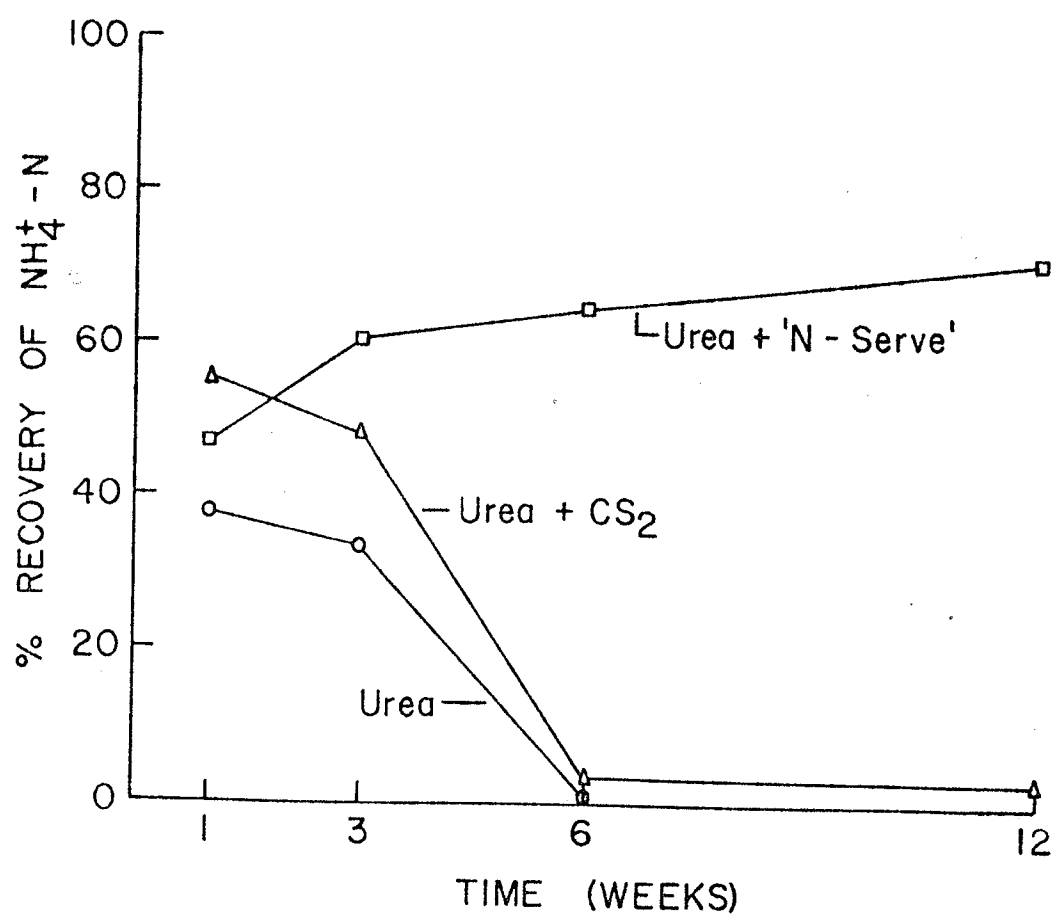


Figure 6A Recovery of $\text{NH}_4^+ - \text{N}$ from banded urea.

that CS_2 was no longer effective. Recovery from the urea-N treated with 'N-Serve' increased from 65 percent at six weeks to 70 percent at twelve weeks. This demonstrated the effectiveness of 'N-Serve' in retaining N in NH_4^+ form.

When added urea-N, either treated or untreated with inhibitor was broadcast, 47-49 percent of the N was recovered as NH_4^+ -N one week after incubation (Fig. 6b). At this date there is no obvious advantage that can be credited to the addition of the inhibitors. By the third week NH_4^+ -N recovery had declined to zero where no inhibitor was applied, indicating that all or most of the added urea-N had been nitrified. In contrast, 27 percent of the applied urea-N treated with CS_2 was recovered as NH_4^+ -N by the third week. This again declined to zero at the sixth week of incubation. Sixty-five percent of added urea-N was recovered in the third week where the fertilizer was treated with 'N-Serve'. By the end of twelve weeks this recovery had increased by about 20 percent.

When urea-N was not treated with inhibitors, recovery of NH_4^+ -N was better with banded than with broadcast application. At three weeks after application recovery from banded was 34 percent of urea-N added, while it was zero with broadcast. This indicated the rapidity with which urea-N nitrifies under broadcast application. It also showed that banding of the fertilizer N below the surface keeps the nitrogen in the ammonium form and thus is less likely to be lost by denitrification.

With 'N-Serve' treated urea-N, recovery of NH_4^+ -N was greater with the broadcast as compared to the banded treatments. The values were 85 and 70 percent for broadcast and banded, respectively, at twelve weeks after application. The data indicated that 'N-Serve' at the rate

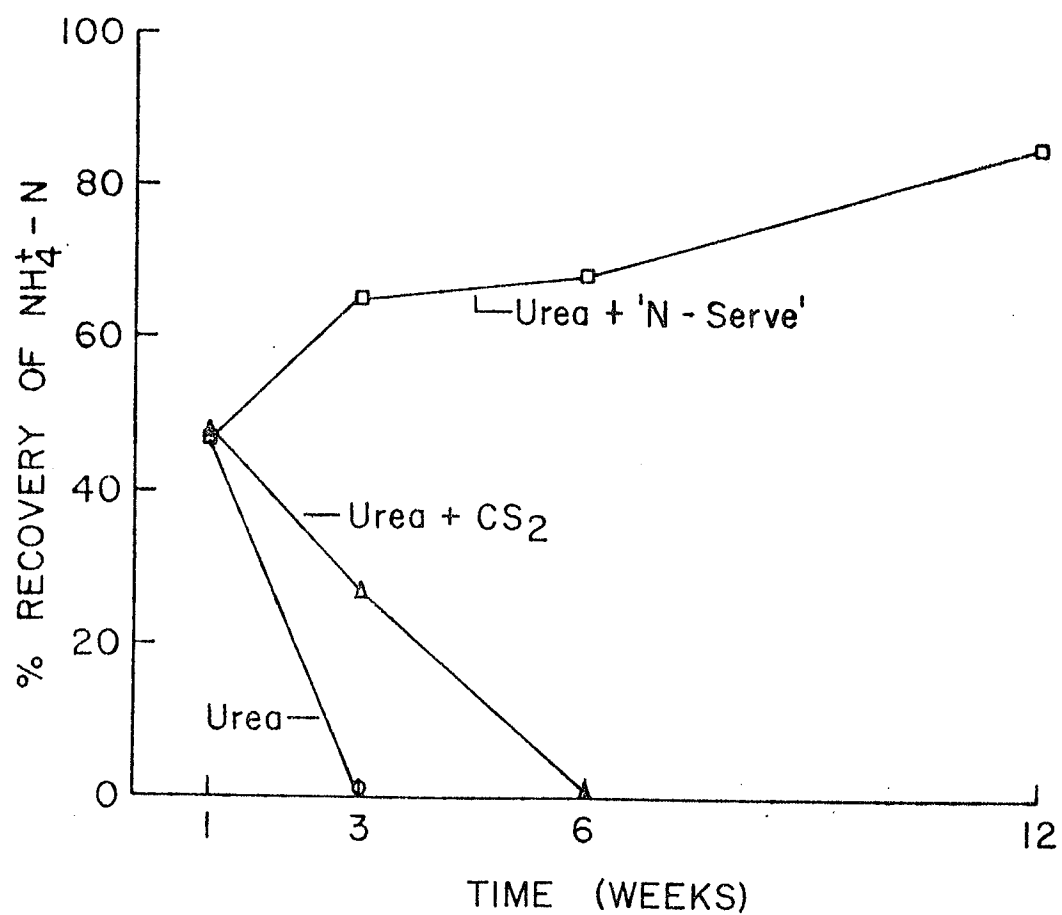


Figure 6B Recovery of $\text{NH}_4^+ - \text{N}$ from broadcast urea.

used was highly effective as a nitrification inhibitor but was not mobile in the soil. These results were in agreement with those obtained by Jana Listanka (1974). The lower effectiveness of 'N-Serve' banded treatments may be related to a slow rate of diffusion out from the fertilizer band.

Distribution and recovery of fertilizer nitrogen

Containers for the incubation study were constructed so that the soils could be sampled at predetermined distances from the point of fertilizer application (Figs. 1 and 2). This permitted a measure of the distribution (by zones) of NO_3^- , NO_2^- and NH_4^+ nitrogen in the containers. The distances in both containers were: zone A - 0 to 1.27 cm; zone B - 1.27 to 3.81 cm; zone C - 3.81 to 6.35 cm; zone D - 6.35 to 8.89 cm. Samples for zone A were obtained from the band or layer of fertilizer placement. Samples for zones B, C and D were taken from bands or layers extending outward and/or downward from zone A.

Data in Tables 4A and 4B showed considerable variation in NO_3^- and NH_4^+ nitrogen distribution. Data for NO_2^- is not shown because the amount of nitrogen recovered in this form was insignificant. Distribution of NO_3^- -N to zone D occurred when urea-N was not treated with 'N-Serve', thus indicating movement of NO_3^- -N from point of application. With 'N-Serve' treatment, a relatively small amount of NO_3^- -N was moved to zone D. Ammonium-N, on the other hand, was sparsely distributed, especially where broadcast urea-N was not treated with 'N-Serve'. Most of the NH_4^+ -N remained within zones A and B, thus indicating the restricted movements of this form of N.

Low recovery of NO_3^- -N occurred at the one week period when urea-N

Table 4a. Percent recovery of urea N as NO_3^- in different zones and at various times during incubation.

Treatments	Zones*	Banded Application				Broadcast Application				
		Time (weeks)				Time (weeks)				
		1	3	6	12	1	3	6	12	
Urea	A	0.3	5.8	4.1	4.7	A	14.8	38.9	47.8	32.4
	B	3.6	34.7	24.8	21.3	B	6.2	38.4	30.2	20.9
	C	1.1	32.2	25.3	24.8	C	-	5.5	9.8	9.5
	D	2.1	15.4	41.3	33.6	D	-	1.3	3.7	5.3
	Total	<u>7.1</u>	<u>88.1</u>	<u>95.5</u>	<u>84.4</u>	Total	<u>21.0</u>	<u>84.1</u>	<u>91.5</u>	<u>68.1</u>
Urea + 'N-Serve'	A	-	0.2	0.2	0.1	A	0.6	0.5	1.2	-
	B	0.9	2.4	0.3	-	B	0.7	0.3	0.8	0.3
	C	2.0	5.4	-	-	C	0.2	0.3	0.8	0.8
	D	3.7	4.2	3.9	-	D	-	0.4	0.6	0.5
	Total	<u>6.6</u>	<u>12.2</u>	<u>4.4</u>	<u>0.1</u>	Total	<u>1.5</u>	<u>1.5</u>	<u>3.4</u>	<u>1.6</u>
Urea + CS ₂	A	0.1	8.9	3.3	4.9	A	8.4	37.9	45.6	40.8
	B	-	37.3	22.6	21.6	B	6.4	23.0	27.1	27.2
	C	1.3	12.1	28.7	24.5	C	-	4.4	9.4	11.7
	D	-	2.5	38.6	42.8	D	-	1.2	3.3	6.5
	Total	<u>1.4</u>	<u>60.8</u>	<u>93.2</u>	<u>93.8</u>	Total	<u>14.8</u>	<u>66.5</u>	<u>85.4</u>	<u>86.2</u>
*Zones										
A - 0 to 1.27 cm										
B - 1.27 to 3.81 cm										
C - 3.81 to 6.35 cm										
D - 6.35 to 8.89 cm										

Table 4b. Percent recovery of urea N as NH_4^+ in different zones and at various times during incubation.

Treatments	Zones*	Banded Application				Broadcast Application			
		Time (weeks)				Time (weeks)			
		1	3	6	12	1	3	6	12
Urea	A	6.1	4.9	0.5	0.4	A	37.6	-	- 3.0
	B	27.2	20.9	-	-	B	10.0	-	-
	C	4.9	8.5	-	-	C	-	-	-
	D	-	-	-	-	D	-	-	-
	Total	<u>38.2</u>	<u>34.3</u>	<u>0.5</u>	<u>0.4</u>	Total	<u>47.6</u>	-	-
Urea + 'N-Serve'	A	4.1	5.6	4.4	4.5	A	26.1	33.9	34.5 29.9
	B	23.8	26.7	22.7	21.8	B	16.9	27.5	18.0 17.7
	C	2.9	17.4	24.3	21.7	C	-	-	-
	D	-	-	-	10.3	D	-	-	-
	Total	<u>30.8</u>	<u>49.7</u>	<u>51.4</u>	<u>58.3</u>	Total	<u>43.0</u>	<u>61.4</u>	<u>52.5</u> <u>47.6</u>
Urea + CS_2	A	6.5	5.4	0.4	0.5	A	36.6	26.9	-
	B	31.6	18.3	3.1	3.1	B	12.7	-	-
	C	7.2	10.2	-	-	C	-	-	-
	D	0.6	-	-	-	D	-	-	-
	Total	<u>45.9</u>	<u>33.9</u>	<u>3.5</u>	<u>3.6</u>	Total	<u>49.3</u>	<u>26.9</u>	-

* Zones

A - 0 to 1.27 cm
 B - 1.27 to 3.81 cm
 C - 3.81 to 6.35 cm
 D - 6.35 to 8.89 cm

was banded without nitrification inhibitor. Nitrate recovery in all zones increased with time. Up to 38% of the added -N was recovered as NH_4^+ -N in the first week. Virtually no NH_4^+ -N was recovered after six weeks of incubation.

With broadcast application of urea-N, recovery of NO_3^- -N was low in the first week, but was greater than from the banded treatment. Nitrate nitrogen recovered increased at the three, six and twelve week periods and was mainly in the top 2 zones. Some added -N was recovered as NH_4^+ -N in the first week, but virtually none occurred thereafter.

Nitrate and ammonium nitrogen recovery from CS_2 treated urea-N was very similar to urea-N without inhibitors. The NO_3^- -N recovered, however, was less and NH_4^+ -N more at the one week period, than in untreated urea-N.

When urea-N was treated with 'N-Serve', very little fertilizer N was recovered as NO_3^- -N in all zones, and with time, from both methods of applications. This indicated the effectiveness of this inhibitor in preventing nitrification. The amount of N recovered as NH_4^+ -N was greater than from other treatments and remained almost constant throughout the 12 week period. Most of the NH_4^+ -N recovered occurred in the top 2 zones with very little in the lower zones.

The total recovery of urea-N as nitrate, nitrite (insignificantly small) and ammonium after one week period was variable and ranged between 37.4 and 47.3 percent for banded and 44.5 to 68.6 percent for broadcast urea-N. This recovery was considerably less than 100 percent. Persistence of unhydrolyzed urea-N after one week of application was unlikely (Gould et al. 1977) as are losses from the system by volatilization since the fertilizer was covered by soil. The presence of

NO_3^- -N in increasing amounts suggested that nitrogen was not lost by denitrification. Thus, some nitrogen transformations probably occurred in the soil. Total recovery of N increased with time until the twelve week period, at which time sampling was discontinued, thus indicating a gradual release of nitrogen with time. Presumably, the low recovery after one week of incubation was due to N-fixation in the soil. Immediate fixation of relatively large amounts of the applied N by clay particles has been reported by Kowalenko and Cameron (1978). They observed that NH_4^+ thus recently fixed was gradually released with time. Total recovery of nitrogen in this experiment was lowest where 'N-Serve' had been applied, more so with banded as compared to broadcast urea-N. This indicated that the presence of 'N-Serve' affected the release of recently fixed NH_4^+ .

Effect of nitrification inhibitors on native soil nitrogen

Broadcast application of 'N-Serve' inhibited nitrification of native soil nitrogen (Fig. 7a). After three weeks of incubation, the control soils had accumulated approximately 7 μg of NO_3^- -N per gram of soil more than the soil treated with 'N-Serve'. At six weeks, the amount of NO_3^- -N accumulated in the control was 14 $\mu\text{g/g}$ soil more than 'N-Serve' treated soil. This value remained constant twelve weeks after incubation. In contrast, CS_2 broadcast had little effect on soil NO_3^- -N when compared with the control up to the six week period. After 6 weeks, a slight increase in soil NO_3^- -N content occurred on soils treated with CS_2 .

When the inhibitors were banded, 'N-Serve' contained 5 μg N per gram soil, and CS_2 treated soils contained 7 μg N per gram soil less than the control after one week (Fig. 7b). The difference between treatments remained constant at the end of the third week. After six weeks, there was more NO_3^- -N in the CS_2 treated soil than in the control. 'N-Serve' treated soil at this period contained slightly less NO_3^- -N than in the control. However, the differences in NO_3^- -N content between the 2 treatments and the control were small.

'N-Serve' was more effective as an inhibitor of nitrification in an unfertilized soil when broadcast than when banded. The inhibitor was effective until the end of the incubation period under the broadcast method and for about 4 weeks when banded in the soil. Conversely, CS_2 was effective for 4 weeks when banded and not at all when applied broadcast.

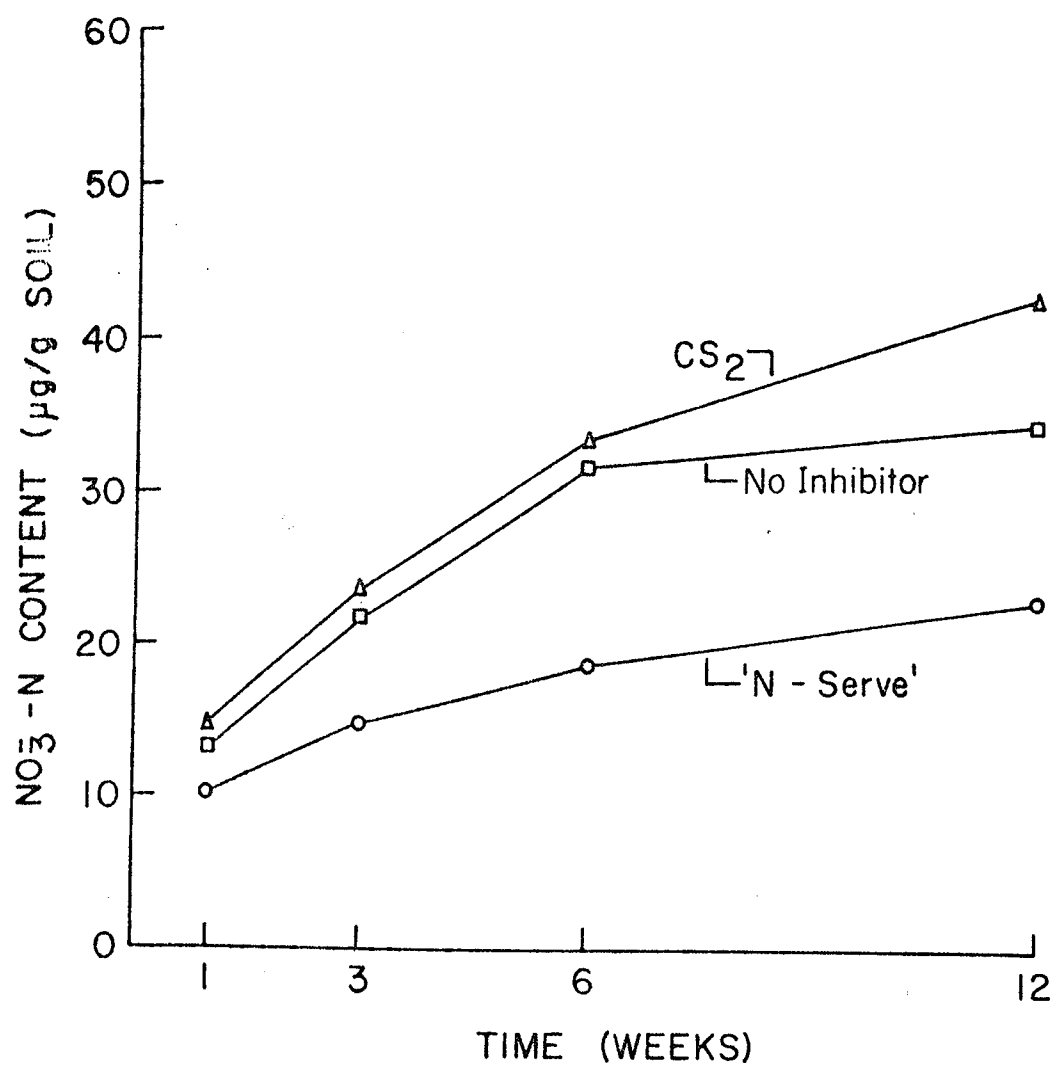


Figure 7A Effect of 'N - Serve' or CS_2 (broadcast) on accumulation of $\text{NO}_3\text{-N}$ in non-fertilized soil.

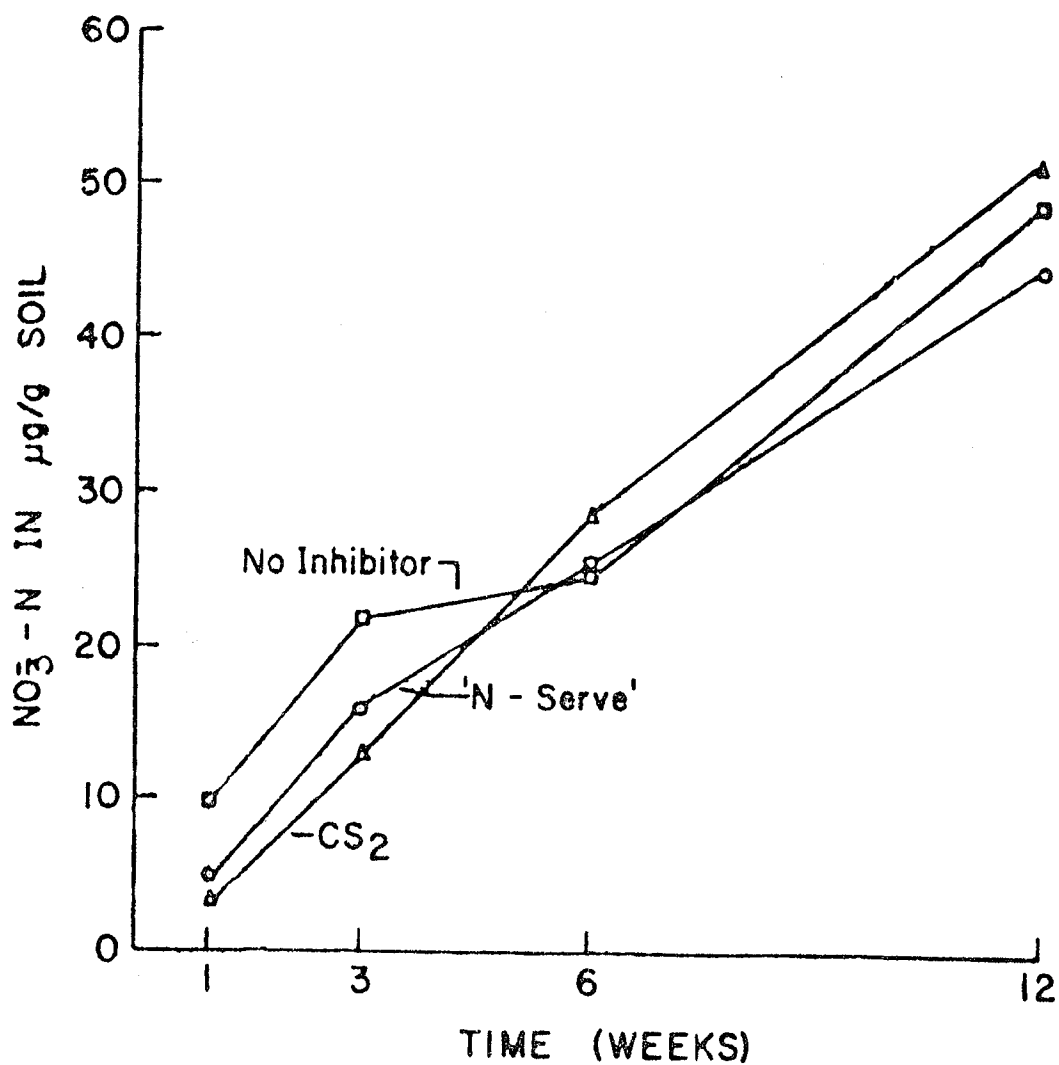


Figure 7B Effect of 'N-Serve' or CS_2 (banded) on accumulation of $\text{NO}_3\text{-N}$ in non-fertilized soil.

Recovery of NH_4^+ -N from urea in 3 soil types treated with 'N-Serve'

Results discussed in previous sections were from treatments conducted on a Wellwood L soil of neutral pH and low lime content. Since Manitoba soils are variable in both pH and lime content, several treatments conducted with Wellwood soil were repeated using an alkaline carbonated black soil (Lakeland) and a non-carbonated slightly acidic (Pine Ridge) soil. The purpose of this was to determine if results obtained would be applicable to a variety of soils. Recovery of NH_4^+ -N from applied urea-N after a three week incubation period was the parameter used as an index of effectiveness of the inhibitor applied.

'N-Serve' was found to be effective in keeping urea-N in the ammonium form on all three soil types (Table 5). Recovery of NH_4^+ -N from urea-N treated with 'N-Serve' was higher than where the fertilizer was not treated. In the Wellwood soil, 61 percent of banded urea-N was recovered as NH_4^+ -N where 'N-Serve' was applied as compared to 34.3 percent when 'N-Serve' was not applied. In Lakeland soil, 50.5 percent recovery of NH_4^+ -N occurred with 'N-Serve' and only 5.1 percent occurred from urea-N without 'N-Serve'. In Pine Ridge soil, 'N-Serve' treatment of urea-N resulted in 73.1 percent recovery of NH_4^+ -N as compared to 53.6 percent recovery from untreated added N.

When urea fertilizer alone was broadcast, no NH_4^+ -N was recovered in Wellwood soil. This indicated a high capacity of Wellwood soil to nitrify urea-N, particularly under this method of application. However, when urea-N was treated with 'N-Serve', 64.8 percent of the added fertilizer was recovered as NH_4^+ -N. Recovery of NH_4^+ -N in Lakeland soil was 48.6 percent from broadcast urea-N treated with 'N-Serve' compared to 22.5 percent from untreated urea-N. In Pine Ridge soil, NH_4^+ -N recovery was 73.9 percent from 'N-Serve' treated urea-N and

Table 5. Recovery of NH_4^+ -N from urea in 3 soil types 3 weeks after application.*

Soil Name	Treatments	*Percent recovery of ammonium nitrogen			
		Banded	Difference between \pm 'N-Serve'	Broadcast	Difference between \pm 'N-Serve'
Wellwood	Urea	34.3		0	
"	Urea + 'N-Serve'	61.0	26.7	64.8	64.8
Lakeland	Urea	5.1		22.5	
"	Urea + 'N-Serve'	50.5	45.4	48.6	26.1
Pine Ridge	Urea	53.6		37.9	
"	Urea + 'N-Serve'	73.1	19.5	73.9	36.0

* Represents average of four sampling zones

37.9 percent when the fertilizer was not treated. The inhibitor was effective on all three soils in keeping urea-N in the ammonium form.

Banded application of urea-N without inhibitors improved NH_4^+ -N recovery more than broadcast in Wellwood and Pine Ridge soils. In contrast, NH_4^+ -N recovered was very low (5.1%) when the fertilizer alone was banded in Lakeland soil. Banding urea-N was therefore least effective on the highly calcareous soil and most effective on the Wellwood soil as a means of reducing nitrification. In Wellwood and Pine Ridge soils, broadcasting urea-N with 'N-Serve' was more effective than banding the fertilizer with the same inhibitor. The difference between 'N-Serve' treated and untreated urea-N in the percentage of NH_4^+ -N recovered was 64.8 percent for broadcast and 26.7 percent for banded in Wellwood soil. With Pine Ridge soil the differences were 36 and 19.5 percent for broadcast and banded treatments, respectively. This is not consistent with Lakeland soil because of low recovery of NH_4^+ -N from banded urea.

EXPERIMENT 2: Field studies

A field experiment was conducted in the spring of 1977 to determine the effect of some nitrification inhibitors on the rate of supply of urea N to barley. Parameters measured at three stages of growth were: yield of plant material, total N content of the plant material, and soil nitrogen. 'N-Serve', Carbon disulphide and Thiourea were the nitrification inhibitors used. The design of the experiment and treatments were described previously.

Effect of urea-N and nitrification inhibitors on yield

Dry matter yield of barley (Table 6) showed that there was a highly significant response to spring applied urea-N at all dates of harvest. No consistent yield benefit was derived from the addition of nitrification inhibitors. At the first harvest date, yields from inhibitor treated plots were greater than yields from plots with no inhibitor applied, but the difference was not statistically significant. The trend was the same at the second harvest date. At the third harvest date, straw and grain yields from plots not treated with inhibitors were higher than yields from 'N-Serve' and CS₂ treated plots, but the differences again were not significant. Olson et al. (1977) in their unpublished report on 'N-Serve' investigation concluded that the inhibitor was only effective when heavy rains produced a saturated atmosphere conducive to denitrification and/or leaching of nitrate nitrogen. Precipitation throughout the period of this experiment was light and occurred in low intensity. Urea fertilizer applied at the time of planting could have been taken up as NH₄⁺-N as soon as it was hydrolysed. Also, both the NH₄⁺ and NO₃⁻ forms of N could be utilized by the plant and the effect of the inhibitors might have

Table 6. Total above ground dry matter yield of barley (kg/ha)*

Treatments	Harvest Period			
	<u>Tillering</u>	<u>Heading</u>	<u>Maturity</u>	
	(July 4)	(July 20)	(Sept 6)	
			<u>Straw</u>	<u>Grain</u>
1. Urea banded	975b	3945b	4944b	4603b
2. Urea + 'N-Serve' banded	1142b	4181b	4860b	4537b
3. Urea + CS ₂ banded	1214b	4406b	4830b	4368b
4. Urea + Thiourea banded	1081b	4035b	5147b	4658b
5. Urea broadcast	1150b	4147b	4999b	4887b
6. Control (no urea)	693a	2250a	3128a	3084a
7. Urea + Sulphur banded	1198b	4220b	4737b	4324b

*Average of six field replicates. Means within columns followed by the same letters are not significantly different at the 0.01 probability level by Duncan's New Multiple Range Test.

been obscured. These results are not unexpected since the fertilizer was applied at seeding time. By the time seeding was done, saturated soil conditions (reducing conditions) did not exist to cause N loss. Denitrification and hence loss of NO_3^- -N is most likely to occur from fall applied nitrogen that has had a chance to nitrify, and then denitrify during saturated soil conditions caused by snow melt and early spring rains.

Yields from plots where urea-N was banded without inhibitor were lower than yields from plots that received the fertilizer N by the broadcast method. However, differences were not significant.

Total N uptake by barley

Addition of urea fertilizer significantly increased N uptake in all treatments at all three harvest dates (Table 7). Addition of nitrification inhibitors with urea-N had no effect on the uptake of N throughout the growing period. This was consistent with the work of Lewis and Stefanson (1975) who observed that application of 'N-Serve' had little effect on improving the overall uptake of nitrogen. This was presumably due to the capacity of plants to take up both NH_4^+ and NO_3^- -N. Providing denitrification did not occur, this would be expected. Total N in the above ground portion of the crop increased with time and this can be attributed to increased plant growth. Total N in the straw at maturity was about 20 percent of the total N in the above ground portion of the plant. By this date, most of the nitrogen taken up earlier had been utilized in grain formation.

Broadcast application of urea N resulted in greater N-uptake than when the fertilizer was banded. This occurred for all three stages of harvest. The differences were, however, not significant except for total N in the straw at maturity.

Table 7. Total N* in above ground portion of plant (in g/0.61 m²).

Treatments	Sampling Times after Seeding				
	(36 days)	(52 days)	<u>100 days</u> (Maturity)		
			Straw	Grain	Total
Urea banded	1.86b	4.69bc	1.36bc	5.57bc	6.93bc
Urea + 'N-Serve' banded	1.99bc	4.41b	1.39bc	5.50bc	6.89bc
Urea + CS ₂ banded	2.26bc	4.61bc	1.39bc	5.30bc	6.69bc
Urea + Thiourea banded	2.03bc	4.61bc	1.48c	5.59bc	7.07bc
Urea broadcast	2.07bc	5.28bc	1.71d	6.07c	7.78c
Control (no urea)	0.99a	2.34a	0.88a	3.49a	4.37a
Urea + Sulphur banded	2.29c	5.57c	1.27b	5.17b	6.44b

*Represents the average of six field replications. Means within columns followed by the same letters are not significantly different at the 0.01 probability level by Duncan's New Multiple Range Test.

Crop recovery of added N

Percent recovery of added N was calculated from the amount of N recovered in the above ground portion of the crop at maturity in urea treated plots less the amount of N uptake from the control plot. Values obtained were expressed as percentages of added urea nitrogen. Percent recovery of added N ranged from 50.6 to 83.2 percent (Table 8), which would be considered normal to high for Manitoba conditions. The Manitoba Soil Testing Laboratory uses an efficiency factor of 52 percent when making N-fertilizer recommendations. Unpublished data of Ridley generally supports an efficiency of recovery of 52 percent, but shows variations ranging from 25-65 percent.

Addition of the nitrification inhibitors did not increase the recovery of added N when compared with plots not treated with inhibitors. These results were in agreement with the observations of Bundy and Bremner (1974). They noted in their investigations that addition of nitrification inhibitors to soil had no effect on the recovery of urea N.

Crop recovery of added N was least where sulphur was added with urea (50.6%). Recovery from the CS_2 treated plot was 56.5 percent. It appeared that sulphur had a depressing effect on the uptake of N. Nyborg and Malhi (1977) reported that addition of CS_2 depressed crop yield in their experiment. The greatest recovery of 83.2 percent of the applied N was from urea-N broadcast. This high recovery may be due to the low amount of rain received throughout the growing period. The first rain after fertilizer application might have been just sufficient to move the broadcast fertilizer a few cm below the soil surface. Nitrogen thus moved might have been immediately available to the growing plant. The banded N, however, was probably not equally affected by light rainfall and therefore remained in a band.

Table 8. Recovery by barley of spring applied urea N as influenced by nitrification inhibitors (average of 6 replicates).

Treatments	N uptake at Maturity (g/0.61 m ²)	% Recovery of applied N
1. Urea banded	6.93	62.5
2. Urea + 'N-Serve' banded	6.89	61.6
3. Urea + CS ₂ banded	6.69	56.5
4. Urea + Thiourea banded	7.07	65.9
5. Urea broadcast	7.78	83.2
6. Control (no urea)	4.37	-
7. Urea + Sulphur banded	6.44	50.6

Effect of nitrification inhibitors on the nitrate nitrogen content of the soil.

Immediately after fertilizer application, the nitrate nitrogen content in the soil ranged from 7.9 to 11.8 ppm (Table 9). The lowest value was from the control plot. At the first harvest date, the NO_3^- -N content of the fertilized soil was still greater than the control and this reflected the treatment effect. The NO_3^- -N content of the unfertilized plot remained essentially unchanged. The highest amount of NO_3^- -N was observed in plots that had urea broadcast. After 36 days, plots which had received urea-N broadcast contained the most NO_3^- -N (19.2 ppm). This may have been due to a more rapid nitrification of NH_4^+ -N when urea-N is broadcast, and this was consistent with results obtained in the laboratory incubation study. The inhibitors had no effect on soil NO_3^- -N at the 36 day harvest period.

The NO_3^- -N content of all the fertilized plots decreased to approximately the NO_3^- -N level of the control plot by the 52 day period. This undoubtedly reflected crop utilization of nitrogen.

At the third date of harvest (maturity), the NO_3^- -N content of the soils was virtually the same regardless of treatments applied.

Addition of inhibitors did not have any apparent effect on the NO_3^- -N content of the soil throughout the growing period. This lack of effect of inhibitor on NO_3^- -N may have been caused by lack of nitrification inhibition, or, there may have been inhibition of nitrification between days 0 and 36 which was never detected. Obviously, at day 0, no difference would be expected. By day 36 differences in soil NO_3^- -N may have been obscured by crop uptake. It has also been suggested (Ashworth et al. 1977, Hendrickson et al. 1977) that losses of applied N in spring through leaching or denitrification on a fine textured soil are unlikely to occur, thus very little benefit from

Table 9. NO_3^- -N content of soil (0-15 cm) in ppm [air-dry basis]*.

Treatments	At Seeding	Days after Seeding		
		36 days	52 days	100 days
Urea banded	10.4	12.2	7.0	6.0
Urea + 'N-Serve' banded	10.2	12.7	7.1	6.8
Urea + CS_2 banded	10.6	12.5	6.9	6.1
Urea + Thiourea banded	8.1	13.1	7.3	6.1
Urea broadcast	9.1	19.2	8.5	5.2
Control (no urea)	7.9	6.4	6.6	5.9
Urea + Sulphur banded	11.8	13.4	7.9	4.9

* Represents the average of six field replications.

an application of inhibitor could be expected. Hence, it was not unusual to observe in this study that no added advantage was derived from spring application of nitrification inhibitors on Wellwood loam.

The ammonium nitrogen content of the soil during the growing period was also monitored but the values obtained were negligibly small. This was an indication that most of the ammonium nitrogen had either been nitrified or taken up by the plant before the 36 day harvest period.

Residual N from added urea

Residual NO_3^- -N and its distribution in the soil profile at final harvest period was monitored in 15 cm increments to 90 cm. The plotted values* of NO_3^- -N derived from added urea-N (NO_3^- -N at appropriate depth less NO_3^- -N in control) ranged between 0 and 2 ppm (Fig. 8). The concentrations of NO_3^- -N were so low that no justifiable conclusion can be made from them. The pattern of distribution does not show any obvious effect of placement of urea-N or effect of the nitrification inhibitors. It is, however, observed that NO_3^- -N content in the 0 to 30 cm depth of urea plus 'N-Serve' plot was greater than the NO_3^- -N content within the same depth in any of the other treatments.

* Represents the average of three field replications.

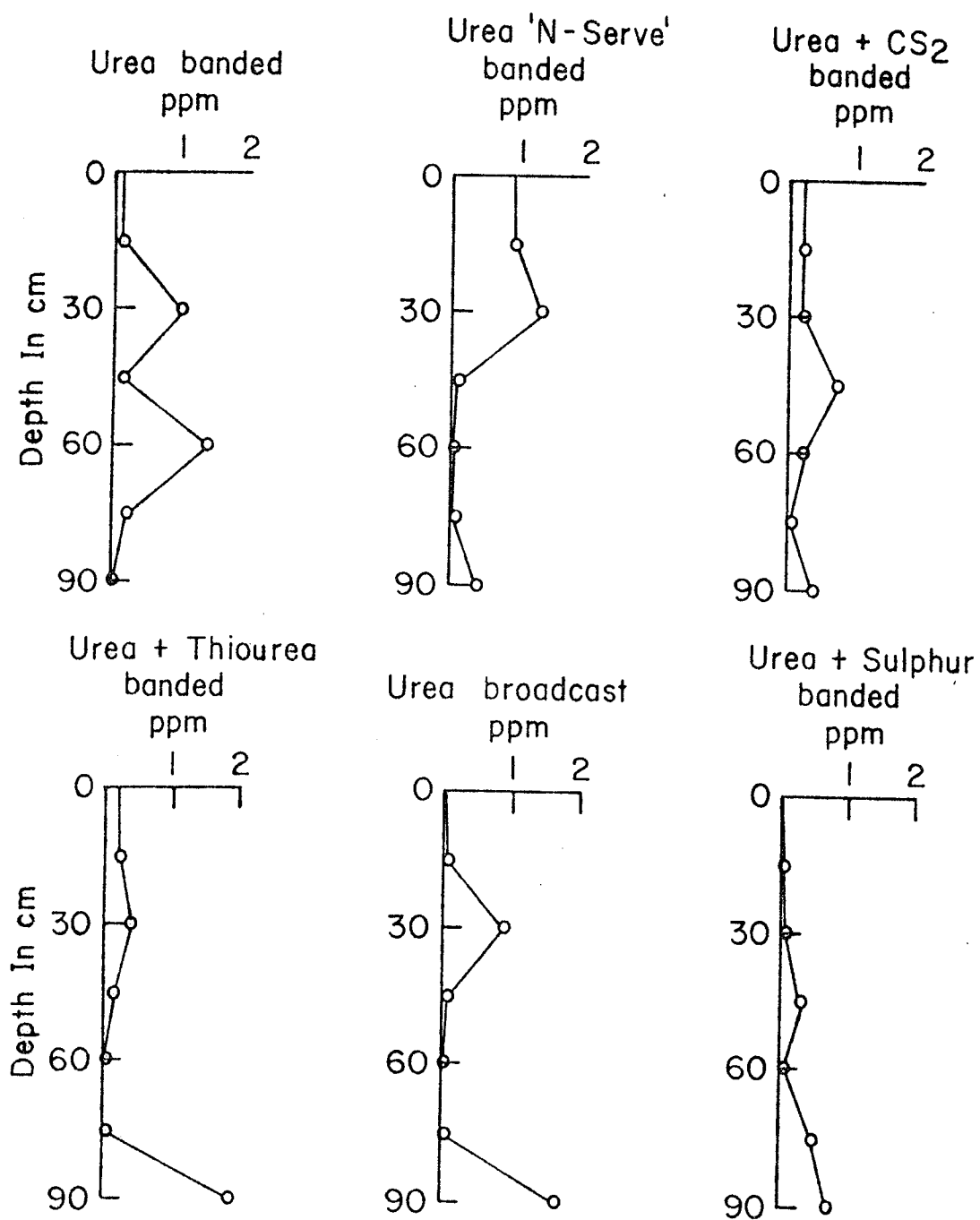


Figure 8 Effect of urea and 'N-Serve' or CS_2 on concentration of $\text{NO}_3\text{-N}$ in the soil profile.

SUMMARY AND CONCLUSION

Urea-N was banded or broadcast with and without nitrification inhibitors in a laboratory study with three soil types: Wellwood L, Lakeland SiC and Pine Ridge S. After 1, 3, 6 and 12 weeks, the amount of NH_4^+ , NO_2^- and NO_3^- -N in the soil at predetermined distances from the point of application was determined for the Wellwood soil. Lakeland and Pine Ridge soils were analysed after 3 weeks of incubation only. This permitted an evaluation of the effects of nitrification inhibitors and placement methods on rate of urea nitrification, distribution of NH_4^+ and NO_3^- -N and recovery of added urea-N.

Nitrification of urea-N alone occurred more rapidly when it was broadcast compared to banded. The proportion of broadcast urea-N which had been nitrified reached 100 percent within three weeks of application. Such high rate of nitrate formation did not occur from banded urea-N until six weeks after application. Addition of nitrification inhibitors reduced the rate of nitrate formation from added N. When the inhibitors were banded with urea-N, CS_2 was initially more effective than 'N-Serve' in retarding nitrification rate, presumably due to its rapid diffusion in the soil. The effectiveness of CS_2 was, however, short-lived as the proportion of urea N which had been nitrified was over 95 percent by six weeks. 'N-Serve' was more persistent and was effective as a nitrification inhibitor for at least twelve weeks. Both inhibitors were more effective when broadcast than when banded. This may have been due to their presence in toxic quantities over a large area of soil. With 'N-Serve', the proportion of broadcast urea-N which had been nitrified did not exceed six percent at any time during the incubation period. At the concentration

used, 'N-Serve' as an inhibitor was more persistent than CS_2 .

Banding urea-N maintained it in the NH_4^+ form for a longer period of time than broadcasting it. At three weeks after application, 34 percent of banded urea-N recovered was in the NH_4^+ form while virtually none was recovered from broadcast urea-N. This indicated that banding urea-N below the soil surface keeps N in the NH_4^+ form and thus less susceptible to loss. Increased recovery of NH_4^+ occurred as a result of treating urea-N with inhibitors.

Distribution and recovery of NO_3^- and NH_4^+ nitrogen in different zones was studied to monitor their movement from the point of fertilizer application. Nitrate-N was well distributed over the zones and its movement from point of application occurred, especially where urea-N was not treated with 'N-Serve'. Ammonium-N, on the other hand, remained close to the point of application. Nitrification inhibitors did not directly affect the movement of the fertilizer-N, but conserved N in the NH_4^+ form, thus reducing its movement away from point of application.

Total recovery of urea-N as nitrate, nitrite (insignificantly small) and ammonium after one week period was considerably less than 100 percent, but increased thereafter. This indicated that nitrogen might have been fixed immediately after application of urea-N. Total recovery of N was lowest where 'N-Serve' was applied, thus indicating that the inhibitor may have reduced the release of recently fixed NH_4^+ .

A three week incubation study was conducted to determine the effectiveness of 'N-Serve' on two soil types other than Wellwood L. The inhibitors were effective in maintaining N in the NH_4^+ form in both Lakeland and Pine Ridge soils. Perhaps the incubation duration should have been longer than three weeks to more definitely establish

the performance of the inhibitor on these soils.

Effect of nitrification inhibitors on native soil nitrogen was also examined. Both 'N-Serve' and CS_2 , when banded in unfertilized soil, retarded nitrification of soil nitrogen for approximately four weeks. Only 'N-Serve' was effective when the inhibitors were broadcast applied, and the effectiveness persisted for twelve weeks. Thus, 'N-Serve', besides conserving fertilizer N in the NH_4^+ form, could also retard nitrification of native soil nitrogen.

A field experiment was conducted to determine the effect of nitrification inhibitors on crop utilization of spring-applied urea-N. Dry matter yield of barley showed that there was a highly significant response to spring applied urea-N, but inhibitors had no effect. Total N uptake and crop recovery of added N was not significantly affected by treating urea-N with nitrification inhibitors. Nitrification inhibitors likely did not increase crop yield or N uptake because the soil at the time of seeding and throughout the growing season was never saturated. In order for substantial losses of NO_3^- -N through denitrification or leaching to have occurred, the soil would have had to be saturated. This was not the case; consequently, there was no particular advantage in retarding the conversion of NH_4^+ to NO_3^- -N. It is also possible that the nitrification inhibitors did not inhibit nitrification. In fact, addition of nitrification inhibitors had no apparent effect on total NO_3^- -N content of the soil or on the distribution of NO_3^- -N in the soil. However, since both NH_4^+ and NO_3^- forms of N would have been taken up by barley, the effect of the inhibitors may have been obscured.

Results of the field experiment suggested that nitrification inhibitors do not increase the efficiency of urea applied at seeding when conditions are moderately dry. Laboratory data, however, suggested

hat the nitrification inhibitor, 'N-Serve' is effective in keeping N in the NH_4^+ form such that N is less susceptible to loss through denitrification and leaching. Therefore, nitrification inhibitors would likely be very useful to farmers who want to increase the efficiency of ammonium producing fertilizer applied in the fall or at seeding when conditions are wetter than normal.

BIBLIOGRAPHY

- Agarwal, A.S., B.R. Singh and Y. Kanehiro. 1972. Differential effect of carbon sources on nitrogen transformation in Hawaiian soils. *Plant and Soil* 36: 529-537.
- Akhundov, F.G. 1965. [Effect of nitrogen fertilizers on rice yield in the Azerbaidzhan SSR]. *Agrokhimiya* 12: 13-16. In Soils and Fert. Abstr. 29, No. 3.
- Alexander, M. 1963. Biochemical ecology of soil microorganisms. *Ann. Rev. Microbiol.* 18: 217-252.
- Allison, F.E. 1955. The enigma of soil nitrogen balance sheets. *Agron.* 7: 213-250.
- Allison, F.E., E.M. Roller and J.E. Adams. 1959. Soil fertility studies in lysimeters containing Lakeland sand. U.S. Dept. Agr. Tech. Bull. No. 1199, pp. 1-62.
- Allison, F.E., J.N. Carter and L.D. Sterling. 1960. The effect of partial pressure of oxygen on denitrification in soil. *Soil Sci. Soc. Amer. Proc.* 24: 283-285.
- Allison, F.E. and C.J. Klein. 1962. Rates of immobilization and release of nitrogen following additions of carbonaceous materials and nitrogen to soils. *Soil Sci.* 93: 383-386.
- Allison, F.E. 1963. Losses of gaseous nitrogen from soils by chemical mechanisms involving nitrous acid and nitrite. *Soil Sci.* 96: 404-409.
- Allison, F.E. 1965. Evaluation of incoming and outgoing processes that affect nitrogen. In Soil Nitrogen, pp. 573-606. Monograph No. 10, Amer. Soc. Agron., Madison, Wisconsin.
- Allison, F.E. 1966. The fate of nitrogen applied to soils. *Adv. Agron.* 18: 219-258.
- Andreeva, E.A. and G.M. Shcheglova. 1967. Utilization of soil nitrogen and fertilizer nitrogen by plants. *Soil Chem. Fert. Trans.* pp. 113-124 (1966).
- Ansorge, H., S. Market and R. Jauert. 1967. Studies on inhibition of nitrification by some chemical preparations, Albrecht-Thaer-Arch 11, 509-516. In Soils and Fert. Abstr. 31: (1) 1968.
- Arnold, P.W. 1954. Losses of nitrous oxide from soil. *J. Soil Sci.* 5: 116-126.
- Ashley, D.A., O.L. Bennett, D.B. Doss and C.E. Scarsbrook. 1965. The effect of N rate and irrigation on yield and residual N recovery by warm season grasses. *Agron. J.* 57: 370-372.
- Ashworth, J., G.G. Briggs and A.A. Evans. 1975. Field injection of CS₂ to inhibit nitrification of ammonia fertilizers. *Chemistry and Industry* No. 6, pp. 749-750.

- Ashworth, J., G.G. Briggs, A.A. Evans and J. Matula. 1977. Inhibition of nitrification by Nitrapyrin, carbon disulphide and frithiocarbonate. *J. Sci. Fd. Agric.* 28: 673-683.
- Bartholomew, W.V. 1971. Soil nitrogen. Supply process and crop requirements. *Int. Soil Fert. Eval. Improv. Progr. Tech. Bull.* No. 6.
- Bollag, J.M., M.L. Orcutt and B. Bollag. 1970. Denitrification by isolated soil bacteria under various environmental conditions. *Soil Sci. Soc. Amer. Proc.* 34: 875-879.
- Bollag, J.M., S. Drzymala and L.T. Kardos. 1973. Biological versus chemical nitrite decomposition in soil. *Soil Sci.* 116: 44-50.
- Boswell, F.C. 1976. Seasonal anhydrous ammonia comparisons for corn with and without a nitrification inhibitor. *Agron. J.* 69: 103-106.
- Briggs, G.G. 1975. The behaviour of the nitrification inhibitor 'N-Serve' in broadcast and incorporated applications to soil. *J. Sci. Fd. Agric.* 26: 1083-1092.
- Broadbent, F.E., W.D. Burge and T. Nakashima. 1961. Factors influencing the reaction between ammonia and soil organic matter. *Trans. 7th Int. Congr. Soil Sci.* 2: 509-516.
- Broadbent, F.E. and F. Clark. 1965. Denitrification. In *Soil Nitrogen* pp. 347-359. Monograph No. 10, Amer. Soc. Agron. Madison, Wisconsin.
- Bremner, J.M. and K. Shaw. 1958b. Denitrification in soil. II. Factors affecting denitrification. *J. Agron. Sci.* 51: 40-52.
- Bremner, J.M. and L.G. Bundy. 1974. Inhibition of nitrification in soils by volatile sulphur compounds. *Soil Biol. Biochem.* 6: 161-165.
- Broadbent, F.E. and T. Nakashima. 1965. Plant recovery of immobilized nitrogen in greenhouse experiments. *Soil Sci. Soc. Amer. Proc.* 29: 55-60.
- Brown, W.T., J.H. Quastel and P.G. Scholefield. 1956. Effects of mercapto compounds on soil nitrification. *Appl. Microbiol.* 2: 235-239.
- Bundy, L.G. and J.M. Bremner. 1973. Inhibition of nitrification in soils. Journal Paper No. J-7428 of the Iowa Agric. and Home Econ. Exp. Sta., Ames, Iowa.
- Bundy, L.G. and J.M. Bremner. 1974. Effects of nitrification inhibitors on transformation of urea nitrogen in soils. *Soil Biol. Biochem.* 6: 369-376.
- Burge, W.D. and F.E. Broadbent. 1961. Fixation of ammonia by organic soils. *Soil Sci. Soc. Amer. Proc.* 25: 199-204.

- Cady, F.B. and W.V. Bartholomew. 1960. Sequential products of anaerobic denitrification in Norfolk soil material. *Soil Sci. Soc. Amer. Proc.* 24: 477-482.
- Cady, F.B. and W.V. Bartholomew. 1961. Influence of low pO_2 on denitrification processes and products. *Soil Sci. Soc. Amer. Proc.* 25: 362-365.
- Carter, J.N. and F.E. Allison. 1960. Investigation on denitrification in well-aerated soils. *Soil Sci.* 90: 173-177.
- Carter, J.N., O.L. Bennett and R.W. Pearson. 1966. Recovery of fertilizer nitrogen under field conditions using Nitrogen-15. *Soil Sci. Soc. Amer. Proc.* 31: 50-56.
- Chai, H.H. and Hou, T.T. 1977. Studies on the volatilization of gaseous nitrogen from ammonium sulfate, urea and sodium nitrate applied to soils. *Soils and Fertilizers in Taiwan. Tech. Bull. Taiwan Fert. Co. No.* 40.
- Chalk, P.M., D.R. Keeney and L.M. Walsh. 1974. Crop recovery and nitrification of fall and spring applied anhydrous ammonia. *Agron. J.* 67: 33-37.
- Chapman, H.D. 1965. Cation-exchange capacity. In Methods of Soil Analysis. Part 2. pp. 891-901. Monograph No. 9, Amer. Soc. Agron., Madison, Wisconsin.
- Cho, C.M. 1976. Mass spectrometric investigation of denitrification. In *Proc. of 20th Manitoba Soil Science Meeting, Winnipeg, Manitoba, December 8 & 9.*
- Clark, F.E. and W.E. Beard. 1960. Influence of organic matter on volatile losses of nitrogen from soil. *Proc. 7th Int. Congr. Soil Sci., Madison, Wisconsin. III.* pp. 501-508.
- Clark, F.E., W.E. Beard and D.H. Smith. 1960. Dissimilar nitrifying capacities of soils in relation to losses of applied nitrogen. *Soil Sci. Soc. Amer. Proc.* 24: 50-54.
- Clark, F.E. 1962. Losses of nitrogen accompanying nitrification. *International Soil Conference Transactions, New Zealand 1962.* pp. 173-176.
- Cooke, G.W. and Cunningham, R.K. 1957. Inorganic nitrogen in soils. *Rothamsted Exp. Sta. Report.* 1956: 53-54.
- Das, B.K., A.K. Sarkar and B.B. Das. 1965. Studies on the effect of nitrogen levels on the field and quality of fibre in varieties of capsularis jute and their residual effect on mustard. *J. Indian Soc. Soil Sci.* 13: 109-114.
- Donald, L., H.J. Stangel and J.T. Pesek. 1963. Advances in knowledge of nitrogen fertilization in the USA since 1950. In Fert. Technology and Usage. pp. 75-129. *Soil Sci. Soc. Amer., Madison, Wisconsin.*
- Dow Chemical Co., 1962. 'N-Serve', *Tech. Bull.* 123, pp. 1-13.

- Ernst, J.W. and H.F. Massey. 1960. The effect of several factors on volatilization of ammonia formed from urea in the soil. *Soil Sci. Soc. Amer. Proc.* 24: 87-90.
- Fenn, L.B. and R. Escarzaga. 1976. Ammonia volatilization from surface application of ammonium compounds on calcareous soil. VI. Effects of initial soil water content and quality of applied water. *Soil Sci. Soc. Amer. J.* 41 (2) 358-363.
- Fredrick, L.R., R.L. Starkey and W. Segal. 1957. Decomposability of some organic sulphur compounds in soil. *Soil Sci. Soc. Amer. Proc.* 21: 287-292.
- Fuller, W.H., A.B. Caster and W.T. McGeorge. 1950. Behaviour of nitrogenous fertilizer in alkaline calcareous soils. I. Nitrifying characteristics of some organic compounds under controlled conditions. *Ariz. Agr. Exp. Sta. Tech. Bull.* 120: 451-467.
- Fuller, W.H. 1963. Reactions of nitrogenous fertilizers in calcareous soils. *J. Agr. Ed. Chem.* 11: 188-193.
- Furuta, T., R.H. Sciaroni and J.R. Breece. 1968. Sulphur coated urea fertilizer for controlled release nutrition of container-grown ornamentals. *Calif. Agr.* 21 (9): 4-5.
- Gama, M.V.Da. 1977. Volatilization losses of urea nitrogen in soils. *Agronomia Lusitana* 37 (4): 269-280.
- Gamboa, J.J., G. Paez and M. Blasco. 1971. A model for describing retention and leaching processes in soils. *Turrialba* 21 (3): 312-316. In *Soils and Fert. Abstr.* 35 (2).
- Gasser, J.K.R. 1964. Some factors affecting losses of ammonia from urea and ammonium sulphate applied to soils. *J. Soil Sci.* 15: 258-272.
- Gasser, J.K.R. and A. Penny. 1964. Inhibiting the nitrification of ammonium salts. *Roth. Exp. Sta. Rep.* 1963. p. 46.
- Gasser, J.K.R. and F.G. Hamlyn. 1968. The effects on winter wheat of ammonium sulphate, with and without a nitrification inhibitor, and of calcium nitrate. *J. Agric. Sci. Camb.* 71: 243-248.
- Gerretsen, F.C. and H. DeHoop. 1957. Nitrogen losses during nitrification in solutions and in acid sandy soils. *Can. J. Microbiol.* 3: 359-380.
- Goring, C.A.I. 1962a. Control of nitrification by 2-chloro-6-(trichloromethyl)-pyridine. *Soil Sci.* 93: 211-218.
- Goring, C.A.I. 1962b. Control of nitrification of ammonium fertilizers and urea by 2-chloro-6-(trichloromethyl)-pyridine. *Soil Sci.* 93: 431-439.

- Gould, W.D., F.D. Cook and G.R.B. Webster. 1977. Factors affecting urea hydrolysis in several Alberta soils. *Plant and Soil* 38: 393-401.
- Greenland, D.J. 1962. Denitrification in some tropical soils. *J. Agr. Sci.* 58: 227-233.
- Harada, T., Y. Oshima, T. Nishihara and Y. Kinoshita. 1964. Control of nitrification in soil by chlorophenyl isothiocyanates. I. Inhibitory effects of mono and di-chlorophenyl isothiocyanates on nitrification in soil. *J. Sci. Soil. Manure Japan* 35, 392-396.
- Hargrove, W.L., D.E. Kissel and L.B. Fenn. 1977. Field measurements of ammonia volatilization from surface application of ammonium salts to a calcareous soil. *Agron. J.* 69: 473-476.
- Hauck, R.D. and M. Koshino. 1971. Slow release and amended fertilizers. In Fertilizer Technology and Use. pp. 455-495. *Soil Sci. Soc. Amer.*, Madison, Wisconsin.
- Hays, J.T. and D.J. Forbes. 1974. Thiourea solutions as nitrification inhibitors. *J. Agr. Ed. Chem.* 22: 468-470.
- Hedlin, R.A. and C.M. Cho. 1974. Fertilizer use and other soil management practices in relation to contamination of ground and surface water with nitrogen and phosphorus. In Allocative Conflicts in Water Res. Man. pp. 303-323. Agassiz Centre for water studies. University of Manitoba, Winnipeg.
- Hendrickson, L., L.M. Walsh and D.R. Keeney. 1977. Effect of 'N-Serve' on nitrification and yield of corn (unpublished) University of Wisconsin, Madison (personal communication).
- Henzel, E.F., A.E. Martin, P.J. Ross and K.P. Haydock. 1964. Isotopic studies on the uptake of nitrogen by pasture grasses. II. Uptake of fertilizer nitrogen by Rhodes grass in pots. *Australian. J. Agr. Res.* 15: 876-884.
- Hughes, T.D. and L.F. Welch. 1968. Potassium azide as a nitrification inhibitor. *Agron. J.* 62: 595-599.
- I.A.E.A. 1969. Coordinated research program on maize fertility using fertilizer containing labelled nutrient elements. *Tech. Rep. Ser. No. 97*: 152-158. *Int. Atom. Energy Agcy.*, Vienna.
- Int. Rice Committee 1966 "on Rice Soils, Water and Fertilizers". International Rice Research, Lake Charles, Louisiana.
- Iswaran. V.B., S.N. Datta; A.K. Rishi and M.A. Iduani. 1961. "Urea-form" - a new fertilizer. *Curr. Sci.* 30, 182-183.
- Janson, S.L., M.J. Hallan, and W.V. Bartholomew. 1955. Preferential utilization of ammonium over nitrate by microorganisms in the decomposition of oat straw. *Plant and Soil* 6: 382-390.

- Jaworski, C.A., and D.J. Morton. 1967. Tomato transplant growth, production and uniformity in relation to sources and levels of nitrogen. Hort. Res. 7: 1-12.
- Joint FAO/IAEA Division 1970. Rice fertilization. Tech. Rep. Ser. No. 108. Int. Atom Energy Agcy., Vienna.
- Jones, R.W. and R.A. Hedlin. 1970a. Ammonium, nitrite and nitrate accumulation in three Manitoba Soils as influenced by added ammonium sulphate and urea. Can. J. Soil Sci. 50: 331-338.
- Kamphake, L.J., S.A. Hannah and J.M. Cohen. 1967. Automated analysis for nitrate by hydrazine reduction. Water Res. 1: 205-216.
- Kilian, K.C. 1964. Use of urea-formaldehyde and other slowly available forms of N for grass. Diss. Abstr. 24, 3485.
- Kinoshita, Y., N. Matsuda and S. Sakai. 1966. Synthesis of isothiocyanates and their inhibitory effects upon soil nitrification. Agr. Biol. Chem. 30: 447-451.
- Kowalenko, C.G. and D.R. Cameron. 1978. Nitrogen transformation in soil-plant systems in three years of field experiments using tracer and non-tracer methods on an ammonium fixing soil. Can. J. Soil Sci. 58: 195-208.
- Kurtz, L.T. and G.E. Smith. 1966. Nitrogen fertility requirements. In Advances in Corn Production. pp. 195-235. Ia. Sta. Univ. Press, Ames, Iowa.
- Lakhdiva, B.A. and R. Prasad. 1969. Effect of urea containing nitrification inhibiting agents on nitrogen uptake and yield of rice, as depending on method and time of application. Z. Pflanzenernaehr. Bodenk. 124: 23-28.
- Lakhdiva, B.A. and R.J. Prasad. 1970. Yield of a tall and dwarf rice as affected by fertilizer nitrogen, with and without nitrification inhibitors. J. Agr. Sci. 75: 375-379.
- Lathwell, D.J., D.R. Bouldin and W.S. Reid. 1970. Effects of nitrogen fertilizer applications in agriculture. In Relationship of Agriculture to Soil and Water Pollution. Cornell Univ., Ithaca, N.Y.
- Linser, H., H.H. Mayer and H. Unzeitig. 1959. Untersuchungen über die Wanderung von Ionen in Bodensäulen. z. Pflanzenernaehr. Dung. Bodenk 86: 57-65. In Soils and Fert. Abstr. 22: No. 6 (1959).
- Listanka, Jana and Jiri Apltauer. 1972. The influence of some factors on transformation and movement of the nitrogen of urea in the soil. Vedecke Prace Vyzkumnych Ustava Rostlinne Vyroby Praha Ruzyně 17: 7-14.

- Listanka, J. 1974. The effect of nitrification inhibitor on the transformation of the nitrogen of urea in grey brown podzolic soil. *Vedecke Prace Vyzkumuych Ustavu Rostlinne Vyroby Praha Ruzyne* 19: 147-154.
- Low, A.J. and F.J. Piper. 1967. Urea as a fertilizer. Laboratory and pot-culture studies. *J. Agr. Sci.* 57: 249-255.
- MacLeod, L.B., J.D.E. Sterling and J.A. MacLeod. 1975. Effects of rate, source and method of application of N, P and K on growth, nutrient uptake and yield of barley. *Can. J. Soil Sci.* 55: 61-67.
- MacVicar, R., W.L. Garman and R. Wall. 1951. Studies on nitrogen fertilizer utilization using ^{15}N . *Soil Sci. Soc. Amer. Proc.* 15: 265-268.
- Martin, J.P. and H.D. Chapman. 1951. Volatilization of ammonia from surface-fertilized soils. *Soil Sci.* 71: 25-34.
- Martin, A.E. and G.W. Skyring. 1962. Losses of nitrogen from the soil plant system. *Commonwealth Bureau Pastures & Field Crops. Bull.* 46: 19-34. Hurley, Berkshire, England.
- Matocha, J.E. 1976. Ammonia volatilization and nitrogen utilization from sulphur-coated urea and conventional nitrogen fertilizers. *Soil Sci. Soc. Amer. Jour.* 40: 597-601.
- McBeath, D.K. 1962. The inhibition of nitrification by thiourea and 2-chloro-6-(trichloromethyl)-pyridine. Ph.D. Thesis Cornell University (reprint 62-5958, University Microfilms, Inc. Ann. Arbor, Mich.).
- McGill, K.S. 1971. Uptake of nitrogen by barley from spring and fall applied urea and ammonium nitrate. M.Sc. thesis -submitted to the Faculty of Graduate Studies and Research, University of Manitoba, Winnipeg, Canada.
- Meyer, R.D., R.A. Olson and H.F. Rhodes. 1961. Ammonia loss from fertilized Nebraska soil. *Agron. J.* 53: 241-244.
- Michalyna, W. and R.A. Hedlin. 1961. A study of moisture storage and nitrate accumulation in soil as related to wheat yields on four cropping sequences. *Can. J. Soil Sci.* 41: 5-15.
- Mikkelsen, D.S. and D.C. Finfrock. 1957. Availability of ammoniacal nitrogen to lowland rice as influenced by fertilizer placement. *Agron. J.* 49: 296-300.
- Millbank, J.W. 1959. The physiology of nitrification in Kenya Highland Soil. *Plant and Soil* 11: 293-311.
- Mitsui, S. 1954. The volatilization of ammonia transformed by urea. *Jour. Sci. Soil and Manure* 25: 17-19. *Chem. Abs.* 48: 11702.

- Mitsui, S. 1956. Inorganic nutrition, fertilization and soil amelioration for lowland rice. Yokendo Press. Tokyo, Japan.
- Mitsui Toatsu Chemical Inc. 1969. Nitrification Inhibitor 'AM' Tech. Bull (1969).
- Morrison, I.K. and N.W. Foster. 1977. Fate of urea fertilizer added to a broad forest Pinus banksiana Lamb stand. Soil Sci. Soc. Amer. Jour. 41: 441-446.
- Mortland, M.M. 1958. Reactions of ammonia in soils. Advances in Agron. 10: 325-348.
- Myers, R.K.J. and E.A. Paul. 1970. Plant uptake and immobilization of ^{15}N -labelled ammonium nitrate in a field experiment with wheat. IAEA-PL-341/5.
- Myers, R.K.J. and J.W. McGarity. 1972. Denitrification in undisturbed cores from a solodized solonetz B. horizon. Plant and Soil 37: 81-89.
- Nelson, D.W. and J.M. Bremner. 1969. Factors affecting chemical transformations of nitrite in soils. Soil Biol. Biochem. 1: 329-239.
- Nelson, D.W. and J.M. Bremner. 1970b. Gaseous products of nitrite decomposition in soils. Soil Biol. Biochem. 2: 203-215.
- Nelson, L.B. and R.E. Uhland. 1955. Factors that influence loss of fall applied fertilizers and their probable importance in different sections of the United States. Soil Sci. Soc. Amer. Proc. 19: 492-496.
- Nielsen, K.F. and R.K. Cunningham. 1964. The effect of soil temperature and form and level of nitrogen on growth and chemical composition of Italian ryegrass. Soil Sci. Soc. Amer. Proc. 38: 213-218.
- Nommik, H. 1956. Investigations on denitrification in soil. Acta Agric. Scand. VI. 2: 195-228.
- Nommik, H. and K.O. Nilson. 1963. Fixation of ammonia by organic fraction of the soil. Acta Agric. Scand. 13: 371-390.
- Nommik, H. 1965. Ammonium fixation and other reactions involving a non-enzymatic immobilization of mineral nitrogen in soil. In Soil Nitrogen, pp. 200-258 Monograph No. 10 Amer. Soc. Agron., Madison, Wisconsin.
- Nyborg, M. 1976. A preliminary report on the effectiveness of nitrogen fertilizer when applied in spring (unpublished). Department of Soil Science, University of Alberta, Edmonton.
- Nyborg, M. and S.S. Malhi. 1977. CS_2 as a source of sulphur for plants. (unpublished). Department of Soil Science, University of Alberta, Edmonton, Alta.

- Olsen, S.R., C.V. Cole, F.S. Watanabe and L.A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dept. Agr. Circ. 939.
- Olson, R.A., A.F. Dreier, C. Thompson, K. Frank and P.H. Grabonski. 1964a. Using fertilizer nitrogen effectively on grain crops. Univ. of Nebr. Agri. Exp. Sta. SB-479 (1964).
- Olson, R.A. 1972. Maximizing the utilization efficiency of fertilizer N. by soil and crop management. Paper No. 3325, Jour. Series. Univ. of Nebr. Agri. Exp. Sta.
- Olson, R.A., K.D. Frank, A.D. Flowerday and A.F. Dreier. 1977. A summary of 'N-Serve' investigations in Nebraska to date. (unpublished) Univ. of Nebr. Agri. Exp. Sta. (1977) (personal communication).
- Owens, L.D. 1960. Nitrogen movement and transformation in soils as evaluated by a lysimeter study utilizing isotopic nitrogen. Soil Sci. Soc. Amer. Proc. 24: 372.
- Pang, P.C., R.A. Hedlin and C.M. Cho. 1973. Transformation and movement of band applied urea, ammonium sulphate and ammonium hydroxide during incubation in several Manitoba soils. Can. J. Soil Sci. 53: 331-341.
- Parish, D.H., L. Ross, C.L. Figon and C. Cavalot. 1965. Comparison between urea and ammonium sulphate as nitrogen sources for sugar cane. I. Effect of ammoniacal and nitrate nitrogen and time of application. Rep. Mauriti. Sug. Ind. Res. Inst. (1965) 48-56.
- Pearson, R.W., H.V. Jordan, O.L. Bennett, C.E. Scarsbrook, W.E. Adams and A.W. White. 1961. Residual effects of fall and spring applied nitrogen fertilizers on crop yields in the southeastern United States. U.S. Dept. Agri. Tech. Bull. 1254.
- Pinck, L.A., F.E. Allison and V.L. Gaddy. 1946. The nitrogen requirement in the utilization of carbonaceous residues in soil. J. Amer. Soc. Agron. 38: 410-420.
- Powlson, D.S. and D.S. Jenkinson. 1971. Inhibition of nitrification in soil by carbon disulphide from rubber bungs. Soil Biol. Biochem. 3: 267-269.
- Prasad, R., B.B. Turkhede and U.K. Das. 1966. 2-chloro-6-(trichloromethyl)-pyridine for reducing nitrogen losses from upland paddy soils. Curr. Sci. 35: 312-313.
- Prasad, R. 1968. Dry-matter production and recovery of fertilizer nitrogen by rice as affected by nitrification retarders 'N-Serve' and 'AM'. Plant and Soil 29: 327-330.
- Prasad, R. and S.S. Bains. 1968. Nitrification Inhibitors for increasing efficiency of fertilizer nitrogen in paddy soils. Fert. News 13 (5): 37-38.

- Prasad, R. and B.A. Lakhdive. 1969. Note on nitrification of ammonium sulphate and subsequent losses of nitrogen under waterlogged conditions as affected by nitrification retarders - 'N-Serve' and 'AM' Indian Journ. Agri. Sci. 39: 259-262.
- Prasad, R. 1970. A Practical Manual for Soil Fertility (Mimeographed), Division of Agronomy. Indian Agri. Res. Inst., New Delhi (1970).
- Prasad, R., G.B. Rajale and B.A. Lakhdive. 1971. Nitrification retarders and slow release nitrogen fertilizers. Adv. Agron. 23: 337-383.
- Prasad, R. and B.B. Turkhede. 1971. Relative efficiency of nitrogen fertilizers for "Ganga 101" maize (zea-mays L.) as influenced by rainfall. Indian Journ. Agri. Sci. 41: 485-489.
- Prasad, R. and G.B. Rajale. 1972. The influence of nitrification inhibitors and slow release nitrogen materials on transformation of fertilizer nitrogen in soils of fluctuating moisture content. Soil Biol. Biochem. 4: 451-457.
- Prasad, M. 1976. Gaseous loss of ammonia from sulphur coated urea, ammonium sulphate and urea applied to calcareous soil. Soil Sci. Soc. Amer. Journ. 40: 130-134.
- Rajale, G.B. and R. Prasad. 1970b. Nitrification/mineralization of urea as affected by nitrification retarders 'N-Serve' and 'AM' Curr. Sci., 39: 211-212.
- Reus, J.O. and R.L. Smith. 1965. Chemical reactions of nitrites in acid soils. Soil Sci. Soc. Amer. Proc. 29: 267-270.
- Ridley, A.O. 1975. Effect of spring and fall applied fertilizer on yield and nitrogen uptake by barley. In Proc. of 19th Manitoba Soil Science Meeting, Winnipeg, Manitoba, December 10-11.
- Ridley, A.O. 1977. Nitrogen Fertilizers, Time and Method of Placement. Manitoba Soil Science Meeting, Winnipeg, December.
- Rindt, D.W., G.M. Blouin and J.G. Getsinger. 1968. Sulphur coating on nitrogen fertilizers to reduce dissolution rate. J. Agr. Fd. Chem. 16: 773-778.
- Russel, E.W. 1973. Nitrogen fertilizers. In Soil Conditions and Plant Growth. pp. 624-628.
- Sabey, B.R. 1968. The influence of nitrification suppressants on the rate of ammonium oxidation in mid-western U.S.A. field soils. Soil Sci. Soc. Amer. Proc. 32: 675-679.
- Sable, W.E. and L.W. Reed. 1964. Investigations concerning nitrogen loss through chemical reactions involving urea and nitrite. Soil Sci. Soc. Amer. Proc. 38: 478-481.
- Sanchez, P.A. and M. DeCalderon. 1971. Timing of nitrogen applications for rice grown under intermittent flooding in the coast of Peru. Proc. Int. Symp. Soil Fert. Evaluation 1: 595-602.

- Scarsbrook, C.E. 1958. Urea-formaldehyde fertilizer as a source of nitrogen for cotton and corn. *Soil Sci. Soc. Amer. Proc.* 22: 442-445.
- Schofield, R.K. and W. Taylor. 1955. The measurement of soil pH. *Soil Sci. Soc. Amer. Proc.* 19: 164-167.
- Schwartzbeck, R.A., J.V. MacGregor and E.L. Schmidt. 1961. Gaseous nitrogen losses from nitrogen fertilized soils measured with infrared and mass spectroscopy. *Soil Sci. Soc. Amer. Proc.* 25: 186-189.
- Shapely, D. 1977. Will fertilizer harm ozone as much as SST's? *Science.* 195: 658.
- Shattuk, G.E. and M. Alexander. 1963. A differential inhibitor of nitrifying micro-organisms. *Soil Sci. Soc. Amer. Proc.* 27: 600-601.
- Smith, D.H. and F.E. Clark. 1960. Volatile losses of nitrogen from acid or neutral soils or solutions containing nitrite and ammonium ions. *Soil Sci.* 90: 86-92.
- Sohn, J.B. and M. Peech. 1958. Retention and fixation of ammonia by soils. *Soil Sci.* 85: 1-9.
- Soper, R.J., G.J. Racz and P.I. Fehr. 1970. Nitrate nitrogen in the soil as a means of predicting the fertilizer nitrogen requirements of barley. *Can. J. Soil Sci.* 51: 45-49.
- Soulides, D.A. and F.E. Clark. 1958. Nitrification in grassland soils. *Soil Sci. Soc. Amer. Proc.* 22: 308-311.
- Sowden, F.J. 1975. Transformation of nitrogen added as ammonium and manure to soil with a high ammonium-fixing capacity under laboratory conditions. *Can. J. Soil Sci.* 56: (4) 319-331.
- Stefanson, R.C. 1972. Soil denitrification in sealed soil-plant systems: 1. Effect of plants, soil water content and soil organic matter content. *Plant and Soil* 33: 113-127.
- Sweezy, A.W. and G.O. Turner. 1962. Crop experiments on the effect of 2-chloro-6-(trichloromethyl)-pyridine for control of nitrification of ammonia and urea fertilizers. *Agron. J.* 54: 532-535.
- Thomas, G.W. 1970. Accumulation and losses. In Nutrient mobility in soils. pp. 1-20. *Soil Sci. Soc. Amer.*, Madison, Wisconsin.
- Turner, G.O., L.E. Warren and F.G. Andriessen. 1962. Effect of 2-chloro-6-(trichloromethyl)-pyridine on the nitrification of ammonium fertilizers in field soils. *Soil Sci.* 94: 270-273.
- Tyler, K.B. and F.E. Broadbent. 1960. Nitrite transformation in California soils. *Soil Sci. Soc. Amer. Proc.* 24: 279-282.

- Ventura, W.B. and T. Yoshida. 1977. Ammonia volatilization from a flooded tropical soil. *Plant and Soil* 46: 521-531.
- Viets, F.G. and R.H. Hagemann. 1971. Factors affecting the accumulation of nitrate in soil, water and plants. U.S. Dept. Agr. Handbook No. 413.
- Vlassak, K. 1964. Effect of 2-chloro-6-(trichloromethyl)-pyridine on nitrification in soil. *Agricultura (Louvain)* 12: 73-89. In Soil and Fertilizer Abstr. 27 No. 4.
- Volk, G.M. 1959. Volatile loss of ammonia following surface application of urea to turf or bare soil. *Agron. J.* 51: 746-749.
- Volk, G.M. 1961. Gaseous loss of ammonia from surface applied nitrogenous fertilizers. *J. Agri. Fd. Chem.* 9: 280-283.
- Waddington, D.V., E.L. Moberg, J.M. Duich and T.L. Watschke. 1976. Long term evaluation of slow-release nitrogen sources on turf-grass. *Soil Sci. Soc. Amer. Jour.* 40: 593-597.
- Wagner, G.H. and G.E. Smith. 1958. Nitrogen losses from soils fertilized with different nitrogen carriers. *Soil Sci.* 85: 125-129.
- Wahab, A., K. Mahmud and M. Ishaq. 1960. Nitrification of urea and its loss through volatilization of ammonia under different soil conditions. *J. Agri. Sci.* 55: 47-51.
- Walker, T.W., A.F.R. Adams and H.D. Orchiston. 1956. Fate of labelled nitrate and ammonium nitrogen when applied to grass and clover grown separately and together. *Soil Sci.* 81: 339-351.
- Walkley, A. and T.A. Black. 1934. An examination of the Degljareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29-38.
- Walunjkar, W.G., W.V. Bartholomew and W.G. Waltz. 1959. Nitrogen interchange in soil affected by soil type, source and rate of nitrogen addition, moisture and time of incubation. *J. Indian Soc. Soil. Sci.* 7: 65.
- Weir, C.C. and J.G. Davidson. 1968. The effect of retarding nitrification of added fertilizer nitrogen on the yield and nitrogen uptake of Pangola grass (*Digitaria decumbens*). *Trop Agri. Trin.* 45: 301-306.
- Wetselaar, R. 1961. Nitrate distribution in tropical soils. II. Extent of capillary accumulation of nitrate during a long dry period. *Plant and Soil* 15: 121-133.
- Wetselaar, R. 1962. Nitrate distribution in tropical soils. III. Downward movement and accumulation of nitrate in the subsoil. *Plant and Soil* 16: 19-31.

- Wetselaar, R. 1974. Increasing the efficiency of nitrogen fertilizers and minimizing losses to the environment. In Fertilizer and Environment, pp. 35-41. Proc. of the Australian Institute of Agri. Sci.
- Wijler, J. and C.C. Delwiche. 1954. Investigations on the denitrification process in soil. *Plant and Soil* 5: 155-169.
- Winsor, G.W. and A.G. Pollard. 1956a. Carbon-nitrogen relationship in soil: the immobilization of nitrogen in presence of carbon compounds. *J. Sci. Fd. Agric.* 7: 134-141.
- Winsor, G.W. and A.G. Pollard. 1956b. Carbon-nitrogen relationship in soil: II. Quantitative relationship between nitrogen immobilized and carbon added to soil. *J. Sci. Fd. Agric.* 7: 142-149.