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EVALUATION OF THE NITRIFICATION INHIBITORS  
N-SERVE AND ATC WITH UREA FERTILIZER

by

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## ABSTRACT

The purpose of using chemical nitrification inhibitors is to delay the oxidation of ammoniacal fertilizers during the early part of the growing season in order to minimize N losses prior to the period of maximum crop uptake. Since  $\text{NH}_4^+$  is electrostatically attracted to soil particles, leaching losses would be minimized, and denitrification losses could not occur in the absence of  $\text{NO}_3^-$ . Thus, smaller amounts of fertilizer N would be required, resulting in lower inputs of money and energy as well as less potential for environmental pollution.

A study (Chapter Two) was initiated in the fall of 1977 to determine if ATC could minimize overwinter losses of fall-applied N. Urea (200 kg N/ha) with or without a 1% coating of ATC (4-amino-1,2,4-triazole) was banded or broadcast onto a silt soil on November 8, when the soil temperature at 10 cm depth was 1.9°C. The soil was sampled to a depth of 90 cm at approximately one month intervals until April, and  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were determined. In the banded plots, some nitrification occurred prior to January, but from this date until March there was very little change in soil  $\text{NH}_4^+$  levels. Overall, from December to April, there were 70 and 48% decreases in the 0-15 cm plots without and with ATC, respectively. In all the broadcast plots, regardless of ATC treatment, nitrification proceeded steadily throughout the sampling period, with 93 and 85% decreases from the December 0-15 cm  $\text{NH}_4^+$  levels in the non-ATC and ATC plots, respectively. It is concluded that ATC is partially effective in minimizing N losses when applied in the fall as a band with urea, but when broadcast there is

no effect on nitrification. Leaching of the water-soluble ATC was the likely cause of its poor effectiveness. Significant leaching of urea from the zone of application was also found to occur during the first month following its application.

A laboratory study (Chapter Three) was conducted to determine the influence of the nitrification inhibitors ATC and N-Serve [2-chloro-6-(trichloromethyl)-pyridine] on urea hydrolysis in a silt soil at 2 and 12°C. There was no delay of ureolysis caused by the presence of these chemicals, even at 20 times the recommended application rate. At 2°C the rate of hydrolysis was about half that at 12°C, with 21 and 7 days being required for complete hydrolysis at 2 and 12°C, respectively. These results suggest that leaching of urea may occur following its application to a cold soil during periods of heavy precipitation as was found in the winter nitrification study (Chapter Two).

A series of field experiments (Chapter Four) was conducted with silage corn (Zea mays L.) to compare the effectiveness of the nitrification inhibitors ATC and N-Serve in a loamy sand and a silt. Urea was coated with the inhibitors at a rate of 1% of active ingredient per weight of N and applied as a band or broadcast in the spring of 1977 and 1978. Neither inhibitor significantly affected nitrification when applied as a broadcast treatment to either soil. In the silt, both inhibitors were equally effective in delaying nitrification when banded, whereas in the loamy sand ATC was much more effective than N-Serve. The effectiveness of N-Serve persisted much longer in the silt (86 days) than in the loamy sand (23 days). This suggested that volatilization of N-Serve severely limited its effectiveness in the loamy sand. There was no significant improvement in crop yields or N content due to inhibitor treatment in either soil.

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## Chapter One

### INTRODUCTION

#### Importance of N Fertilizer

Plants, like all organisms, require nitrogen (N) for their growth and reproduction. Nitrogen is a constituent of all protein, all enzymes, many of the metabolic intermediates involved in synthesis and energy transfer, and even of the deoxyribonucleic acids making up the genetic code itself. Of the elements necessary for higher plant growth, N is usually required in larger quantities than any other element absorbed from the soil. For a 9400 kg/ha yield of corn grain (Zea mays L.), 146 kg N, 28 kg P, 39 kg K, 17 kg Ca, and 24 kg Mg are removed per hectare (Martin et al., 1976).

Some soils can still supply all of the N needs of the crop. This is most probable where moisture deficit limits crop yields, and losses of N are minimal, such as the steppe and prairie regions of the world. Areas of higher rainfall, such as the coastal regions of North America, generally require N applications for optimum yields since crop growth is not limited by lack of moisture, and N losses by leaching and denitrification are significant.

Under favorable conditions, 80% or more of the fertilizer N may be recovered by the crop to which it was applied. However, under many soil and cropping conditions, efficiencies of 50% or less are not uncommon (Allison, 1955; Prasad et al., 1971).

#### Loss Mechanisms for N Fertilizer

Most N fertilizers are subject to certain chemical, physical and biochemical events which can result in significant losses of N from the soil-

root zone after application. Losses occur principally through (i) leaching of nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^+$ ); (ii) biological denitrification of both  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ; (iii) volatilization of ammonia ( $\text{NH}_3$ ) following improper application of anhydrous or aqua  $\text{NH}_3$  and surface application of urea and other ammoniacal N sources to neutral or alkaline soils; and (iv) chemical denitrification according to mechanisms proposed by Allison (1963). Fertilizer N can also be lost through (v) surface runoff and erosion, (vi) interlattice fixation of ammonium ( $\text{NH}_4^+$ ) by clay minerals, (vii) microbiological immobilization, and (viii) chemical immobilization involving reactions of fertilizer N with soil organic components. The latter three mechanisms represent temporary losses, since fixed or immobilized N is gradually released over time.

#### Reasons for Increasing Fertilizer N Efficiency

At least three good reasons exist for improving the efficiency of N fertilizer applications. Increased efficiency would (i) save money due to lower application rates, (ii) conserve some of the energy which is currently used for N fertilizer production, and (iii) reduce the environmental pollution which sometimes results from N fertilizers.

From the farmer's viewpoint, saving money is of greatest importance. The cost of N fertilizer has increased greatly during recent years, from \$105 per metric ton of urea (23¢/kg N) in 1975 to \$270 per metric ton (60¢/kg N) in 1980 (prices in British Columbia). In the past, N fertilizer was relatively inexpensive, so farmers often used an excess to ensure optimum yields. But the greatly increased cost of N fertilizer has caused farmers to be more conservative in their application rates, which may lead to reduced yields unless the efficiency can be improved.

The manufacture of N fertilizers requires a great deal of energy, generally in the form of natural gas. This is one reason for the rapid increase in price. During 1972 in the United States, 10.4 million metric tons of anhydrous ammonia was produced for N fertilizer, requiring 12.8 billion  $\text{m}^3$  of natural gas. This usage accounted for 2 percent of the 600 billion  $\text{m}^3$  of gas consumed that year (Jones, 1979). The single largest energy input for corn production is the energy required to produce fertilizer N. This energy amounts to over 30 percent of the estimated total 2.9 million kilocalories required to produce 9400 kg/ha of corn, using 125 kg/ha of N fertilizer (Pimentel et al., 1973). Thus, reduction of N fertilizer rates would significantly decrease the energy requirement for agriculture. However, N fertilizer efficiency would have to be increased in order that crop yields would not be lowered by using lower N fertilizer rates.

Reduction of environmental contamination is another important reason for decreasing N application rates. Normally, all forms of N fertilizer are converted to nitrates, primarily by the soil bacteria Nitrosomonas sp. (oxidizes  $\text{NH}_4^+$  to  $\text{NO}_2^-$ ), and Nitrobacter sp. (oxidizes  $\text{NO}_2^-$  to  $\text{NO}_3^-$ ). Nitrates are very soluble in water, and since they are negatively charged, they are not electrostatically attracted to the negatively charged soil colloids. Thus,  $\text{NO}_3^-$  is very susceptible to leaching in the event of precipitation or irrigation. Leaching of  $\text{NO}_3^-$  can lead to contamination of drinking water supplies, and an allowable limit for  $\text{NO}_3^-$ -N in drinking water of 10 mg/liter has been adopted by

many agencies. Enrichment of lakes with  $\text{NO}_3^-$  can lead to increased eutrophication rates as well as more rapid growth of algae and weeds. Several sources of drinking water in California (Ward, 1970) and Illinois (Harmeson et al, 1971) have been found to be contaminated with  $\text{NO}_3^-$  originating from fertilizer applications.

Under partially anaerobic conditions, certain soil bacteria can use  $\text{NO}_3^-$  as an electron acceptor in place of oxygen which leads to the reduction of  $\text{NO}_3^-$  to nitrogen ( $\text{N}_2$ ) or nitrous oxide ( $\text{N}_2\text{O}$ ). As  $\text{N}_2\text{O}$  rises to the stratosphere it is photochemically oxidized to form nitric oxide ( $\text{NO}$ ), which in turn may react with the ozone layer. Destruction of the ozone layer could lead to increased ultraviolet radiation on the earth's surface, and thus a higher incidence of human skin cancer (McElroy et al, 1977).

#### Approaches to Improving N Fertilizer Efficiency

An efficient means of using N fertilizers is to apply a portion of the N shortly before the crop is planted and then apply side dressings of N during the growing season. This minimizes N losses, simply because the crop is able to absorb the N before it can be leached or denitrified. However, it is costly in terms of labor and equipment for the farmer to make several N applications, and soil compaction would also be increased. This practice is generally more appropriate for home gardeners or vegetable farmers.

Spring or summer N fertilizer applications are almost always more efficient than fall applications, since less time is available for losses of N to occur. Stevenson and Baldwin (1969) found that fall-applied

ammonium nitrate, urea, and anhydrous ammonia all resulted in significantly lower corn grain yields than spring-applied N on clay, clay loam and silt loam soils in southern Ontario over a period of four years. Relative efficiencies of fall-applied vs. spring-applied N ranged from 0.30 to 0.87 at the various locations, with the lower efficiencies being found in the clay soils, presumably due to greater denitrification losses. Similar results have been found by numerous other researchers, such as Welch et al (1971) in Illinois and Frye (1977) in Tennessee.

The use of coatings on N fertilizer pellets to decrease their solubility and thereby reduce leaching losses is another approach to improving N fertilizer efficiency. A commercially available example of this is sulfur-coated urea (SCU), which has coatings of sulfur, wax, and a microbiocide to delay the oxidation of S. The urea is not susceptible to hydrolysis and subsequent oxidation to nitrate until the sulfur is oxidized, which may require several weeks depending on the soil temperature and other factors. Use of SCU has been shown to decrease the loss of  $\text{NH}_3$  via volatilization which often occurs following surface applications of urea (Matocha, 1976) and to decrease leaching of N from a sandy soil (El Wali et al, 1980). However, studies by some researchers (Terman and Allen, 1974) have shown a decrease in N recovery by corn when SCU was compared with conventional N sources. A possible explanation for these findings is that the release of N from the SCU is not rapid enough to adequately supply a rapidly growing plant such as corn. Another major drawback of SCU is its cost. The 1980 price per kg of N as SCU is \$2.50 compared with \$0.60 for urea (Green Valley Fertilizer, 1980).

During the last few years, several slowly available forms of N have been developed, such as urea-formaldehyde compounds, metal ammonium phosphates, oxamide, crotonylidene diurea, isobutylidene diurea, thiourea, urea pyrolyzate, dicyandiamide, and calcium cyanamide. With the exception of urea-formaldehyde, most of these are still in the experimental stage. It is not likely that any of them will ever be low enough in cost for agronomic applications.

### Nitrification Inhibitors

The use of chemical nitrification inhibitors (NI) which can be coated onto or mixed with ammoniacal fertilizers is a promising approach to improving the efficiency of N fertilizer applications. The function of NI is to delay the oxidation of ammonium-based fertilizers in order to minimize leaching and denitrification losses of N prior to the period of maximum crop uptake. Ideally, a NI should meet several criteria:

- (i) it should persist in the soil long enough to prevent N losses, but it should be biodegradable so that it does not persist in the soil;
- (ii) it should be specific for Nitrosomonas, but not have any deleterious effect on other soil microorganisms;
- (iii) it should be non-toxic to plants, animals, or humans;
- (iv) its cost should be low enough to make it economical to use.

N-Serve or nitrapyrin [2-chloro-6-(trichloromethyl)pyridine] was the first patented chemical NI (Dow Chemical Co., Midland, Michigan). According to Goring (1962) N-Serve is a highly specific Nitrosomonas inhibitor which has a low order of toxicity to the general fungus and

bacterial populations as well as the seedlings of many plants. Its main disadvantage is that it is somewhat volatile, and for maximum effectiveness, it needs to be covered with soil (Briggs, 1975).

More recently, Bundy and Bremner (1973) tested 24 potential NI in a laboratory study. With the soils used, 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-6-methyl-pyrimidine (AM)>sulfathiazole (ST)>sodium diethyldithiocarbamate.

#### Field Studies with Nitrification Inhibitors

Most of the published field experiments with N-Serve have been done using anhydrous  $\text{NH}_3$  as the N source. This inhibitor may be mixed in the tank with the  $\text{NH}_3$  or it can be applied separately, but simultaneously, in the fertilizer band using separate metering equipment. Since the injection equipment normally applies the  $\text{NH}_3$  at a depth of 12 to 15 cm, volatilization of N-Serve is greatly minimized.

A few field experiments have shown increased crop yields following fall applications (Warren et al, 1975) or spring applications (Swezey and Turner, 1962) of N-Serve with anhydrous  $\text{NH}_3$ . However, many other studies, such as those by Cochran et al (1973), Hendrickson et al (1978a), and Touchton et al (1979a) have failed to demonstrate any



significant yield increases resulting from fall or spring applications of N-Serve with anhydrous  $\text{NH}_3$ . Increased yields resulting from NI applications can usually be attributed to effective inhibition of nitrification with a subsequent reduction in N losses. The lack of a positive yield response to NI may be due to either ineffective control of nitrification or to no loss of N because of prevailing soil and climatic conditions.

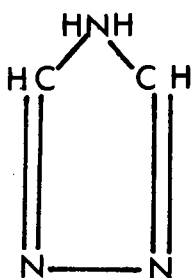
Only a few field experiments have been conducted where N-Serve has been applied in the fall with a solid N fertilizer. Huber et al (1969) reported a 15% increase in winter wheat yields averaged over three years when N-Serve (0.67 kg/ha) was band-applied with ammonium sulfate (67.5 kg N/ha) in the fall on an Idaho silt loam. Soil samples taken in March from the N-Serve plots had three times higher  $\text{NH}_4$  levels in the surface 15 cm than the plots with no inhibitor. Touchton et al (1979b) found that N-Serve (2.24 kg/ha) increased corn grain yields by 27% when broadcast and incorporated in the fall with 67 kg/ha urea-N applied to an Illinois silt loam when compared to a similar application without N-Serve. In contrast, Boswell et al (1976) found no improvement in winter wheat yields in Georgia during a three-year study when fall-applied N-Serve (1.11 kg/ha) and ammonium sulfate (84 kg N/ha) were broadcast and incorporated onto a loamy sand and a sandy loam. Soil samples taken in January revealed somewhat higher  $\text{NH}_4$  levels in the N-Serve plots, but by March there was no difference. The poor effectiveness of N-Serve in the Georgia soils was likely due to the warmer soil temperatures, coarser soil, and higher rainfall, which together would promote more rapid nitrification and percolation losses of N.

Studies where solid N fertilizers have been applied in the spring with N-Serve have generally shown disappointing results. Hendrickson et al (1978b) found that the effectiveness of N-Serve was very short-lived when it was applied with ammonium sulfate to an irrigated loamy sand, probably due to its low organic matter content (1%) which limited adsorption of N-Serve as well as its coarse texture which allowed greater volatilization of the inhibitor. Also, the low cation exchange capacity and the low water holding capacity of this soil permitted appreciable movement of  $\text{NH}_4$  below the N-Serve treated zone. Other field experiments, such as those by Spratt and Gasser (1970), Touchton et al (1979b), and Boswell et al (1976) have failed to show any improvement in crop yield following the spring application of N-Serve with solid urea or ammonium sulfate.

#### ATC Nitrification Inhibitor

ATC (4-amino-1,2,4-triazole) is a more recently patented (Ishihara Sangyo Kaisha Ltd., Tokyo, Japan) NI which is also specific for Nitrosomonas. According to the manufacturer, ATC is not phytotoxic to seedlings, and it has no effect on the growth of soil fungi or other soil bacteria. Laboratory studies (Bundy and Bremner, 1973) have shown it to be almost as effective as N-Serve when coated onto urea or ammonium sulfate and incubated with 10 g soil samples in small covered flasks. The limited air circulation in these containers would have the effect of artificially prolonging the effectiveness of the N-Serve since volatilization losses

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



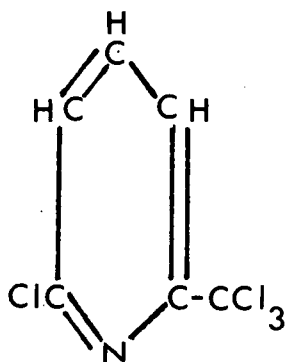
Molecular formula:  $C_2H_4N_4$

Molecular weight: 84.1

Water solubility: 420 g/100 ml at 20°C

Melting point: 81°C

N-SERVE [2-chloro-6-(trichloromethyl) pyridine]



Molecular formula:  $C_5H_3NCl_4$

Molecular weight: 230.9

Water solubility: 0.004 g/100 ml at 20°C

Melting point: 62°C

FIGURE 1:1 Chemical structure and properties of ATC and N-Serve

would be minimized. Thus, under field conditions, it is possible that ATC might be more persistent than N-Serve and thereby control nitrification for a longer period. The chemical structures of ATC and N-Serve are shown in Figure 1.

### Purpose of this Study

As of this date, there have been no results published from field studies where ATC has been used as a NI. Due to its non-volatile nature, this inhibitor should be more suitable than N-Serve for applications with solid N fertilizers, such as urea or ammonium sulfate.

With this in mind, a series of experiments was designed to test the effectiveness of ATC and N-Serve. In the first experiment (Chapter Two), ATC was applied with urea as a fall application to determine if use of this inhibitor could minimize losses of N during the winter and spring. In the second experiment (Chapter Three) a laboratory incubation study was conducted to determine if ATC or N-Serve affected the rate of urea hydrolysis at low soil temperatures. In Chapter Four, a series of field experiments with silage corn are discussed. The purpose of these experiments was to compare the effectiveness of ATC and N-Serve when applied in the spring with urea. Urea was chosen as the N source for these experiments since it is rapidly becoming the most popular solid N fertilizer in British Columbia, primarily since it has the lowest cost per kg of N. Anhydrous  $\text{NH}_3$  was not considered, since very little of this form of N is used in British Columbia. The use of anhydrous  $\text{NH}_3$  is generally only practical on large acreages, since costly, pressurized

or refrigerated equipment is necessary for the storage and application of this fertilizer.

The chapters presented in this thesis were each written in a style suitable for publication in the Soil Science Society of American Journal (American Society of Agronomy, 1976).

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## Chapter Two

### EFFECTS OF 4-AMINO-1,2,4-TRIAZOLE ON TRANSFORMATIONS OF FALL-APPLIED UREA-N

#### ABSTRACT

The objectives of this study were: (1) to determine if the nitrification inhibitor ATC (4-amino-1,2,4-triazole) could minimize overwinter N losses from fall-applied urea; and (2) to monitor the transformations of fall-applied urea-N.

Urea (200 kg N/ha) with or without a 1% (by weight of N) coating of ATC was applied as band and broadcast applications to a silt soil in November, 1977, when the soil temperature at 10 cm was 1.9°C. The soil was sampled to a depth of 90 cm at approximately one month intervals until April and analyzed for  $\text{NH}_4$ - and  $\text{NO}_3$ -N.

With the banded applications, some nitrification occurred prior to January, but from this date until March there was little change in soil  $\text{NH}_4$  levels. As the soil warmed from March to April (4.7 to 8.5°C) there were 50 and 35% decreases in the 0-15 cm  $\text{NH}_4$  levels in the non-ATC and ATC treatments, respectively. Overall, from December to April there were 70 and 48% decreases in the 0-15 cm soil  $\text{NH}_4$  levels of the non-ATC and ATC plots, respectively.

With the broadcast applications, regardless of ATC treatment, nitrification proceeded steadily throughout the sampling period, with 93 and 85% decreases from the December 0-15 cm  $\text{NH}_4$  levels in the non-ATC and ATC

plots, respectively. It is concluded that ATC is partially effective in minimizing N losses when applied in the fall as a band with urea, but when broadcast there is no effect on nitrification. Leaching of the water-soluble ATC is the likely cause of its poor effectiveness.

Significant leaching of urea from the soil surface was found to occur during the first month following its application.

## INTRODUCTION

Fall applications of nitrogenous fertilizers are not generally recommended, particularly in areas such as coastal British Columbia where the soil seldom freezes for extended periods, soil temperatures are often high enough during the winter for slow nitrification to occur, and the intense winter rainfall can lead to considerable loss of N by leaching. The high soil moisture levels and relatively warm soil temperatures which occur in the spring are also conducive to denitrification losses of  $\text{NO}_3\text{-N}$ .

However, several potential advantages exist for fall fertilizer applications. Manufacturers and dealers prefer to have their sales distributed throughout the year; farmers would like to spread their labor requirements more evenly through the year; the soil is often in a better physical condition in the fall for field operations.

Chemical inhibition of nitrification of fall-applied ammoniacal fertilizers offers a potential means of decreasing N losses from the soil by preventing formation of the highly labile nitrate ion. Ammonium is not subject to denitrification loss, and leaching of  $\text{NH}_4$  usually occurs only in coarse-textured soils having low cation exchange capacities.

Several researchers have investigated the use of N-Serve [2-chloro-6-(trichloromethyl)pyridine] as a nitrification inhibitor which can be applied in the fall with ammoniacal fertilizers. Most of the published studies have been done using anhydrous ammonia as the N source, since N-Serve cannot be easily applied with solid fertilizers due to its volatility (Bremner et al, 1978; Briggs, 1975).

Results from many researchers (Hendrickson et al., 1978; Touchton et al., 1978, 1979; Warren et al., 1975) have shown that N-Serve applied in the fall with anhydrous  $\text{NH}_3$  can significantly decrease the rate of nitrification and thus increase the proportion of fall-applied N which is available in the soil for plant uptake during the summer. However, fall N-Serve applications have not always resulted in improved crop yields the following season. Some possible explanations for the lack of crop response to fall-applied N-Serve are: (1) climatic conditions which were not conducive to N losses by leaching or denitrification; (2) lower than average yields due to drought or disease; (3) high rates of soil organic N mineralization during the summer.

ATC (4-amino-1,2,4-triazole) is a more recently developed nitrification inhibitor which is also specific for Nitrosomonas sp. It has the advantage of being non-volatile, and thus is more appropriate to use with solid fertilizers. Its cost is expected to be less than that of N-Serve. Laboratory incubations (Bundy and Bremner, 1973) and field studies (Guthrie and Bomke, 1980) have demonstrated that ATC is at least as effective as N-Serve when coated onto urea.

The objectives of the present study were: (1) to monitor the transformations and movement of urea-N during the winter and spring; (2) to determine the effectiveness of ATC in minimizing losses of N following fall application of urea as a band or broadcast onto a silt soil in the humid coastal region of the Pacific Northwest.

## METHODS AND MATERIALS

The experimental site was located 50 km south of Vancouver, B.C. on a poorly drained alluvial silt soil classified as a Typic Fluvaquent (Rego Humic Gleysol, Can.). The field had been under continuous silage corn production for three years and had received heavy annual manure applications from the associated dairy operation. Some of the important physical and chemical properties of the soil used in this study are listed in Table 2.1. Bulk densities were determined using the core method, and particle size analysis was done using the hydrometer technique (Black, 1965a). Soil pH was determined in 0.01 M  $\text{CaCl}_2$  (soil:solution ratio 1:2), total C by combustion in a Leco induction furnace, total N by a semimicro-Kjeldahl digestion, and CEC by a neutral 1 N ammonium acetate extraction (Black, 1965b).

The average annual precipitation at this site is 1270 mm, with 870 mm occurring between November 1 and April 30, almost all in the form of rain. The mean annual air temperature is 10 °C, with an average temperature of 5 °C from November through April.

The N source for the experiment was fertilizer grade (46% N) prilled urea (1.4 to 3.0 mm) which was applied on 8th November 1977 at rates of 0 or 200 kg N/ha (360 g N/18 m<sup>2</sup> plot). This was applied either as a broadcast treatment which was raked into the soil or as a narrow (5 cm) band (two 6 m bands per plot) which was covered with 8 cm of soil. Half of the fertilized plots received urea which had been coated with ATC (one kg ATC per 100 kg urea-N) using the following procedure. The required

Table 2.1. Selected physical and chemical properties at different depths of soil used in winter nitrification study

Depth	Bulk Density	Water content at -33 kPa <sup>+</sup>	Silt	Clay	Total C	Total N	CEC	pH CaCl <sub>2</sub>
cm	kg/m <sup>3</sup>			%			meq/100 g	
0-15	840	53.1	85	5	6.78	0.60	39.1	4.6
15-30	960	54.3	88	5	5.84	0.48	36.1	4.3
30-60	1100	N.D. <sup>‡</sup>	N.D.	N.D.	2.94	0.20	23.4	3.6
60-90	1200	N.D.	N.D.	N.D.	2.03	0.15	15.4	3.4

<sup>‡</sup> N.D. indicates that value was not determined.

<sup>+</sup> 100 kPa = 1 Bar

quantity of ATC (36% w/v aqueous solution) was sprayed with a chromatography spray gun onto a tray of urea prills (one kg) which were shaken by a mechanical shaker. Following thorough mixing, the coated urea was dried overnight using a fan at room temperature, then sealed into plastic bags. The treatments were arranged in a completely random design with three replications.

At approximately one month intervals, soil samples were taken from each plot to a depth of 90 cm in 15 cm increments. Six 2.5 cm cores were randomly obtained using a hand sampler from each broadcast plot, while the banded plots were sampled directly in the center of the fertilizer bands, which had been marked with nylon strings tightly stretched between pairs of wooden stakes. The samples from each plot were mixed and either extracted on the sampling day or refrigerated ( $2^{\circ}\text{C}$ ) no more than one day prior to extraction. Fresh soil (10 g) was subsampled and extracted with 2 N KCl (100 ml), and the filtrate was collected for  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$  analysis by Technicon Autoanalyzer. The same filtrates were also used for pH determinations. Separate 10 g subsamples were oven-dried ( $105^{\circ}\text{C}$ ) for gravimetric moisture determinations to correct the N data to a dry weight basis.

Precipitation data were obtained from a raingauge installed at the experimental site. Soil temperatures at 10, 20, 40 and 75 cm depths were measured weekly using silicone diodes (Hinshaw and Fritschen, 1970) inserted along two sides of the experimental area. In addition, a soil degree-day integrator was installed at a depth of 10 cm. These data are summarized in Table 2.2.

An analysis of variance was performed on the data from each sampling



depth, and treatment means were tested for significant differences by Duncan's multiple range test.

Table 2.2 Soil moisture, precipitation, and average soil temperatures  
between sampling dates, 1977-1978

Sampling date	Elapsed time	Precipitation	Depth of Measurement							
			10 cm	20 cm	40 cm	75 cm	0-15 cm	15-30 cm	30-60 cm	60-90 cm <sup>#</sup>
	days	mm	average °C				% moisture <sup>‡</sup>			
8 Nov.	0	-	1.9	3.0	5.6	8.0	62.0	60.7	72.6	78.4
5 Dec.	27	194 <sup>§</sup>	1.3	2.1	4.5	6.6	70.7 <sup>+</sup>	63.8	73.0	-
16 Jan.	69	199 <sup>§</sup>	0.9	0.4	1.9	3.9	92.4 <sup>+</sup>	65.5	79.2	84.5
13 Feb.	97	89 <sup>§</sup>	1.2	0.5	1.0	2.8	69.0	65.0	75.4	79.7
14 Mar.	126	62	4.7	3.1	3.7	4.3	67.0	62.5	72.7	76.2
4 Apr.	147	64	8.5	5.1	5.3	5.0	68.6	64.5	71.9	78.6

<sup>+</sup> Surface (3-4 cm) frozen on sampling date.

<sup>§</sup> A small portion (< 20%) of this precipitation was snow, which melted prior to sampling.

<sup>‡</sup> Water retention of 0-15 cm horizon is 62.5% of dry weight at -10 kPa (0.1 bar) tension.

<sup>#</sup> The water table was between 75 and 80 cm depth during most of the sampling period.

## RESULTS AND DISCUSSION

### Banded fertilizer application (Table 2,3 and Figure 2.1)

One month following urea application (December 5) the  $\text{NH}_4$  concentrations were very similar in the ATC and non-ATC plots. It is likely that the low average 0-15 cm soil temperature ( $1.3^\circ\text{C}$ ) and high  $\text{NH}_4$  concentrations in the bands ( $> 600$  ppm) combined to effectively prevent any nitrification. Previous researchers (Anderson and Boswell, 1964; Wetselaar *et al.*, 1972) have demonstrated that high local  $\text{NH}_4$  concentrations can inhibit nitrification, probably due to the low osmotic potential of solution in the immediate vicinity of N fertilizer band. Inhibition caused by high pH or nitrite formation resulting from the high concentrations of urea was not a factor, since the pH of the soil extracts never exceeded 5, and soil  $\text{NO}_2\text{-N}$  levels never exceeded 1 ppm (data not shown).

On the December sampling date the average  $\text{NH}_4$  concentrations of the 15-30 cm and 30-60 cm layers were 60 and 18%, respectively, of the average  $\text{NH}_4$  concentration in the 0-15 cm layers of the fertilized plots. It is not likely that there was any significant movement of  $\text{NH}_4$  in this silt soil due to the high cation exchange capacity (39 meq/100 g). A more plausible explanation for the high  $\text{NH}_4$  levels below the surface 15 cm is that unhydrolyzed urea was leached down the profile by the 194 mm of rainfall which occurred during this time interval. The low initial soil temperatures ( $1.9$  and  $3.0^\circ\text{C}$  at 10 and 20 cm depth) would greatly decrease the rate of urea hydrolysis (Overrein and Moe, 1967). Urea is known to be only weakly adsorbed by soil organic matter (Chin and Kroontje, 1962), and it moves

Table 2.3 Ammonium-N and nitrate-N concentrations in banded and control plots on various sampling dates as affected by urea-N and ATC nitrification inhibitor, 1977-1978

Nitrogen	ATC	Sampling depth	Sampling date (days from N application)											
			8 Nov. (0)		5 Dec. (27)		16 Jan. (69)		3 Feb. (97)		14 Mar. (126)		4 Apr. (147)	
			NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
— kg/ha —		cm	µg N/g dry soil <sup>‡</sup>											
0	0	0-15	4	40	25	10	8	6	11	6	7	7	8	8
		15-30	2	41	12	26	8	10	9	9	5	9	6	10
		30-60	6	30	16	32	11	25	9	20	7	17	7	13
		60-90	8	23	- <sup>+</sup>	-	7	32	11	21	14	18	7	20
200	0	0-15	4	30	626	11	316	35	363	42	377	60	189	28
		15-30	2	33	351	28	299	42	303	49	219	82	246	75
		30-60	7	32	79	27	110	30	84	32	87	51	105	59
		60-90	6	19	-	-	18	21	28	21	17	24	23	29
200	2.0	0-15	5	33	603	8	476	18	498	23	482	49	313	56
		15-30	2	39	387	24	272	30	213	32	260	52	137	96
		30-60	6	33	138	27	72	29	84	25	105	30	104	62
		60-90	6	20	-	-	19	20	18	20	19	25	23	31

<sup>+</sup> Samples not obtained.

<sup>‡</sup> Values represent average of three replicate plots.

through the soil almost as easily as  $\text{NO}_3$  in response to water movement (Wagenet et al., 1977). Thus, conditions were favorable for leaching of the applied urea. Leaching of  $\text{NO}_3$  was also evident, since the concentration of  $\text{NO}_3$  in the 0-15 and 15-30 cm layers was considerably reduced between November 8 and December 5. Samples were not taken from the 60-90 cm depth on the latter date, but it is likely that a good portion of the  $\text{NO}_3$  in the 0-60 cm zone was leached away. Denitrification was probably not an important factor causing loss of  $\text{NO}_3$  from the 0-30 cm zone, since the low temperature ( $< 2^\circ\text{C}$ ) would result in very slow rates of denitrification (Craswell, 1978; Stanford et al., 1975). However, there was a greater potential for denitrification in the 30-90 cm zone, where the average temperature was  $5-6^\circ\text{C}$  during this period, and organic matter (4.3%) was probably not a limiting factor.

Between December 5 and January 16 there were 21 and 50% decreases in the 0-15 cm soil  $\text{NH}_4$  levels of the ATC and non-ATC treated plots, respectively. Some of this decrease was likely due to diffusion of  $\text{NH}_4$  away from the zone of high concentration in the band. This decrease in  $\text{NH}_4$  concentration would have made conditions more favorable for nitrification by improving the osmotic potential as well as increasing the availability of the  $\text{NH}_4$  substrate to the nitrifying microbes. The greater decrease in  $\text{NH}_4$  and increase in  $\text{NO}_3$  levels associated with the non-ATC plots suggests that the ATC was having some effect as an inhibitor. The  $\text{NO}_3$  increases were not sufficient to account for the decrease in  $\text{NH}_4$ , but it is probable that a large portion of any  $\text{NO}_3$  formed was leached out of the profile by the 199 mm of precipitation. Soil moisture levels increased throughout the

profile, and the 60-90 cm layer was saturated (Table 2.2) indicating a potential for leaching losses.

From January 16 to March 14 there was very little change in soil  $\text{NH}_4$  concentrations in the 0-15 cm and 15-30 cm layers under either treatment. The cold soil temperatures during this time served as an effective nitrification inhibitor. Precipitation was less intense during this period, and  $\text{NO}_3$  leaching did not appear to occur, since  $\text{NO}_3$  levels in the 0-15 and 15-30 cm layers did not decrease. Soil moisture levels decreased throughout the profile during this time.

During the 21 days between March 14 and April 4 there were 35 and 50% decreases in soil  $\text{NH}_4$  concentrations in the 0-15 cm layers of the ATC and non-ATC plots, respectively. The average 10 cm soil temperature during this time was  $8.5^\circ\text{C}$ , which has been shown to be high enough for fairly rapid nitrification (Anderson and Boswell, 1964). Furthermore, although the average temperature was  $8.5^\circ\text{C}$ , temperatures during the daytime would have been higher. On a sunny day (March 14) the soil temperature at 10 cm depth increased from  $1.9$  to  $8.8^\circ\text{C}$  between the hours of 1000 and 1400. Campbell et al. (1973) have demonstrated in growth chamber experiments that fluctuating ( $3$  to  $14^\circ\text{C}$ ) temperatures can result in higher nitrification rates than the corresponding mean temperature ( $8.5^\circ\text{C}$ ). Thus, nitrification may have proceeded at a faster rate than would be predicted from the mean soil temperature alone.

The smaller percentage decrease in the  $\text{NH}_4$  concentration of the ATC plots could have been due to some residual effect of the ATC inhibitor, or it could have been caused by the inhibitory effect of the higher  $\text{NH}_4$

concentration. It is likely that much of the water-soluble ATC was leached out of the soil by the 610 mm of precipitation recorded through April 4. However, there is no published literature dealing with the mechanisms of ATC adsorption and transport in the soil. A number of studies (Anderson and Boswell, 1964; Wetselar et al., 1972) have demonstrated that nitrification rates tend to decrease as  $\text{NH}_4$  substrate levels increased beyond the optimum concentration.

Nitrate levels did not show the consistent increases which should have been associated with the accelerated nitrification rates. It is probable that much of the  $\text{NO}_3$  which formed was lost by leaching or denitrification. Some leaching did occur, as evidenced by the increased soil moisture levels (Table 2.2). The high soil moisture and organic matter levels throughout the profile provided ideal conditions for denitrification to occur, and the increasing soil temperatures during this time would have stimulated denitrification rates, particularly during sunny days when the soil surface was warmed considerably.

#### Broadcast Fertilizer Application (Table 2.4 and Figure 2.1)

On the first sampling date following urea application (December 5),  $\text{NH}_4$  levels in the 0-15 cm layers of the non-ATC plots were much higher than those in the ATC plots. This was unexpected, since the ATC treatments should have resulted in higher  $\text{NH}_4$  levels. It is possible that at the low soil temperature ( $< 2^\circ\text{C}$ ) ATC may have inhibited urea hydrolysis for a period of time following application. The 194 mm of rain which fell during November could have leached a large portion of any unhydrolyzed urea out of

Table 2.4 Ammonium-N and nitrate-N concentrations in broadcast and control plots on various sampling dates as affected by urea-N and ATC nitrification inhibitor, 1977-1978

		Sampling date (days from N application)												
Nitrogen	ATC	Sampling depth	8 Nov. (0)		5 Dec. (27)		16 Jan. (69)		3 Feb. (97)		14 Mar. (126)		4 Apr. (147)	
			NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
— kg/ha —		cm	kg N/ha <sup>‡</sup>											
0	0	0-15	5	51	31	12	10	8	14	8	9	9	10	10
		15-30	4	59	17	38	12	15	13	13	7	12	9	14
		30-60	19	99	53	105	37	82	30	66	22	56	23	44
		60-90	28	82	- <sup>+</sup>	-	25	115	41	74	51	64	24	70
		0-90	56	291	-	-	84	219	98	161	89	142	66	137
200	0	0-15	4	30	246	12	164	37	62	30	51	41	18	28
		15-30	5	62	66	33	36	35	17	35	8	42	10	55
		30-60	23	96	51	86	40	83	31	79	20	75	33	109
		60-90	20	71	-	-	37	66	36	68	35	74	23	89
		0-90	52	259	-	-	277	220	146	212	113	231	83	280
200	2.0	0-15	4	50	81	15	58	27	36	17	12	31	12	38
		15-30	3	62	18	51	14	33	13	35	8	34	9	49
		30-60	17	113	36	106	32	123	33	100	23	95	24	109
		60-90	31	75	-	-	40	96	42	82	37	88	26	114
		0-90	56	300	-	-	144	279	123	235	80	248	71	310

<sup>+</sup> Samples not obtained.

<sup>‡</sup> Values represent average of three replicate plots.



the top 60 cm. In the non-ATC plots hydrolysis was apparently sufficiently rapid to prevent much movement of N. In the banded plots any inhibitory effect of ATC on ureolysis was masked by the strong osmotic inhibition caused by the concentrated fertilizer bands.

During the four months from December 5 to April 4 there was a steady decrease in the  $\text{NH}_4$  content of the 0-15 cm layers under both treatments, with  $\text{NH}_4$  decreasing from 81 to 12 and 246 to 18 kg N/ha in the ATC and non-ATC plots, respectively. Similar  $\text{NH}_4$  decreases were observed in the 15-30, 30-60 and 60-90 cm layers, thus indicating that nitrification was occurring continuously despite the low soil temperatures (Table 2.2). Leaching and denitrification probably removed a substantial portion of the nitrate which was formed, since nitrate levels did not show the consistent increases which would be expected from nitrification.

On the last sampling date (April 4) there were 203, 363, and 381 kg/ha of  $(\text{NH}_4 + \text{NO}_3)\text{-N}$  remaining in the upper 90 cm of the control, non-ATC and ATC treatments, respectively. This represented losses of 144 (41%), 148 (29%), and 175 (31%) kg/ha of the N which was present following the November 8 urea applications to these plots. Of the total mineral N remaining in the upper 90 cm of the fertilized plots on April 4, an average of 79% was in the form of  $\text{NO}_3$  and 71% was below 30 cm. There was no difference due to the presence of ATC. Since at least two more months would elapse before any substantial crop uptake of N might occur, it is unlikely that much of this N would be available to a crop considering the potential for leaching and denitrification losses during this period of warmer soil temperatures and heavy rainfall (average April and May precipitation = 122 mm).

The broadcast ATC treatment had no effect on nitrification rates in the surface 15 cm. The high solubility of ATC in water would render it susceptible to leaching losses. Before the urea hydrolyzed, it is possible that it and ATC may have moved together through the soil, but once  $\text{NH}_4$  formed ATC would have leached away. ATC may have had some effect at 30-60 cm, since the rate of  $\text{NH}_4$  loss was much slower at this depth in the ATC plots than the non-ATC plots, particularly during the period from December 5 to February 13. This could have been due to leaching of the unhydrolyzed urea and ATC to this depth.

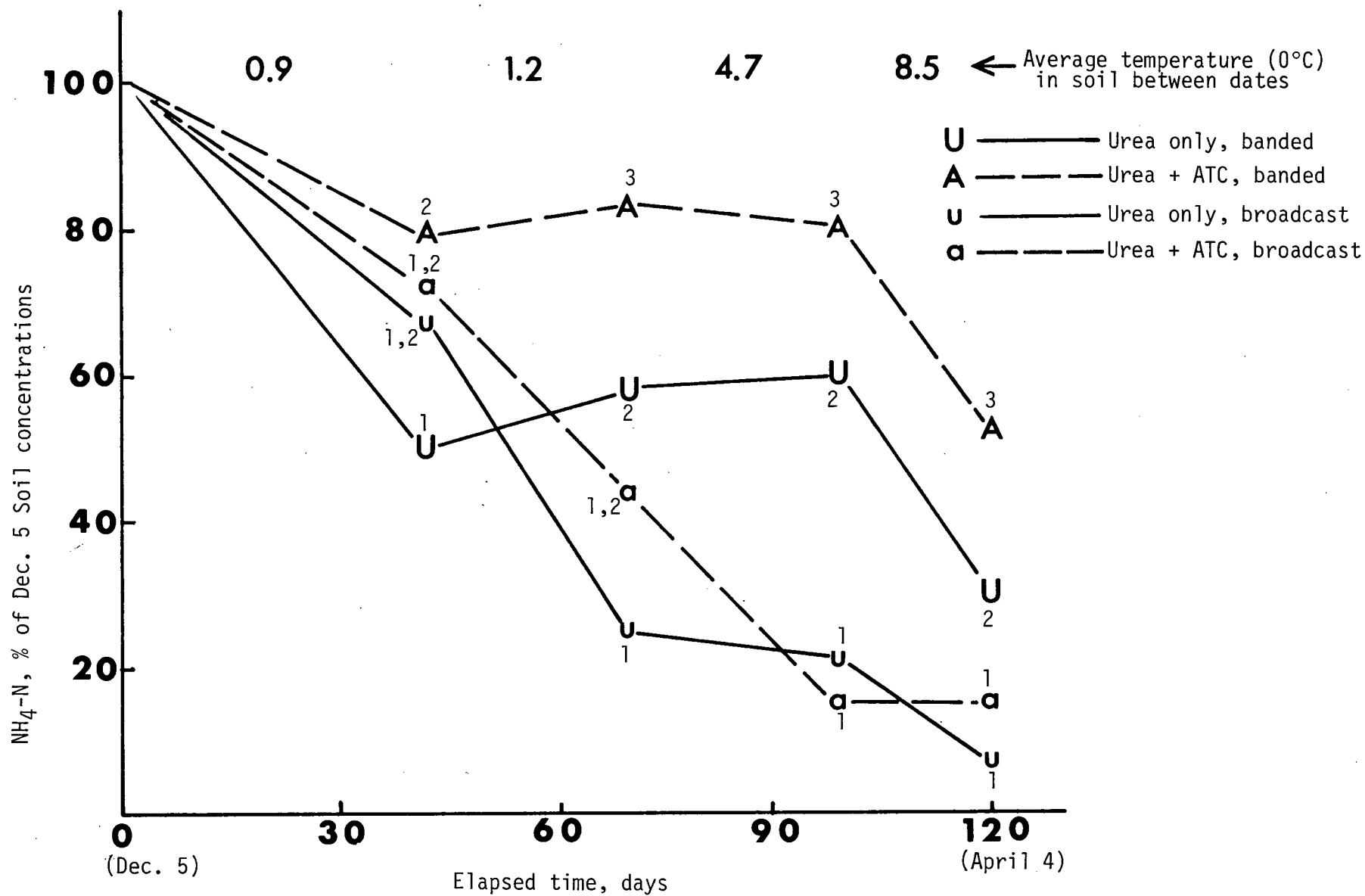


Fig. 2.1.  $\text{NH}_4\text{-N}$  in the 0-15 cm horizons on various sampling dates expressed as % of  $\text{NH}_4\text{-N}$  present in Dec. 5 samples, 1977-78. Data points for each sampling date accompanied by the same number are not significantly different ( $p \leq 0.05$ ).

## CONCLUSIONS

When urea was applied on November 8 as a band,  $\text{NH}_4$  concentrations one month following the N application were similar regardless of ATC treatment, but after two months the  $\text{NH}_4$  concentration in the 0-15 cm layers with ATC was significantly higher. There was no nitrification in this layer between January 16 and March 14 when the soil temperature averaged  $3^\circ\text{C}$ . Between March 14 and April 4 when the temperature of the 0-15 cm layer averaged  $8.5^\circ\text{C}$ , nitrification proceeded at a rapid rate, but there was a greater percentage loss of  $\text{NH}_4$  from the surface layer of the non-ATC plots. These results suggest that fall application of urea with ATC as a band may be somewhat effective in minimizing N losses, although spring applications would certainly be more efficient.

One month after N application a substantial portion of the  $\text{NH}_4$  was found below 15 cm in both banded and broadcast plots, indicating that leaching of unhydrolyzed urea had taken place. This suggests that urea should be applied earlier in the fall when the soil is warm enough for more rapid hydrolysis, although this would also increase the risk of nitrification. Safer fertilizers to use would be ammonium sulfate or anhydrous ammonia, which could be applied late in the year with little possibility of leaching.

In contrast to the banded urea, nitrification of broadcast urea proceeded continuously throughout the winter regardless of ATC treatment. If  $\text{NH}_4\text{-N}$  is expressed as a percentage of the amount present in the 0-15 cm layer on December 5, by April 4 there were 7, 15, 30 and 52% remaining in the broadcast -ATC, broadcast +ATC, banded -ATC, and banded +ATC plots, respectively. (Figure 2.1).

Thus, broadcasting urea in the fall leads to large losses of N, even in the presence of ATC. It is possible that a nitrification inhibitor with a low water solubility, such as N-Serve, might be more effective under the intense leaching conditions existing during the Pacific Northwest winters.

These results also have important implications for spring N applications. Urea should only be applied in the spring when the soil has warmed enough for rapid hydrolysis. Otherwise, leaching of unhydrolyzed urea may take place if rainfall occurs shortly after N application.

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### Chapter Three

#### EFFECTS OF LOW TEMPERATURES AND NITRIFICATION INHIBITORS ON UREA HYDROLYSIS

##### ABSTRACT

The results of a urea hydrolysis study conducted at 2 and 12°C using a silt soil indicated that there was no effect of the nitrification inhibitors ATC (4-amino-1,2,4-triazole) and N-Serve [2-chloro-6-(trichloromethyl)pyridine] on urea hydrolysis at two or twenty times the recommended application rate. The rate of hydrolysis at 2°C was about half that at 12°C, suggesting that leaching of urea might occur following its application to a cold soil. However, use of nitrification inhibitors should not increase leaching losses of urea.



## INTRODUCTION

Urea is very soluble in water (78 g/100 ml at 5 °C) and is only weakly adsorbed by soil organic matter (Chin and Kroontje, 1962). Thus, it moves through the soil almost as readily as  $\text{NO}_3$  in response to water movement (Wagenet et al., 1977). It is therefore important that urea hydrolyzes rapidly following its application, since unhydrolyzed urea may move through the soil profile with percolating water. The use of nitrification inhibitors (NI) such as N-Serve [2-chloro-6-(trichloromethyl)pyridine] and ATC (4-amino-1,2,4-triazole) has been suggested as a means of increasing the efficiency of fall-applied or spring-applied ammoniacal N by delaying the formation of nitrate. Due to the potential for leaching of urea, it is important to determine if these inhibitors have any delaying effect on urea hydrolysis, particularly at the low soil temperatures found in the late fall or early spring. An earlier study (Bundy and Bremner, 1974) dealt with the effects of NI on urea hydrolysis at 30 °C. At this temperature complete hydrolysis occurred within three days regardless of the presence of ATC or N-Serve. The purpose of the present study was to determine if ATC or N-Serve have any delaying effect on urea hydrolysis at 2 or 12 °C, temperatures which are commonly found in the soil during the late fall or early spring.

## METHODS AND MATERIALS

The soil used in this study was collected from the surface 15 cm of a silt classified as a Rego Humic Gleysol (Typic Fluvaquent, U.S.). Some of the important properties of this soil are as follows: soil pH in 0.01 M  $\text{CaCl}_2$  (soil:solution ratio 1:2), 4.8; total C, 4.9%; total N, 0.47%; CEC, 32.6 meq/100 g; sand, 8%; silt, 87%; moisture content at -10 kPa (0.1 bar), 59.9%; bulk density, 840 kg/m<sup>3</sup>. Particle size analysis was determined by the hydrometer method, and moisture retention at -10 kPa by the pressure membrane method (Black, 1965a). Total C was determined using a Leco induction furnace, total N by semi-micro-Kjeldahl digestion, and CEC by neutral 1N ammonium acetate extraction (Black, 1965b).

The incubation procedure was a slight modification from that of Mulvaney and Bremner (1977). Five gram portions of air-dried and sieved (1 mm) soil were weighed into 60 ml screw-cap plastic bottles. Distilled water (1 ml) was added to all the bottles, which were then capped, shaken, and preincubated 3 days at either 2 or 12 °C (70 bottles per temperature). Following the preincubation, 1 ml of an aqueous solution containing 2000 µg urea (reagent grade) with either no NI, 10 µg ATC, 10 µg N-Serve, 100 µg ATC, or 100 µg N-Serve was added, with each treatment being applied to 28 samples. The final water content was 40% by weight, which was 2/3 of field capacity. These NI additions were equivalent to 2.5 and 25 kg/ha of active ingredient, which is two and twenty times the recommended application rate for soils with high organic matter content.

Half of the bottles were incubated at 2 °C and half at 12 °C, using

thermographs to continuously record the temperatures, which did not vary more than 1 °C from the desired settings. Each day the bottle tops were removed for a few seconds to allow gaseous exchange in order to prevent anaerobiosis. Loss of water from the samples, which was determined gravimetrically, was not significant.

On each sampling date (0, 2, 3, 4, 7, 11, 21 days), 10 bottles (5 treatments x 2 replicates) were removed from each incubator. Fifty ml of 2 N KCl (containing 5 ug/ml phenylmercuric acetate as a urease inhibitor) was added to the bottles, which were mechanically shaken for 1 hour. The extracts were filtered and analyzed by the diacetyl monoxime colorimetric procedure (Douglas and Bremner, 1970). Percent hydrolysis (% H) was calculated using the formula  $\% H = (\text{mg urea lost} / 2.00 \text{ mg}) \times 100$ . The zero day extraction was immediately after the addition of urea. The purpose of this extraction was to determine the actual urea content in the soils at this time, which was found to range from 1.94 to 2.04 mg/5 g of soil, with a mean of 1.98 mg.

## RESULTS AND DISCUSSION

As shown in Table 3.1 after two days of incubation, there was no significant effect from either ATC or N-Serve on the hydrolysis of urea. After 1 day, there were some differences in the % hydrolysis between treatments. At 2 °C the NI treatments all had about half the % hydrolysis of the no NI control, whereas there was no such trend at 12 °C. By the second day there was very little difference in hydrolysis rates due to NI

Table 3.1. Effects of temperature, N-Serve and ATC on urea hydrolysis in a silt soil.<sup>+</sup>

		Elapsed time following urea addition, days												
Temperature	Chemical added	Conc.	1		2		4		7		11		21	
°C		µg/g	% urea hydrolysis (standard deviation) <sup>‡</sup>											
2	None	0	15.4	(2.1)	19.8	(2.1)	37.9	(1.2)	55.3	(0.4)	77.3	(1.1)	99.1	(0.2)
	ATC	2	7.9	(4.2)	14.5	(1.3)	37.9	(1.2)	55.5	(2.1)	76.4	(2.5)	98.5	(0.2)
	N-Serve	2	5.4	(0.7)	19.2	(2.8)	37.9	(1.2)	51.7	(0)	75.1	(0.7)	98.5	(0.1)
	ATC	20	7.8	(1.4)	18.3	(6.8)	37.0	(0)	54.3	(1.7)	78.4	(0.7)	98.2	(0.4)
	N-Serve	20	6.9	(0)	15.4	(5.4)	39.2	(1.6)	54.6	(1.2)	77.9	(1.1)	98.5	(0)
	Average		8.7		17.4		38.0		54.3		77.0		98.6	
12	None	0	17.3	(0)	36.6	(0)	72.5	(3.9)	97.7	(1.1)	100	(0)	-	-
	ATC	2	11.1	(0.7)	38.5	(2.7)	66.5	(5.1)	96.2	(3.3)	100	(0)	-	-
	N-Serve	2	18.0	(6.7)	38.5	(0)	71.4	(1.8)	96.8	(0.3)	100	(0)	-	-
	ATC	20	21.1	(1.3)	36.5	(5.4)	70.0	(0)	96.4	(0.9)	100	(0)	-	-
	N-Serve	20	15.9	(2.0)	39.5	(1.3)	63.7	(2.8)	93.0	(1.3)	100	(0)	-	-
	Average		16.7		37.9		68.3		96.0		100		-	-

<sup>+</sup>Soil samples (5 g air-dry) were incubated (2 or 12 °C, 2 ml of water) after treatment with 2 mg of urea and 0, 10 or 100 µg of compound specified.

<sup>‡</sup>% urea hydrolysis = (mg urea lost/2.00mg) x 100, values represent average of duplicate samples.

treatment. Thus, any inhibition of hydrolysis caused by ATC or N-Serve was of very short duration. These results indicate that use of ATC or N-Serve at the rates used in this study should not promote leaching losses of N by delaying the hydrolysis of urea.

The lower rate of NI in this study ( $2 \mu\text{g/g}$  soil) approximates concentrations in the soil following broadcast applications. The higher rate ( $20 \mu\text{g/g}$  soil) would be more comparable to that found in the soil in the zone of banded applications. As an example, during a study of NI degradation rates in a silty clay loam, Touchton et al. (1978) found approximately  $10 \mu\text{g}$  N-Serve /g soil 15 days after a banded application of N-Serve ( $0.56 \text{ kg/ha}$ ). During the first few days after the application the concentration of N-Serve could have been much greater. Thus, if N-Serve or ATC were to cause any delay in urea hydrolysis, the effect would be greatly accentuated in banded applications due to the much higher local concentrations of these chemicals in the band.

Urea hydrolysis was strongly temperature dependent, which confirms the results of previous researchers (Overrein and Moe, 1967). On each sampling date the average % hydrolysis of the  $12^\circ\text{C}$  samples was approximately twice that of the  $2^\circ\text{C}$  samples, which agrees well with theoretical calculations for enzymatic reactions. The added urea was almost completely hydrolyzed within 7 days at  $12^\circ\text{C}$ , whereas at  $2^\circ\text{C}$ , 21 days were required for complete hydrolysis. Soils having less organic matter should hydrolyze urea more slowly due to lower urease activity (Bundy and Bremner, 1974; Conrad, 1940).

These results suggest that when the soil temperature is below  $12^\circ\text{C}$ ,

urea should not be applied in areas where heavy rainfall occurs. At 12 °C 7 days may be required for complete hydrolysis, during which time any unhydrolyzed urea would be susceptible to leaching losses. A field experiment (T.F. Guthrie, unpublished data) demonstrated that urea-N which was applied to a silt in the fall in coastal British Columbia (2 °C soil temperature at 10 cm depth) was leached more than 30 cm following 194 mm of rainfall.

Loss of urea-N by  $\text{NH}_3$  volatilization is recognized as a serious problem, particularly following surface applications when the soil is relatively dry and warm (Volk, 1959). For this reason, it has been recommended that urea be applied to a cool soil followed by rainfall or irrigation, but this would tend to promote leaching of the urea. If irrigation is applied following urea application, the amount of water used should be minimized to prevent excessive leaching of urea.

Urea applications ideally should be made when the soil is warm enough ( $> 12$  °C) for rapid hydrolysis in order to minimize urea leaching. However, this temperature would also favor nitrification, and the resulting  $\text{NO}_3$  would be easily leached. Thus, fall applications of urea where heavy winter rainfall occurs would probably result in large N leaching losses regardless of the soil temperature at the time of urea application. The best approach for spring applications would be to apply urea to a warm ( $> 12$  °C) moist soil to encourage rapid hydrolysis and, if  $\text{NH}_3$  volatilization is a problem, to cover the urea with 2 to 4 cm of soil as suggested by the results of Ernst and Massey (1960).

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## Chapter Four

### NITRIFICATION INHIBITION BY N-SERVE AND ATC IN SOILS OF VARYING TEXTURE

#### ABSTRACT

Although numerous laboratory studies have demonstrated the effectiveness of certain nitrification inhibitors, many field studies have failed to show any significant crop response to inhibitor treatments. Most field studies to date have only evaluated N-Serve [2-chloro-6-(trichloromethyl)pyridine], which cannot be conveniently applied with solid fertilizers due to its volatility. ATC (4-amino-1,2,4-triazole) is a non-volatile, water-soluble nitrification inhibitor which can be easily coated onto solid fertilizers without volatilization loss. The objective of this research was to compare the effect of N-Serve and ATC on silage corn (Zea mays L.) production and nitrification rates in two soils (silt and loamy sand). Urea was coated with the inhibitors at a rate of 1% of active ingredient per weight of N and applied as a band or broadcast in the spring of 1977 and 1978. The  $\text{NH}_4\text{-N}/\text{NO}_3\text{-N}$  ratio in the soil was calculated for each sampling date as an indicator of inhibitor effectiveness. Neither inhibitor significantly affected nitrification when applied as a broadcast treatment to either soil. In the silt, both inhibitors were equally effective in delaying nitrification when banded, but in the loamy sand ATC had a five times higher  $\text{NH}_4/\text{NO}_3$  ratio than N-Serve three weeks following application. The effectiveness of N-Serve persisted much longer in the silt (86 days) than in the loamy



sand (23 days). This suggested that volatilization of N-Serve severely limited its effectiveness in the loamy sand. There was no significant improvement in crop yields or N content due to inhibitor treatment in either soil.

ATC is recommended for further field evaluation in conjunction with band-applied solid fertilizers, particularly in coarse-textured soils.

## INTRODUCTION

There are a number of potential advantages associated with delaying nitrification of ammonium-based fertilizers through the use of chemical nitrification inhibitors (NI). By preventing rapid formation of nitrate in the soil, leaching and denitrification losses of N should be limited, thus increasing the efficiency of N fertilizers. Lower concentrations of nitrate in the soil should result in less contamination of the ground water with this chemical as well as reduced emissions of nitrous oxide ( $N_2O$ ) from denitrification. Inhibition of nitrification would also decrease the emission of  $N_2O$  which has been found to occur during the biological oxidation of ammonium (Bremner and Blackmer, 1978). Reduction of  $N_2O$  emissions could be important due to the current hypothesis that  $N_2O$  released to the atmosphere may ultimately lead to partial destruction of the ozone layer (Hutchinson and Mosier, 1979; McElroy et al., 1977).

Use of NI to increase plant uptake of  $NH_4$  relative to  $NO_3$  has been shown to reduce the risk of toxic accumulation of  $NO_3$  in plant tissue (Mills et al., 1976; Turner and Macgregor, 1978). Increasing plant uptake of  $NH_4$  has also been shown to decrease the incidence of stalk rot in corn (Warren et al., 1975), but high  $NH_4/NO_3$  ratios have resulted in decreased yields of potatoes (Hendrickson et al., 1978).

Since Goring (1962) first reported the results of his studies with N-Serve [2-chloro-6-(trichloromethyl) pyridine], the first patented chemical inhibitor specific for Nitrosomonas sp., a number of other inhibitors have been developed. Bundy and Bremner (1973) evaluated 24 possible NI using

laboratory soil incubations and concluded that N-Serve and ATC (4-amino-1,2,4-triazole) were the most effective under their experimental conditions.

The NI which has been tested in almost all field studies to date has been N-Serve; there have been no published field experiments involving the use of ATC. ATC is much easier to work with since it can be coated onto solid fertilizers and applied to the soil without risk of volatilization losses. In addition, its high water solubility (420 g/100 ml H<sub>2</sub>O at 20°C) would enable this inhibitor to diffuse through the soil as rapidly as the N fertilizer. This chemical is not commercially available, but its cost is expected to be lower than that of N-Serve. Thus, ATC would appear to be a good candidate for field evaluation. The purpose of this study was to compare the effectiveness of ATC and N-Serve when applied to two different soils in the humid environment of coastal British Columbia.

## METHODS AND MATERIALS

The experiments were conducted for two years (1977-78) at two sites within 50 km of Vancouver, British Columbia. Site 1 was a tile drained lowland silt formed from alluvial deposits; U.S. classification was a Typic Fluvaquent (Rego Humic Gleysol, Can.). This soil had been under continuous corn for three years as part of a commercial dairy operation and had received heavy annual manure applications. Rooting depth was estimated to be about 70 cm, since below this depth excessive moisture restricted root respiration. Site 2 was a well-drained upland loamy sand formed from glacial till; U.S. classification was a Typic Haplohumod (Humic Podzol, Can.). Rooting depth was restricted to the upper 45 cm due to the high bulk density ( $1400 \text{ kg-m}^{-3}$ ) of the Ae horizon. Pertinent surface (0-15 cm) soil properties for the silt and loamy sand, respectively, were: soil pH in  $0.01M \text{ CaCl}_2$  (soil:solution ratio 1:2), 4.5 and 5.4; total C, 4.9% and 4.5%; total N, 0.47% and 0.27%; CEC, 32.6 and 23.9 meq/100 g; bulk density, 842 and  $1160 \text{ kg-m}^{-3}$ ; sand, 8% and 76%; silt, 87% and 18%. Total C was determined using a Leco induction furnace, total N by a semimicro-Kjeldahl digestion, and CEC by a neutral  $1N$  ammonium acetate extraction (Black, 1965).

The N source for all experiments was fertilizer grade prilled urea (1.4 to 3.0 mm), applied in the spring at rates of 0, 50, or 100 kg N/ha. The highest rate is somewhat lower than that commonly used for silage corn in this area (130 kg N/ha), but the purpose of this study was to compare the yields of corn with and without the inhibitors at lower than optimum N application rates. Nitrogen was applied either as a broadcast treatment

which was raked into the soil or as a narrow (5 cm) band which was covered with 7.5 cm of soil 30 cm from the seed row. The location of each band was marked by stretching a nylon string between two wooden stakes.

Nitrification inhibitor treatments consisted of 1% of active ingredient per weight of N of either N-Serve or ATC. The required quantity of ATC (36% w/v aqueous solution) was sprayed with a chromatography spray gun (S.S. Malhi, personal communication) onto a tray of urea prills which were shaken by a mechanical shaker. Following thorough mixing, the coated urea was dried overnight at 23°C, then sealed in plastic bags. Due to the volatility of N-Serve a different method (L.D. Bailey, personal communication) was necessary for coating this chemical onto the urea. One kg batches of urea were weighed into clean 3.78 liter paint tins, the calculated quantity of N-Serve (22.2% w/v in xylene) was added, and the cans were tightly sealed and shaken for 10 minutes. The batches were all mixed together in a large glass dessicator where they were stored. Within 24 hours of field application, the N-Serve plus urea treatments were weighed out into triple thickness plastic bags.

The details of each experiment are given in Table 4.1. In 1977 a completely random design was used, whereas randomized, complete blocks were used in 1978, with three replications in all experiments. Individual plots consisted of four rows of silage corn (Zea mays L., DeKalb 22) planted 84 or 75 cm apart, with an average seeding rate of 69,000 or 55,000 plants/ha in Sites 1 and 2, respectively. In 1977 (Exp. 1) urea with and without 1% ATC was either broadcast or banded when applied to the silt soil in a single June application when the plants were 30 cm high. In 1978 1% N-Serve was added as another inhibitor treatment in the silt, but all treatments were banded

Table 4.1. Experimental conditions prevailing during studies of the effects of ATC and N-Serve on nitrification and corn production.

Variable	Experiment			
	1	2 ‡	3	4
Soil texture	silt	silt	loamy sand	loamy sand
Plot size, m	7.6 x 3.35	7 x 3.35	6 x 3	3 x 2
Bands/plot x length, m	4 x 7.6	4 x 7.0	4 x 6.0	2 x 3.0
N fertilizer rate, kg/ha	0, 50, 100#	0, 50, 100#	0, 50, 100#	0, 100
Nitrification inhibitor	ATC, none	ATC, N-S <sup>§</sup> , none	ATC, N-S, none	ATC, N-S, none
N placement	band, broadcast	band only	band only	band, broadcast
N application date	14 June 1977	12 June 1978	9 May 1978	9 May 1978
Planting date	26 May 1977	24 May 1978	10 May 1978	fallow

‡Manure application to silt in 1977, but not in 1978.

#In addition, 12 kg N/ha applied as starter band 5 cm to the side and 5 cm below the seed.

§N-Serve is abbreviated as N-S.

(Exp. 2). The results of other researchers (Briggs, 1975; Boswell et al., 1976) have shown that N-Serve is relatively ineffective when broadcast, and our 1977 results indicated that the same is true for ATC. In 1978 N-Serve and ATC were also compared when applied to the loamy sand at Site 2 (Exp. 3). At this site the corn was hand planted, and the N treatments were applied on the day following seeding. All corn plots received a starter band application of N and P (12 and 26 kg/ha, respectively) at seeding. Potassium (80 kg K/ha) was broadcast at this time also. The corn plots at Site 1 received a post-emergence treatment of 2 kg/ha atrazine for weed control. Adjacent to the corn field at Site 2 a fallow field (Exp. 4) was also treated with N-Serve or ATC-coated urea which was either banded or broadcast. The purpose of this fallow experiment was to eliminate the effect of crop uptake of N in order to more accurately assess soil N transformations.

The plots were sampled (six 2.5 cm diameter cores/plot) at two or three week intervals to a depth of 30 cm (Exp. 1, 3, 4) or 60 cm (Exp. 2). Banded plots were sampled directly in the center of the marked bands, whereas broadcast plots were randomly sampled. The samples were separated into 15 cm increments which were refrigerated ( $2^{\circ}\text{C}$ ) and extracted within 48 hours using 2N KCl (10 g moist soil:100 ml KCl). The soil extracts were analyzed for  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  using a Technicon Autoanalyzer II. A separate 10 g sample of each soil was oven-dried ( $105^{\circ}\text{C}$ ) to determine the moisture content in order to calculate the N concentrations on a dry weight basis as well as to determine soil moisture tensions using soil water retention curves. The pH of the extracts was also determined but the data is not reported since there was very little variation, with values ranging between 4 and 5.

The leaf opposite and below the ear was sampled at silking time (August), and ears plus stover were harvested from the two center rows of each plot in mid-September. Fresh weights of the ears plus stover were taken in the field, and subsamples were obtained for N analysis and water content. Total Kjeldahl N (including  $\text{NO}_3$ ) (Bremner, 1965) was determined on the ear leaf and ear plus stover samples following drying ( $70^{\circ}\text{C}$ ) and grinding in a stainless steel Wiley mill. Nitrate in the ear leaf was determined by shaking 0.5 g samples of the ground leaves with 100 ml distilled water, followed by filtration and analysis on the Autoanalyzer II.

Air temperature and precipitation records were obtained from monitoring stations located 5 km and 0.1 km, respectively, from Sites 1 and 2. Soil temperatures at 10, 20 and 40 cm were monitored using silicone diodes (Hinshaw and Fritschen, 1970) installed in the experimental area. In addition, a soil degree-day integrator was installed at the 10 cm depth of Site 2 in 1978 (Table 4.2).

An analysis of variance was performed on the data from each experiment, and treatment means were tested for significant differences by Duncan's multiple range test.



Table 4.2. Soil moisture tension, average soil temperature (10 cm depth) and cumulative precipitation between sampling dates at Sites 1 and 2, 1977 and 1978.

1977 Site 1					1978 Site 1					1978 Site 2				
Sample date	Soil temp. <sup>#</sup>	Moisture tension		Pptn. <sup>†</sup>	Sample date	Soil temp.	Moisture tension		Pptn.	Sample date	Soil temp.	Moisture tension		Pptn.
		0-15	15-30				0-15	15-30				0-15	15-30	
		cm	cm				cm	cm				cm	cm	
	°C	— kPa <sup>§</sup> —		cm		°C	— kPa —		cm		°C	— kPa —		cm
14 June	13.5	30	15	-	12 June	17.0	60	20	-	9 May	13.0	30	15	-
30 June	15.0	30	15	0.6	4 July	17.2	110	40	0	1 June	13.2	35	20	10.8
13 July	14.5	50	25	2.1	25 July	19.5	270	200	0.3	16 June	17.4	40	25	2.6
27 July	15.4	170	110	1.4	15 Aug.	18.9	160	200	4.8	11 July	19.2	25	40	1.4
10 Aug.	19.9	250	190	0	6 Sept.	16.0	30	25	9.6	7 Aug.	20.8	100	50	0.4
6 Sept.	16.7	50	120	13.2	-	-	-	-	-	29 Aug.	17.4	25	20	12.7

<sup>#</sup>Average soil temperature since previous sampling date, value for first date is actual temperature when N applied.

<sup>†</sup>Supplemental irrigation was not applied to any of the fields.

<sup>§</sup>100 kPa = 1 bar tension

## RESULTS AND DISCUSSION

Three possible measures of nitrification inhibitor effectiveness were considered: (1) concentration of  $\text{NH}_4$ ; (2) sum of concentrations of  $\text{NH}_4$  and  $\text{NO}_3$  ( $\Sigma\text{N}$ ); (3) ratio of  $\text{NH}_4/\text{NO}_3$ . The first two of these parameters would obviously have much higher values in samples from plots where the N was applied at the higher rate or banded, regardless of the inhibitor treatment. The ratio of  $\text{NH}_4/\text{NO}_3$  should be more independent of rate of N or method of application, and thus would be a better measure of inhibitor effectiveness. Use of this ratio could help to lessen the inherent variability associated with sampling a fertilizer band. Concentration of  $\text{NO}_3$  by itself was not considered a good measure of nitrification inhibition due to its greater potential for loss, either by leaching, denitrification or plant uptake.

The discussion which follows will focus on the data from the 0-15 cm soil samples and the 100 kg N/ha treatments. Seldom were significant differences due to inhibitor treatments found below 15 cm. Trends observed at the lower rate of N application were similar to those of the higher N rate, but the differences between treatments were smaller. Values given for  $\text{NO}_3$  include  $\text{NO}_2$ , but  $\text{NO}_2\text{-N}$  was not found to exceed one ppm in any sample.

### 1977 Silt (Experiment 1) Soil Results

A significantly higher ( $p \leq 0.01$ )  $\text{NH}_4/\text{NO}_3$  ratio due to the presence of ATC was found in all 0-15 cm samples taken from the banded N plus ATC plots during the entire 84 day sampling period (Fig. 4.1). No significant differences were observed when the N and ATC were broadcast. The elevated  $\text{NH}_4/\text{NO}_3$

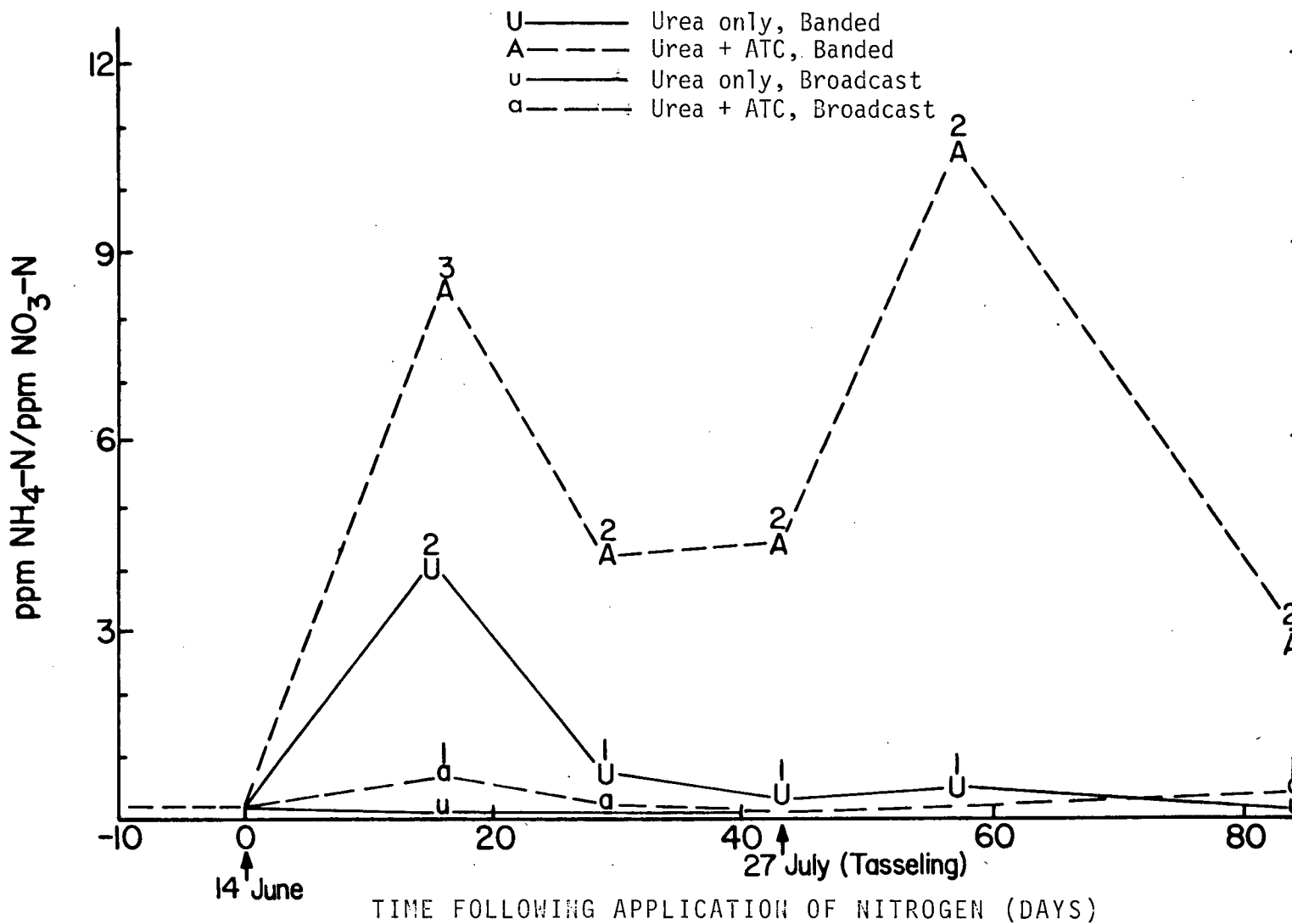


Figure 4.1. Ratio of ppm  $\text{NH}_4\text{-N/ppm NO}_3\text{-N}$  in 0-15 cm depth of 1977 silt as affected by method of N application, presence of nitrification inhibitor, and time. In this and subsequent figures data points for each sampling date accompanied by the same number are not significantly different ( $P \leq 0.05$ ).

ratio associated with the banded ATC treatment indicates that some inhibition of nitrification persisted throughout the growing season.

On the first sampling date (16 days following N application), urea banded without ATC had a significantly higher  $\text{NH}_4/\text{NO}_3$  ratio than the broadcast urea plots, but by the second sampling date (29 days) this difference was negligible (Fig. 4.1). This inhibition of nitrification caused by high local urea concentrations has been reported previously (Wetselaar *et al.*, 1972) and is thought to be caused primarily by the low osmotic potential of solution in the immediate vicinity of the N fertilizer band. Inhibition caused by high pH and  $\text{NO}_2^-$  accumulation was not likely in this situation since the pH of the soil extracts never exceeded 5, and soil  $\text{NO}_2\text{-N}$  concentrations never exceeded 1 ppm.

The concentration of  $\text{NH}_4$  in the 0-15 depth showed a similar response to the presence of ATC (Fig. 4.2). With the exception of the first sampling date, throughout the growing season there was a significantly higher ( $P \leq 0.05$ )  $\text{NH}_4$  concentration in the banded plots which received ATC than in the banded plots which did not. Again there was no significant difference in the broadcast plots due to application of ATC. Soil  $\text{NO}_3$  levels (0-15 cm) were consistently significantly lower in the banded ATC plots than in those without ATC, but there were no consistent differences between the broadcast treatments (data not shown).

The sum of  $\text{NH}_4$  plus  $\text{NO}_3$  was a poor indicator of inhibitor effectiveness, since it did not reveal any significant differences due to the presence of ATC until 57 days following N addition (Fig. 4.3). This indicates that there was probably little loss of  $\text{NO}_3$  by leaching or denitrification prior to

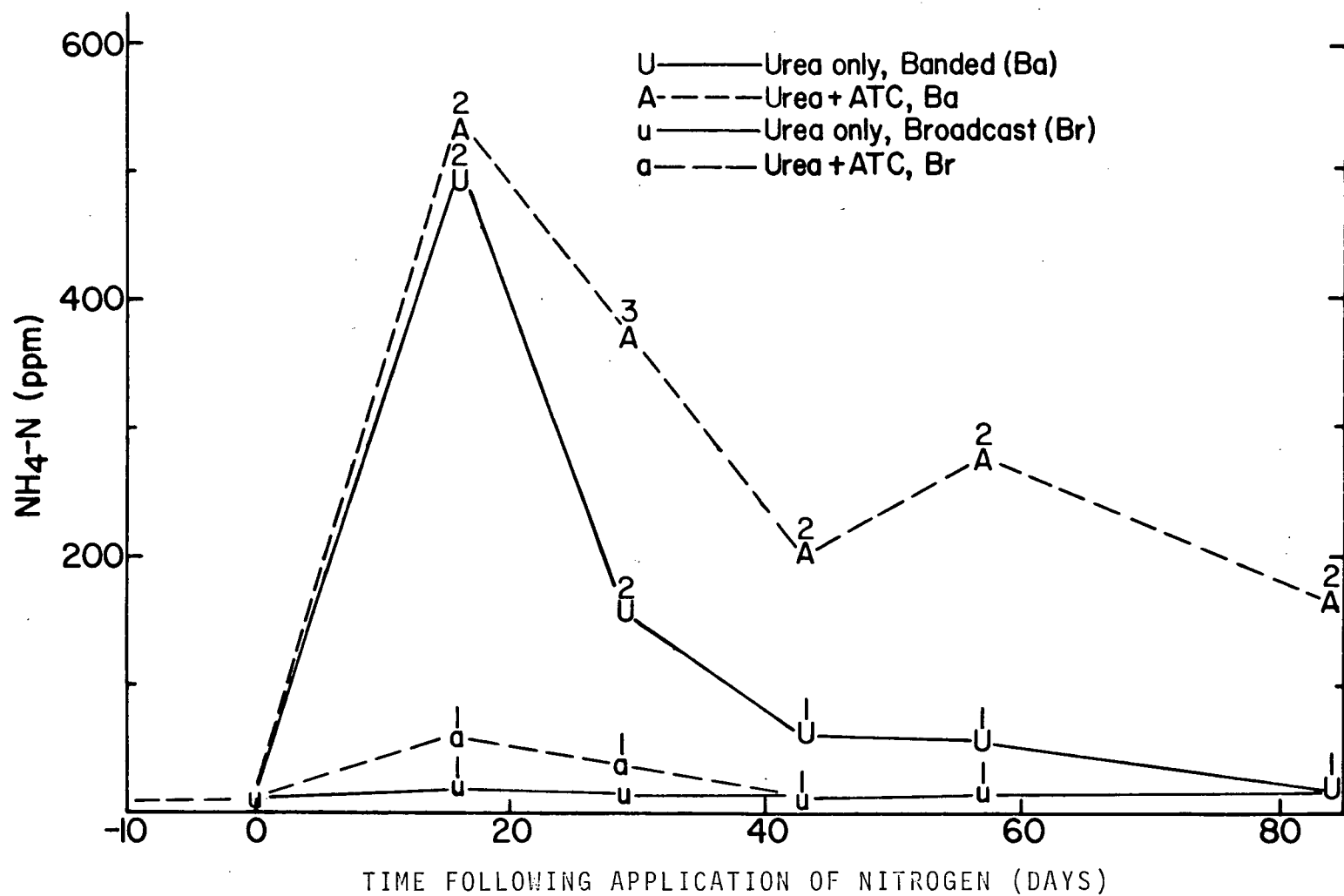


Figure 4.2. Concentration of  $\text{NH}_4\text{-N}$  (ppm) in 0-15 cm depth of 1977 silt as affected by method of N application, presence of nitrification inhibitor, and time.

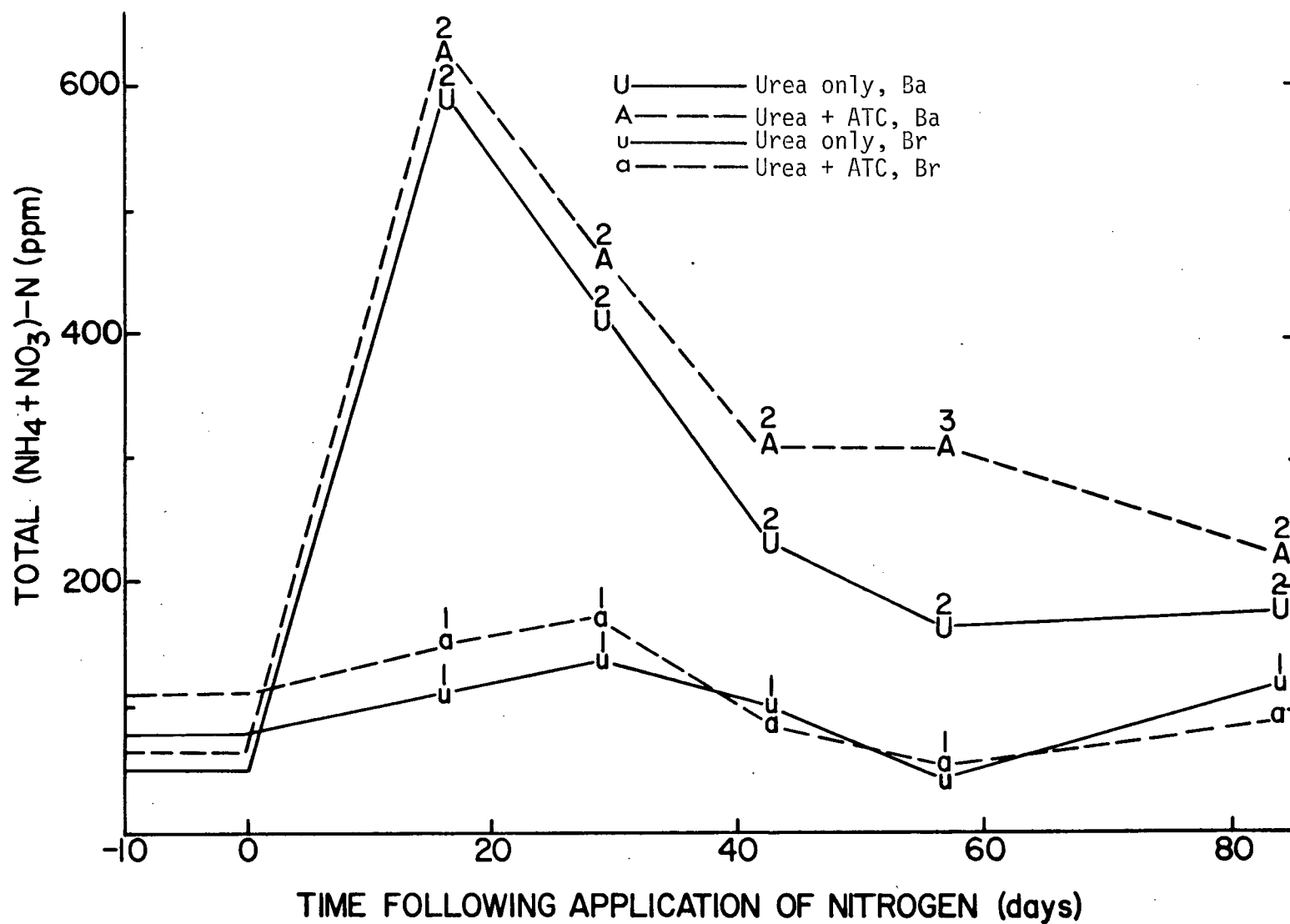


Figure 4.3. Sum of exchangeable (ppm NH<sub>4</sub>+NO<sub>3</sub>) - N in 0-15 cm depth of 1977 silt as affected by method of N application, presence of nitrification inhibitor, and time.

this date. Leaching losses were not likely, since only 4.1 cm of rainfall was recorded through July 27 (Table 4.2) and most of this would have been used by the crop. Thus, even though there was more rapid nitrification in the non-ATC plots, conditions were not favorable for  $\text{NO}_3$  loss, and the  $\Sigma\text{N}$  was not significantly lower. However, on the August 10 sampling date there was a significantly higher  $\Sigma\text{N}$  in the banded plots with ATC than in the plots without ATC. On the same date there was also a much higher  $\text{NH}_4/\text{NO}_3$  ratio in the banded ATC plots than on the previous sampling date. These data suggest that in the banded ATC plots between July 27 and August 10 there was either a decrease in the nitrification rate compared to the rate of  $\text{NH}_4$  formation or else there was an increase in the plant uptake of  $\text{NO}_3$  relative to  $\text{NH}_4$ .

Increased soil temperatures between July 27 and August 15 (Table 4.2) should have resulted in more rapid mineralization of soil organic N, but higher soil moisture tensions in this non-irrigated field (170 to 250 kPa) could have caused accumulation of  $\text{NH}_4$  due to the greater sensitivity of the nitrifying population to moisture stress, as suggested by other researchers (Miller and Johnson, 1964; Reichman *et al.*, 1966). However, if this were true, then all of the treatments should have exhibited an increased  $\text{NH}_4/\text{NO}_3$  ratio, whereas only the banded ATC treatment had a significant increase.

Plant uptake of relatively immobile ions such as  $\text{NH}_4$  is regulated by the diffusion rate as well as by the rate of root interception of these ions, whereas mobile ions such as  $\text{NO}_3$  are free to move to the roots by mass flow. Thus, during the period of maximum N uptake it is possible that the  $\text{NH}_4/\text{NO}_3$  ratio in the soil could be increased by more rapid crop removal of  $\text{NO}_3$  than  $\text{NH}_4$ . However, if the concentration of  $\text{NH}_4$  is already very low, then

there would be less of an effect on the  $\text{NH}_4/\text{NO}_3$  ratio. The banded ATC plots which had a high  $\text{NH}_4$  concentration (200 ppm) on July 27 showed a large increase in the  $\text{NH}_4/\text{NO}_3$  ratio, whereas in the banded plots without ATC and the broadcast plots which had much lower  $\text{NH}_4$  concentrations (60 and 10 ppm, respectively) there were much smaller ratio increases. The period from July 27 to August 10 corresponded to the time of tassel and silk formation, which is thought to be the time of maximum N uptake by the corn plant (Terman and Niggle, 1973; Bar-Yosef and Kafkafi, 1972).

A third hypothesis for the increased  $\text{NH}_4/\text{NO}_3$  ratio in the banded ATC plots is the possibility that high ambient concentrations of  $\text{NH}_4$  may restrict  $\text{NO}_3$  uptake, as suggested by Jackson (1978). This inhibition of  $\text{NO}_3$  uptake might be reversed when the  $\text{NH}_4$  concentration relative to the  $\text{NO}_3$  concentration drops below a certain level, thus increasing the  $\text{NO}_3$  uptake and consequently the  $\text{NH}_4/\text{NO}_3$  ratio in the soil (W.A. Jackson, personal communication).

The remainder of this discussion will focus on the  $\text{NH}_4/\text{NO}_3$  ratio in the soil, since this parameter had higher F test values than the  $\text{NH}_4$  concentration alone, and provided a better separation of the treatment means. The ratio appears to be a more sensitive indicator of inhibitor effectiveness, particularly during the first half of the growing season before the time of maximum crop uptake of N.

#### 1978 Silt (Experiment 2) Soil Results

As shown in Fig. 4.4 the  $\text{NH}_4/\text{NO}_3$  ratio in the banded ATC plots was significantly higher for 86 days than in the plots without inhibitor,



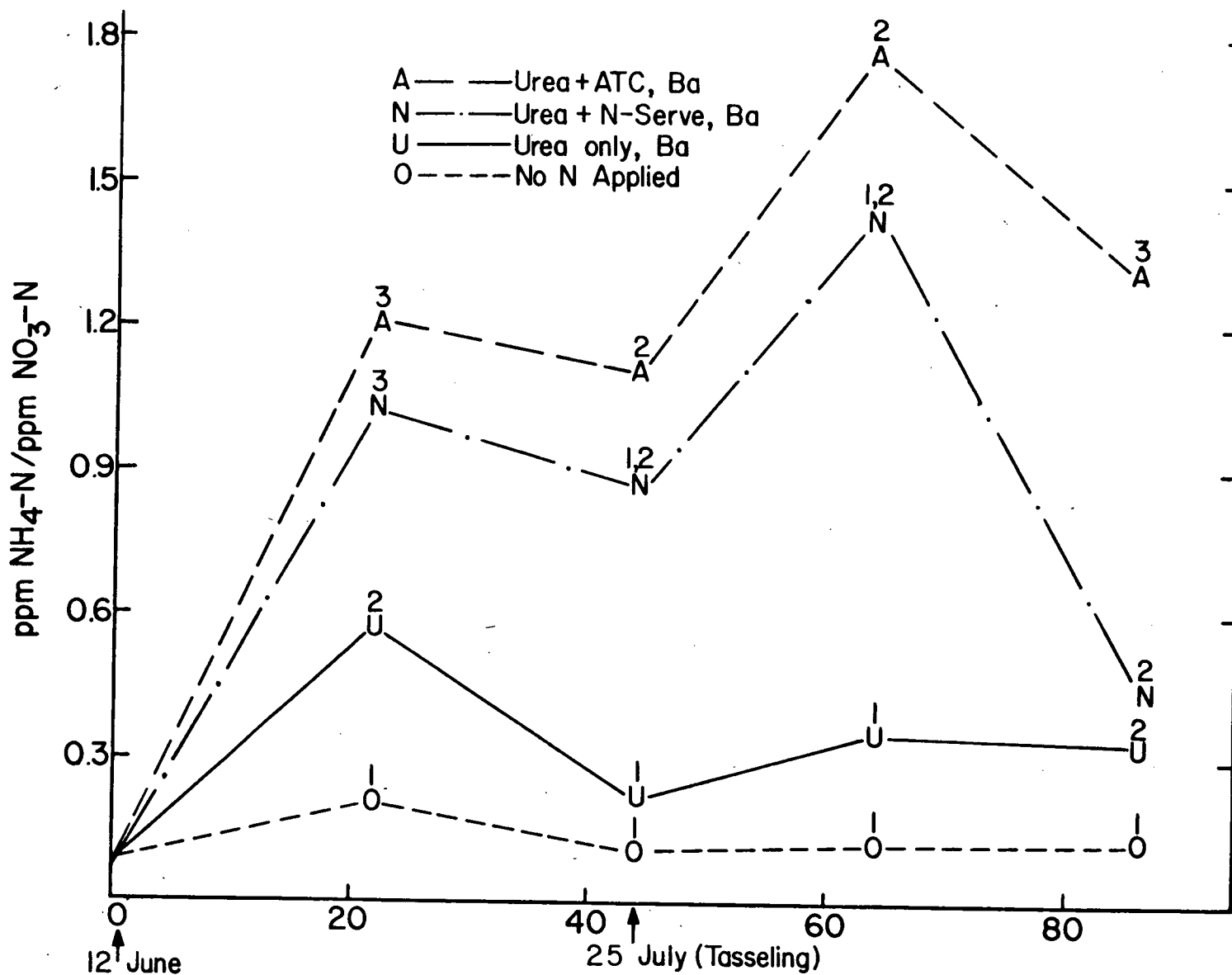


Figure 4.4. Ratio of ppm  $\text{NH}_4\text{-N/ppm NO}_3\text{-N}$  in 0-15 cm depth of 1978 silt as affected by method of N application, presence of nitrification inhibitor, and time.

indicating that ATC was again an effective nitrification inhibitor for the entire season. The banded N-Serve ratios were consistently lower than the ATC ratios, but not significantly lower until the last sampling date. Thus ATC and N-Serve were equally effective nitrification inhibitors for the first 64 days following N addition.

Both of the banded inhibitor treatments had large increases in their  $\text{NH}_4/\text{NO}_3$  ratios between July 25 and August 15, as seen at the same period in the 1977 banded ATC plots. Again, this is probably largely a function of preferential plant uptake of  $\text{NO}_3$  relative to  $\text{NH}_4$  during this period of rapid N and water uptake. There was precipitation during this time, and the soil water content increased (Table 4.2) so nitrification would not have been limited by low soil moisture. Leaching of  $\text{NO}_3$  out of the 0-15 cm zone was probably not a factor, since there was no increase in soil moisture (Table 4.2) or  $\text{NO}_3$  concentration (data not shown) in the 15-30 cm zone on August 15. Denitrification could also be a cause of  $\text{NO}_3$  disappearance, but it is unlikely that the small increase in soil moisture (31.4% to 38.1% of dry weight) would be enough to stimulate a large increase in the denitrification rate.

#### 1978 Cropped Loamy Sand (Experiment 3) Soil Results

The  $\text{NH}_4/\text{NO}_3$  ratios in Fig. 4.5 indicate that banded ATC was a much more effective inhibitor than banded N-Serve for the first 63 days following application in the loamy sand. Neither inhibitor was effective after 63 days, as the  $\text{NH}_4/\text{NO}_3$  ratios were not significantly higher than those of banded urea alone on this date. There was no nitrification inhibition associated with the banded urea-no inhibitor treatment, since the  $\text{NH}_4/\text{NO}_3$  ratio of this treatment

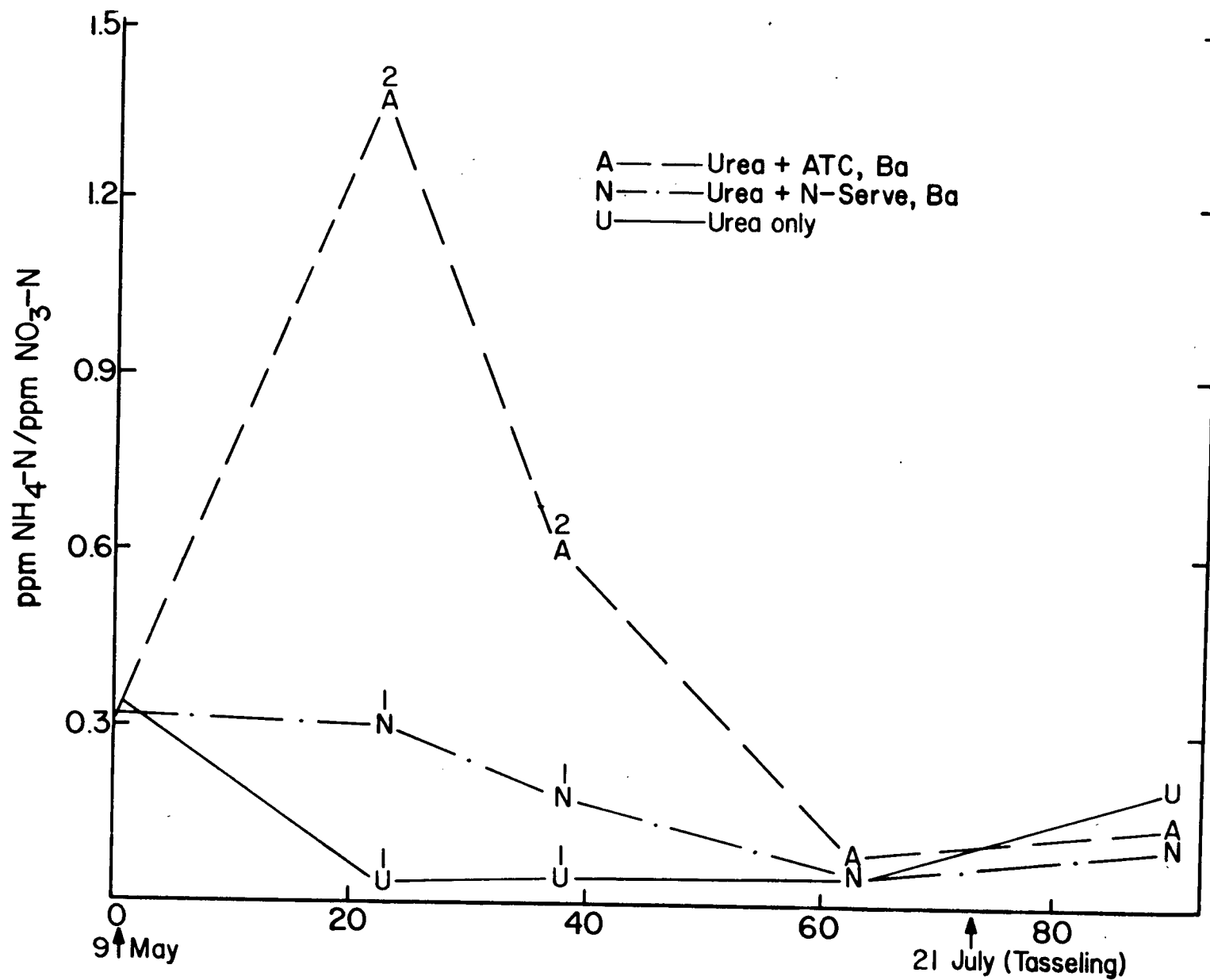


Figure 4.5. Ratio of  $\text{ppm NH}_4\text{-N/ppm NO}_3\text{-N}$  in 0-15 cm depth of 1978 cropped loamy sand as affected by method of N application, type of nitrification inhibitor, and time.

was no higher than that of the broadcast urea treatment (data not shown). It is likely that the rainfall (10.8 cm) between N application and the first sampling date tended to dilute the fertilizer band and decrease the osmotic potential of the soil solution. Also, there would be greater movement of both water and salts in this coarse-textured soil than in the silt. More than half of the 10.8 cm precipitation occurred on the fifth day following urea application. It is not likely that much nitrification would have occurred by this time even in the plots without inhibitor treatments, thus little  $\text{NO}_3$  should have been leached at this time.

Leaching seemed to have little influence on the effectiveness of the highly water-soluble ATC. The  $\text{NH}_4/\text{NO}_3$  ratios of the banded ATC plots three weeks following application were approximately the same in both the silt and the loamy sand, even though there was no leaching in the silt.

The reduced effectiveness of N-Serve in the loamy sand compared to the silt could be a factor of the loamy sand's lower organic matter content, coarser texture, or both. Previous researchers (Briggs, 1975; Toughton et al., 1978) have found that N-Serve is more effective in soils having higher organic matter due to greater sorption by the organic fraction which helps to prevent volatilization loss. However, the somewhat higher carbon content of the silt soil is probably not enough to account for the great difference in N-Serve effectiveness. The large textural difference between the two soils offers a more plausible explanation. Hendrickson et al. (1978) applied urea coated with N-Serve as a sidedress band to an irrigated loamy sand and found only small increases in soil  $\text{NH}_4$  or  $\text{NH}_4/\text{NO}_3$  ratios due to the inhibitor. They concluded that the poor effectiveness of the inhibitor in this soil was due to

leaching of the N fertilizer out of the N-Serve treated zone as well as rapid volatilization of the N-Serve. Gaseous diffusion in the loamy sand would be enhanced by its abundance of connected air-filled pore space. Volatilization of N-Serve might readily occur in this soil even if placed well below the surface, since a direct pathway may exist between the incorporated N-Serve and the atmosphere. Leaching of the urea away from the N-Serve may also have occurred in the loamy sand.

The greater persistence of the effectiveness of both N-Serve and ATC in the silt is especially striking since the inhibitors and urea were applied to the silt one month later when the soil was appreciably warmer (Table 4.2). Laboratory studies (Bundy and Bremner, 1973; Goring, 1962) have shown that the effectiveness of both inhibitors decreases with increasing soil temperature. But the difference in texture between these two soils is apparently a more important factor than the temperature in determining the persistence of the inhibitor activity. Laboratory studies (Bundy and Bremner, 1973; Goring, 1962) have indicated that N-Serve is more effective in coarse-textured soils, but the confined nature of these studies prevented gaseous loss of N-Serve from the soil. Also, unlike the situation in the field, there would be little movement of N or inhibitor through the soil by leaching.

In contrast to the results from the silt soil there was only a small increase in the  $\text{NH}_4/\text{NO}_3$  ratios between July and August in the loamy sand plots with inhibitors. By the July sampling date (63 days), both inhibitors had completely lost their effectiveness, and the level of  $\text{NH}_4$  was less than 10 ppm in all plots (data not shown). Thus, even though crop uptake lowered the  $\text{NO}_3$  concentrations considerably, the  $\text{NH}_4/\text{NO}_3$  ratios increased only slightly.

#### 1978 Fallow Loamy Sand (Experiment 4) Soil Results

As in the cropped loamy sand, the banded ATC treatment initially had a much higher  $\text{NH}_4/\text{NO}_3$  ratio than the other treatments (Fig. 4.6). The ratios for all treatments were 5-10 times higher than those in the adjacent cropped experiment. A possible explanation for this is the different band spacing in the two experiments. Due to space limitations, smaller plots were used in the fallow experiment, and more concentrated bands of urea fertilizer were applied (22.2 g urea compared to 16.7 g urea per m of band). The results of Wetselaar et al. (1972) have shown that nitrification rates can be reduced by increasing the distance between bands while maintaining equal rates of N application per ha (i.e., increasing the local concentration of fertilizer N).

Both broadcast inhibitor treatments had higher  $\text{NH}_4/\text{NO}_3$  ratios for the first 63 days than the broadcast treatment without inhibitor, but the differences were not significant. Thus, broadcasting the inhibitor treatments was not an effective means of slowing nitrification in either soil. This agrees with the findings of Briggs (1975), who showed that broadcast N-Serve was rapidly lost by volatilization, while incorporation at 3 cm depth greatly retarded its loss. The explanation for the poor response of broadcast ATC treatments may be due to its high solubility in water. When the ATC plus urea is broadcast, each fertilizer granule is exposed to a much larger volume of soil than when it is banded. Thus there would be a greater dilution of the ATC by the surrounding soil moisture. In addition, broadcast treatments of either inhibitor would be more susceptible to biological degradation, since each granule is exposed to a greater number of soil microorganisms.

N-Serve was more persistent in the fallow field than in the cropped

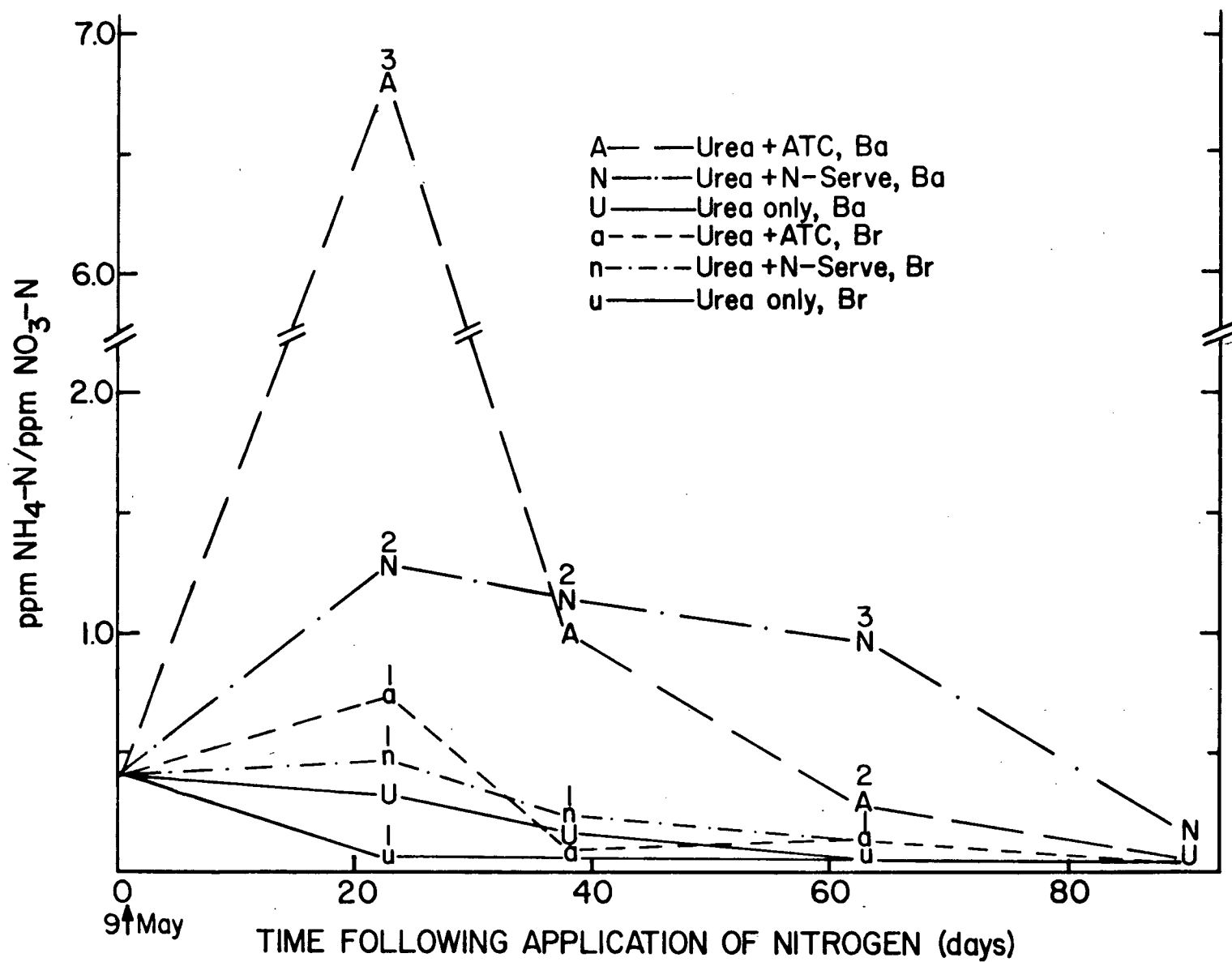


Figure 4.6. Ratio of ppm  $\text{NH}_4\text{-N/ppm NO}_3\text{-N}$  in 0-15 cm depth of 1978 fallow loamy sand as affected by method of N application, type of nitrification inhibitor, and time.

field. In the cropped field both N-Serve and ATC lost their effectiveness within 63 days, whereas in the fallow field ATC became ineffective after 63 days, but the activity of N-Serve persisted for 90 days. This finding has not been previously reported in the literature. It is possible that the greater microbial activity associated with the rhizosphere of the corn roots led to more rapid degradation of N-Serve but had no effect on ATC. Previous research (Redemann et al., 1965) has shown that N-Serve can be taken up by plant roots, but no studies have been reported on plant uptake of ATC.

No August increase in the  $\text{NH}_4/\text{NO}_3$  ratios of the banded ATC or N-Serve plots occurred in the fallow field. This suggests that preferential crop removal of  $\text{NO}_3$  was probably the primary cause of the increased  $\text{NH}_4/\text{NO}_3$  ratios at this same time in the cropped fields.

### Crop Results

In 1977 at Site 1 there were no significant differences due to N rate or inhibitor for either yield of dry matter or % total N in the harvested crop or the leaves at silking (Table 4.3). This was probably due to the heavy addition of manure during the previous winter and the consequent high rate of organic N mineralization. Total mineral N in the control plots (0-15 cm) averaged 97 ppm on July 13 and only decreased to 65 ppm by September 6 (data not shown). Thus, the rate of N mineralization from the manure and soil organic matter was sufficient for maximum yield of silage corn.

Although no manure was added to the silt prior to the 1978 season, residual N mineralization rates were still too high to reveal any significant differences due to treatments for yield of dry matter or % total N in the crop



Table 4.3. Yield of silage dry matter, % total N in harvest and silk leaves in Experiments 1, 2 and 3 as affected by rate of N, type of NI and placement of N.<sup>s</sup>

Treatment	Experiment 1 (1977 silt)			Experiment 2 (1978 silt)			Experiment 3 (1978 l. sa.)		
	Yield <sup>†</sup>	Total N	Total N	Yield	Total N	Total N	Yield	Total N	Total N
		crop <sup>‡</sup>	leaf <sup>#</sup>		crop	leaf		crop	leaf
	t/ha	———— % ————	————	t/ha	———— % ————	————	t/ha	———— % ————	————
0 N Control	20.9	1.05	2.82	18.8	1.04	2.82	12.7a <sup>##</sup>	0.96	2.28a
50 N Ba <sup>†</sup>	18.1	1.17	2.76	18.4	1.06	2.71	15.3b	0.92	2.27a
50 N Ba + ATC	18.4	1.10	2.95	19.7	1.06	2.86	16.8b	1.01	2.42a
50 N Ba + N-S	-	-	-	19.8	1.02	2.78	17.0b	1.00	2.41a
50 N Br	20.3	1.19	2.82	-	-	-	-	-	-
50 N Br + ATC	18.3	1.18	2.71	-	-	-	-	-	-
100 N Ba	18.9	1.08	2.68	19.6	1.05	2.80	18.5c	1.15	2.88b
100 N Ba + ATC	17.9	1.26	2.92	20.7	1.08	2.88	17.5bc	1.03	2.87b
100 N Ba + N-S	-	-	-	18.7	1.10	2.91	18.4c	1.17	3.01b
100 N Br	19.7	1.23	2.89	-	-	-	-	-	-
100 N Br + ATC	19.1	1.22	2.81	-	-	-	-	-	-

<sup>s</sup>Data values represent average of 3 replicate plots.

<sup>†</sup>Ba represents banded plots, Br represents broadcast plots.

<sup>‡</sup>Includes ears plus stover.

<sup>#</sup>Leaves harvested at time of silking.

<sup>##</sup>Values in each column accompanied by the same letter or without a letter are not significantly different ( $P \leq 0.05$ ).

or silk leaves. The  $\Sigma N$  in the control plots was lower than in 1977 (maximum of 36 ppm during the season, data not shown), but still too high to show any yield response to added N.

In the loamy sand there were significant responses to rate of N for yield of corn dry matter and total % N in the silk leaves, but not for total % N in the crop. There was still no significant response to inhibitor treatment, but where 50 kg urea-N/ha was applied, there was a 10% increase in both yield of dry matter and % N in the crop when either ATC or N-Serve were added with the urea. This suggests that the efficiency of the urea fertilizer was increased sufficiently to improve the yield at the lower rate of N.

At the higher rate of N, even though there were large significant differences in the soil  $NH_4$  and  $NH_4/NO_3$  ratios due to the inhibitor treatments, there were only small differences in the  $\Sigma N$  (0-30 cm) due to inhibitor treatments (data not shown). Apparently, there was insufficient leaching or denitrification of  $NO_3$  to lower the yields in the non-inhibitor plots. If there had been more precipitation, greater loss of  $NO_3$  might have occurred, and the presence of the inhibitors might have resulted in yield increases.

The concentration of  $NO_3$  in the ear leaves at silking was not significantly affected by the inhibitor treatments in any of the experiments (data not shown). Conditions were apparently sufficiently favorable for nitrate reductase activity that the higher levels of  $NO_3$  absorbed by the plants in the non-inhibitor plots were reduced to levels similar to those in the inhibitor plots.

Dry matter yields in all experiments were somewhat above those commonly

obtained by farmers in this area (13-16 t/ha). The only 0 N control treatment with a lower yield was that in the loamy sand (12.7 t/ha). These yields reflect the high rates of organic N mineralization in these soils and help to explain the lack of response to the nitrification inhibitors.

## CONCLUSIONS

The  $\text{NH}_4/\text{NO}_3$  ratio appears to be a better indicator of nitrification inhibitor effectiveness than  $\text{NH}_4$  concentration alone or the sum of  $\text{NH}_4$  plus  $\text{NO}_3$ , particularly in the earlier part of the growing season. This ratio tended to increase in the cropped plots during the period of maximum N uptake, but showed no increase in the fallow plots during the same period.

Both ATC and N-Serve were equally effective nitrification inhibitors when banded in the silt, but ATC was more effective than N-Serve in the cropped loamy sand, probably due to more rapid volatilization of N-Serve in the coarse-textured soil or leaching of urea out of the zone of N-Serve application. Neither inhibitor was effective when broadcast. The effectiveness of both inhibitors persisted longer in the silt (86 days) than the loamy sand (63 days). Since ATC is much easier to coat onto solid fertilizers, it appears that this inhibitor is a good candidate for further field evaluation in conjunction with band-applied solid fertilizers.

There was no significant improvement in crop yield or N content due to inhibitor treatment in either soil. This was apparently due to conditions which favored high mineralization rates of soil organic N as well as little loss of  $\text{NO}_3$  from the soil. Some improvement in crop yield might have been seen if the soil had a lower organic N content or if conditions had been more favorable for leaching and denitrification losses of  $\text{NO}_3$ .

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## Chapter Five

### SUMMARY AND CONCLUSIONS

The aim of this thesis was to determine if the nitrification inhibitors N-Serve and ATC could increase the efficiency of urea fertilizer so that farmers might use lower N application rates, thereby saving money, energy, and decreasing the potential negative impacts on the aquatic and atmospheric environment.

In Chapter Two, an experiment was described where urea was applied to a silt loam near Vancouver, B.C. in the fall as a band or broadcast treatment with or without ATC nitrification inhibitor. When the urea was broadcast, either with or without ATC, nitrification proceeded steadily from November until April despite near-freezing soil temperatures. This finding suggests that other forms of N, including manure-N, may also nitrify if broadcast in the fall under similar climatic conditions. Any nitrate which forms would be highly susceptible to loss in the spring via leaching or denitrification due to the heavy precipitation which normally occurs.

The banded applications of urea resulted in very little nitrification until March, probably due to  $\text{NH}_4^+$  toxicity as well as osmotic inhibition of the nitrifiers caused by the high salt concentration in the band. This suggests that banding ammoniacal fertilizers may be one way of decreasing N losses from fall applications.

ATC had no effect on nitrification when broadcast with urea, but there was some inhibition when it was banded, as indicated by higher

$\text{NH}_4^+$  levels in the spring. Leaching of the water-soluble ATC was the probable cause of its poor effectiveness. Leaching of urea was also found to occur, as evidenced by increased  $\text{NH}_4^+$  levels at the 30-60 cm depth, particularly with the banded treatments.

In Chapter Three, a laboratory study was described where ATC and N-Serve were applied at two different rates with urea to a silt and incubated at 2 and 12°C. The purpose of this experiment was to determine if either of these NI have any effect on the hydrolysis rate of urea, as well as to examine the effect of soil temperature on the rate of urea hydrolysis.

The results indicated that neither NI had any effect on hydrolysis, but low temperatures greatly delayed the rate. This suggests that if urea is applied to a cold soil (<12°C) a potential for leaching loss of N exists should a heavy rainfall occur, as was observed in the winter nitrification study (Chapter Two).

In Chapter Four, a series of summer experiments with silage corn (Zea mays L.) were described where urea was applied with or without ATC or N-Serve as a band or broadcast treatment on two soils, a silt and a loamy sand. The inhibitors were much more effective when banded than when broadcast. A possible explanation for this is that when the inhibitors were banded they were exposed to a smaller number of soil microorganisms, and thus biological degradation would have taken place more slowly.

Contrary to expectations, both inhibitors were more effective in the silt than the loamy sand. The coarser texture of the loamy sand



apparently resulted in greater volatilization of the N-Serve and allowed more extensive leaching and diffusion of the ATC. The higher organic matter content of the silt may have resulted in stronger adsorption of the organic inhibitors, which would have prolonged their effectiveness.

In comparing the two inhibitors, ATC was slightly more effective than N-Serve in the silt soil, but in the loamy sand ATC was much more effective. The effectiveness of N-Serve was of much shorter duration than ATC in the loamy sand, undoubtedly due to its volatilization from the coarse-textured soil.

Although the soil analyses indicated that the inhibitors were effective in delaying nitrification, particularly in the silt, the crop data revealed no significant differences due to either NI. Manure applications which occurred prior to initiation of the experiments on the silt resulted in high rates of organic N mineralization. Because of this there was no possibility of obtaining growth response from N fertilizer or NI, since even the unfertilized plots had high yields. In the loamy sand there was a significant response to N, but still no response to NI. This was partly because the NI were less effective in this soil. A more important factor which was probably partly responsible for lack of crop response to NI in both soils was the relatively dry weather which prevailed during both summers of the study. Higher rainfall would have caused greater loss of  $\text{NO}_3^-$  by leaching and denitrification which would have increased the possibility of a yield response to NI.

Although crop yields were not affected, ATC and N-Serve did delay nitrification for more than 60 days in the loamy sand and more than 80 days in the silt. Thus, use of NI does have the potential for increasing the efficiency of N fertilizer. As the cost of N fertilizer continues to rise, the use of NI will become more economically viable. If the cost of urea-N is assumed to be 60¢/kg, then 100 kg N/ha would cost \$60/ha. The current price of N-Serve is \$21/kg of active ingredient. By using N-Serve it may be possible to obtain an optimum crop yield by using only 50 kg N/ha (\$30) and 0.5 kg/ha N-Serve (\$10.50) for a total N fertilizer cost of \$40.50 per ha, or a savings of almost \$20/ha. The cost of ATC is not available at this time, but it is expected to be somewhat lower than N-Serve according to the manufacturer.

Further studies involving ATC and N-Serve remain to be done. Optimization of the rate of NI applications for different soils would require determining the effect of adding various rates of N-Serve and ATC to soils. Also, other reduced forms of N fertilizer such as anhydrous ammonia and ammonium sulphate could be combined with ATC or N-Serve. It would also be of considerable interest to compare the efficiency of sulfur-coated urea with that of urea coated with inhibitors. Finally, the effect of varying the width of band spacing of ammoniacal fertilizers on nitrification rates should be examined as an alternate means of improving N fertilizer efficiency.

Appendix 1.1 Field description of silt soil used in study

Soil Classification: Rego Humic Gleysol, Can. (Typic Fluvaquent, U.S.)

Location: 600 m W of King George Highway, 300 m N of Nicomekl River in  
Surrey, B.C. Kitzel farm at 13975 40th Avenue.

HORIZON (U.S.)	Can.	DEPTH (cm)	DESCRIPTION
(Ap)	Ap	0-20	Dark brown (10 YR 4/2.5, m); silt; weak, medium granular; very friable; many fine and medium roots; diffuse, wavy boundary to:
(Ah)	Ah	20-35	Brown (10 YR 4/3, m); silt; weak, medium subangular blocky; friable; many fine roots; abrupt, wavy boundary to:
(C1g)	Cg1	35-70	Grayish-brown (2.5 Y 5/2, m); silt loam; common, coarse, distinct pale yellow mottles (5 Y 7/4, m) in the form of slightly hard tubes around old root channels; moderate, coarse, subangular blocky; firm; many roots in upper part thinning to few in lower part; diffuse wavy boundary to:
(C2g)	Cg2	70+	Dark gray (10 YR 4/1, m); silt loam; many coarse, prominent pale yellow mottles (5 Y 7/4, m) in the form of slightly hard tubes around old root channels; moderate, coarse, subangular blocky; firm; occasional fine roots in upper part; lower boundary undetermined.

## Appendix 1.2 Field description of loamy sand soil used in study

Soil Classification: Humic Podzol, Can. (Typic Haplohumod, U.S.)

Location: University of British Columbia, 110 m N of Meteorological Station,  
30 m W from road

HORIZON (U.S.)	Can.	DEPTH (cm)	DESCRIPTION
(A <sub>p</sub> )	A <sub>p</sub>	0-40	Very dark grayish brown (10 YR 3/2, m); loamy sand; single grain; loose; very friable; abundant fine roots; some thin lenses of decayed wood and bark at the abrupt wavy boundary to:
(E)	A <sub>e</sub>	40-48	Dark grayish brown (10 YR 3.5/2, m); loamy sand; granular; friable; few fine roots; abrupt wavy boundary to:
(B <sub>h</sub> )	B <sub>h</sub>	48-60	Dark brown (7.5 YR 3/1, m); loamy sand; weak medium subangular blocky breaking to fine to medium granular; firm to friable; roots absent; some lenses of strong brown (7.5 YR 5/6 m); gradual wavy boundary to:
(B <sub>hir</sub> )	B <sub>f</sub>	60-80	Dark yellowish brown (10 YR 4/6, m); sand; angular blocky breaking to single grain; firm; roots absent; abrupt wavy boundary to:
(II. C <sub>lg</sub> )	II C <sub>gl</sub>	80-100	Grayish brown matrix (2.5 Y 5/3, m); loam; with many distinct medium yellowish red (5 YR 5/8, m); mottles; strong coarse platy breaking to medium angular blocky; firm; roots absent; diffuse boundary to:

HORIZON (U.S.)	Can.	DEPTH (cm)	DESCRIPTION
(II C <sub>2g</sub> )	II C <sub>g2</sub>	100-110 <sup>+</sup>	Grayish brown matrix (2.5 Y 5/1, m); silt loam, with many distinct coarse yellowish red mottles (5 YR 5/8, m); strong coarse platy breaking to medium angular blocky firm; roots absent; lower boundary undetermined.

Appendix 2.1. Ammonium-N and nitrate-N concentrations in 1977 silt (Experiment 1) on various sampling dates as affected by rate of urea-N, presence of ATC nitrification inhibitor (NI), and method of application.

Rate of N	NI *	Appl. ** Method	Sampling date (days from N application)											
			27 May (-18)		30 June (16)		13 July (29)		27 July (43)		10 Aug. (57)		6 Sept. (84)	
			NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
kg/ha			µg N/g dry soil <sup>+</sup>											
0 to 15 cm														
0	None	-	8	76	16	76	10	87	3	45	5	26	5	60
50	None	BA	10	46	213	123	71	185	24	120	41	75	9	84
50	ATC	BA	7	70	225	73	175	109	39	58	34	31	41	57
100	None	BA	8	55	506	23	154	255	59	172	54	107	16	160
100	ATC	BA	8	40	536	63	370	88	201	51	275	31	167	54
50	None	BR	8	57	18	73	19	108	5	57	6	24	5	71
50	ATC	BR	7	65	35	69	17	106	83	42	13	24	15	45
100	None	BR	7	73	17	95	14	124	10	88	16	33	16	104
100	ATC	BR	7	103	61	90	33	138	10	75	13	42	16	71
15 to 30 cm														
0	None	-	4	36	4	31	11	27	5	23	5	13	6	15
50	None	BA	4	39	19	37	14	26	24	52	5	8	7	19
50	ATC	BA	3	35	8	28	16	24	39	40	6	10	10	24
100	None	BA	10	26	14	19	15	18	87	117	31	21	11	31
100	ATC	BA	3	39	14	26	16	16	124	58	82	24	42	24
50	None	BR	3	44	6	37	13	23	7	28	6	13	6	21
50	ATC	BR	4	37	7	26	15	20	9	20	4	9	7	15
100	None	BR	4	54	6	34	11	28	11	29	5	8	11	21
100	ATC	BR	5	79	5	36	16	47	15	23	5	6	13	22

\* Nitrification inhibitor rates were 1% of N applied as active chemical ingredient.

\*\* Broadcast treatments indicated by BR, banded treatments by BA. Bands were spaced 85 cm apart.

+ Values represent averages of three replicate plots, rounded to nearest integer.

Appendix 2.2. Ammonium-N and nitrate-N concentrations in 1978 silt (Experiment 2) on various sampling dates, as affected by rate of urea-N, presence and type of nitrification inhibitor (NI).

Rate of N	NI*	Sampling date (days from N application)									
		12 June (0)		4 July (22)		25 July (43)		15 Aug. (64)		6 Sept. (86)	
		NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
kg/ha		µg N/g dry soil <sup>+</sup>									
0 to 15 cm											
0	None	4	44	5	23	3	28	4	32	4	29
100	None	3	44	92	163	22	105	38	109	28	83
100	ATC	3	46	163	135	71	64	98	55	69	53
100	N-Serve	7	49	107	104	35	56	65	45	24	61
50	None	4	35	72	140	15	56	28	75	5	66
50	ATC	3	42	151	178	5	21	29	54	13	43
50	N-Serve	3	42	140	111	33	37	34	42	24	30
15 to 30 cm											
0	None	7	26	4	21	2	9	2	7	4	8
100	None	5	26	6	34	2	15	8	31	4	25
100	ATC	8	21	9	36	4	15	7	11	6	13
100	N-Serve	6	24	7	33	3	17	6	14	5	21
50	None	7	26	4	28	5	17	6	7	5	12
50	ATC	7	27	7	22	2	5	6	8	4	17
50	N-Serve	6	22	7	24	6	11	6	9	4	12
30 to 60 cm											
0	None	6	21	4	31	4	31	6	15	2	13
100	None	5	24	51	76	5	52	33	38	5	18
100	ATC	8	26	76	42	42	39	25	21	5	12
100	N-Serve	5	29	32	29	21	38	31	24	5	15
50	None	6	19	30	67	36	67	16	24	3	12
50	ATC	4	21	61	47	16	39	19	22	3	16
50	N-Serve	2	23	40	40	24	39	17	28	8	14

\* Nitrification inhibitor rates were 1% of N applied as active chemical ingredient. All N and NI applications were banded with 85 cm spacing.

<sup>+</sup> Values represent averages of three replicate plots, rounded to nearest integer.

Appendix 2.3. Ammonium-N and nitrate-N concentrations in 1978 cropped loamy sand (Experiment 3) on various sampling dates as affected by rate of urea-N, presence and type of nitrification inhibitor (NI), and method of application.

Rate of N	NI*	Appl.** Method	Sampling date (days from N application)											
			9 May (0)		1 June (23)		16 June (38)		11 July (63)		7 Aug. (90)		29 Aug. (112)	
			NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
kg/ha			µg N/g dry soil <sup>+</sup>											
0 to 15 cm														
0	None	-	4	12	5	13	2	14	3	11	2	4	3	3
50	None	BA	4	9	5	80	2	45	2	55	2	8	3	3
50	ATC	BA	4	13	11	72	3	104	3	36	2	4	3	4
50	N-Serve	BA	5	10	10	61	4	76	5	38	4	4	3	3
100	None	BA	4	13	5	158	3	68	3	62	2	11	3	4
100	ATC	BA	4	14	139	101	106	179	4	50	3	25	3	11
100	N-Serve	BA	4	12	29	98	26	143	6	89	3	27	3	9
100	N-Serve	BR	5	13	9	40	3	49	5	44	2	13	3	4
100	None	BR	4	11	5	64	2	81	2	46	2	11	3	7
15 to 30 cm														
0	None	-	6	6	3	10	7	11	3	6	1	3	2	3
50	None	BA	7	6	3	19	9	12	2	6	2	9	2	2
50	ATC	BA	8	6	3	24	8	24	2	8	5	6	4	3
50	N-Serve	BA	6	7	4	22	11	18	2	5	12	5	3	3
100	None	BA	6	7	3	54	11	42	3	13	2	7	3	4
100	ATC	BA	5	6	3	34	6	40	2	12	2	8	2	7
100	N-Serve	BA	7	7	27	69	7	71	8	30	1	6	2	5
100	N-Serve	BR	7	6	2	9	9	8	2	6	2	8	3	3
100	None	BR	6	9	3	19	6	20	3	13	2	5	3	6

\* Nitrification inhibitor rates were 1% of N applied as active chemical ingredient.

\*\* Broadcast treatments indicated by BR, banded treatments by BA. Bands were spaced 75 cm apart.

<sup>+</sup> Values represent averages of three replicate plots, rounded to nearest integer.



Appendix 2.4. Ammonium-N and nitrate-N concentrations in 1978 fallow loamy sand (Experiment 4) on various sampling dates as affected by presence and type of nitrification inhibitor (NI) and method of application.

Rate of N	NI*	Appl. ** Method	Sampling date (days from N application)											
			9 May (0)		1 June (23)		16 June (38)		11 July (63)		7 Aug. (90)		29 Aug. (112)	
			NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
kg/ha			μg N/g dry soil <sup>+</sup>											
0 to 15 cm														
0	None	-	6	12	3	8	2	11	4	24	2	27	3	18
100	None	BA	5	15	40	125	41	246	8	154	2	98	4	36
100	ATC	BA	6	18	385	57	166	169	55	206	6	135	9	99
100	N-Serve	BA	6	14	137	106	183	161	130	134	15	97	18	38
100	None	BR	6	15	3	47	2	40	3	48	2	43	4	20
100	ATC	BR	6	14	39	52	8	56	11	83	2	37	4	33
100	N-Serve	BR	8	15	21	45	9	48	10	60	2	43	3	23
15 to 30 cm														
0	None	-	6	5	2	12	3	9	2	9	2	16	2	20
100	None	BA	6	8	2	34	2	93	2	41	2	37	2	48
100	ATC	BA	5	6	7	39	4	29	3	36	2	43	2	54
100	N-Serve	BA	5	6	6	39	5	53	5	42	3	37	3	38
100	None	BR	5	5	2	18	3	9	4	11	3	9	3	34
100	ATC	BR	6	4	2	14	2	9	3	12	2	21	5	42
100	N-Serve	BR	5	6	2	16	2	7	2	11	2	15	3	29

\* Nitrification inhibitor rates were 1% of N applied as active chemical ingredient.

\*\* Broadcast treatments indicated by BR, banded treatments by BA. Bands were spaced 100 cm apart.

+ Values represent averages of three replicate plots, rounded to nearest integer.

Appendix 3. Selected physical and chemical properties of soils used in thesis research, 1977-1978.

Texture	Depth cm	Sand —— % ——	Silt	Bulk Dens. —— kg/m <sup>3</sup> ——	Part. Dens.	-10 kPa	-33 kPa	-1500 kPa	Exch. Na	Exch. K	Exch. Ca	Exch. Mg	CEC, pH7	Total C	Total N	pH CaCl <sub>2</sub>
						—— % H <sub>2</sub> O ——			me/100 g					—— % ——		
Silt	0-15	8	85	840	2390	59.9	53.1	24.1	0.22	0.97	10.3	1.83	39.1	6.8	0.60	4.6
	15-30	7	88	960	2450	60.8	54.3	26.3	0.28	0.80	8.3	1.61	36.1	5.8	0.48	4.3
	30-60	N.D.	N.D.	1100	2650	N.D.	N.D.	N.D.	0.42	0.33	2.5	1.23	23.4	2.9	0.20	3.6
	60-90	N.D.	N.D.	1200	N.D.	N.D.	N.D.	N.D.	0.64	0.28	1.2	0.98	15.4	2.0	0.15	3.4
Loamy sand	0-15	76	18	1160	2450	42.0	31.2	13.1	0.08	0.68	8.5	0.78	23.9	4.5	0.27	5.4
	15-30	N.D.	N.D.	N.D.	2630	33.5	24.3	10.9	0.09	0.56	6.7	0.66	22.9	4.3	0.26	5.3