CHANGES IN UREASE ACTIVITY AND AMMONIA VOLATILIZATION INDUCED BY RESIDUE MANAGEMENT SYSTEMS FERTILIZED WITH UREA

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INTRODUCTION

This dissertation provides laboratory experimental evidence on the potential for ammonia volatilization from urea fertilizer due to chemical and biological changes induced by residue accumulation in reduced and no-till systems for winter wheat production.

The body of this document has been divided into two chapters. The first chapter presents data indicating changes in the activity of the soil enzyme urease in the zone of fertilizer application in residue management systems. The second chapter illustrates the systematic study of the effect of surface wheat residue on ammonia volatilization under controlled laboratory conditions. These experiments were designed to study individual factors and their role in the ammonia volatilization process and the distribution of mineral N as affected by urea-N rates in the presence and absence of surface wheat residue.

Chapters I and II are presented in a format suitable for publication in a professional journal.

CHAPTER I

Changes in Soil Urease Activity Induced by Wheat Residue Management Systems

ABSTRACT

Reduced and no-till cropping systems are conducive to surface residue accumulation and nutrient stratification of broadcast fertilizers. Urease contained in crop residues increases the rate of urea hydrolysis which can increase the potential for ammonia volatilization. Significant increases in urease activity were measured in the surface 10 mm of Norge clay loam (fine-silty, mixed, thermic udic Paleustoll) and Grant silt loam (fine silty, mixed, thermic udic Argiustoll) which have been in reduced- and no-till management for over four years. Increases in soil urease activity were found where accumulation of residue occurred. Urease activity was uniformly distributed with soil depth under conventional tillage. Average urease activity in the surface 10 mm of soil under conventional-, reduced-, and no-till residue management systems were, 12.1, 41.4, and 45.2 ug NH_4-N g^{-1} h^{-1} for Norge clay loam and 9.7, 12.4, and 35.0 ug NH_4-N g^{-1} h^{-1} for Grant silt loam, respectively. Urease activity of mature undecomposed residue grown at the site was 376.2 ug NH4-N g^{-1} h^{-1} which was 28 times larger than the average activity found in soil. Increase in soil urease activity appeared to be the result of urease contained in the residue itself and not the result of microbial activity during residue decomposition.

Additional Index Words: ammonia volatilization, urea hydrolysis, wheat residue, tillage.

INTRODUCTION

Urea must first undergo hydrolysis by the enzyme urease to make its N available for plant uptake. Urease is synthesized by microbes and plants and is commonly found in soils associated with both organic and inorganic soil fractions (Paulson and Kurtz, 1970). Gibson (1930) indicated that urea decomposition was faster in pasture than in cultivated soils. Conrad (1940a, 1940b) reported urease activity in mineral soils to be less than in organic soils. Paulson and Kurtz (1970) demonstrated that urease in soil exists as the product of microbial activity in both intracellular and extracellular forms. Extracellular urease activity has been shown to be associated with clay-organic matter complexes (Paulson and Kurtz, 1969, 1970; Burns et al., 1972a, 1972b; Gould et al., 1973; Lloyd, 1975; Dalal, 1975). Pinck and Allison (1961) demonstrated that urease readily complexes with 2:1 and 1:1 clay minerals. They observed that H^+ treated montmorillonite adsorbed more urease than kaolinite and suggested an explanation based on the amphoteric nature of urease and clay minerals. McLaren et al. (1975), reported that the sedimentation rate of soil urease activity following high speed centrifugation was greater than that of organic matter suggesting that urease and organic matter colloids are not uniformly associated.

Extracellular urease activity has been shown to be positively correlated with both soil organic matter and clay content (Dalal, 1975; Tabatabai, 1973; Zantua et al., 1977). Myers and McGarity (1968) indicated higher urease activity of surface soil and a decrease in activity with increased soil depth. They indicated that urease activity closely followed the organic carbon distribution within the soil profile.

Conrad (1942) recognized that natural soil urease activity was highly resistant to proteolytic degradation and that pure urease added to soil was inactivated after application. The stable forms of soil urease appear to be associated with adsorbed clay-organic matter complexes that are resistant to a wide range of extreme soil conditions (Zantua and Bremner, 1977). Reports of soil urease activity at temperatures as low as -20 C have been presented by Bremner and Zantua (1975). However, accounts of soil urease stability and persistance vary widely. Skujins and McLaren (1969) identified urease activity in geologically preserved permafrost samples as old as 9550 years. On the other hand, Pancholy and Rice (1972) indicated loss of urease activity from an Oklahoma mollisol when stored dry in open containers for as little as four weeks. Soils appear to have a definite but limited capacity to adsorb urease. Urease adsorbed by soil colloids is apparently protected from microbial degradation (Paulson and Kurtz, 1969; Roberge, 1970; Lloyd, 1975; Pettit et al., 1976).

Frankenberger and Tabatabai (1982) reported urease activity associated with tissue of 21 diverse plants ranging from alfalfa (*Medicago sativa L.*) to sorghum (*Sorghum bicolor* L. Moench). Torello and Wehner (1983) measured urease activity in Kentucky bluegrass turf (*Poa pratensis* L.) which they reported to be 25 times larger than urease activity of soil. Goos (1985) reported urease activity associated with cereal residues of winter wheat (*Triticum aestivum* L.), winter rye (*Secale cereale* L.) and spring wheat (*Triticum aestivum* L.). He indicated that urease activity of the residue increased with increased saprophytic colonization during residue aging and decomposition under field conditions.

Increasing urease activity of soil by additions of urease has generally resulted in only temporary increases in the rate of urea hydrolysis as the soil appears to inactivate or destroy added urease (Conrad, 1940b; Stojanovic, 1959). Zantua and Bremner (1976) reported increases in soil urease activity upon addition of readily decomposable carbon materials such as glucose. However, they observed a tendency of the soil to return to the level of activity originally present. Burns et al. (1972b) indicated that proteolysis appeared to be a major mechanism in the inactivation of added urease to soil. Stojanovic (1959) reported seasonal changes in soil urease activity.

Pancholy and Rice (1973) reported that in an old field succession in Oklahoma, urease activity increased from April to October followed by a gradual decline during the winter months. These reports all indicate the dynamic nature of urease activity in soil. Increases in urease activity can affect ammonia volatilization from surface-applied urea by increasing the rate of urea hydrolysis (Hargrove et al., 1987) and the initial rate of ammonia loss (Moe, 1967).

In no-till winter wheat production in Oklahoma, urea is broadcast during late fall at a time when large amounts of crop residue remain on the soil surface. Changes in urease concentration in the zone of fertilizer placement can increase NH_3-N losses from broadcast urea. Therefore, detailed information on the distribution of urease activity in residue management systems is needed in the implementation of efficient methods of application for urea fertilizer.

The objective of this research was to characterize the distribution of urease activity in the surface to 75 mm of two Oklahoma mollisols which have been in conventional, reduced and no-till wheat residue management for over four years.

MATERIALS AND METHODS

Soils from established field experiments at the North Central Research Station at Lahoma, Oklahoma (Grant silt loam, fine, silty, mixed, thermic Udic Argiustoll) and the Agronomy Research Station at Stillwater, Oklahoma (Norge clay loam, fine, silty, mixed, thermic Udic Paleustoll) were collected in the fall of 1986. Intact soil cores, 75 mm deep, were randomly taken from plots which had been under conventional- (CT), reduced- (RT), and no-till (NT) management since 1982. The CT plots had been disked twice after harvest each year which resulted in complete incorporation of crop residues. Reduced till plots were V-bladed twice after harvest which partially incorporated residues. The no-till plots remained untilled except for the narrow band opened by the double disk openers during seeding. Each plot received 168 kg urea-N ha^{-1} and winter wheat (Triticum aestivum L. TAM W 101) was planted every year.

Wheat residue samples were collected at maturity following the 1986 wheat harvest at Stillwater. Straw samples were dried at 40 C, ground, and stored in closed containers until analyzed for urease activity.

Prior to taking a soil sample, all standing residue over the soil surface was removed. Soil samples were collected within 48 h of a saturating rain in order to obtain samples with moisture near "field capacity". Intact soil samples were taken and encased in aluminum cylinders which were sealed immediately using plastic lids. Before analysis, seven soil cores from each tillage level were separated into 10 mm increments and screened to pass a 2 mm sieve. Screened samples for each tillage and depth were stored moist in closed containers and kept refrigerated at 5 C until analyzed for urease activity (Zantua and Bremner, 1975a). At the time of analysis, samples were taken from each container and urease activity was determined in soils and residue according to the procedure outlined by Tabatabai and Bremner (1972). Data were analyzed statistically as a split plot with soils and tillage levels in the main units and soil depth in the subunits using ANOVA procedures outlined by the SAS Institute (Statistical Analysis System Institute, 1982).

RESULTS AND DISCUSSION

Urease activity averaged over soils, tillages, and depths was 13.5 ug NH_4-N g^{-1} h^{-1}. This value is within the range of activities reported for soils by Tabatabai and Bremner (1972) and Zantua and Bremner (1975b). Table 1. depicts the analysis of variance table for urease activity as affected by soil, tillage, and soil depth. Significant changes in urease activity due to tillage level and soil depth were observed.

Both reduced and no-till management leave residue over the soil surface; therefore, comparisons of CT vs. RT and NT at each soil depth were used in evaluating the effect of tillage on soil urease activity. Contrasts of CT vs. RT and NT, and RT vs. NT residue management systems for each depth interval are shown in Tables 2 and 3 for Norge cl and Grant sil, respectively.

The uppermost 10 mm layer of NT- treatments in both soils consistently showed higher urease activity compared to CT- treatments. Urease activity distribution with soil depth depended on tillage system. Urease activity distribution in the top 51 mm of soil as affected by tillage system and depth is presented in Figs. 1 and 2 for Norge cl and Grant sil, respectively. Under NT the highest urease activity was observed in the top 10 mm of soil and tended to

TABLE 1. ANALYSIS OF VARIANCE TABLE FOR SOIL UREASE ACTIVITY AS AFFECTED BY SOIL, TILLAGE, AND DEPTH

Source	df	Mean square	F Value	
Treatments				
Soil	1	2.037	0.06	
Tillage	2	639.501	18.71	**
Error (a)	2	34.188		
Depth	5	919.536	7.81	**
Soil x Depth	5	324.334	2.75	
Tillage x Depth	10	316.022	2.68	
Error (b)	10	117.731	7.34	
Subsample error	108	16.033		
Total	143			

df - degrees of freedom.

** Indicates significance at 0.01 probability level.

TABLE 2. SINGLE DEGREE OF FREEDOM CONTRASTS OF UREASE ACTIVITY BY DEPTH IN NORGE CLAY LOAM

Contrast	Sum of Squares	F Value
CT vs. RT and NT		
0 - 10 mm.	650.46	5.52 *
11 - 20 mm.	0.06	0.00
21 - 30 mm.	13.05	0.11
31 - 40 mm.	0.63	0.01
41 - 50 mm.	24.50	0.21
51 - 60 mm.	7.65	0.06
RT vs. NT		
0 - 10 mm.	30.03	0.26
11 - 20 mm.	7.08	0.06
21 - 30 mm.	107.34	0.91
31 - 40 mm.	154.56	1.31
41 - 50 mm.	96.13	0.82
51 - 60 mm.	19.05	0.16

*, ** Indicates significance using Error (b)= 117.73 with 10 df at 0.05 and 0.01 probability level, respectively.

TABLE 3. SINGLE DEGREE OF FREEDOM CONTRASTS OF UREASE ACTIVITY BY DEPTH IN GRANT SILT LOAM

Contrast	Sum of Squares	F Value
CT vs. RT and NT		
0 - 10 mm.	130.87	1.11
11 - 20 mm.	7.20	0.04
21 - 30 mm.	20.12	0.17
31 - 40 mm.	0.26	0.00
41 - 50 mm.	1.63	0.01
51 - 60 mm.	4.63	0.04
RT vs. NT		
0 - 10 mm.	1022.15	8.68 *
11 - 20 mm.	360.14	3.06
21 - 30 mm.	140.72	1.20
31 - 40 mm.	160.81	1.37
41 - 50 mm.	49.94	0.42
51 - 60 mm.	53.09	0.45

*, ** Indicates significance using Error (b)= 117.73 with 10 df at 0.05 and 0.01 probability level, respectively.

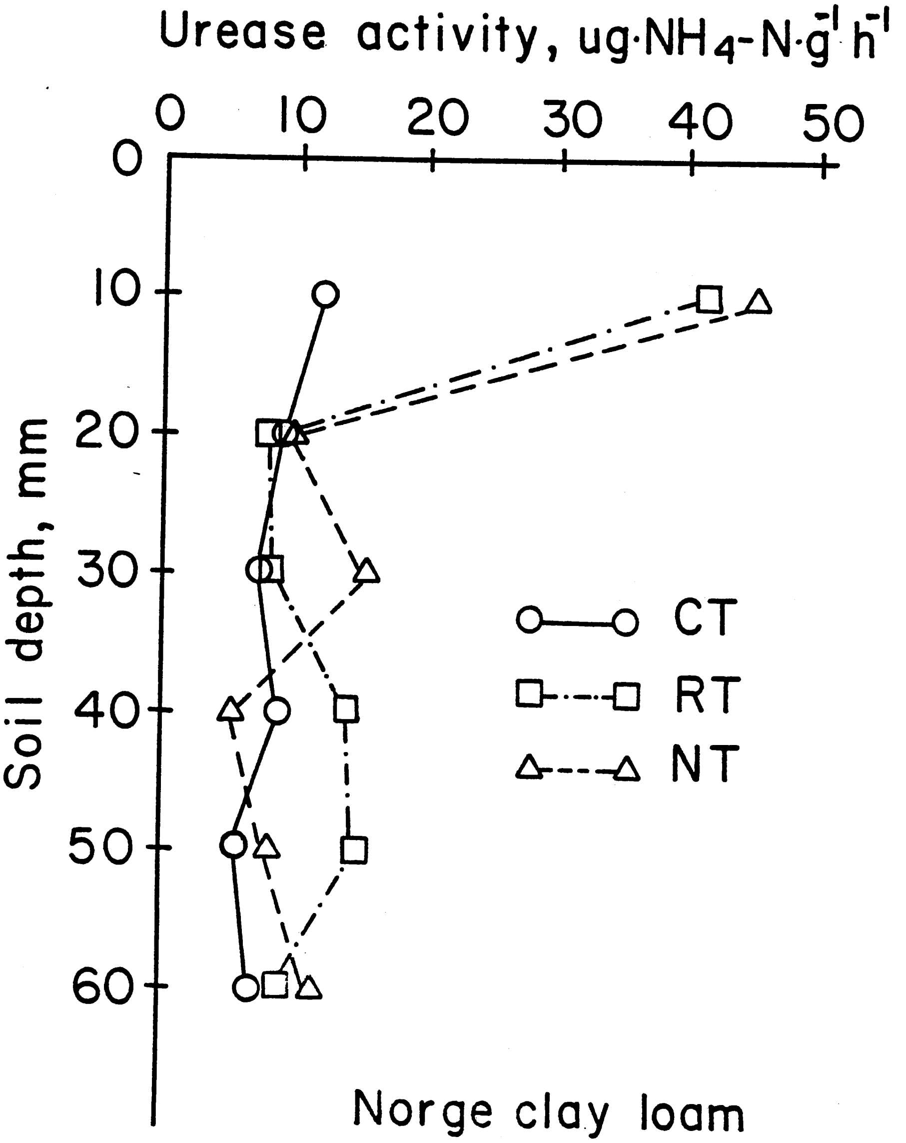

Fig. 1. Effect of residue management system on soil urease activity of Norge clay loam

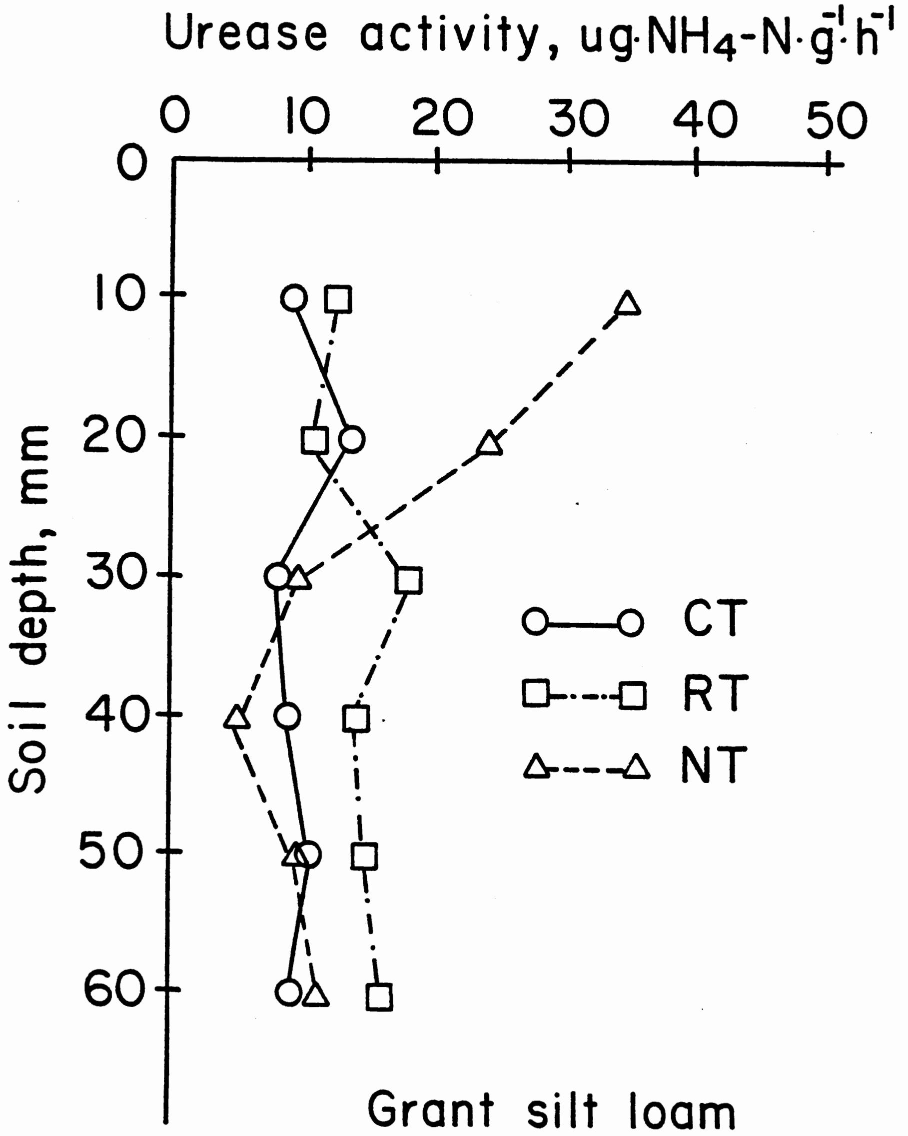

Fig. 2. Effect of residue management system on soil urease activity of Grant silt loam

Under CT urease activity distribution in both soils was uniform over the entire depth range while in RT urease distribution depended on the soil. Reduced tillage samples from Grant sil showed regular distribution of soil urease activity with depth. However, RT samples from Norge cl showed high urease activity in the top 10 mm of soil. Comparisons of urease activity between soils revealed significant differences between RT only on the 0 to 100 mm depth as shown in table 4. There appeared to be a direct relationship between the presence of residue in the soil samples and the increase in urease activity.

Addition of urease to soil has been shown to increase soil urease activity at least on a temporary basis (Conrad, 1942; Stojanovic, 1959; Moe, 1967; Zantua and Bremner, 1976). However, urease activity in soil can also increase due to microbial activity during decomposition (Zantua and Bremner, 1976; Goos, 1985). Doran, (1980) reported increases in microbial activity at the surface of soils under reduced and no till management.

Urease activity measured in undecomposed wheat straw was 376 ug NH_4-N g^{-1} h^{-1} which is approximately 28 times greater than the average activity of soil. This agrees with results by Torello and Wehner (1983) on Kentucky bluegrass turf (*Poa pratensis* L.). High urease activity in wheat residue suggests that the observed increases in soil activity are related to urease addition where the residue itself

TABLE 4. SINGLE DEGREE OF FREEDOM CONTRASTS OF UREASE ACTIVITY BETWEEN SOILS

Norge clay loam vs. Grant silt loam		
Contrast	Sum of Squares	F Value
CT		
0 - 10 mm.	11.05	0.09
11 - 20 mm.	58.99	0.50
21 - 30 mm.	2.67	0.02
31 - 40 mm.	0.40	0.00
41 - 50 mm.	56.07	0.48
51 - 60 mm.	9.52	0.08
RT		
0 - 10 mm.	1675.28	14.23 **
11 - 20 mm.	21.03	0.18
21 - 30 mm.	203.21	1.73
31 - 40 mm.	0.07	0.00
41 - 50 mm.	0.02	0.00
51 - 60 mm.	114.40	0.97
NT		
0 - 10 mm.	208.49	1.77
11 - 20 mm.	436.90	3.71
21 - 30 mm.	63.48	0.54
31 - 40 mm.	0.00	0.00
41 - 50 mm.	6.71	0.06
51 - 60 mm.	0.99	0.01

*, ** Indicates significance using Error (b)= 117.73 with 10 df at 0.05 and 0.01 probability level, respectively.

contained the enzyme. Greater urease activity can increase the rate of urea hydrolysis increasing the potential for ammonia volatilization. McInnes et al. (1986), indicated the direct relationship between ammonia volatilization and the pattern of urea hydrolysis.

Urea hydrolysis occurring at the soil-residue interface can increase the potential for ammonia volatilization since residue has little adsorption capacity for NH_4^+. Since urea can move freely with percolating water, hydrolysis is likely to occur deeper into the soil (Fenn and Miyamoto, 1981). However, NH_4^+, due to its charge, is likely to diffuse more slowly and to remain closer to the soil surface where it might be lost as NH_3-N.

CONCLUSION

These results support the idea that soil urease activity under RT and NT management can increase from addition of residue over several years. They also point to wheat residue as the source of the observed increase in enzymatic activity.

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CHAPTER II

Effect of Wheat Straw on Ammonia Volatilization From Surface-Applied Urea

ABSTRACT

Laboratory experiments were conducted to determine the effect of surface wheat residue on NH_3-N volatilization from urea. Urea was applied to the surface of Norge clay loam (fine, silty, mixed, thermic Udic Paleustoll) and Grant silt loam, (fine, silty, mixed, thermic Udic Argiustoll) at rates equivalent to 84, 168, and 252 kg N ha^{-1}. Urea-N treatments were applied to both bare and mulched soils. Ammonia loss, soil NH_4-N, and NO_3-N were monitored over selected time intervals following urea application. Results indicated that wheat residue on the soil surface affected the pattern and magnitude of NH_3-N loss. Two ammonia volatilization patterns were observed for mulched and bare soil. Ammonia loss from bare soil started slow and increased to a maximum between 3 to 6 d after urea application. In mulched soil, the rate of NH_3-N volatilization was highest during the first day and was followed by a steady decline with time to almost zero after 7 d. Similar patterns of NH_3-N volatilization were observed in undisturbed soil cores fertilized with 224 kg N ha^{-1} from soils which had been under conventional-till (CT) and no-till (NT) for four years. Ammonia volatilization losses averaged 6.7 and 12.7% of the applied urea-N for soils in CT and NT, respectively. Differences in rate of NH_3-N volatilization for CT and NT soils appeared due to changes in the rate of urea hydrolysis. Urea hydrolysis averaged over soils was 45% of the applied N in the initial 24 h after urea application in NT soils while only 16% was hydrolyzed in CT soils. Differences in the pattern of NH_3-N loss were directly related to changes in the pattern of urea hydrolysis as a result of increased urease activity from residue additions.

Additional Index Words: urease, N immobilization, urea hydrolysis, inorganic N, tillage, wheat residue.

INTRODUCTION

Research regarding the ammonia volatilization loss process has received considerable interest in the past 25 years. Terman (1979) and Freney et al. (1983) provided literature reviews on the loss of NH_3 from surface applications of urea. For the most part, the study of the ammonia volatilization process has been conducted as a systematic study of soil and environmental components under laboratory conditions (Terman, 1979; McInnes et al., 1986; Young, 1978). Among the most important soil factors cited are soil pH (Du Plessis and Kroontje, 1964; Ernst and Massey, 1960), soil moisture (Ernst and Massey, 1960; Chao and Kroontje, 1964; Fenn and Escarzaga, 1976), soil temperature (Ernst and Kroontje, 1960; Fenn and Kissel, 1974), cation exchange capacity (Fenn and Kissel, 1976), urease activity (Terman, 1979), $CaCO_3$ content (Fenn and Kissel, 1975; Stumpe et al., 1984), and hydrogen buffering capacity (Ferguson et al., 1984; Avnimelech and Laher, 1977). Other environmental factors include rate of soil drying (Chao and Kroontje, 1964; Volk, 1959), depth of fertilizer placement (Fenn and Kissel, 1976; Nommik, 1973; Overrein and Moe, 1967), and rate of N application (Fenn and Kissel, 1974; Overrein and Moe, 1967).

The mechanism of ammonia volatilization following urea application to soil can be summarized as follows.

$$CO(NH_2)_2 + 2H^+ + 2H_2O \xrightarrow{\text{urease}} 2NH_4^+ + H_2CO_3$$

Soon after application, urea is hydrolyzed by the enzyme urease. The products of this reaction are ammonium ion and one or more carbon species. The reaction consumes hydrogen ions therefore an increase in soil pH is usually observed (Ferguson et al., 1984; Overrein and Moe, 1967; Young, 1978). When a given ammonium ion concentration is established, the fraction of applied ammonium ion that is in the form of ammonia is determined by the pH of the soil solution, rate of N application, depth of movement into the soil, and buffering capacity (Avnimelech and Laher, 1977; Young, 1978). An equilibrium partial pressure of ammonia that is a function of the ammonium ion concentration in the soil solution is established in the air over the soil to maintain the equilibrium described by Henry's Law (Nelson, 1982). In the soil solution, the equilibrium of ammonium ion, H ion, and ammonia concentration may be generalized by the following reaction.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \quad k = 1.75 \times 10^{-5}$$

This reaction indicates that the larger the increase in the concentration of ammonium ion, the larger concentration of ammonia in the soil solution will be present at a given solution pH.

Research has demonstrated that ammonia volatilization from urea is mainly a surface application problem as it has been repeatedly shown that adequate incorporation of fertilizer with soil can significantly reduce gaseous losses (Bouwmeester et al., 1985; Fenn and Miyamoto, 1981; Terman, 1979; Young, 1978). However, in reduced and no-till management, urea fertilizer is generally broadcast on undecomposed organic residues lying on the soil surface (Keller and Mengel, 1986). Since the fertilizer remains unincorporated, significant NH_3 losses can occur (Bandel et al., 1980; Harding et al., 1963; Keller and Mengel, 1986; Meyer et al., 1961; Mengel et al., 1982).

Residue accumulation on the soil surface can affect soil properties and the availability of plant nutrients (Doran, 1980). Keller and Mengel (1986), indicated lower use efficiency of urea when applied directly on the surface residue in no-till corn. They indicated that ammonia volatilization might account for the lower efficiency observed when using urea. Volk (1959) reported significant losses of NH_3 when urea was broadcast over turf. Moe (1967) showed that changes in the rate of ammonia volatilization loss occurred as a result of surface urea application over fresh corn mulch. Meyer et al. (1961) indicated significant losses of NH_3 from urea-ammonium nitrate solutions when broadcast over wheat straw residue. Nelson et al. (1980) reported greater NH_3 volatilization when urea was applied to turf than when urea was applied to bare soil. Hargrove et al. (1987) reported that as much as 41% of applied urea-N could be lost as NH_3 within 7 d after application to mulched soil. McInnes et al. (1986) indicated close relationship between the pattern of urea hydrolysis and ammonia loss. Titko et al. (1987) indicated that as much as 60% of surface applied urea-N could be lost through volatilization upon application to turfgrass. Hargrove et al. (1987) summarized the effect of crop residues in increasing NH_3 loss from urea by portraying their role in preventing physical access to the soil, maintaining continuous moist conditions on the soil surface, and increasing urease activity.

Urease activity associated with crop residues has been reported by Frankenberger and Tabatabai (1982), Torello and Wehner (1983), and Goos (1985). Biological activity resulting from decomposition of carbonaceous materials on the soil surface has been shown to increase urease activity in soil (Zantua and Bremner, 1976).

The presence of a mulch over the soil surface can increase NH_3 loss from urea as a result of inadequate contact of hydrolysis products with the underlying soil. However, the degree to which residue management modifies the profile distribution of N fractions and how both interact to increase NH_3 loss from urea has not been adequately documented. Therefore, three laboratory experiments were planned to attain the following objectives:

1) To evaluate the effect of wheat straw mulching on NH_3 loss and soil mineral N in soils fertilized with several urea-N rates.

2) To evaluate NH_3 loss and rate of urea hydrolysis on the movement of urea hydrolysis products following surface application of urea to soils which have been under clean- and no-till residue management for over four years.

MATERIALS AND METHODS

Experiments No.1 and 2

Bulk soil samples (0 to 15 cm) of Norge clay loam (fine-silty, mixed, thermic Udic Paleustoll) and Grant silt loam (fine silty, mixed, thermic Udic Argiustoll) were collected from the Agronomy Research Station at Stillwater, Oklahoma and the North Central Agronomy Research Station at Lahoma, Oklahoma, respectively, in the spring of 1985. Table 1. shows selected chemical properties of the soils used in the study. Soils were air dried and screened to pass a 2 mm sieve. Following the 1985 wheat harvest, straw from winter wheat (*Triticum aestivum* L. TAM W 101), was collected at Stillwater. The straw was chopped, screened to pass a 5 mm sieve, dried at 40 C, and stored in a closed container.

The ammonia volatilization apparatus consisted of an acid scrubber, a conditioning chamber, a volatilization chamber, and an ammonia collection flask. The system is illustrated in Fig. 1. Compressed air was scrubbed through 0.125 M H_2SO_4, passed through a conditioning flask containing distilled deionized water, and blown in the enclosed vapor space inside the volatilization chamber which contained the soil sample. The resulting ammonia-carrying air stream was bubbled into 40 ml of 2% boric acid solution

TABLE 1. SELECTED CHEMICAL PROPERTIES OF THE SOILS USED IN THE STUDIES

Soil	pH 1:1	Total-N g kg^{-1}	Organic C g kg^{-1}	P	K
				kg ha^{-1}	
Norge clay loam	5.6	0.90	9.8	81	546
Grant silt loam	5.8	1.10	11.2	60	658

Total N methodology by Bremner (1965)
Organic C methodology by Nelson and Sommers (1982)
P and K indices determined using Bray and Kurtz (1945) no. 1 extract (1:20) dilution and 1 M neutral NH_4OAc (Knudsen et al., 1982), respectively.

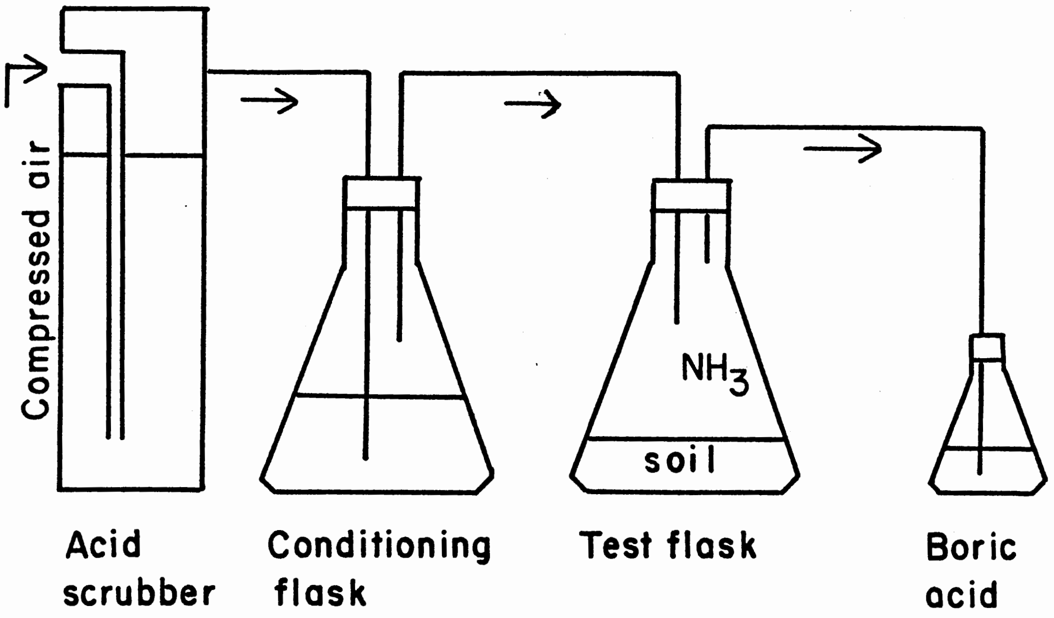

Fig. 1. Laboratory apparatus used to measure NH_3-N volatilization from urea in experiments No.1 and 2

to collect volatilized ammonia. Sixteen volatilization systems were assembled, tested for air leaks, and connected to the compressed air source. Compressed air connected to each one of the assembled systems was calibrated to deliver a flow rate of 1.5 L min^{-1}. Air flow rate was monitored twice daily using a Visi-Flow flowmeter (model VFB-65, Dwyer Instruments, Inc.) and adjusted when necessary. The air volume above the soil inside the volatilization chamber was approximately 600 cc. The rate of volume exchange was approximately 2.5 chamber volumes per minute.

In experiment No 1, 500 g of oven dried soil was placed into eight 1 L erlenmeyer flasks. In experiment No 2, Nalgene plastic tubes 2.5 cm in diameter were cut to 5 cm in length and filled with 25 g of oven dried soil. Six tubes supported by a foam rubber stand were placed inside each of eight volatilization chambers. The soil inside each system was leveled by gently shaking it until the surface was even. Enough deionized distilled water was added to bring the soil to -33 kPa soil moisture content (20% water by weight). An amount of dry wheat residue equivalent to 3.9 Mg ha^{-1} was applied evenly over the exposed soil surface for treatments requiring mulching. The amount of residue required for treatment was calculated on the basis of exposed surface area for each experiment. In each case, it resulted in a mulch layer of approximately 2 mm thick. Chambers from experiment No. 1 received 5 ml of water and those from experiment No. 2 received 0.25 ml of water as a fine mist covering the entire soil surface. Following equilibration for 48 h, urea solutions were prepared and applied to deliver 0, 43.1, 86.2, and 129.2 ug N g^{-1} of soil. These rates were equivalent to 0, 84, 168, and 252 kg N ha^{-1} for both experiments. After boric acid collecting flasks were installed, all systems were immediately closed and timing started. In both experiments, boric acid traps were collected every 24 h during the 14 d span of the experiment. Boric acid traps were analyzed for NH_3-N content by titration with standardized H_2SO_4. In experiment No. 2, a plastic tube was removed from each system at selected time intervals of 1, 3, 5, 7, 9, and 11 d. Soil samples were immediately extracted with 2 M KCl containing phenylmercuric acetate (a urease inhibitor). Samples were analyzed for NH_4-N, NO_2-N, and NO_3-N using Technicon Autoanalyzer methodology (Henriksen and Selmer-Olsen, 1970; Selmer-Olsen, 1971).

Due to the number of treatments and limitations in the number of volatilization systems, only one complete replication or block for each soil could be conducted for a given two week period. In each block, treatment combinations were assigned at random to each one of the eight volatilization systems. The experiment was conducted as a split plot in time with the main units (N rates applied over mulched or bare soil) in factorial arrangement and sampling times as the main plot subunits. Data were analyzed statistically using ANOVA procedures of the SAS Institute (Statistical Analysis System Institute, 1982).

Experiment No. 3

Soil samples from two established field experiments at the North Central Research Station at Lahoma, Oklahoma and the Agronomy Research Station at Stillwater, Oklahoma were collected in the fall of 1986. Thirty two cores from each soil were taken from plots which had been under conventional (CT) and no-till (NT) treatments since 1982. Soils were collected within 48 h of a saturating rain to obtain samples with adequate moisture. Prior to sampling, all standing residue was removed. Intact soil cores, 5 cm in diameter and 7.5 cm deep were taken and encased in aluminum cylinders. Soil samples were sealed in the field using plastic lids and taken to the lab where they were kept frozen until needed.

The ammonia volatilization apparatus used in this experiment was a modification of the system previously described. A diagram illustrating the volatilization system is shown in Fig. 2. The major modification consisted in the type of volatilization chamber used. Plastic bottles (500 cc), fitted with rubber stoppers with holes for air inlet and outlet, were carefully cut in half. A soil sample

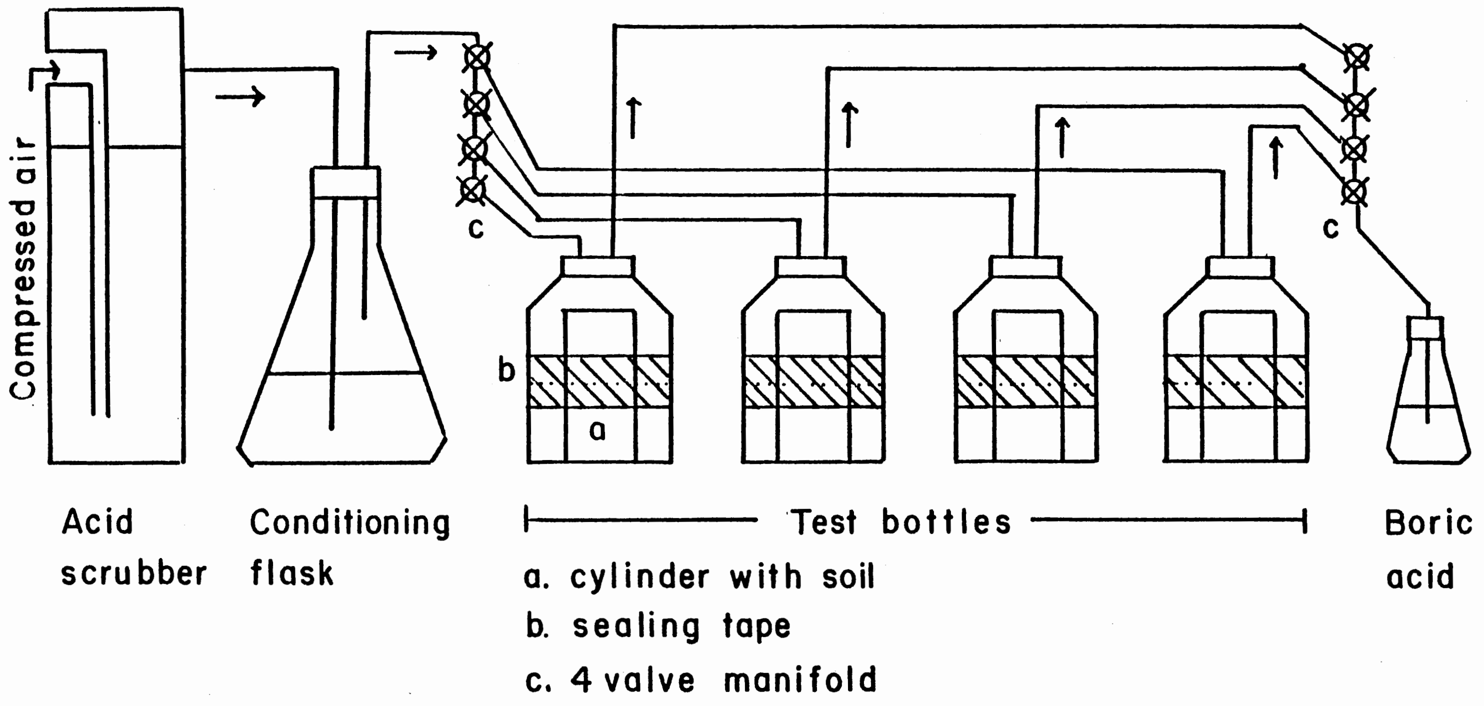

Fig. 2. Laboratory apparatus used to measure NH_3-N volatilization from urea in experiment No.3

contained in an aluminum cylinder was placed inside each plastic bottle and the bottle carefully sealed around the cut seam using wide plastic tape. A manifold provided with four controlling valves was fitted with plastic tubing and connected to the inlet coming from the conditioning chamber. The manifold allowed separation of a single air stream into four individual streams each connected to each of the four volatilization chambers. The stopper on each chamber had a piece of tubing which was connected to a second four-valve manifold. Every time a soil sample was taken, the inlet valve corresponding to the chamber to be sampled was closed. The individual air stream arrangement allowed uninterrupted air flow for the remaining chambers in the system every time a soil had to be sampled. The air stream coming out of the second manifold bubbled into 40 ml of 2% boric acid solution. The procedure used to regulate and monitor the air delivery system was identical to the one used for experiments 1 and 2. However, the volume exchange rate was set at 7.5 chamber volume per minute which was three times higher than the one used in experiments No. 1 and No. 2.

Eight systems were assembled which provided four replications of the two tillage treatments for a given soil. Treatment combinations were randomly assigned to each of the eight systems. Forty eight h prior to initiation of the experiment, each chamber received 2 ml of water applied over the soil surface. A watch glass was used to tap over the surface. This was necessary to provide an even surface in no-till treatments whose surface had been disturbed due to residue sticking to the plastic lid used to seal each cylinder. Urea-N solution was prepared to deliver 224 Kg N ha^{-1} calculated on a surface basis. The N fertilizer treatment was applied in 0.5 ml of solution applied evenly over the exposed soil surface. At selected time intervals of 1, 3, 5, and 7 d following urea application, a soil core was taken from each of the eight systems. Soil cores from were separated into 15 mm increments and screened to pass a 2 mm sieve. Samples were immediately taken for water calculations. A soil sample of moist soil from each layer was weighed and extracted in 2 M KCl containing 5 ug g^{-1} of phenyl mercuric acetate (a urease inhibitor). Soil leachates were stored in the refrigerator at 5 C prior to being analyzed for NH_4-N and NO_3 using Technicon Autoanalyzer methodology (Henriksen and Selmer-Olsen, 1970; Selmer-Olsen, 1971).

The experiment was conducted as a split plot in time with soils and tillage levels in the main plots, soil depths in the subplots and sampling times in the sub-subplots. Data were analyzed statistically using ANOVA procedures of the SAS Institute (Statistical Analysis System Institute, 1982).

RESULTS AND DISCUSSION

Experiment No. 1

Effect of N Rates and Mulching on NH_3-N Loss

Ammonia volatilization was significantly affected by N rate, mulching, and time of incubation as indicated in the analysis of variance table presented in Table 2. The effect of urea-N rate on the rate of ammonia loss is illustrated in Figs. 3 and 4 for bare and mulched soil, respectively. These data indicate that both, the quantity and pattern of ammonia volatilization were affected by N rate and the presence of mulch. Ammonia loss from check treatments (no N applied) remained undetectable over the two week incubation period.

The pattern of NH_3-N loss from urea applied to bare soil displayed a slow build up during the early stages of incubation reaching a maximum between 5 to 8 d. The time of maximum NH_3-N loss rate depended on N rate. Ammonia loss decreased with time reaching very low levels (<1% of applied N) by two weeks. Ammonia volatilization in the presence of mulch reached a maximum during the first two days of incubation and was followed by a steady decline with time. Less than 0.5 % of applied N was lost by the end of 1 week.

TABLE 2. ANALYSIS OF VARIANCE TABLE FOR RATE OF NH_3-N LOSS FROM EXPERIMENT NO.1

Source	df	Mean square	F value	
Rep	2	0.424		
Soil	1	0.145	1.00	
N Rate	3	22.091	153.31	**
Mulch	1	29.14	202.24	**
Soil x N rates	3	0.078	0.54	
Soil x Mulch	1	0.347	2.41	
N rate x Mulch	3	8.162	56.64	**
Soil x N rate x Mulch	3	0.088	0.61	
Error (a)	30	0.144		
Time	13	6.069	113.90	**
Error (b)	26	0.053		
Soil x Time	13	0.055	1.66	
N rate x Time	39	1.435	43.44	**
Mulch x Time	13	6.891	208.65	**
Error (c)	130	0.033		
N rate x mulch x Time	39	1.789	73.77	**
Soil x Mulch x Time	13	0.045	1.84	
Soil x N rate x Time	39	0.029	1.21	
Soil x N rate x Mulch x Time	39	0.035	1.46	
Error (d)	260	0.024		

df - degrees of freedom

*, ** - Significant at 0.05 and 0.01 probability level, respectively.

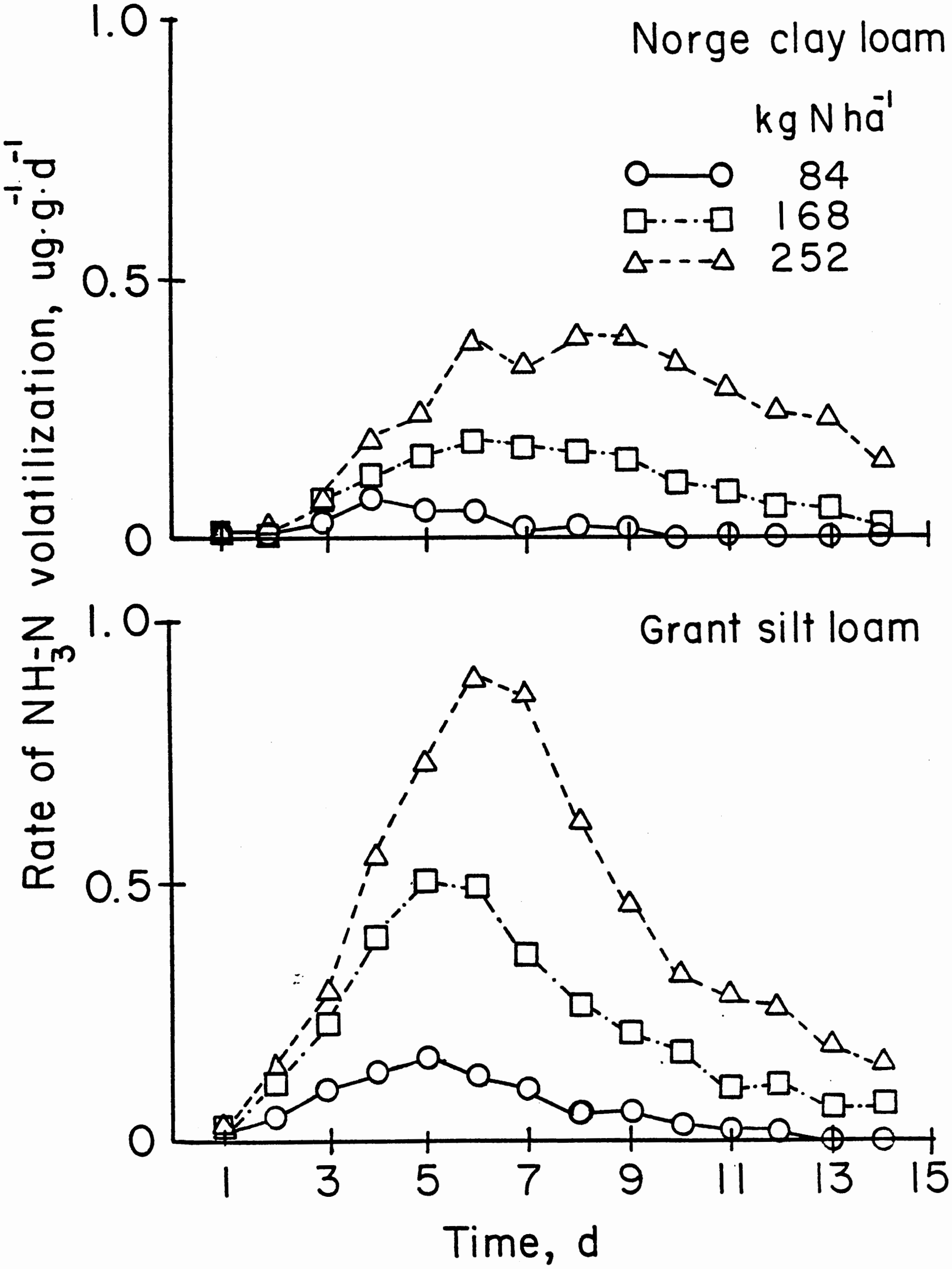

Fig. 3. Effect of urea-N rates applied to bare soil on NH_3-N volatilization over time for Norge clay loam and Grant silt loam

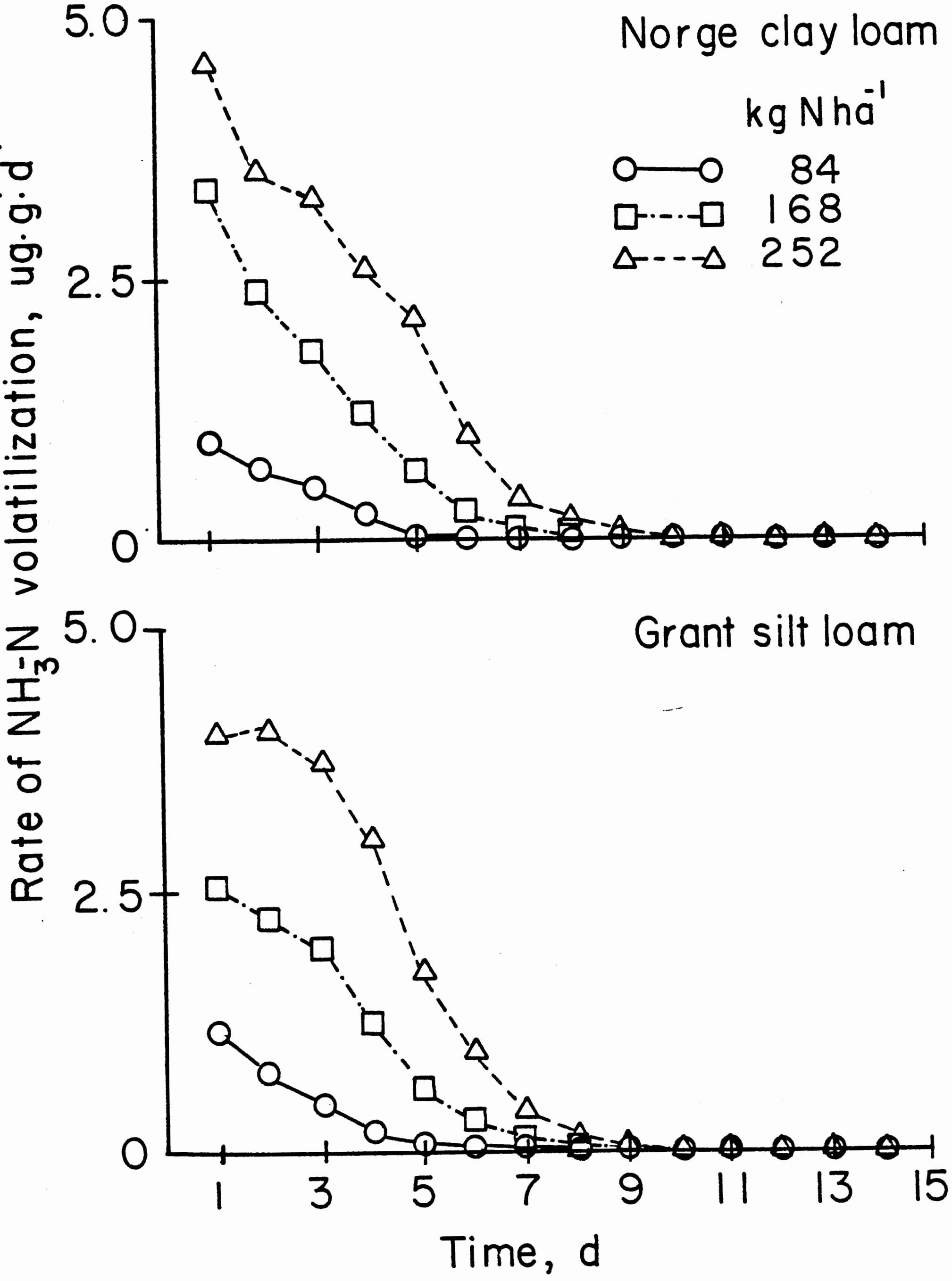

Fig. 4. Effect of urea-N rates applied to mulched soil on NH_3-N volatilization over time for Norge clay loam and Grant silt loam

Volatilization patterns for bare and mulched soil appeared consistent across soils for all N rates. Analysis of variance table for cumulative (14 d) NH_3-N losses is presented in Table 3. There were no differences in total NH_3-N loss between soils. Means averaged over soils for cumulative NH_3-N losses as affected by N rate and mulch are presented in Table 4. Total ammonia loss increased with N rate. However, mulched soils lost significantly more NH_3-N than did bare soils. Total NH_3-N loss from both soils ranged from 1.5 to 14.1 % of applied N. Ammonia loss from urea applied to bare soil was less than 5% of applied N regardless of N rate.

Urea applied to wheat straw hydrolyses very fast due to high urease activity in residue. This causes soil NH_4-N concentration to elevate rapidly increasing the potential for NH_3 volatilization (Hargrove et al., 1987; Moe, 1967). When urea was applied to bare soil, lower urease activity of soil with respect to residue allowed urea to diffuse into the soil. This resulted in hydrolysis occurring within the soil rather than at the soil surface which increased the possibility of NH_4^+ being adsorbed by the soil, immobilized, or nitrified.

TABLE 3. ANALYSIS OF VARIANCE TABLE FOR CUMULATIVE NH_3-N LOSS (14 D) FROM EXPERIMENT NO.1

Source	df	Mean square	F value	
Rep	2	7.899		
Soil	1	2.711	1.05	
N Rate#	2	280.562	108.97	**
Mulch	1	543.977	211.28	**
Soil x N rates	2	1.319	0.51	
Soil x Mulch	1	6.554	2.55	
N rate x Mulch	2	103.437	40.18	**
Soil x N rate x Mulch	2	1.047	0.41	
Error	22	2.575		

Check treatments (no N applied) were excluded.
*, ** - Denote significance at 0.05 and 0.01 probability level, respectively.

TABLE 4. CUMULATIVE NH_3-N LOSS (14 D) AS AFFECTED BY N RATE AND MULCHING FOR EXPERIMENT NO.1.

	Cumulative NH_3-N loss after 336 h $\mu g\ g^{-1}$	
N rate $Kg\ ha^{-1}$	Mulched Soil	Bare Soil
84	2.8 (6.5)#	0.7 (1.5)
168	9.7 (11.2)	2.4 (2.7)
252	18.3 (14.1)	4.5 (3.4)
LSD (0.05)	2.7	

numbers in parenthesis represent NH_3-N loss as % of urea-N applied.

Experiment No. 2

Effect of N Rates and Mulching on Soil NH_4-N

Initial concentrations of soil NH_4-N were 35.4 and 65.7 ug g^{-1} respectively, for Norge cl and Grant sil. The analysis of variance table for soil NH_4-N as affected by Nrate, mulching, and time is presented in Table 5. Soil NH_4-N as affected by treatments is illustrated in Figs. 5 and 6 for Norge cl and Grant sil, respectively. A significant N rate x mulch x time interaction ($P < .001$) constrains any generalizations about main factor effects. However, single degree of freedom comparisons were used with means across blocks for each sampling time as a method for determining treatment differences. These comparisons are presented in Tables 6, 7, 8, 9, 10, and 11 for 1, 3, 5, 7, 9, and 11 d of incubation, respectively.

During the first day of incubation there were differences between check and fertilized treatments indicating that urea was significantly hydrolyzed as early as 24 h after application in both soils. However, differences among N rates were not yet apparent indicating that hydrolysis was not yet complete. Samples taken at 3 d indicated significant linear effect due to N rates but no effect due to mulch. Comparisons among N rates in Norge cl showed no significant differences among N rates on either mulched or bare soil. However, significant differences

TABLE 5. ANALYSIS OF VARIANCE TABLE FOR SOIL NH_4-N FROM EXPERIMENT NO.2

Source	df	Mean square	F value	
Rep	2	805.31		
Soil	1	95826.76	278.52	**
N Rate	3	119335.86	346.85	**
Mulch	1	1853.14	5.39	**
Soil x N rates	3	1932.39	5.62	**
Soil x Mulch	1	335.12	0.97	
N rate x Mulch	3	96.02	0.27	
Soil x N rate x Mulch	3	44.80	0.13	
Error (a)	30	344.05		
Time	5	18482.48	77.26	**
Error (b)	10	239.21		
Soil x Time	5	459.29	5.44	**
N rate x Time	15	2698.02	31.95	**
Mulch x Time	5	967.10	11.45	**
Error (c)	50	84.43		
N rate x mulch x Time	15	196.87	3.94	**
Soil x Mulch x Time	5	56.11	1.12	
Soil x N rate x Time	15	114.31	2.29	*
Soil x N rate x Mulch x Time	15	45.80	0.92	
Error (d)	100	49.92		

df - degrees of freedom

*, ** - Denote significance at 0.05 and 0.01 probability level, respectively

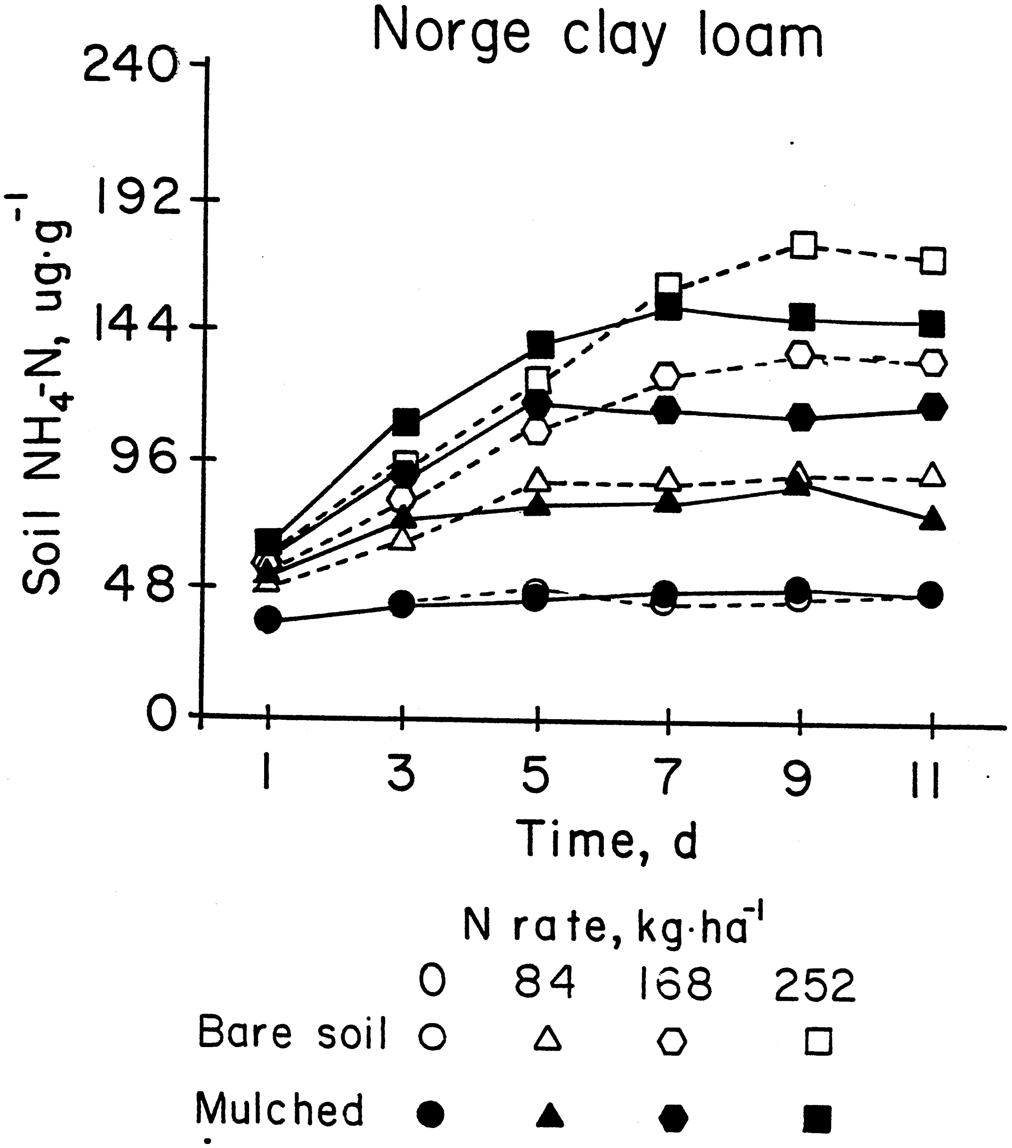

Fig. 5. Effect of urea-N rates and mulch on soil NH_4-N with time in Norge clay loam

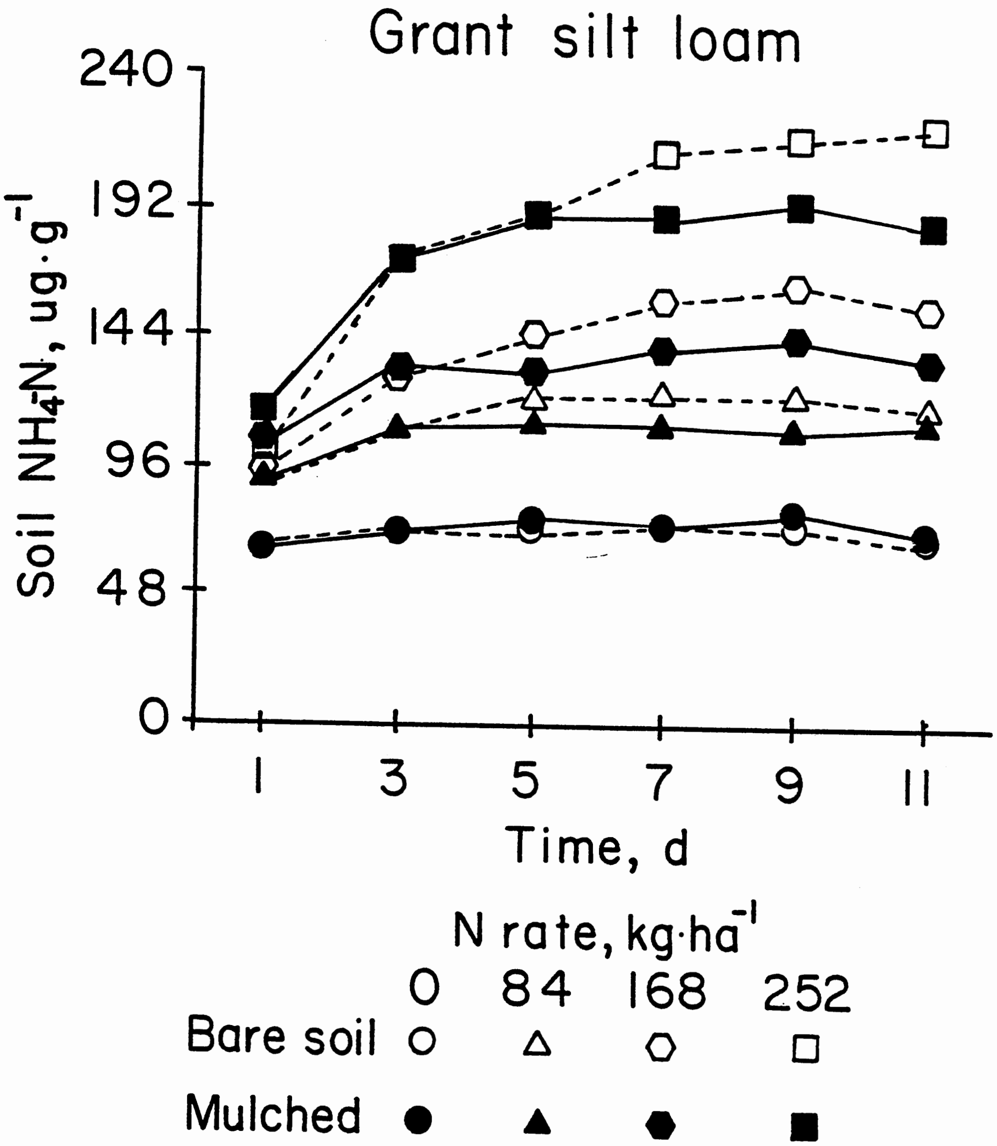

Fig. 6. Effect of urea-N rates and mulch on soil NH_4-N over time in Grant silt loam

TABLE 6. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 1 D INCUBATION

Contrast	df	sum of squares	F value
Norge clay loam			
- Orthogonal -			
Bare soil vs. mulch	1	91.014	0.26
Rates (linear)	1	1986.006	5.77 *
Rates (quadratic)	1	172.169	0.50
Rates (cubic)	1	64.778	0.19
Mulching x rate (l)	1	16.297	0.05
Mulching x rate (q)	1	1.972	0.01
Mulching x rate (c)	1	4.048	0.01
- Non Orthogonal -			
Check vs. Fertilized	1	1951.282	5.67 *
Bare : 84 vs. 168	1	25.129	0.07
Bare : 168 vs. 252	1	34.849	0.10
Mulch: 84 vs. 168	1	16.965	0.05
Mulch: 168 vs. 252	1	65.677	0.19
Fertilized: Bare soil vs. Mulch	1	110.053	0.32
Grant silt loam			
- Orthogonal -			
Bare soil vs. mulch	1	153.015	0.44
Rates (linear)	1	5934.642	17.25 **
Rates (quadratic)	1	359.306	1.04
Rates (cubic)	1	74.258	0.22
Mulching x rate (l)	1	259.696	0.75
Mulching x rate (q)	1	1.018	0.00
Mulching x rate (c)	1	0.662	0.00
- Non Orthogonal -			
Check vs. Fertilized	1	5305.839	15.42 **
Bare : 84 vs. 168	1	53.229	0.15
Bare : 168 vs. 252	1	61.748	0.18
Mulch: 84 vs. 168	1	243.194	0.71
Mulch: 168 vs. 252	1	235.501	0.68
Fertilized: Bare soil vs. Mulch	1	274.155	0.80

F values were calculated using mean square error(A) = 344.1 with 30 df.

TABLE 7. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 3 D INCUBATION

Contrast	df	sum of squares	F value
Norge clay loam			
- Orthogonal -			
Bare soil vs. mulch	1	574.096	1.67
Rates (linear)	1	10967.175	31.88 **
Rates (quadratic)	1	275.790	0.80
Rates (cubic)	1	73.163	0.21
Mulching x rate (l)	1	313.229	0.91
Mulching x rate (q)	1	9.575	0.03
Mulching x rate (c)	1	15.455	0.04
- Non Orthogonal -			
Check vs. Fertilized	1	8633.309	25.09 **
Bare : 84 vs. 168	1	267.614	0.78
Bare : 168 vs. 252	1	218.165	0.63
Mulch: 84 vs. 168	1	360.980	1.05
Mulch: 168 vs. 252	1	533.946	1.55
Fertilized: Bare soil vs. Mulch	1	841.320	2.45
Grant silt loam			
- Orthogonal -			
Bare soil vs. mulch	1	2.209	0.01
Rates (linear)	1	31879.964	92.66 **
Rates (quadratic)	1	3.301	0.01
Rates (cubic)	1	421.279	1.22
Mulching x rate (l)	1	0.197	0.00
Mulching x rate (q)	1	42.032	0.12
Mulching x rate (c)	1	2.355	0.01
- Non Orthogonal -			
Check vs. Fertilized	1	20321.784	59.07 **
Bare : 84 vs. 168	1	636.355	1.85
Bare : 168 vs. 252	1	2920.259	8.49 **
Mulch: 84 vs. 168	1	733.676	2.13
Mulch: 168 vs. 252	1	2114.666	6.15 *
Fertilized: Bare soil vs. Mulch	1	7.778	0.02

F values were calculated using mean square error(A)= 344.1 with 30 df.

TABLE 8. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH$_4$-N AFTER 5 D INCUBATION

Contrast	df	sum of squares	F value
Norge clay loam			
- Orthogonal -			
Bare soil vs. mulch	1	50.052	0.15
Rates (linear)	1	24356.643	70.79 **
Rates (quadratic)	1	544.154	1.58
Rates (cubic)	1	5.268	0.02
Mulching x rate (l)	1	328.018	0.95
Mulching x rate (q)	1	29.965	0.09
Mulching x rate (c)	1	87.718	0.25
- Non Orthogonal -			
Check vs. Fertilized	1	18211.193	52.93 **
Bare : 84 vs. 168	1	530.160	1.54
Bare : 168 vs. 252	1	469.245	1.36
Mulch: 84 vs. 168	1	1908.844	5.55 *
Mulch: 168 vs. 252	1	721.387	2.10
Fertilized: Bare soil vs. Mulch	1	107.165	0.31
Grant silt loam			
- Orthogonal -			
Bare soil vs. mulch	1	232.560	0.68
Rates (linear)	1	39841.784	115.80 **
Rates (quadratic)	1	96.108	0.28
Rates (cubic)	1	981.844	2.85
Mulching x rate (l)	1	8.922	0.03
Mulching x rate (q)	1	127.914	0.37
Mulching x rate (c)	1	23.680	0.07
- Non Orthogonal -			
Check vs. Fertilized	1	24662.539	71.68 **
Bare : 84 vs. 168	1	686.940	2.00
Bare : 168 vs. 252	1	3030.349	8.81 **
Mulch: 84 vs. 168	1	441.698	1.28
Mulch: 168 vs. 252	1	5190.747	15.09 **
Fertilized: Bare soil vs. Mulch	1	215.696	0.63

F values were calculated using mean square error(A)= 344.1 with 30 df.

TABLE 9. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 7 D INCUBATION

Contrast	df	sum of squares	F value
		Norge clay loam	
- Orthogonal -			
Bare soil vs. mulch	1	293.307	0.85
Rates (linear)	1	40473.338	117.64 **
Rates (quadratic)	1	10.324	0.03
Rates (cubic)	1	0.895	0.00
Mulching x rate (l)	1	37.273	0.11
Mulching x rate (q)	1	32.762	0.10
Mulching x rate (c)	1	9.373	0.03
- Non Orthogonal -			
Check vs. Fertilized	1	24788.626	72.05 **
Bare : 84 vs. 168	1	2404.802	6.99 *
Bare : 168 vs. 252	1	1607.174	4.67 *
Mulch: 84 vs. 168	1	1780.927	5.18 *
Mulch: 168 vs. 252	1	2099.599	6.10 *
Fertilized:			
Bare soil vs. Mulch	1	340.527	0.99
		Grant silt loam	
- Orthogonal -			
Bare soil vs. mulch	1	914.542	2.66
Rates (linear)	1	50540.761	146.90 **
Rates (quadratic)	1	120.745	0.35
Rates (cubic)	1	305.474	0.89
Mulching x rate (l)	1	398.843	1.16
Mulching x rate (q)	1	12.373	0.04
Mulching x rate (c)	1	0.688	0.00
- Non Orthogonal -			
Check vs. Fertilized	1	29689.971	86.29 **
Bare : 84 vs. 168	1	1802.389	5.24 *
Bare : 168 vs. 252	1	4443.284	12.91 **
Mulch: 84 vs. 168	1	1199.638	3.49
Mulch: 168 vs. 252	1	3660.540	10.64 **
Fertilized:			
Bare soil vs. Mulch	1	1228.295	3.57

F values were calculated using mean square error(A)= 344.1 with 30 df.

TABLE 10. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 9 D INCUBATION

Contrast	df	sum of squares	F value
		Norge clay loam	
- Orthogonal -			
Bare soil vs. mulch	1	954.678	2.77
Rates (linear)	1	42835.268	124.50 **
Rates (quadratic)	1	40.529	0.12
Rates (cubic)	1	50.786	0.15
Mulching x rate (l)	1	627.891	1.82
Mulching x rate (q)	1	3.655	0.01
Mulching x rate (c)	1	120.745	0.35
- Non Orthogonal -			
Check vs. Fertilized	1	27500.050	79.93 **
Bare : 84 vs. 168	1	2967.305	8.62 **
Bare : 168 vs. 252	1	2297.088	6.68 *
Mulch: 84 vs. 168	1	813.636	2.36
Mulch: 168 vs. 252	1	1992.576	5.79 *
Fertilized: Bare soil vs. Mulch	1	1189.744	3.46
		Grant silt loam	
- Orthogonal -			
Bare soil vs. mulch	1	1415.854	4.12
Rates (linear)	1	53790.684	156.34 **
Rates (quadratic)	1	272.161	0.79
Rates (cubic)	1	111.134	0.32
Mulching x rate (l)	1	301.467	0.88
Mulching x rate (q)	1	0.089	0.00
Mulching x rate (c)	1	6.627	0.02
- Non Orthogonal -			
Check vs. Fertilized	1	29876.435	86.84 **
Bare : 84 vs. 168	1	2539.984	7.38 *
Bare : 168 vs. 252	1	4543.607	13.21 **
Mulch: 84 vs. 168	1	1535.040	4.46 *
Mulch: 168 vs. 252	1	3874.009	11.26 **
Fertilized: Bare soil vs. Mulch	1	1526.060	4.44 *

F values were calculated using mean square error(A)= 344.1 with 30 df.

TABLE 11. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 11 D INCUBATION

Contrast	df	sum of squares	F value
Norge clay loam			
- Orthogonal -			
Bare soil vs. mulch	1	1253.552	3.64
Rates (linear)	1	43382.609	126.09 **
Rates (quadratic)	1	0.512	0.00
Rates (cubic)	1	33.445	0.10
Mulching x rate (l)	1	288.626	0.84
Mulching x rate (q)	1	11.110	0.03
Mulching x rate (c)	1	21.739	0.06
- Non Orthogonal -			
Check vs. Fertilized	1	25682.278	74.65 **
Bare : 84 vs. 168	1	2613.717	7.60 **
Bare : 168 vs. 252	1	2289.346	6.65 *
Mulch: 84 vs. 168	1	2478.268	7.20 *
Mulch: 168 vs. 252	1	1553.329	4.51 *
Fertilized: Bare soil vs. Mulch	1	1505.907	4.38 *
Grant silt loam			
- Orthogonal -			
Bare soil vs. mulch	1	1369.374	3.98
Rates (linear)	1	55097.945	160.14 **
Rates (quadratic)	1	368.864	1.07
Rates (cubic)	1	515.891	1.50
Mulching x rate (l)	1	867.832	2.52
Mulching x rate (q)	1	44.791	0.13
Mulching x rate (c)	1	3.863	0.01
- Non Orthogonal -			
Check vs. Fertilized	1	31186.407	90.64 **
Bare : 84 vs. 168	1	2039.095	5.93 *
Bare : 168 vs. 252	1	6610.054	19.21 **
Mulch: 84 vs. 168	1	861.122	2.50
Mulch: 168 vs. 252	1	3993.376	11.61 **
Fertilized: Bare soil vs. Mulch	1	1703.295	4.95 *

F values were calculated using mean square error(A)= 344.1 with 30 df.

among N rates in Grant sil suggested that hydrolysis was more advanced in this soil.

A significant effect due to mulching (Table 5) suggested changes in urea hydrolysis in the presence of residue. Nevertheless, NH_3-N volatilization losses contributed to deplete the soil NH_4-N pool. Therefore, the measurement of NH_4-N alone provided an incomplete picture of the effect of mulch on urea hydrolysis. Indirect evidence of greater urea hydrolysis under mulch is provided by levels of soil NH_4-N which reached stable levels earlier in the incubation period under mulch while NH_4-N in bare soil continued to increase (Figs. 5 and 6). Leveling of soil NH_4-N would suggest completion of urea hydrolysis. After 11 d, lower soil NH_4-N was measured in mulched soils at N rates greater than 84 kg N ha^{-1} as presented in Table 12.

Soil NH_4-N expressed as % of applied N after 11 d and corrected for initial NH_4-N in untreated soil is presented in Table 13. Nitrogen immobilization at the surface of a mulched soil has been shown to be an important mechanism reducing N recovery by crops (Doran, 1980; Cochran et al., 1980; Rice and Smith, 1984). Lower soil NH_4-N from mulched soils might reflect greater NH_3-N loss and/or immobilization of NH_4-N. Whether or not NH_3-N volatilization and/or immobilization were responsible for lower NH_4-N under mulch cannot be directly answered from the results of experiment No. 2 alone due to difficulties encountered in the

TABLE 12. SOIL NH_4-N AS AFFECTED BY N RATE AND MULCH AFTER 11 D INCUBATION

Treatment	N rate kg ha^{-1}		
	84	168	252
	Norge clay loam		
Bare soil	91.6	133.3	172.4
Mulched	76.3	117.0	149.2
Difference	15.3	16.3	23.2
	Grant silt loam		
Bare soil	118.4	155.3	221.6
Mulched	112.5	136.4	188.0
Difference	5.9	18.8	33.6

TABLE 13. NH_4-N RECOVERY AS % OF APPLIED N AFTER 11 D INCUBATION

Treatment	N rate kg ha^{-1}		
	84	168	252
	Norge clay loam		
Bare soil	98.4	97.6	95.3
Mulched	69.8	82.1	79.6
	Grant silt loam		
Bare soil	105.0	95.3	114.9
Mulched	96.1	75.9	90.5

assessment of NH_3-N losses. Although ammonia measurements were conducted in experiment No.2, the results became unreliable after the second soil sampling (3 d). It appeared that the amount of soil left in the volatilization chambers after removal of 2 soil samples, would not volatilize enough NH_3-N to be picked up during titration. However, correlation data from experiments No. 1 and 2 over the first 2 d of incubation indicated close agreement on NH_3-N loss from mulched soils. The correlation coefficient between ammonia loss from mulched treatments for experiment No. 1 and No. 2 for the first 2 d incubation was 0.98.

Based on results from experiment No. 1, NH_3-N loss could account for some of the differences in soil NH_4-N between mulched and bare soil observed in experiment No. 2. The remaining N unaccounted for might have been immobilized by microorganisms active in the decomposition of the residue.

Effect of N Rates and Mulching on Soil NO_3^--N

Nitrification of applied N was low during the 11 d of incubation. The analysis of variance table is presented in Table 14. Although significant effects due to soil, N rates, and time were observed, the magnitude of changes in NO_3-N among treatments for each soil was very small. Soil NO_3-N values in the experiment ranged from 1.2 to 4.0 ug g^{-1} and from 10.9 to 15.2 ug g^{-1} for Norge cl and Grant sil, respectively. Since changes in soil NO^3-N due to treatments were very small compared to changes in other N fractions such as NH_4-N or NH_3-N, it was assumed that nitrification was negligible during the span of the experiment and no detailed analysis of treatment differences were conducted.

Soil NO_3-N averaged over N rates, time, and mulch treatments were 2.8 and 13.8 ug g^{-1} for Norge cl and Grant sil, respectively. Soil extracts were analyzed for NO_2-N and no significant accumulation was measured.

TABLE 14. ANALYSIS OF VARIANCE TABLE FOR SOIL NO_3-N FROM EXPERIMENT NO.2

Source	df	Mean square	F value	
Rep	2	10.53		
Soil	1	8771.28	4287.7	**
N Rate	3	10.38	5.07	**
Mulch	1	0.12	0.06	
Soil x N rates	3	21.82	10.67	**
Soil x Mulch	1	0.24	0.12	
N rate x Mulch	3	0.74	0.36	
Soil x N rate x Mulch	3	0.80	0.39	
Error (a)	30	61.37		
Time	5	2.83	4.62	**
Error (b)	10	0.61		
Soil x Time	5	0.94	2.14	
N rate x Time	15	1.00	2.27	*
Mulch x Time	5	2.81	6.38	**
Error (c)	50	0.44		
N rate x mulch x Time	15	0.53	1.82	
Soil x Mulch x Time	5	1.05	3.58	
Soil x N rate x Time	15	0.78	2.64	**
Soil x N rate x Mulch x Time	15	1.15	3.91	**
Error (d)	100	0.29		

df - degrees of freedom
*, ** - Denote significance at 0.05 and 0.01 probability level, respectively

Experiment No. 3

Effect of Tillage on NH_3-N Loss

The rate of NH_3-N volatilization was significantly affected by soil, tillage, and time of incubation as indicated in the analysis of variance table presented in Table 15. The rate of NH_3-N loss under CT and NT over a 7 d period is presented in Fig. 7 for both soils. The rate of NH_3-N volatilization was greatest during the first day of incubation under NT reaching values of 10.2 and 12.7 ug NH_3-N g^{-1} d^{-1} for Norge cl and Grant sil, respectively. Table 16 presents single degree of freedom comparisons between soils. The rate of NH_3-N loss was consistent between soils under NT even though volatilization rates differed during days 1 and 3. Under CT higher NH_3-N loss occurred in Norge cl compared with Grant sil during days 2, 3, and 4. Maximum volatilization under CT took place at 3 and 5 d for Norge cl and Grant sil, respectively. The high rate of NH_3-N loss (8.2 ug g^{-1} d^{-1} or 3.3 % of N applied) observed in Norge cl during the third day under CT was unexpected. However, the pattern of NH_3-N loss for Norge cl under CT remained similar to that of urea applied to bare soil; that is, a build up to a maximum followed by a steady descent.

The analysis of variance table for cumulative NH_3-N losses after 7 d is presented in Table 17. Total NH_3-N loss

TABLE 15. ANALYSIS OF VARIANCE TABLE FOR RATE OF NH_3-N LOSS FROM EXPERIMENT NO.3

Source	df	Mean square	F value	
Rep	3	1.33		
Soil	1	12.55	9.60	**
Till	1	122.43	93.61	**
Soil x Till	1	9.33	7.13	*
Error (a)	9	1.31		
Time	6	67.77	61.17	**
Error (b)	18	1.11		
Soil x Time	6	16.12	15.18	**
Till x Time	6	125.19	117.91	**
Soil x Till x Time	6	4.87	4.59	**
Error (c)	54	1.06		

df - degrees of freedom
*, ** - Denotes significance at 0.05 and 0.01 probability level, respectively.

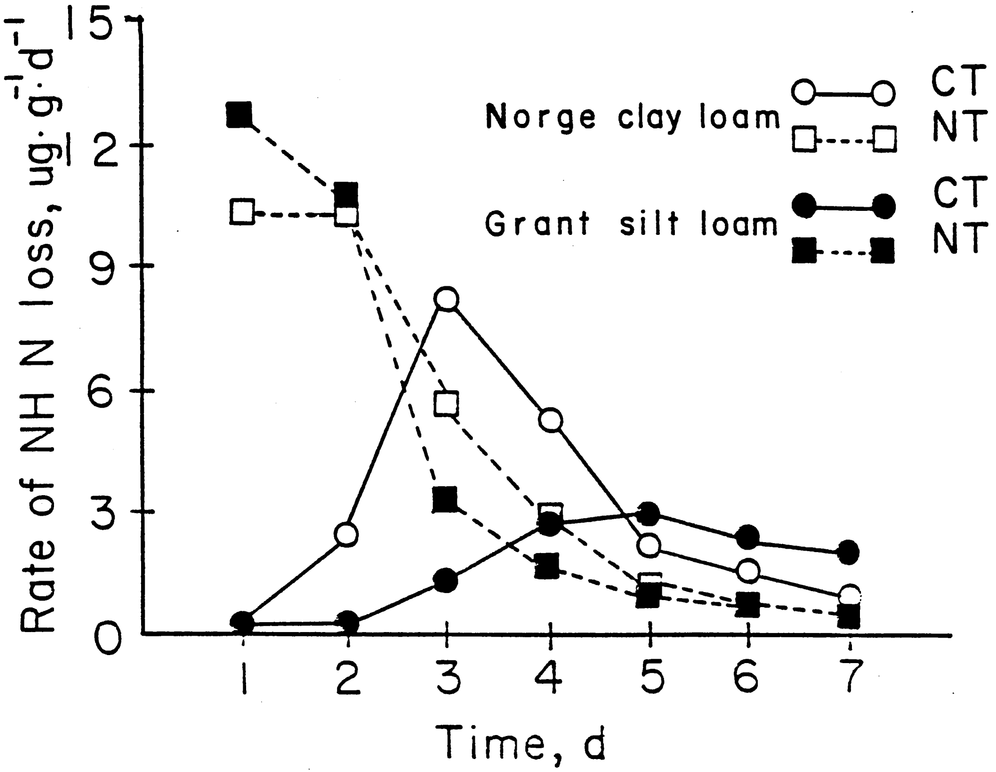

Fig. 7. Effect of soil and tillage on NH_3-N volatilization from surface-applied urea in experiment No. 3

TABLE 16. SINGLE DEGREE OF FREEDOM CONTRASTS BETWEEN SOILS FOR RATE OF NH_3-N LOSS FROM EXPERIMENT NO.3

Contrast	Tillage	Day	Sum of squares	F value
Norge vs. Grant	NT	1	12.341	9.42 **
Norge vs. Grant	NT	2	0.442	0.34
Norge vs. Grant	NT	3	10.663	8.14 **
Norge vs. Grant	NT	4	3.026	2.31
Norge vs. Grant	NT	5	0.226	0.17
Norge vs. Grant	NT	6	0.049	0.04
Norge vs. Grant	NT	7	0.027	0.02
Norge vs. Grant	CT	1	0.008	0.01
Norge vs. Grant	CT	2	9.314	7.11 **
Norge vs. Grant	CT	3	94.256	71.95 **
Norge vs. Grant	CT	4	12.044	9.19 **
Norge vs. Grant	CT	5	1.394	1.06
Norge vs. Grant	CT	6	1.483	1.13
Norge vs. Grant	CT	7	2.504	1.91

F values were calculated using mean square error (A) = 1.31 with 18 df.

TABLE 17. ANALYSIS OF VARIANCE TABLE FOR CUMULATIVE NH_3-N LOSS (7 D) FROM EXPERIMENT NO. 3

Source	df	Mean square	F value
Rep	3	9.32	
Soil	1	87.98	9.62 **
Till	1	857.90	93.80 **
Soil x Till	1	65.29	7.14 *
Error (a)	9	9.15	

df - degrees of freedom
*, ** - Denotes significance at 0.05 and 0.01 probability level, respectively.

depended on soil and tillage. Cumulative NH_3-N losses (7 d) under NT ranged from 12.5 to 12.8 % of applied urea-N for Grant sil and Norge cl, respectively. Cumulative NH_3-N losses (7 d) under CT were 4.9 and 8.5 % of applied N for Norge cl and Grant sil, respectively.

The pattern of ammonia volatilization for CT treatments resembled that of previous experiments where urea was applied to bare soil while the pattern under NT resembled that of urea applied to mulched soil. Increased NH_3-N volatilization under NT are consistent with published results (Hargrove et al.,1987; Keller and Mengel, 1986; Meyer et al.,1961; Nelson et al.,1980; Titko et al.,1987).

The maximum rates of volatilization from experiment No.3 were higher than those measured in previous experiments due, in part to the higher air exchange rate used in experiment No. 3. (7.5 volume exchanges min^{-1} as opposed to 2.5 exchanges min^{-1} for experiments No. 1 and 2). This is expected and in agreement with the relationship between air exchange rate and ammonia volatilization described by Kissel et al. (1977).

The agreement between the results obtained through laboratory experiments with simulated tillage systems and the results using soils under actual NT strengthens the idea that residue on the soil surface plays a critical role in increasing ammonia volatilization from surface-applied urea.

Effect of Tillage on Soil NH_4-N Distribution With Depth

Analysis of variance table for soil NH_4-N as affected by soil, tillage, depth, and time is presented in Table 18. Significant effects due to soil, tillage, and depth were observed. A significant ($P < 0.05$) Tillage x Depth x Time restricts any generalizations due to main effects in the distribution of soil NH_4-N. Soil NH_4-N as affected by tillage and depth for each sampling time is illustrated in Figs. 8 and 9 for Norge cl and Grant sil, respectively. Single degree of freedom comparisons of tillages at each depth and sampling time are presented in Tables 19, 20, 21, and 22 for days 1, 3, 5, and 7, respectively.

Significantly higher soil NH_4-N in the 0 to 15 mm layer under NT compared to CT was the result of increased hydrolysis during the first day after urea application. Ratios [NH_4-N]-NT/ [NH_4-N]-CT were 2.4 and 3.6 in the 0 to 15 mm layer for Norge cl and Grant sil, respectively. This indicated urease activity was 2 to 3 times larger in NT compared to CT. After 3 d, significantly higher soil NH_4-N was found in the top 0 to 15 mm of CT compared to NT as an effect of NH_3-N volatilization. Significantly more NH_4-N moved into the 16 to 30 mm depth in CT compared to NT in Norge cl. It is likely that this increase was due to movement of urea and NH_4-N into the soil which decreased the likelihood of ammonia volatilization. It appears that

TABLE 18. ANALYSIS OF VARIANCE TABLE FOR SOIL NH_4-N FROM EXPERIMENT NO. 3

Source	df	Mean square	F value
Rep	3	2159.07	
Soil	1	273000.30	131.90 **
Tillage	1	21772.05	10.52 **
Soil x Tillage	1	20191.29	9.76 *
Error (a)	9	2069.69	
Depth	3	3252621.91	1441.37 **
Soil x Depth	3	115428.96	51.15 **
Tillage x Depth	3	6349.64	2.81
Soil x Tillage x Depth	3	14346.33	6.36 **
Error (b)	36	2256.62	
Time	3	78105.92	46.62 **
Error (c)	9	1675.51	
Soil x Time	3	27874.12	10.68 **
Tillage x Time	3	83774.38	32.09 **
Depth x Time	9	25671.10	9.83 **
Soil x Tillage x Time	3	12501.66	4.79 *
Error (d)	54	2610.53	
Soil x Depth x Time	9	14262.97	4.78 **
Tillage x Depth x Time	9	65490.24	21.94 **
Soil x Tillage x Depth x Time	9	4984.61	1.67
Error (e)	81	2985.53	

df - degrees of freedom
*, ** - Denotes significance at 0.05 and 0.01 probability level, respectively.

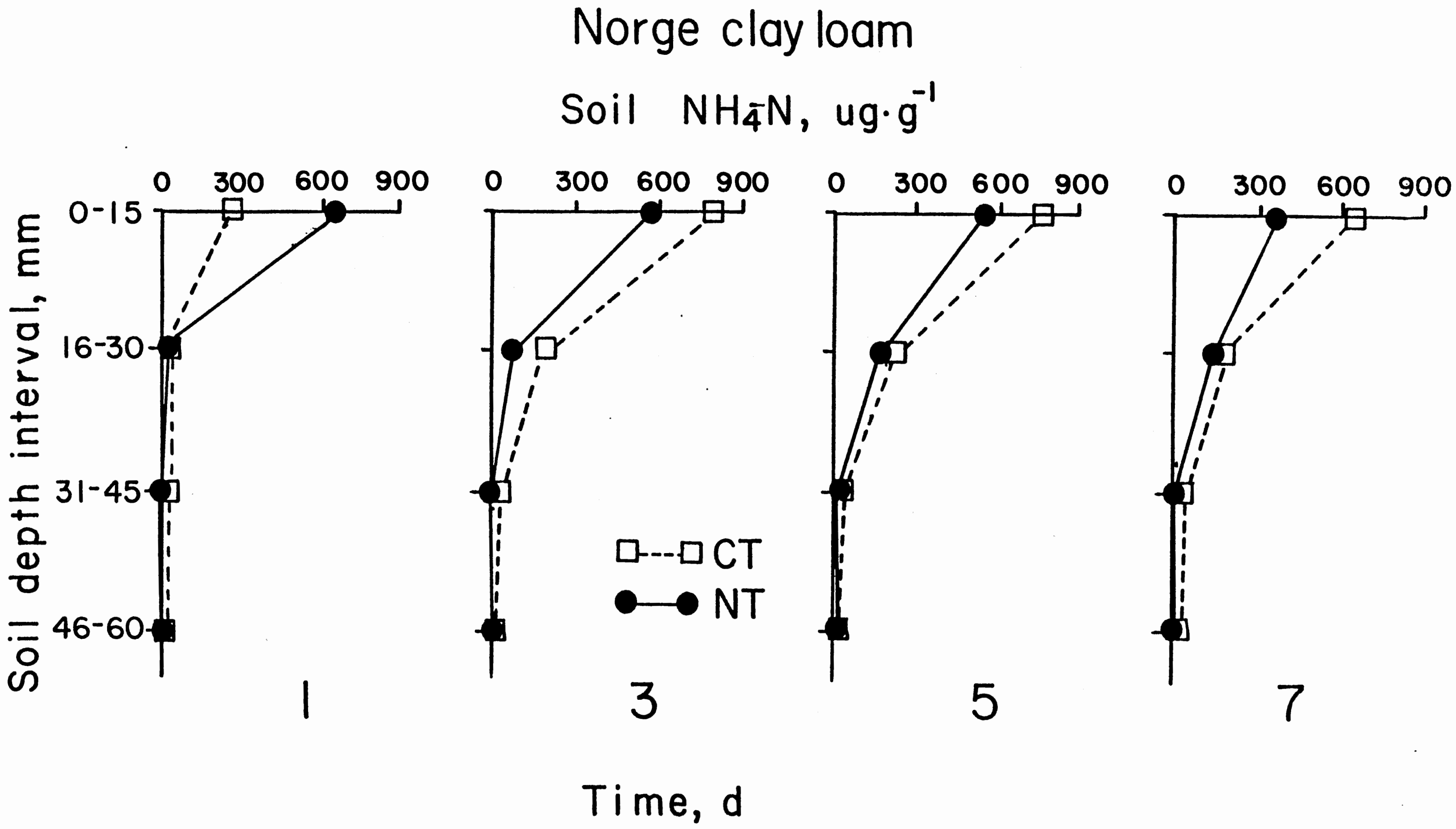

Fig. 8. Effect of tillage and depth on NH_4-N distribution after 1, 3, 5, and 7 d in Norge clay loam

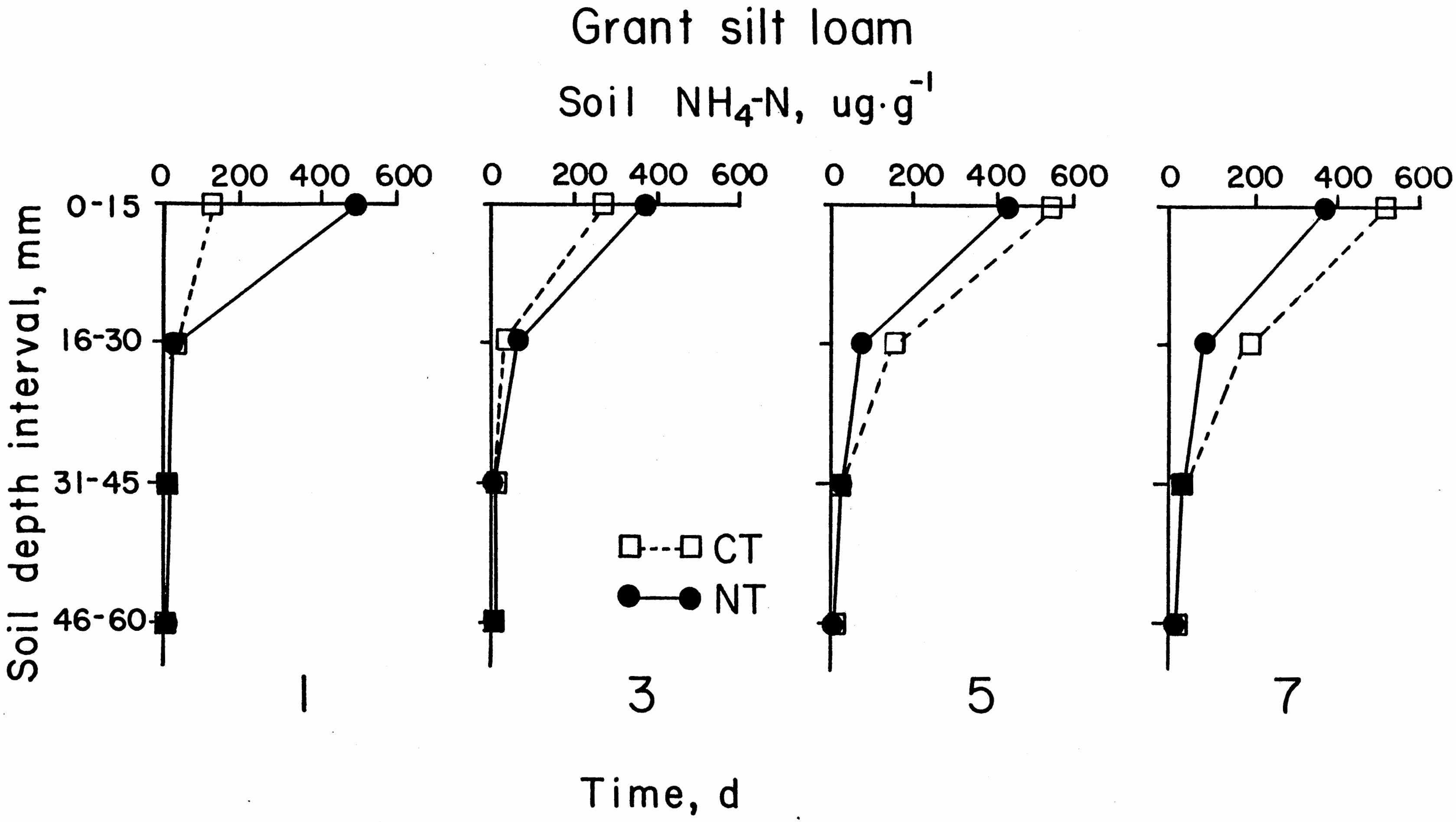

Fig. 9. Effect of tillage and depth on NH_4-N distribution after 1, 3, 5, and 7 d in Grant silt loam

TABLE 19. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 1 D INCUBATION; EXPERIMENT NO. 3

Contrast	df	sum of squares	F value
		Norge clay loam	
CT vs. NT (0-15 mm)	1	303169.714	146.48 **
CT vs. NT (16-30 mm)	1	16.188	0.01
CT vs. NT (31-45 mm)	1	86.251	0.04
CT vs. NT (46-60 mm)	1	262.388	0.13
		Grant silt loam	
CT vs. NT (0-15 mm)	1	253509.025	122.49 **
CT vs. NT (16-30 mm)	1	135.532	0.07
CT vs. NT (31-45 mm)	1	93.352	0.05
CT vs. NT (46-60 mm)	1	130.088	0.06

F values were calculated using mean square error(A) = 2069.69 with 9 df.

TABLE 20. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 3 D INCUBATION; EXPERIMENT NO. 3

Contrast	df	sum of squares	F value
		Norge clay loam	
CT vs. NT (0-15 mm)	1	97749.196	47.23 **
CT vs. NT (16-30 mm)	1	22255.858	10.75 **
CT vs. NT (31-45 mm)	1	1347.843	0.65
CT vs. NT (46-60 mm)	1	969.409	0.47
		Grant silt loam	
CT vs. NT (0-15 mm)	1	18782.321	9.07 *
CT vs. NT (16-30 mm)	1	45.716	0.02
CT vs. NT (31-45 mm)	1	32.096	0.02
CT vs. NT (46-60 mm)	1	17.170	0.01

F values were calculated using mean square error(A) = 2069.69 with 9 df.

TABLE 21. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 5 D INCUBATION; EXPERIMENT NO. 3

Contrast	df	sum of squares	F value
		Norge clay loam	
CT vs. NT (0-15 mm)	1	71121.061	34.36 **
CT vs. NT (16-30 mm)	1	8626.674	4.17
CT vs. NT (31-45 mm)	1	56.882	0.03
CT vs. NT (46-60 mm)	1	23.025	0.01
		Grant silt loam	
CT vs. NT (0-15 mm)	1	24026.512	11.61 **
CT vs. NT (16-30 mm)	1	10061.846	4.86
CT vs. NT (31-45 mm)	1	55.272	0.03
CT vs. NT (46-60 mm)	1	15.390	0.01

F values were calculated using mean square error(A) = 2069.69 with 9 df.

TABLE 22. SINGLE DEGREE OF FREEDOM CONTRASTS OF SOIL NH_4-N AFTER 7 D INCUBATION; EXPERIMENT NO. 3

Contrast	df	sum of squares	F value
	Norge clay loam		
CT vs. NT (0-15 mm)	1	152115.836	73.50 **
CT vs. NT (16-30 mm)	1	2277.315	1.10
CT vs. NT (31-45 mm)	1	21.820	0.01
CT vs. NT (46-60 mm)	1	442.234	0.21
	Grant silt loam		
CT vs. NT (0-15 mm)	1	38293.067	18.50 **
CT vs. NT (16-30 mm)	1	21305.434	10.29 *
CT vs. NT (31-45 mm)	1	105.560	0.05
CT vs. NT (46-60 mm)	1	2.654	0.00

F values were calculated using mean square error(A) = 2069.69 with 9 df.

indicated ongoing hydrolysis. Hydrolysis appeared near completion by 5 d in CT- Norge cl since NH_4-N decreased from 813 to 752 ug g $^{-1}$ in the 0 to 15 mm layer. After 7 d, significantly more NH_4-N within the 0 to 60 mm depth in CT compared to NT seemed to reflect higher losses by NH_3-N volatilization under NT. The increase in NH_4-N at depths below 15 mm for both tillages was due to diffusion of urea and/or NH_4-N. However, this was especially noticeable in CT Grant sil after 7 d.

Distribution of NH_4-N with depth followed the pattern of urea hydrolysis. Maximum accumulation of hydrolysis products coincided with the time for maximum NH_3-N volatilization under both tillages. In NT maximum NH_3-N loss occurred during the first 2 d of incubation at a time when soil NH_4-N was at its peak. Similarly, the top NH_3-N loss in CT occurred at the time of high NH_4-N accumulation. The movement of urea and NH_4-N below 15 mm significantly reduced NH_3-N losses. Differences in rates of NH_3-N volatilization observed between soils under CT could be explained based on the relative magnitude of soil NH_4-N concentration in the top 15 mm.

Effect of Tillage on Soil NO_3-N Distribution With Depth

Analysis of variance for soil NO_3-N as affected by soil, tillage, depth, and time is presented in Table 23.

TABLE 23. ANALYSIS OF VARIANCE TABLE FOR SOIL NO_3-N FROM EXPERIMENT NO.3

Source	df	Mean square	F value
Rep	3	2492.33	
Soil	1	2819.72	2.01
Tillage	1	2.60	0.00
Soil x Tillage	1	1187.43	0.85
Error (a)	9	1399.98	
Depth	3	7824.33	25.58 **
Soil x Depth	3	1377.17	4.50 *
Tillage x Depth	3	17.59	0.06
Soil x Tillage x Depth	3	87.72	0.29
Error (b)	36	305.85	
Time	3	6480.83	5.44 *
Error (c)	9	1190.17	
Soil x Time	3	1288.80	5.16 *
Tillage x Time	3	480.87	1.92
Depth x Time	9	1862.77	7.45 **
Soil x Tillage x Time	3	182.53	0.73
Error (d)	54	249.88	
Soil x Depth x Time	9	344.09	2.52
Tillage x Depth x Time	9	17.85	0.13
Soil x Tillage Depth x Time	9	56.71	0.42
Error (e)	81	136.41	

df - degrees of freedom

*, ** - Denotes significance at 0.05 and 0.01 probability level, respectively.

Significant soil x depth and depth x time interactions were due to differences in initial NO_3-N content between soils and the effect of nitrification of applied N.

There was no significant effect of tillage on NO_3-N production. However, there was nitrification occurring in the top layer of soil 7 d after urea application. Nitrate-N in the 0 to 15 mm depth of Norge cl increased from 21.6 to 96.2, and from 15.2 to 80.2 ug g^{-1} for NT and CT, respectively. Similarly, Grant sil NO_3-N in the 0 to 15 mm depth increased from 44.3 to 81.0 and from 37.1 to 79.2 ug g^{-1} for NT and CT, respectively. It was evident that NO_3-N accumulation was restricted to the 0 to 15 mm layer in both soils as little change in NO_3-N occurred at depths below 15 mm during the incubation period.

Recovery of Applied Nitrogen

Nitrogen recoveries by N fraction over time are presented in Table 24 for experiment No. 3. Low recoveries during the first 3 d following application were due to incomplete urea hydrolysis. There was a general trend for both tillages and soils to achieve maximum N recovery after 5 d following urea application but later decreased after 7 d. There is no simple explanation for this behavior; however, it is possible that other N processes such as immobilization acted upon the NH_4-N pool reducing recovery when measured by conventional laboratory means. Nitrogen recoveries under CT after 7 d were 87.9 and 104.2 % for Grant sil and Norge cl, respectively. Recoveries of applied N under NT after 7 d were 72.9 and 83.1% for Grant sil and Norge cl, respectively. Lower total recovery in NT compared to CT after correction for NH_3-N volatilization indicates N immobilization and/or denitrification losses. However, conditions during the experiment were not favorable for denitrification.

TABLE 24. RECOVERY OF APPLIED UREA-N BY N FRACTION FROM EXPERIMENT NO. 3

Tillage	Days	NH4-N#	NO3-N#	NH3-N	N recovery
		% of N applied			
			Norge cl		
NT	1	63.4	10.2	4.2	77.7
	3	62.2	14.3	10.6	87.1
	5	69.8	12.5	12.3	94.7
	7	49.0	21.3	12.8	83.1
CT	1	32.0	7.7	0.1	39.7
	3	96.0	11.7	4.4	112.1
	5	91.0	14.9	7.4	113.3
	7	78.4	17.4	8.5	104.2
LSD (5%)		8.0	7.8	1.0	
CV %		8.0	38.6	9.0	
			Grant sil		
NT	1	45.5	12.5	5.2	63.1
	3	39.4	12.5	10.8	62.8
	5	49.0	18.1	11.9	79.1
	7	43.2	17.3	12.5	73.0
CT	1	16.9	11.3	0.1	28.3
	3	31.4	15.8	0.7	48.0
	5	65.6	21.4	3.1	90.0
	7	65.0	18.0	4.9	87.9
LSD (5%)		17.3	7.2	1.4	
CV %		26.4	31.1	15.9	

Numbers include initial soil NH_4-N and NO_3-N.

CONCLUSIONS

The results from these laboratory experiments indicated that wheat residue on the soil surface influences the pattern and amount of NH_3-N loss from surface-applied urea. Experiments with simulated mulching revealed different patterns of ammonia loss for mulched and bare soil. Ammonia loss from bare soil started slow and increased to a maximum between 3 to 6 d after urea application. In mulched soil, the rate of NH_3-N volatilization showed a sharp increase the first day and was followed by a continuous decrease over time. After 2 weeks, NH_3-N loss from bare soil averaged 1.5, 2.7, and 3.4 % of N applied and under mulching 6.5, 11.2, and 14.1 % respectively for N rates of 84, 168, and 252 kg N ha^{-1}.

An experiment using intact soil cores from established tillage experiments corroborated the results of the experiments with simulated tillages. The pattern of ammonia volatilization when urea was surface-applied to soils under conventional tillage resembled that of urea applied to bare soil. Ammonia loss from urea applied to no-till soils resembled the pattern of NH_3-N volatilization of urea applied to wheat residue mulch. Ammonia losses averaged 6.7 and 12.7 % of the applied N for soils under CT and NT, respectively.

Differences in rate of NH_3-N volatilization due to tillage were explained by changes in the rate of urea hydrolysis. Urea hydrolysis in the initial 24 h after application averaged 55 and 42% of the applied N for no-till Norge cl and Grant sil, respectively. Urea hydrolysis in conventional till Grant sil and Norge cl averaged 11 and 21%, respectively. Hydrolysis increased as a result of high urease activity existing in the wheat residue. Both lower urease activity and diffusion of urea and NH_4-N below 15 mm contributed to reduce NH_3-N loss under conventional till.

Seven days after urea application, N recoveries of (NH_4 + NO_3 + NH_3)-N were 87.9 and 104.2% for conventional till Grant sil and Norge cl, respectively. Under no-till, N recoveries were 72.9 and 83.1% for Grant sil and Norge cl, respectively. Lower N recoveries in no-till suggested immobilization of soil NH_4-N by soil microbes.

It was concluded that NH_3-N volatilization and N immobilization were responsible for reducing availability of mineral N from urea under no-till residue management.

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