SECTION V

AMMONIA VOLATILIZATION FROM SURFACE – APPLIED UREA IN SOUTHWESTERN NORTH DAKOTA

AMMONIA VOLATILIZATION FROM SURFACE - APPLIED UREA IN SOUTHWESTERN NORTH DAKOTA[1]

By

David Alan Claypool

Research Specialist I

Dickinson Research Center

Department of Soil Science

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ABSTRACT

Claypool, David Alan, M. S., Department of Soil Science, College of Agriculture, North Dakota State University, April, 1990.   Ammonia Volatilization from Surface-applied Urea in Southwestern North Dakota. Major Professor: Dr. R. J. Goos.

Loss of urea-N through the process of NH_3 volatilization can represent a significant agronomic and economic loss. These losses have not been measured under unmodified field conditions in North Dakota. The objectives of the current research were to estimate ammonia volatilization losses and to identify the environmental conditions which facilitate ammonia losses from urea in southwestern North Dakota. Microplot cylinder studies were established on barley (*Hordeum vulgare L.*) stubble, tilled soil, and native pasture. ^{15}N-labelled ammonium nitrate and urea were applied as 0.01 g pellets at a rate of 100 kg N ha^{-1} on three dates in the spring and three dates in the fall of 1986. Ammonia loss was estimated as the difference in N recovery between ammonium nitrate and urea treatments for both mineral N and ^{15}N. Statistically significant (P=0.10) ammonia volatilization loss estimates ranged from 12.1 to 44.0% by the mineral N method and from 20.3 to 26.7% by the ^{15}N method. Significant volatilization losses were associated with high urease activity and drying conditions. The mineral N method generally gave larger estimates of ammonia loss than the ^{15}N method. No difference in precision between the two methods was apparent.

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INTRODUCTION

Urea is a widely used nitrogen fertilizer in southwestern North Dakota. The loss of urea-N through the process of NH_3 volatilization can represent a significant agronomic and economic loss of N. No measurements of NH_3 volatilization losses have been made under unmodified field conditions in North Dakota. An experiment was designed to study these losses in southwestern North Dakota.

The objectives of the current research were to:

1. Estimate NH_3 volatilization losses from tilled soil, small grain stubble, and native pasture, and

2. Identify the environmental conditions which facilitate NH_3 losses in southwestern North Dakota.

MATERIALS AND METHODS

Microplot cylinder studies were established to measure the recovery of ^{15}N-labelled ammonium nitrate and urea. The working assumption of the study was that the $^{15}NH_4^+$ in the ammonium nitrate was subject to minimal NH_3 volatilization while the ^{15}N-labelled urea was subject to NH_3 volatilization (Fenn and Kissel, 1973).

The use of microplots and ^{15}N recovery in this experiment was patterned after the technique used by Nommick (1973). The use of microplots allows the study of NH_3 losses under natural, undisturbed soil conditions. The ratio of ^{14}N:^{15}N in the atmosphere is almost constant at 272:1. The natural abundance of ^{15}N in atmospheric N_2 is defined to be 0.3663% (Buresh et al., 1982). Unlabelled N and ^{15}N recovery methods may give similar results (Hargrove et al., 1987).

Field Procedures

Three experimental sites of differing soil cover types were selected at the Dickinson Research Center Ranch near Manning, ND. The three sites were standing barley (*Hordeum vulgare L.*) stubble, tilled soil (barley stubble which had been disked 3 to 4 times), and native mixed grass pasture. The tilled soil and barley stubble sites were located 3.5 km east of the Ranch Headquarters at NE 1/4 Sec. 24, Township

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143N., Range 96W., Dunn County, ND. The native pasture site was located 4.0 km west of the Ranch Headquarters at NE 1/4 Sec. 19, Township 143N., Range 96W., Dunn County, ND. The stubble used for the spring treatments was from the 1985 barley crop and the stubble used for the fall treatments was from the 1986 barley crop. The tilled soil and stubble sites were kept free of living vegetation with glyphosate [N- (phosphonomethyl) glycine] during the experiment.

Thirty-six aluminum microplot cylinders (30.5-cm diam. by 20.3-cm long) were pressed into the soil at each soil cover type site on April 1, 1986, and again on September 4, 1986. Approximately 2 cm of each cylinder was left sticking above the soil surface. Each microplot was randomly assigned one of three treatments:

1. Control (no N added),

2. Urea (N labelled at 4.394 atom % ^{15}N),

3. Ammonium nitrate (NH$_4$-N labelled at 2.480 atom % ^{15}N).

The experimental design was a randomized complete-block design with three replicates. The labelled fertilizers were applied as 0.01 g pellets at a rate of 100 kg N ha^{-1}. The fertilizers were pelleted by Mr. George Jones, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, AL.

Fertilizer pellets were applied to the soil surface inside the microplots when soil conditions were suitable for the use of commercial fertilization equipment preferably 2 to 3 d after rain and at least 3 to 4 d before rain was predicted. Spring applications were made on 1, 16, and 27 May. No treatment was applied to pasture on 27 May because most native pasture in the area is fertilized earlier in the season. The experimental sites were moved approximately 25 m for fall applications and fertilizer treatments were applied on 4 September, 6 October, and 13 October. Treatment periods lasted for 9 to 14 d after fertilizer application during which the fertilizer was left exposed to the weather. The microplot cylinders were dug out at the end of the treatment period and the entire soil volume of each microplot was passed through a

0.64-cm sieve and air-dried. After drying, the soil was ground to pass a 2mm-sieve, mixed well, and subsampled for laboratory analysis.

Gravimetric soil water at 0 to 5, 5 to 10, 10 to 15, and 15 to 30 cm was measured adjacent to the microplots when fertilizer was applied and again when the microplots were removed. The thatch layer of the pasture site was excluded from soil water samples.

Environmental conditions were recorded by instruments located at the research sites. Air temperature and relative humidity were recorded by hygrothermograph. Soil temperature at 10 cm was measured by recording soil thermometers. Cumulative precipitation was recorded weekly and at the beginning and end of each treatment period. Daily precipitation values were recorded at the Ranch Headquarters.

Laboratory Procedures

Inorganic N, NH_4^+-N and $(NO_2^-+NO_3^-)$ –N, content of the soil samples was determined on 10 g subsamples of the microplots by extraction with KC1 and steam distillation with MgO and Devarda's alloy (Keeney and Nelson, 1982).

Soil to be used for total N analysis was ground with a mortar and pestle to pass a 500-µm sieve. Plant matter in these samples was ground separately to pass a 286-µm sieve and then mixed into the soil sample. Separate mortars and pestles were used for each fertilizer treatment to minimize ^{15}N cross-contamination. Total N was determined by the permanganate-reduced iron modification of the semimicro-Kjeldahl method to include nitrate and nitrite (Bremner and Mulvaney, 1982). Control treatment samples were distilled first, followed by the ammonium nitrate samples, and then the urea-treated samples to prevent cross-contamination of ^{15}N. Samples were distilled into 10 mL of 0.01 M H_2SO_4 and back titrated with 0.03 M NaOH.

The distillate from the total N procedure was acidified with 0.1 mL of 0.05 M H_2SO_4 to prevent loss of NH_3 and evaporated at 90°C. The dried residue was analyzed for ^{15}N content by Isotec, Inc. Analytical Services, Miamisburg, OH.

Percent recovery of applied mineral N (PMR) was calculated according to the formula:

$$PMR = [(a – b)\ c/d]\ 100, \text{ where}$$

a = mineral N in treated sample, mg kg^{-1}

b = mineral N in check sample, mg kg^{-1}

c = weight of oven-dry soil in treated microplot, kg

d = weight of N applied, mg

The weight of ^{15}N recovered (WNR) in mg was calculated according to the formula:

$$WNR = e\ (f/100)\ [(g-h)\ /100]\ 1000, \text{ where}$$

e = weight of soil in treated microplot, g

f = total N content of treated soil, %

g = ^{15}N content of treated soil, %

h = ^{15}N content of check soil, %

The percent recovery of applied ^{15}N (P15R) was calculated according to the formula:

$$P15R = 100i/\ [j\ (k/100)\ (l/100)\ 1000], \text{ where}$$

i = ^{15}N recovered (WNR from previous equation), mg

j = fertilizer applied, g

k = N content of fertilizer (46.64% for urea and 35.00% for ammonium nitrate)

l = ^{15}N content of fertilizer (4.3938% for urea and 2.4797% for ammonium nitrate)

Relative N recovery (RNR) was estimated for both the mineral N and ^{15}N recovery data as the difference in recovery between ammonium nitrate and urea treatments by the formula:

$$RNR = m–n, \text{ where}$$

m = recovery for urea treatment, %

n = recovery for ammonium nitrate treatment, %

A negative RNR was assumed to be an estimate of NH_3 volatilization loss for the purpose of determining when an NH_3 volatilization event occurred.

Site Characterization

Soil samples from each experimental site were taken in April 1986 for the purpose of characterizing the soils. A second set of characterization samples were taken at the end of the experiment. Sampling increments were 0 to 5, 5 to 10, 10 to 15, and 15 to 30 cm. Samples were analyzed for pH, urease activity, CEC, organic matter and particle size (Table 1). Samples of standing barley stubble and native pasture thatch were also taken and analyzed. Soil pH was determined by glass electrode on a 1:1 soil: water slurry. Urease activity was determined by ammonium production upon incubation with an unbuffered urea solution at 20°C for 16 h (Tabatabai, 1982). Cation exchange capacity was determined by the Bower procedure (U.S. Salinity Lab Staff, 1969). Organic matter was determined with the modified Walkley-Black method (Chapman and Pratt, 1961). Particle size distribution (Table 2) was determined with the pipette method (Day, 1965).

Soil water retention was determined at -33.3 and -1500 kPa potential with pressure plates. Samples for the spring and fall tilled soil and stubble sites were combined into one composite sample of the 0- to 15-cm depth. Water retention at -33.3 and -1500 kPa potential was 164 and 89 g kg^{-1}, respectively. The soil water retention sample for the native pasture site was a composite of the 0- to 15-cm depths of the fall and spring experimental sites. Soil water retention for the pasture site at -33.3 and -1500 kPa potential was 221 and 127 g kg^{-1}, respectively. The soils at each site were classified by Mr. D. G. Hopkins of the North Dakota State University (NDSU) Department of Soil Science (Table 3).

The plant species in order of occurrence at the spring pasture site were crested wheatgrass [*Agropyron desertorum* (Fisch. ex Link) Schult.], Kentucky bluegrass (*Poa pratensis* L.), smooth bromegrass (*Bromus inermis* Leyss), and fringed sage (*Artemisia frigida* Willd.). Plant species in order of occurrence at the fall pasture site were crested wheatgrass, Kentucky bluegrass, sandberg bluegrass (*Poa sandbergii* Vasey), white prairie aster (*Aster ericoides* L.), purple coneflower [*Echinacea angustifolia* (D.C.) Heller], hairy golden aster [*Chrysopsis villosa* (Pursh) Nutt.], prairie birdsfoot trefoil [*Lotus americanus* (Nutt.) Bisch.], longheaded coneflower [*Ratibida columnifera* (Nutt.) Wooton & Standl], and western snowberry

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(*Symphoricarpos occidentalis* Hook.). Identification was made by Mr. Phillip Sjursen of the NDSU

Department of Animal and Range Science.

Statistical analyses were calculated using Lotus 1-2-3® release 2.01 spreadsheets designed by the author

and based on procedures for the randomized complete-block and split-plot designs (Little and Hills,

1978). Regression analysis was performed using the regression feature of the 1-2-3 program.

Table 1.   Selected Soil Chemical Properties of the Research Sites

Site	Depth cm	Organic matter %	CEC cmol (p⁺) kg⁻¹	Urease activity μg N g⁻¹h⁻¹	pH
			Spring		
Tilled Soil	0-5	3.2	18.3	13.59	6.3
	5-10	2.4	17.6	7.07	6.1
	10-15	2.6	18.0	--	6.0
	15-30	1.9	21.6	--	6.3
Stubble	straw	--	--	201.43	--
	0-5	2.6	18.2	11.59	6.2
	5-10	2.3	18.2	7.16	6.1
	10-15	2.8	17.8	--	6.3
	15-30	2.4	17.5	--	5.9
Pasture	thatch	--	--	78.88	--
	0-5	5.2	21.0	19.18	6.0
	5-10	3.7	18.6	10.85	6.5
	10-15	2.3	19.4	--	6.5
	15-30	1.9	18.8	--	6.8
			Fall †		
Tilled Soil	0-5	2.7	19.4	6.15	6.2
	5-10	2.1	19.4	6.12	6.0
	10-15	2.7	19.0	--	6.0
	15-30	2.6	20.8	--	6.2
Stubble	straw	--	--	184.47	--
	0-5	2.8	18.6	6.23	6.4
	5-10	2.6	18.7	5.48	6.3
	10-15	2.5	18.6	--	6.0
	15-30	2.8	20.5	--	5.9
Pasture	thatch	--	--	57.95	--
	0-5	4.2	20.0	12.62	6.2
	5-10	2.7	19.0	4.46	6.0
	10-15	1.8	18.5	--	6.0
	15-30	1.7	19.7	--	6.3

†Sampled at the end of the experiment.

Table 2.   Soil Textural Classes of the Research Sites

Depth cm	Tilled Soil	Stubble	Pasture
	Spring		
0-5	loam	loam	sandy clay loam
5-10	loam	loam	loam
10-15	loam	loam	sandy loam
15-30	clay loam	loam	sandy loam
	Fall		
0-5	loam	loam	loam
5-10	loam	sandy loam	loam
10-15	loam	loam	loam
15-30	loam	loam	loam

Table 3.   Soil Classification of Research Sites

Site	Soil Series	Classification
	Spring	
Tilled Soil	Farland	Fine-silty, mixed Typic Argiboroll
Stubble	Reeder	Fine-loamy, mixed Typic Argiboroll
Pasture	Amor	Fine-loamy, mixed Typic Haploboroll
	Fall	
Tilled Soil	Shambo	Fine-loamy, mixed Typic Haploboroll
Stubble	Shambo	Fine-loamy, mixed Typic Haploboroll
Pasture	Shambo	Fine-loamy, mixed Typic Haploboroll

RESULTS

The results will be presented by fertilizer treatment period. First, the environmental conditions during each period will be presented, followed by estimates of NH_3 loss. Then, loss estimates will be discussed in relation to the environmental conditions.

1 to 12 May

The soil surface was moist at fertilizer application (Table 4) and soil water content was greater than -33.3 kPa potential. Temperatures were warm for the first 4 d of fertilizer exposure, with air temperatures reaching 30°C on 3 to 4 May. The weather then changed dramatically, with rain mixed with snow falling 5 May and air temperatures declining to below 10°C on 7 to 8 May. The remainder of the period was continuously wet with air temperatures warming to above 20°C on 10 to 11 May. Total precipitation for the period was 6.15 cm at the tilled soil and stubble sites and 6.38 cm at the pasture site (Table 4). The relative precipitation distribution at the Ranch Headquarters for the period was 49.5% on 5 May, 46.0% on 7 to 9 May, and 4.5% on 11 May.

No statistically significant (P=0.10) losses of NH_3 were estimated by either the mineral N method (Table 5) or the ^{15}N method (Table 6). The combination of wet soil, rain, and cool temperatures prevented volatilization losses. Significant volatilization losses did not occur in response to the high temperatures on 3 to 4 May. Significant urea hydrolysis was possible between 1 to 4 May, because of the moist soil and warm conditions, but it seems that significant NH_3 volatilization was prevented by the precipitation that began on 5 May.

Recovery of mineral N from urea treatments was superior to ammonium nitrate on the tilled soil giving an apparent gain in N of 22.1%. Total precipitation was heavy and soil water content increased for the period, except for the 0- to 5-cm of the tilled soil (Table 4). The NO_3^- of the ammonium nitrate may have been subject to leaching or denitrification giving the appearance of a relative N increase.

Table 4. Weather and Soil Condition Summary for the 1 to 12 May Treatment Period

	Site		
Parameter	**Tilled Soil**	**Stubble**	**Pasture**
Total precipitation (cm)	6.15	6.15	6.38
First precipitation after treatment† (d)	5	5	5
Air temperature (°C)			
Maximum	33	33	31
Minimum	1	1	1
Mean	9.6†	9.6†	10.3
Mean relative humidity (%)	NA	NA	74.8
Mean soil temperature (°C)	7.9	8.0	9.1
Initial soil water ($g\ kg^{-1}$)			
0-5 cm	210	212	238
5-10 cm	209	227	201
10-15 cm	220	225	175
15-30 cm	223	224	164
Net soil water change for period ($g\ kg^{-1}$)			
0-5 cm	-5	21	40
5-10 cm	11	0	21
10-15 cm	3	10	16
15-30 cm	11	-1	17

†   Ranch headquarters records.

NA = data not available or incomplete.

Table 5.   Relative Nitrogen Recovery Estimated by the Mineral N Method †

	Site		
Dates	**Tilled Soil**	**Stubble**	**Pasture**
	- % -		
1-12 May	22.1 *	-17.4 NS	26.1 NS
16 -27 May	16.4 +	-12.1 +	-10.8 NS
27 May-5 June	-6.3 NS	-44.0 *	----
4-18 Sept.	4.4 NS	-2.0 NS	-15.3 NS
6-16 Oct.	-13.8 NS	-34.6***	-30.7 +
13-23 Oct.	4.9 NS	-29.6 *	-15.9 NS

+, *, **, *** Significant at the 0.10, 0.05, 0.01, and 0.001 probability levels, respectively; NS = not significant.

†   Negative numbers represent NH_3 loss.

Table 6.   Relative Nitrogen Recovery Estimated by the ^{15}N Method †

Dates	Site		
	Tilled Soil	**Stubble**	**Pasture**
	- % -		
1-12 May	11.3 NS	-13.1 NS	-0.9 NS
16-27 May	2.0 NS	-10.8 NS	2.6 NS
27 May-5 June	13.6 *	-26.7 +	----
4-18 Sept.	9.6 NS	10.5 NS	35.2 **
6-16 Oct.	0.2 NS	-23.2 +	-20.3 *
13-23 Oct.	12.5 NS	-22.7 *	6.9 NS

+, *, ** Significant at the 0.10, 0.05, and 0.01 probability levels, respectively; NS = not significant.
†   Negative numbers represent NH_3 loss.

16 to 27 May

Maximum daily air temperatures increased from the teens at fertilizer application to 20 to 25°C on 18 to 21 May (Table 7). The first precipitation fell 19 May and totaled 0.05 at the pasture site and 0.30 cm at the tilled soil and stubble sites.

Heavy rainfall was observed on 22 May (4.0 cm recorded at Ranch Headquarters) and precipitation was recorded daily through 24 May. Total precipitation was substantial at all sites. Air temperatures dropped during the rainy days but rose above 20°C for 25 to 27 May. Mean daily relative humidity ranged from 55 to 100%. Soil water content at fertilizer application was near -33.3 kPa potential and increased for the period through the 15- to 30-cm depth of the microplots.

Mineral N analysis indicated a statistically significant loss of NH_3 (12.1%) on stubble (Table 5). No statistically significant losses were detected by the ^{15}N method (Table 6). The light rainfall of 19 May was not sufficient to prevent NH_3 loss. The heavy rain of 22 May was adequate to terminate NH_3 loss. Thus, it is likely that the NH_3 loss observed on stubble occurred between 16 to 22 May.

Recovery of mineral N was superior with urea on tilled soil giving an apparent gain in N (16.4%). The rainfall of 22 to 24 May possibly caused some NO_3^- leaching or dentrification loss of N on tilled soil.

Table 7.   **Weather and Soil Condition Summary for the 16 to 27 May Treatment Period**

Parameter	Site		
	Tilled Soil	**Stubble**	**Pasture**
Total precipitation (cm)	4.34	4.34	4.34
First precipitation after treatment† (d)	4	4	4
Air temperature (°C)			
Maximum	27	27	25
Minimum	1	1	-2
Mean	14.9	14.9	13.6
Mean relative humidity (%)	76.0	76.0	73.7
Mean soil temperature (°C)	NA	13.3	11.2
Initial soil water (g kg^{-1})			
0-5 cm	174	151	198
5-10 cm	191	191	187
10-15 cm	206	208	160
15-30 cm	223	204	159
Net soil water change for period (g kg^{-1})			
0-5 cm	-25	31	32
5-10 cm	8	25	1
10-15 cm	13	10	17
15-30 cm	6	5	9

†   Ranch headquarters records.
NA = data not available or incomplete.

27 May to 5 June

Air temperatures for the period were hot with daily high temperatures staying above 22°C until 5 June and reaching a maximum of 34°C on 31 May and 2 June (Table 8). No rainfall was recorded until 4 June. The amount of rainfall was small (0.38 cm) and fell too late in the period to stop NH_3 loss before the microplots were retrieved. Soil water content (0 to 5 cm) at fertilizer application was slightly below -33.3 kPa potential on tilled soil and slightly above that level on stubble. Soil water content for the period declined through the 15- to 30-cm depth.

Significant NH_3 losses from stubble were detected by both methods. A loss of 44.0% was estimated by the mineral N method (Table 5) and a loss of 26.7% was estimated by the ^{15}N method (Table 6). No significant losses were estimated on the tilled soil for this period.

The combination of high temperatures and drying conditions apparently induced NH_3 loss from stubble. Recovery of urea-^{15}N was superior on tilled soil resulting in an apparent gain in N (13.6%). An explanation for this result is not evident.

Table 8.   Weather and Soil Condition Summary for the 27 May to 5 June Treatment Period

Parameter	Site	
	Tilled Soil	**Stubble**
Total precipitation (cm)	0.38	0.38
First precipitation after treatment† (d)	8	8
Air temperature (°C)		
Maximum	34	34
Minimum	11	11
Mean	21.0	21.0
Mean relative humidity (%)	70.5	70.5
Mean soil temperature (°C)	23.8	21.3
Initial soil water (g kg^{-1})		
0-5 cm	149	183
5-10 cm	199	215
10-15 cm	219	218
15-30 cm	228	208
Net soil water change for period (g kg^{-1})		
0-5 cm	-7	-44
5-10 cm	-28	-45
10-15 cm	-39	-31
15-30 cm	-30	-11

†   Ranch headquarters records.

4 to 18 September

The soil surface was very dry at all sites at fertilizer application (Table 9) and the soil water content was less than the -1500 kPa potential content at the 0- to 10-cm depth.

Air temperatures remained above freezing for the period but fluctuated widely with maximum daily air temperatures for the period ranging from 9 to 23°C. Precipitation on 5 September totaled 1.07 at the pasture site and 1.02 cm at the tilled soil and stubble sites. Precipitation fell almost daily 9 to 18 September. Soil water content for the period increased through the 10- to 15-cm depth on tilled soil and the 15- to 30-cm depth at the other sites.

No statistically significant NH_3 losses were detected by either method (Tables 6 and 7). A statistically significant increase in NH_3 at the pasture site was indicated by the ^{15}N method. Volatilization did not occur because the soil was too dry initially to hydrolyze the urea and sufficient rain fell to dissolve the urea and move it into the soil.

Table 9.   Weather and Soil Condition Summary for the 4 to 18 September Treatment Period

	Site		
Parameter	**Tilled Soil**	**Stubble**	**Pasture**
Total precipitation (cm)	2.90	2.90	3.40
First precipitation after treatment† (d)	2	2	2
Air temperature (°C)			
Maximum	23	23	23
Minimum	3	3	2
Mean	11.4	11.4	10.6
Mean relative humidity (%)	72.9	72.9	77.5
Mean soil temperature (°C)	10.9	12.7	10.8
Initial soil water (g kg^{-1})			
0-5 cm	59	59	58
5-10 cm	88	76	69
10-15 cm	108	91	70
15-30 cm	119	105	78
Net soil water change for period (g kg^{-1})			
0-5 cm	143	154	200
5-10 cm	62	97	132
10-15 cm	4	18	52
15-30 cm	0	2	10

†   Ranch headquarters records.

6 to 16 October

Air temperatures at all sites reached 23°C on 6 October and declined the first 3 d of the period. Minimum daily air temperatures remained near or below freezing 8 to 15 October. Temperatures warmed to 20°C or higher the last 2 d of the period. Rainfall of 0.23 cm fell 7 October and fog was recorded on 9 October. The following two days were windy. Soil water content at fertilizer application was above -33.3 kPa potential at the tilled soil and stubble sites and slightly below -33.3 kPa potential at the pasture site (Table 10). Although air temperatures were generally cool for the period, there was a net soil water loss at all sites.

Ammonia loss from stubble was statistically significant. The mineral N method estimated an NH_3 loss of 34.6% (Table 5) and the ^{15}N method estimated a loss of 23.3% (Table 6). Losses estimated on pasture were 30.7% by the mineral N method and 20.3% by the ^{15}N method. No statistically significant losses were observed on tilled soil by either method.

The light precipitation and humid conditions on 8 to 9 October apparently activated urease activity and hydrolyzed the urea but did not wash it into the soil. The subsequent windy conditions and rising temperatures dried the soil despite cool air temperatures and induced NH_3 volatilization.

Table 10.   **Weather and Soil Condition Summary for the 6 to 16 October Treatment Period**

	Site		
Parameter	Tilled Soil	Stubble	Pasture
Total precipitation (cm)	0.23	0.23	0.23
First precipitation after treatment† (d)	2	2	2
Air temperature (°C)			
Maximum	24	24	23
Minimum	-6	-6	8
Mean	7.7	7.7	6.5
Mean relative humidity (%)	57.1	57.1	68.5
Mean soil temperature (°C)	7.1	6.4	3.2
Initial soil water (g kg^{-1})			
0-5 cm	172	191	226
5-10 cm	190	194	189
10-15 cm	197	207	180
15-30 cm	205	232	181
Net soil water change for period (g kg^{-1})			
0-5 cm	-25	-17	-31
5-10 cm	-13	3	-22
10-15 cm	-6	-3	-22
15-30 cm	3	-3	-11

†   Ranch headquarters records.

13 to 23 October

No precipitation fell during the period. Maximum daily air temperatures were typically 20 to 23°C after warming for the first 3 d of the period. Minimum daily air temperatures for 13 to 15 October were at or below freezing. The mean relative humidity for the period was low compared to the other periods (Table 11). Soil water content at fertilizer application was near or slightly above -33.3 kPa potential. All sites lost soil water to 30 cm.

No statistically significant losses were detected on tilled soil or pasture. Statistically significant NH$_3$ loss estimates indicated on stubble were 29.6% by the mineral N method (Table 5) and 22.8% by the ^{15}N method (Table 6). The urea apparently absorbed enough moisture on the stubble site to be hydrolyzed and the warm, drying conditions induced NH$_3$ volatilization.

At fertilizer application, the thatch layer of the pasture site was dry. Because the thatch layer kept the

fertilizer pellets separated from the moist soil and there was no precipitation, the rate of hydrolysis must

have been slow. Perhaps the slow rate of hydrolysis prevented a sufficient rise in the soil pH to permit

significant volatilization. The absence of significant volatilization losses from the tilled soil can best be

attributed to the low urease activity of the soil surface (Table 1).

Table 11.   Weather and Soil Condition Summary for the 13 to 23 October Treatment Period

Parameter	Site		
	Tilled Soil	Stubble	Pasture
Total precipitation (cm)	0.0	0.0	0.0
First precipitation after treatment† (d)	--	--	--
Air temperature (°C)			
Maximum	24	24	23
Minimum	-4	-4	-6
Mean	10.7	10.7	9.6
Mean relative humidity (%)	60.1	60.1	66.4
Mean soil temperature (°C)	9.0	6.3	4.1
Initial soil water (g kg^{-1})			
0-5 cm	172	191	219
5-10 cm	187	190	210
10-15 cm	201	213	201
15-30 cm	203	247	191
Net soil water change for period (g kg^{-1})			
0-5 cm	-40	-36	-31
5-10 cm	-16	-15	-22
10-15 cm	-11	-5	-22
15-30 cm	-1	-6	-11

†   Ranch headquarters records.

DISCUSSION

In general, significant NH$_3$ volatilization losses occurred under drying conditions and high urease activity. Substantial precipitation during a fertilizer exposure period minimized or prevented NH$_3$ losses.

Ammonia Loss Events by Treatment Period

The treatment period 6 to 16 October had the most volatilization loss events which were statistically significant. Losses were detected at the stubble and pasture sites according to both the mineral and ^{15}N methods. Significant loss events were also detected by both methods for the periods 27 May to 5 June and 13 to 23 October. All three periods were characterized by 0.38 cm or less precipitation, soil water content near -33.3 kPa potential at fertilizer application, and substantial soil water loss to at least 15 cm (Tables 8, 10, and 11). Soil water content of -33.3 kPa potential apparently was sufficient for urea hydrolysis to take place.

Drying conditions were more important to the volatilization process than actual air temperature and relative humidity. The 6 to 16 October period was cooler than 13 to 23 October and 27 May to 5 June was warmer and more humid than the periods in October. Yet, drying conditions and NH$_3$ loss events occurred during each of these periods. Ellington (1986) reported that large volatilization losses occurred with high evaporation rates.

Light precipitation of approximately 0.2 cm falling 1 d after application during the 6 to 16 October period also would have activated urea hydrolysis. Cool temperatures during 6 to 16 October did not prevent volatilization, although the rate could possibly have been slowed. This result is similar to those of Bowman et al. (1987) who found that in irrigation treatments on urea-fertilized pasture, maximum NH$_3$ loss occurred after 0.2 cm of water had been applied. Most NH$_3$ was lost in the first 24 h. Volatilization decreased with greater or lesser amounts of irrigation and minimal loss was achieved with a 1-cm water application.

In the cases of 27 May to 5 June and 13 to 23 October, the soil was moist at fertilizer application and precipitation was lacking or fell at the end of the treatment period. Sufficient time passed for hydrolysis and volatilization to take place before either precipitation fell or the microplots were removed from the field. Black et al. (1987) concluded that the timing of water application was critical in reducing volatilization losses when urea was applied to moist soil in a pasture. If the urea had already hydrolyzed before irrigation, the benefits of additional water in reducing volatilization losses were lessened. When urea was applied to moist soil without subsequent watering NH_3 losses peaked 2 d after urea application and were slow by the fifth day.

Statistical analysis for the fall application dates on stubble indicates a highly significant ($P=0.001$) interaction for fertilizer application date x fertilizer treatment for the mineral N method. This interaction was also significant ($P=0.01$) for the ^{15}N method. Statistical analysis for the spring application dates on stubble indicates a significant ($P=0.001$) interaction for fertilizer application date x fertilizer treatment for the mineral N method but this interaction was not significant for the ^{15}N method. Volatilization loss from stubble during 6 to 16 October appears to be greater than that of 13 to 23 October because of inhibition of volatilization due to a faster soil drying rate caused by warmer temperatures during the latter period. Air temperatures were generally cooler during 6 to 16 October which could have slowed the rates of hydrolysis and soil drying and prolonged the period of NH_3 volatilization. If soil dries before hydrolysis is complete, volatilization is reduced (Reynolds and Wolf, 1987a). The magnitude of volatilization loss depends on the amount of urea hydrolyzed before drying occurs. Immediate soil drying can reduce NH_3 volatilization by inhibition of urea hydrolysis.

Ammonia Loss Events by Soil Cover Type

The magnitude of NH_3 volatilization losses could not be statistically compared between soil cover types due to the design of the experiment. Comparisons of variations in NH_3 loss events between experimental sites can only be qualitatively made.

More NH$_3$ loss events were detected on stubble than tilled soil or pasture. Stubble has a higher volatilization potential than tilled soil due to the combination of high urease activity and slower soil drying rate. Following precipitation, bare soil dries faster than soil covered by stubble especially for the first 5 d after precipitation. Stubble cover slows the rate of soil drying by decreasing wind speed at the soil surface (Enz et al., 1988). Soil drying can inhibit urease activity and, therefore, slow hydrolysis and volatilization (Reynolds and Wolf, 1987a). The tilled soil in the current research would have dried at a faster rate than stubble, shortening the period during which volatilization could take place, and effectively reducing or preventing NH$_3$ volatilization losses. Bacon et al. (1986) reported greater NH$_3$ losses from standing stubble than tilled stubble and attributed this to less moisture loss from the untilled stubble and NH$_3$ lost from urea held in the stubble.

Fewer loss events occurred on pasture than on stubble. The pasture site was expected to produce more NH$_3$ loss events than the tilled soil and stubble sites due to high urease activity of the thatch layer (Bowman et al., 1987). The higher CEC at the pasture site may be partially responsible for this result. A high CEC gives the soil greater potential to adsorb NH$_4^+$ after urea hydrolysis and to prevent NH$_3$ losses (Reynolds and Wolf, 1987b; Nelson, 1982).

The moisture dynamics of the thatch layer may also have reduced the number of NH$_3$ loss events on pasture. The water content of soil or crop residues influences the rate of urea hydrolysis (Ferguson et al., 1988). The fertilizer was in direct contact with the thatch rather than the soil surface. The thatch was usually drier at fertilizer application than the soil. The urea, as a result, would have hydrolyzed slowly. Subsequent heavy rains could have moved the unhydrolyzed urea into the soil without volatilization losses taking place.

Ammonia "Increase" Events

The experimental data occasionally showed greater recovery of urea-N over ammonium nitrate-N. Such anomalies deserve discussion. The mineral N method compared inorganic N recovery of urea versus

ammonium nitrate, without regard to the ^{15}N label. Any set of environmental conditions leading to nitrate loss (leaching or denitrification) would favor loss from ammonium nitrate over urea, particularly if nitrification of the added urea-N was not complete.

Heavy rainfall (over 6 cm) fell during the 1 to 12 May exposure period and leaching or denitrification could have occurred. Correspondingly, there was superior recovery of mineral N from urea than ammonium nitrate on tilled soil (Table 5). Substantial rainfall (over 4 cm) fell during the 16 to 27 May exposure period, and again mineral N recovery for urea was greater than ammonium nitrate on untilled soil. Leaching or denitrification is the most likely explanation for these two results.

A statistically significant greater recovery of ^{15}N from the urea treatment than from ammonium nitrate was estimated for tilled soil during the 27 May to 5 June period and for the pasture site during the 4 to 18 September period (Table 6). An explanation for these results is not evident, as the ^{15}N-labelled urea and the ^{15}N-labelled ammonium in the ammonium nitrate should have been equally subject to transformations such as immobilization, nitrification, and subsequent leaching or denitrification. The only possible explanation for these two anomalous results is that some undetected error occurred during the many steps needed to prepare soil samples for ^{15}N analysis or during distillation.

Comparison of ^{15}N and Mineral N Methods

The relative N recoveries of the mineral N and ^{15}N methods are compared in Figure 1. The quadratic model describes the relationship better than the linear model and the best fit was obtained with the equation:

$$Y = 6.526 + 0.309X - 0.015X^2, \text{ where}$$

X = relative N recovery detected by the mineral N method, %

Y = relative N recovery detected by the ^{15}N method, %.

The coefficient of determination (r^2) for this equation is 0.78. The value of the pasture site for 4 to 18 September was an outlier and excluded from calculation of the regression line. Almost all points fall above the 1:1 line, indicating that the mineral N method gives, in general, larger estimates of NH_3 loss than the ^{15}N method. The best agreement between the two methods was when both detected an NH_3 loss and drying conditions had occurred. The relationship for these data points is almost linear. This indicates that wet weather conditions may have affected mineral N recovery more than ^{15}N recovery.

The coefficients of variability (CV) of the two methods were similar for each individual treatment period and site. The average CV for both methods were approximately 10%, indicating no difference in precision between the two methods.

The mineral N method is simple and inexpensive. The inorganic N fraction, however, is subject to losses other than those of NH_3 volatilization such as immobilization losses, other gaseous losses, plant uptake, and leaching, which would cause lower N recovery values (Black et al., 1985). The ^{15}N method is less subject to errors from N transformations (e.g., immobilization) but involves expensive and more complex analyses through which errors can be introduced during sample preparation and in laboratory determinations (Buresh et al., 1982).

A suggested improvement in this research for future studies is to compare mineral N recovery of urea to ammonium chloride instead of ammonium nitrate. Then, both N sources would supply all of the N in the ammonium form, and chloride recovery could serve as an independent measure of leaching.

The thatch layer of the pasture site should have been sampled for water content because it may have insulated the urea from moist soil and slowed hydrolysis. Also, the determination of urease activity at each fertilizer application would give a better indication of the importance of this soil property for each period. Determination of H^+ buffering capacity would give an indication of NH_3 volatilization potential of the soils and help explain differences in results between different sites.
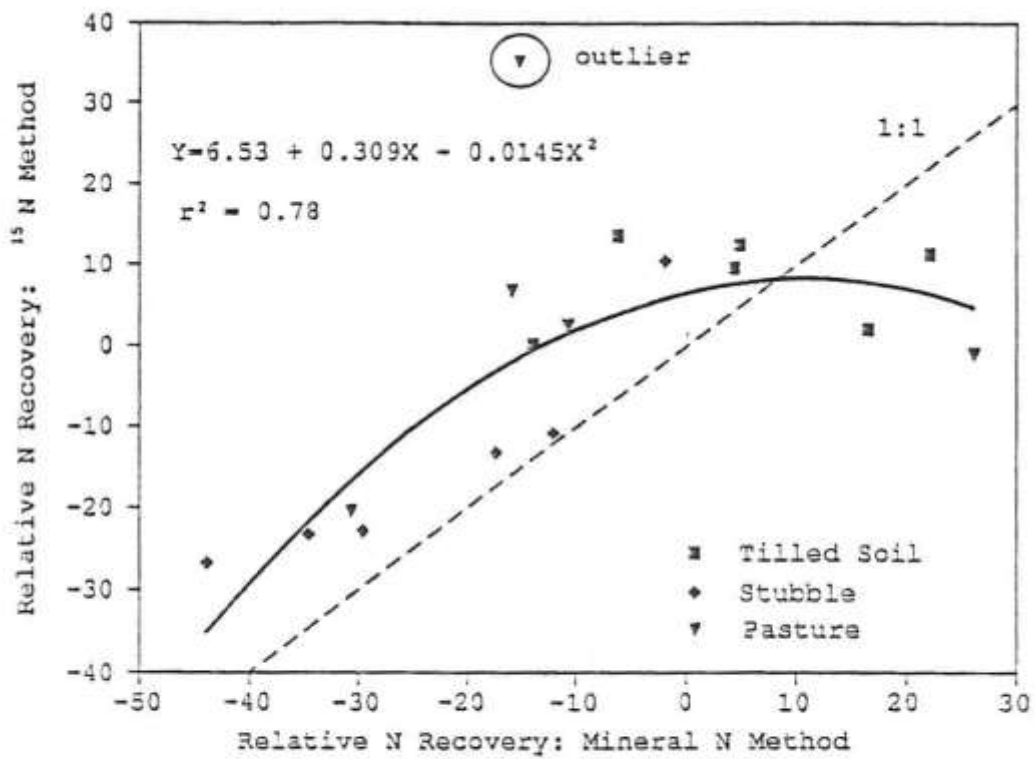
Figure 1. Comparison of mineral N and ^{15}N methods used to estimate NH_3 volatilization losses for three soil cover types.

CONCLUSIONS

Significant NH_3 volatilization losses were found to occur on barley stubble and native pasture in southwestern North Dakota. Loss events were associated with high urease activity and drying conditions. Soil water content near -33.3 kPa potential at fertilizer application appeared to be sufficient for urea hydrolysis. Ammonia volatilization losses occurred when drying conditions followed urea applications made to moist soil.

Urea applied to tilled soil was not subject to significant NH_3 volatilization on the soils tested due to low soil pH, low urease activity, and a rapid rate of drying which inhibited urea hydrolysis and NH_3 volatilization. Ammonia increase events on tilled soil were apparently caused by NO_3^- leaching from the ammonium nitrate treatment.

Low water content of the thatch layer of the pasture site at fertilizer application reduced the number of NH_3 volatilization loss events by slowing the rate of urea hydrolysis. Volatilization was possibly reduced in part by the relatively high CEC of the pasture soil.

The two methods used to estimate NH_3 volatilization losses were equally precise in this study although the mineral N method gave higher estimates of NH_3 loss. The mineral N method was easier to use, less costly, and less subject to analytical errors. Inorganic N is subject to losses other than volatilization, e.g., immobilization and denitrification, which can cause overestimation of volatilization losses.

The ^{15}N method, while less subject to some of the problems of the mineral N method, is costly, time-consuming, and subject to analytical errors due to the many steps involved in the analysis. Experience in using this technique is the best means of preventing errors. A N recovery technique, such as that used in this experiment, cannot account for all possible sources of variability in the results.

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