Recovery of Nitrogen by Corn from Solid Fertilizers and Solutions

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Four greenhouse pot experiments were conducted to measure recovery of applied N by corn (*Zea mays*) from various solid N sources and solutions. Crop recovery was low from sources containing amino N, such as urea, formamide, hexamine, and oxamide surface-applied to both acid and alkaline soils. Much higher recovery resulted from mixing these fertilizers with the soils. Greatest recovery (least loss, presumably by NH_3 volatilization) resulted from NH_4NO_3 and $NH_4H_2PO_4$. Similar results were obtained with solid and solution sources. Volatilization loss as NH_3 increased in the laboratory to a maximum of 9% over a 41-day period at 24° C. with increase in proportion of urea in solutions and was less with moist than with drier (70% RH) aeration. Much greater loss was indicated by lower N recovery by corn grown after a 1-week drying period (24° to 32° C.) prior to planting. Guanyl urea nitrate, guanyl urea phosphate, and potassium dicyandiamide were toxic for corn growth.

Use of N solutions for fertilizing various crops has been increasing rapidly over the past several years. Surface application to the soil accounts for much of the tonnage applied, although some may be incorporated into the soil during plowing or cultivation. Results summarized by Gasser (1964), Terman (1965), and others indicate that volatilization losses as NH_3 may be serious from urea surface-applied to both acid and alkaline soils and from ammonium fertilizers on alkaline soils. However, results are commonly satisfactory with urea and other N fertilizers surface-applied for grass or small grains during late winter and early spring when cool, moist conditions prevail.

Rather variable results have been obtained in comparisons of solution and solid sources of N surface-applied to various crops and soils (Nowakowski et al., 1967; Volk, 1966). Results are apparently influenced by type of soil and crop, temperature, moisture, and other factors.

This paper summarizes results from four greenhouse pot and laboratory experiments carried out to evaluate volatilization losses and crop recovery of N from several potential new N fertilizers. These were compared with standard sources applied in both solution and solid forms as sources of N for corn.

EXPERIMENTS AND RESULTS

Fertilizers Compared. Standard N fertilizers compared in the experiments (Table I) included ammonium nitrate [AN, NH_4NO_3], ammonium sulfate [AS, $(NH_4)_2SO_4$], monoammonium phosphate [MAP, $NH_4H_2PO_4$], diammonium phosphate [DAP, $(NH_4)_2HPO_4$], ammonium phosphate nitrate (APN, largely AN and MAP), and urea [U, $CO(NH_2)_2$].

Urea-AN suspension (UAN, 37% N) was developed recently by TVA as a high analysis fluid N source. Other suspension fertilizers made with 12-40-0 and clay were also included in experiment 3. The 12-40-0 suspension and solid ammonium polyphosphate (APP) are produced by TVA by ammoniation of superphosphoric acid (Scott

et al., 1967). Formamide and UAN-formamide solutions (Jones et al., 1966), as well as solids such as oxamide and hexamine (hexamethylenetetramine), are potential fertilizer materials. Humic acid is a potential slow-release N fertilizer.

Guanylurea nitrate, guanylurea phosphate, and potassium dicyandiamide were included in experiment 3, since little information was available on the agronomic effects of these compounds.

EXPERIMENT 1. Hartsells fine sandy loam (pH 5.2, CEC of 7.6 meq. per 100 grams, Colbert County, Alabama) was limed to pH 6.3 with 3.75 grams of a 4 to 1 mixture of $CaCO_3$ and $MgCO_3$ per pot for two series of treatments. For a third series, 2.5 cm. of the soil limed to pH 7.5 was placed over the pH 6.3 soil in pots.

Sufficient concentrated superphosphate to supply a total of 500 mg. of P was mixed with 3 kg. of soil per pot. In series 1, various N fertilizers (Table I) were mixed with the entire amount of soil to supply 300 and 600 mg. of N (100 and 200 p.p.m.) per pot on September 19, 1963. Water was then added to bring the soil to 18% moisture ($^1/_3$ atm.). For series 2 and 3, first the water was surface-applied and then fertilizers were applied to the moist soil surface. After 7 days on greenhouse benches, during which 150 ml. of water per can were added so as to avoid contact with the fertilizers on the surface, corn was pushed 2.5 cm. deep into the soil on September 26, with minimum disturbance of the soil. For a duplicate series of pots receiving granular urea and AS, the surface 2.5 cm. of soil was mixed just prior to planting. All pots also received K_2SO_4 in solution to supply 200 mg. of K per pot. The crop was harvested on November 12, at which time all of the plants were N-deficient.

All treatments, including no applied N, were replicated three times in experiments 1 to 4 in 4-liter greenhouse pots lined with polyethylene bags and containing 3 kg. of dry soil per pot. Seven hybrid corn seeds were planted and plants were later thinned to five per pot. Water was surface-applied as needed to bring each soil to $^1/_3$-atm. moisture tension. Yields of dry corn forage and content of N (by a micro-Kjeldahl procedure) were determined by individual pots in all experiments.

Crop uptake of N was linear with amount applied in all

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Table I. Properties of Fertilizers Compared as N Sources in Experiments

N Source	Symbol	Total N, %	N as NO₃, %	Total P, %	pH[a]	Experiment in Which Compared
Solids, mesh size						
NH₄NO₃, −6 +14	AN	33.8	16.9	...	5.8	1, 2, 3
(NH₄)₂SO₄, −6 +14[b]	AS	20.9	0	...	5.3	1, 2
Ammonium phosphate nitrate						
(25–25–0), −6 +14	APN	26.5	9.5	11.0	6.2	1
(NH₄)₂HPO₄, −6 +14	DAP	20.9	0	22.9	7.7	2
NH₄H₂PO₄, −6 +14	MAP	11.7	0	22.1	4.5	2
Urea, −6 +14[b]	U	46.5	0	...	8.8	1, 2
Oxamide, −100[b]	Oxamide	31.8	0	...	4.6	1
Hexamide, −14 +20[b]	Hex.	40.0	0	...	7.6	1
Ammonium polyphosphate	APP	11.8	0	26.5	4.3	3
Humic acid[b]	HA	20.3	0	...	...	3
Guanyl urea nitrate	...	37.1	7.4	...	...	3
Guanyl urea phosphate	...	27.8	0	15.5	...	3
Potassium dicyandiamide	...	38.9	0	...	...	3
Solutions						
8–24–0	...	7.8	0	10.5	...	3
Formamide[b]	...	30.6	0	...	6.6	1, 3
Urea, 100%	U	23.3	0	...	...	1
Urea-AN	UAN	32.0	7.8	...	...	1
UAN-formamide	UANF	35.5	3.5	...	...	1
AN, 100%	AN	20.5	10.3	...	5.8	1, 4
75% AN, 25% urea	...	19.5	7.3	...	6.1	4
25% AN, 75% urea	...	20.2	2.5	...	6.9	4
Urea, 100%	U	20.5	0	...	8.8	4
UAN suspension	UAN	36.8	5.0	...	7.1	4
12–40–0 + UAN suspension	...	31.8	<4	3.8	5.7	4
12–40–0 + UAN suspension	...	28.1	<4	6.1	5.6	4

[a] pH of solid materials was that of saturated aqueous solutions.
[b] From commercial sources. Other fertilizers prepared by TVA.

experiments. Consequently, apparent N recoveries were calculated by the least squares method, using a concurrent linear regression model. This model accounted for 92 to 98% of the variation in crop uptake of N from the various soils and placements of N.

Yields of dry corn forage shown in Figure 1 were similar among the various N fertilizers mixed with the soil. However, marked differences in yields occurred among the fertilizers surface-applied to the soil at pH 6.3 and 7.5. Interpretations based on either curvilinear yields of forage or linear uptake of N were similar.

Apparent recoveries of applied N calculated by the least squares method (Table II) from fertilizers mixed with the soil at pH 6.3 ranged from 68 to 79%. Recovery from liquid and granular urea and from granular AS and APN mixed with the soil was higher than from the other fertilizers. No explanation for this result is apparent.

With surface application, recoveries of N varied widely from a low recovery of 15% from urea solution to 78% with granular APN. The orders of recoveries were as follows:

pH 6.3. APN > solution and granular AN = granular AS > urea-AN solution = hexamine > urea-AN-formamide > formamide = oxamide > solution or granular urea.

pH 7.5. APN > solution and granular AN = granular AS > hexamine > urea-AN > urea-AN formamide > oxamide > formamide > solution and granular urea.

These results are consistent with previously published

Table II. Apparent Recoveries of N from Fertilizers Mixed with and Surface-Applied to Hartsells Fine Sandy Loam (Experiment 1)

N Source	Recovery of Applied N, %		
	Mixed, pH 6.3	Surface, pH 6.3	Surface, pH 7.5
Formamide (solution)	74 a, b[a]	32 e	26 g
AN (solution)	...	75 a, b	73 a, b
Urea (solution)	79 a	21 f	17 h
Urea-AN (solution)	69 b	56 c	45 d
Urea-AN-formamide (solution)	68 b	43 d	39 e
AN (granular)	71 b	71 b	70 b
Urea (granular)	75 a	23 f	15 h
AS (granular)	76 a	71 b	68 b
APN (granular)	77 a	78 a	77 a
Oxamide (fine)	72 b	34 e	32 f
Hexamine (granular)	71 b	52 c	61 c

[a] Recoveries in each column followed by the same letter are not significantly different at the 5% level of probability in this table and Tables III, IV, and VI.

results (Terman and Hunt, 1964) and indicate greatest N volatilization loss from urea and least from APN and AN. All of the compounds which contain NH_2 groups—urea, formamide, oxamide, and hexamine—resulted in poorest crop recovery of N, if surface-applied to soil. Recovery from all of these compounds was lower at higher soil pH.

Compounds such as AS and DAP are also subject to NH_3 loss from reaction with Ca compounds in neutral
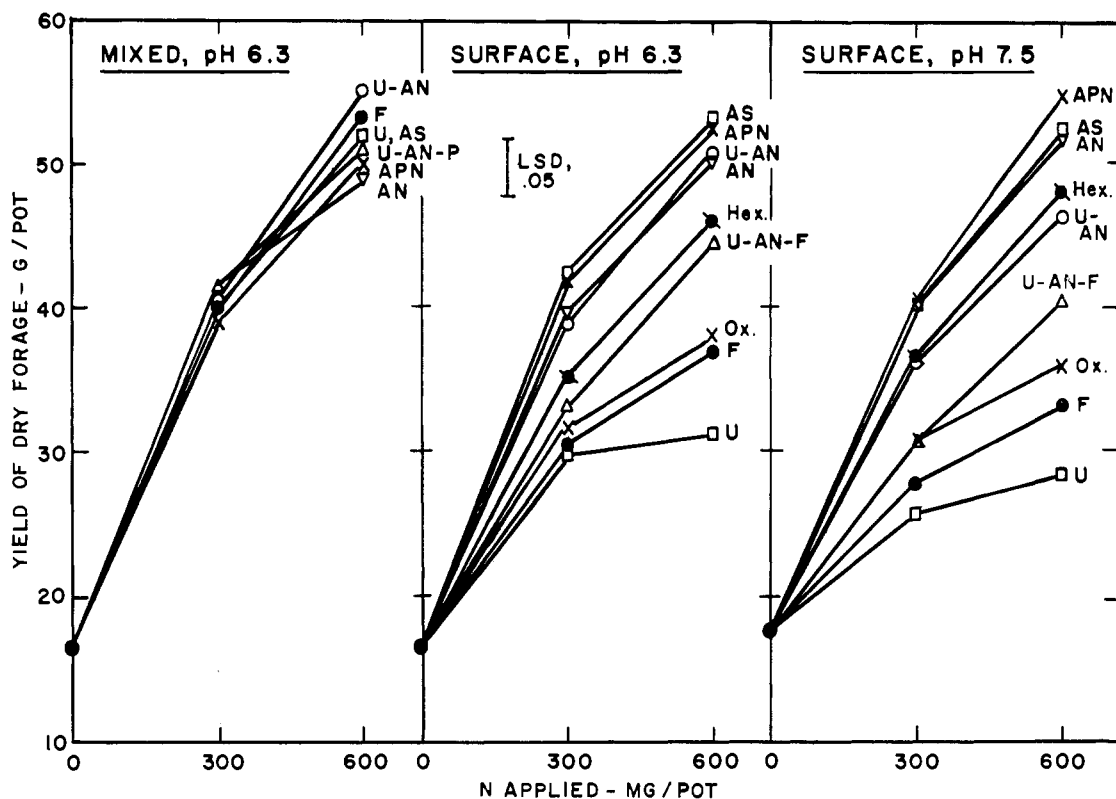
Figure 1. Effect of source, rate, and method of application of N fertilizers on yields of dry forage

Experiment 1

to calcareous soils (Larsen and Gunary, 1962). Losses of N as NH_3 from MAP, AN, APP, and APN in most soils are low or negligible because of chemical reactions which form nonvolatile intermediate products (Terman and Hunt, 1964).

Yields and uptake of N from cultures in which the surface soil was mixed just prior to planting (data not shown) were not appreciably greater than from unmixed cultures. This indicates that the major volatilization losses of N as NH_3 occurred during the 7-day drying period prior to planting and subsequent surface watering.

EXPERIMENT 2. Hartsells soil limed to pH 6.3 (2.5 kg.) was placed in all pots. Then 0.5 kg. of the following soils was placed on top of the Hartsells soil: Gila sand (Arizona), pH 8.5; Platner silt loam (Colorado), pH 8.2; Wisner silt loam (Michigan), pH 8.0; and Webster silty clay loam (Iowa), pH 8.3.

After watering to 18% moisture, N fertilizers (Table I) were surface-applied to supply 300 and 600 mg. of N per pot. One week later (February 24, 1964), corn seeds were pushed into the soil to a depth of 2.5 cm. Monocalcium phosphate in solution was added to the surface in four weekly increments of 300 mg. of P as necessary to equalize all pots to a total of 1200 mg. of P. K_2SO_4 was added to supply 200 mg. of K. The crop was harvested on April 10.

Average apparent recoveries of N by corn from the four soils (Table III) were in the following order: AN = MAP > AS > DAP > urea. Differences in yields of dry matter were in the same order.

Recovery of N from AN was considerably lower than in experiment 1 with application to Hartsells fine sandy

Table III. Apparent Recoveries of N Surface-Applied to Four Calcareous Soils (Experiment 2)

Solid N Source	Recovery of Applied N, %				
	Gila s	Platner sil	Wisner sil	Webster sicl	Av.
AN	54 a	60 a	61 a, b	52 a	57
MAP	52 a	60 a	65 a	56 a	58
AS	37 b	59 a	53 c	36 c	46
DAP	26 c	55 a	58 b	34 c	43
Urea	27 c	44 b	32 d	44 b	37

loam limed to pH 6.3 and 7.5. Moreover, recovery of N from MAP was lower than has been observed following application to a heavily limed Hartsells soil. Since the corn was very N-deficient (yellowed) at harvest in both experiments, the lower recovery in experiment 2 indicated greater N loss by volatilization from these naturally calcareous soils. The lower recoveries from the ammonium N sources, AS and DAP, indicate greater reaction of these compounds to form unstable $(NH_4)_2CO_3$. Urea, from which the lowest average recovery of N was obtained, hydrolyzes directly to $(NH_4)_2CO_3$. The cause of the differences in N recoveries among soils was not determined. Factors in addition to soil texture appear to be involved. Court et al. (1963) found that in England response of corn to urea was positively correlated with clay content of 42 soils but not with organic matter content, pH, exchangeable H^+, CEC, or moisture content.

EXPERIMENT 3. Mountview silt loam (pH 5.0 and

CEC of 12.6 meq. per 100 grams; Lawrence County, Tennessee) was limed to pH 6.5 for this experiment. Sufficient concentrated superphosphate was added for each treatment to equalize the total to 1348 mg. of P per pot. K_2SO_4 to supply 200 mg. of K and $ZnSO_4$ to supply 15 mg. of Zn were also added per pot. The N sources (Table I) were either surface-applied (except AN) to supply 300 and 600 mg. of N per pot or covered with soil to a depth of 5 cm. just prior to planting corn and watering to 18% moisture on May 5, 1964. Corn forage was harvested on June 15.

Yields of dry corn forage (Figure 2) were highest and similar for AN, 8-24-0, ammonium polyphosphate (APP), and formamide layered in the soil. Yields were lower with surface-applied 8-24-0 solution, formamide, and humic acid than with layering of these N sources in the

soil. Yields with APP were only slightly lower with surface application.

Apparent recovery of N from surface-applied formamide (Table IV) was only 29%, as compared to 77% when layered. These results verify that the poor recovery obtained with surface-applied formamide in experiment 1 was due largely to volatilization loss of N. Recoveries from APP and 8-24-0 sources were also lower with surface application, but to a lesser degree. The low N recovery from humic acid either surface-applied or layered (40%) indicates that much of this N remained in the soil in an organic form not readily available to crop plants. It is also possible that microbial degradation of humic acid could have produced certain phytotoxic constituents that limited plant growth (Wang et al., 1967).

Recovery from guanyl urea nitrate, initially slightly toxic to growth at both N levels, was lower than from humic acid. Recovery was still lower from guanyl urea phosphate, which remained sufficiently toxic to produce a slight yield depression. Potassium dicyandiamide was much more toxic to growth and marked yield depression resulted (Figure 2).

EXPERIMENT 4. On August 23, 1966, N solutions (Table I) were surface-applied to Hartsells fine sandy loam (pH 6.3) containing 18% moisture, into which had been mixed the following per pot: 3.75 grams of a 2-to-1 mixture of $CaCO_3$ and $MgCO_3$, 200 mg. of K as K_2SO_4, P equalized to 500 mg. with concentrated superphosphate, and 300 mg. of a mixture of all essential micronutrients. Rates of N were 300 and 600 mg. per pot.

Polyethylene lids with inlet and outlet hoses were then

Table IV. Apparent Recoveries of N Surface-Applied and Layered in Mountview Silt Loam (Experiment 3)

N Source	Recovery of Applied N, %	
	Surface-applied	Layered
AN	. . .	74 a
Liquid 8-24-0	60 b	80 a
Formamide	29 d	77 a
Humic acid	40 c	40 b
APP	70 a	76 a
Guanyl urea nitrate	22 e	18 c
Guanyl urea phosphate	19 e	5 d
Potassium dicyandiamide	0	0

Table V. Yields of Dry Corn Forage, N Volatilized as NH_3 during 41-Day Aeration, and Uptake of N by Corn Following Aeration (Experiment 3)

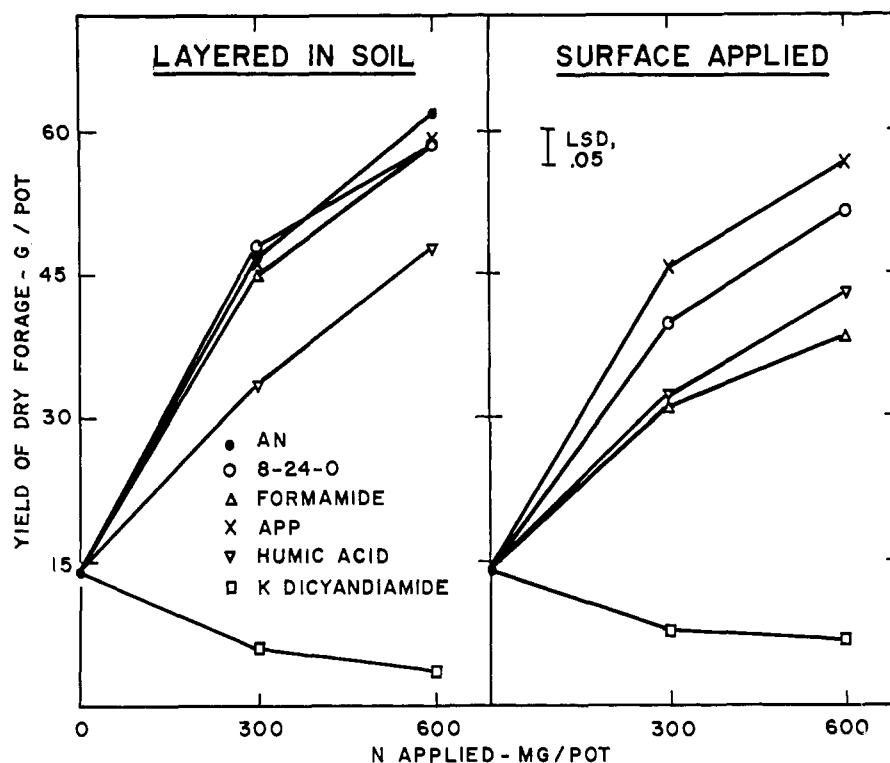| N Source	N Applied, Mg./Pot	Moist Aeration			Dry Aeration		
		Dry forage, g./pot	N evolved, mg./pot	N uptake by corn, mg./pot	Dry forage, g./pot	N evolved, mg./pot	N uptake by corn, mg./pot
100% AN	300	38	2	268	39	1	271
	600	56	1	518	51	1	477
75% AN, 25% urea	300	39	1	271	38	1	288
	600	53	2	461	53	2	470
25% AN, 75% urea	300	38	7	258	38	4	261
	600	54	16	484	51	28	455
100% urea	300	38	9	271	39	6	272
	600	53	45	466	52	55	413
UAN suspension	300	36	5	282	34	2	244
	600	55	20	481	53	22	440
32-8-0	300	38	3	272	38	3	272
	600	50	17	458	51	22	403
28-14-0	300	39	4	280	39	2	262
	600	54	16	462	52	18	484
No N	0	13	1	77	14	1	80
LSD, 5% level		4	. . .	83	4	. . .	83
CV, %		4.8	. . .	13.9	4.8	. . .	13.9

Figure 2. Effect of N source and placement on yields of dry corn forage

Experiment 3

Table VI. Apparent Recoveries of Applied N by Corn Forage and Totals Recovered during Aeration and by Corn (Experiment 4)

N Source	Moist Aeration, %		Dry Aeration, %	
	Recovery by corn	Aeration loss + recovery by corn	Recovery by corn	Aeration loss + recovery by corn
100% AN	73 a	74 a	65 a	69 a
75% AN, 25% urea	65 b	66 b	65 a	67 a, b
25% AN, 75% urea	67 b	71 a	61 b	67 a, b
100% urea	66 b	73 a	57 b, c	65 b
UAN suspension	68 b	72 a	58 b, c	63 b, c
32-8-0	65 b	68 a, b	55 c	60 c
28-14-0	66 b	69 a, b	65 a	69 a

fitted to the pots. One series was continuously force-aerated with NH₃-free, H₂O-saturated air near 100% relative humidity and a second series with NH₃-free drier air (70% RH) at an ambient temperature of 24° C. The rate of air flow was sufficient to change the volume above the soil four times per hour. The evolved NH₃ was trapped in dilute HCl and the amount determined at eight intervals over a 41-day period.

Weights at the end of the drier aeration period showed that the soil lost from 70 to 85 grams of H₂O (a reduction from 18 to 15% moisture content). With moist aeration, there was no change in soil moisture content.

After the aeration period, the surface 2.5 cm. of soil was

mixed and corn planted on October 5. The crop was harvested November 23.

Loss of NH₃ during Aeration. As shown in Table IV, only 1 to 2 mg. of N was lost with no applied N and with 300 or 600 mg. of N applied as the 100% AN and 75% AN-25% urea fertilizers. Losses from 300 mg. of N as the other fertilizers ranged from 2 to 7 mg. of N (maximum of 2% loss). Losses from the 600-mg. rate ranged from 16 to 55 mg. (maximum of 9%) and increased in general with the content of urea. Losses were slightly higher with drier (70% RH) than with moist aeration. Cumulative losses from 600 mg. of N with the drier aeration shown in Figure 3 increased over the entire 41-day aeration period from solutions containing urea.

Response by Corn. Yields of dry corn forage (Table V) ranged from 34 to 39 grams per pot with 300 mg. of applied N and from 50 to 56 grams with 600 mg. Thus, there was a marked effect of rate of applied N, but rather minor differences among N sources. This apparently resulted largely from the rather small differences in volatilization losses prior to cropping. Total aeration losses and uptake of N by corn were also rather similar among sources.

With moist aeration, the highest recovery after the drier aeration was only 66%. An explanation is not apparent for this result, although possibly greater immobilization of NH₃ N in dry soil (Parr and Papendick, 1966) and/or volatilization losses by other pathways may be the cause (Allison, 1963). Recoveries from the other solutions were lower but not related to urea content.

With the drier aeration, recoveries of N by corn decreased with increase in urea content of the AN-urea solutions, reflecting the increase in NH₃ volatilization.
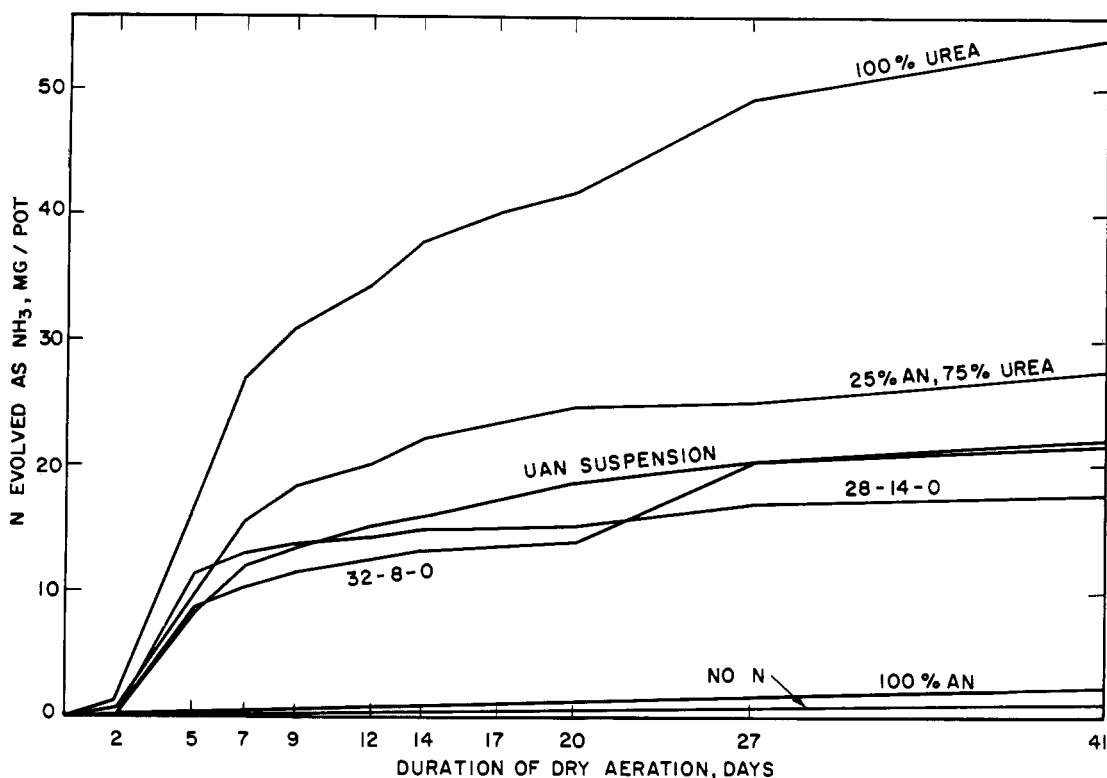
Figure 3. N volatilized as NH_3 during 41 days of dry aeration from 600 mg. of N per pot

Experiment 4

Recoveries from other solutions did not appear to be related to urea content. Lowest recovery was from the 32-8-0 solution (Table VI).

Recoveries by corn plus losses during the prior aeration period differed appreciably among N sources. As for the generally lower total recovery following dry aeration, no explanation is apparent.

CONCLUSIONS

Volatilization of N as NH_3 from surface-applied urea and NH_4 N sources under laboratory conditions show small percentage losses of the applied N unless air exchange is very rapid (Overrein and Moe, 1967). Losses in some pot and field tests are also low; in others, losses are high. For example, similar yield responses to urea and other N sources have been reported with late winter or early spring topdressings for grass or small grains (Devine and Holmes, 1965). Cool, humid weather generally prevails during this period. Results from field experiments carried out at Muscle Shoals, Ala. (TVA, 1967), in 1965-67 also indicate that urea topdressed for grass in winter and early spring is nearly as effective as other N sources. In England, Cooke (1964) reported that urea averaged about 80% as effective as AN per unit of N for grassland. In contrast, high volatilization losses of N as NH_3 have been reported during high temperature drying conditions.

The present studies on crop recovery of applied N suggest that high temperatures, accompanied by rapid drying, are very important in N losses as NH_3 from surface-applied urea and other compounds containing NH_2 N. The same is true for NH_4 N sources on calcareous soils. Low volatilization losses under laboratory conditions

can be attributed largely to lower ambient temperatures and reabsorption of NH_3 by the soil in the closed systems employed.

Except for guanyl urea nitrate, guanyl urea phosphate, and potassium dicyandiamide, to which corn exhibited varying degrees of toxicity, roots completely permeated the soil mass. Thus, the poor recovery of surface-applied N cannot be attributed to ammonium toxicity or poor moisture supply near the soil surface. Surface application of water also made this possibility unlikely.

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