

Ammonia Losses from Surface-Applied Urea and Ammonium Fertilizers as Influenced by Rate of Soluble Calcium¹

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ABSTRACT

Previous research has shown that applying large amounts of soluble Ca with urea and NH_4 fertilizers depressed ammonia (NH_3) losses extensively. This paper reports effects of varying amounts of Ca on reduction of this loss. Ammonia loss was progressively less with increasing Ca/N ratios. In the greenhouse, a Ca/urea-N equivalent ratio of 0.25 reduced NH_3 losses to 11% of applied N. In the laboratory, this ratio reduced NH_3 -N losses to 42% of applied N; without Ca, N losses were 75%.

Soluble Ca was effective in reducing NH_3 losses from urea when surface applied to both acid and calcareous soils. Increased acidity from the application of soluble Ca salts on acid soils reduced the amount required to reduce NH_3 losses. Soluble Ca applied with $(\text{NH}_4)_2\text{SO}_4$ (AS) and NH_4NO_3 (AN) also reduces NH_3 losses from calcareous soils. Reduction of NH_3 losses from AN was due solely to lowered soil pH values. However, reduction of NH_3 loss from urea and AS was possibly due both to CaCO_3 precipitation and soil pH depression.

Additional Index Words: NH_3 loss, Ca/N ratios, Mg/N ratios, N fertilizers, plant N uptake, sodalgrass.

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REACTIONS OF N FERTILIZERS with water-soluble and exchangeable Ca and Mg are not well documented. An increase in solution pH due to anhydrous ammonia (NH_3) added to irrigation waters has been shown by Miyamoto et al. (7) to precipitate Ca and Mg as carbonates; addition of sulfuric acid prevented the precipitation. Increase in soil CO_2 levels caused a steady decrease in NH_3 lost from Ca-saturated soils, leading DuPlessis et al. (1) to postulate that increasing CO_2 precipitated more Ca as CaCO_3 . Removal of Ca adsorbed on clay particles resulted in Ca being replaced by NH_4 .

Fenn and Kissel (2) showed that NH_4F , $(\text{NH}_4)_2\text{SO}_4$, or $(\text{NH}_4)_2\text{HPO}_4$ applied to calcareous soil increased soil pH to 8.9 as a result of production of $(\text{NH}_4)_2\text{CO}_3$ (AC). Other work (6) showed that AC formed from applied urea raised soil pH to 9.2 in both acid and calcareous soils. Such pH increases cause Ca and Mg precipitation, allowing NH_3 to occupy CEC sites on a relatively noncompetitive basis. Desorption of NH_3 under these conditions will occur only when Ca and Mg are reintroduced, or when NH_3 is nitrified.

Surface applications of soluble Ca and Mg nitrates or chlorides at an equivalent ratio of urea-N reduced NH_3 losses 90% when compared with urea alone (6). Ammonia loss was reduced by both CaCO_3 precipitation

and reduction of soil pH by soluble Ca and Mg, but the exact contribution of each remains obscure.

Previous research (5, 6) has shown a relationship between changes in NH_3 losses and extractable soil Ca and Mg. It seems probable that inclusion of soluble Ca and Mg salts with N-fertilizers could be economical if Ca/N ratios < 1 adequately inhibit NH_3 losses.

The objective of this study was to determine volatilization losses of NH_3 from surface-applied urea and NH_4 -N fertilizers, as affected by Ca/N ratios.

MATERIALS AND METHODS

Laboratory Study

A series of laboratory experiments was conducted to determine NH_3 losses from urea, AS, and AN (NH_4NO_3) surface applied to wet Harkey silt, Darco fs, and Beaumont c at 550 kg of NH_4 -N or NH_3 -N/ha (Table 1). All soils were oven-dried at 105°C, sieved through a 1-mm screen, and 1.0% organic matter (bluegrass clippings) added. Then 2.5 cm of soil (250 g) were placed in columns on sand which had been previously leached and saturated with distilled water. The experimental soil was kept moist by water from the subsoil for 10 to 14 days. Calcium carbonate (15% by weight) was blended with Harkey silt whereas acidic Darco fs and Beaumont c were not limed.

Equivalent (eq) ratios of 0:1 to 2:1 of Ca [CaCl_2 or $\text{Ca}(\text{NO}_3)_2$] to NH_4 -N were surfaced applied in 3 to 5 ml solution of urea or AN to each soil. Ammonium sulfate and CaCl_2 or $\text{Ca}(\text{NO}_3)_2$ were surfaced applied in separate solutions as they could not be mixed due to CaSO_4 precipitation.

Volatilized NH_3 was collected for periods of 10 to 14 days at 32°C. The studies were terminated when NH_3 -N loss was < 1%/day of applied N. The physical arrangement for NH_3 collection was described previously (2). All tests were replicated four times.

Soil pH was measured daily for 3 days on a paste of 26.6 g of soil consisting of 2 parts Harkey silt and 1 part water with and without Ca as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The 26.6 g soil was used as an approximation of the top 3 mm of experimental soil. Soil pH was similarly measured on comparable soil-CaCl₂ mixture which received 452 mg N (550 kg N/ha) as AC. Exchangeable (including water soluble) Ca and Mg were subsequently determined on samples shaken for 30 minutes and extracted with 2N KCl on a vacuum filter. Calcium plus Mg were determined by titration with 0.01N EDTA in the presence of Eriochrome Black T and $\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer (3).

Greenhouse Study

Greenhouse pots (30 cm by 30 cm) were filled with calcareous sand to within 5 cm of the top and leached with water. Triple superphosphate (5 g) was added to the surface and sudangrass seed [*Sorghum bicolor* (L.) c Bunchmore] was sown and covered with the final 2.5 cm. of sand. This sand had been previously adjusted to 15% CaCO_3 by weight and received 1% new organic matter. Total soil weight was 10 kg/pot. All tests, replicated six times, consisted of ad-

Table 1—Selected physical properties of experimental soils.

Soil	Soil classification	Soil pH	CEC	
			%	meq/100 g
Beaumont c	Fine, montmorillonitic, thermic, Entic Peluderts	4.8	4.8	24.6
Darco fs	Loamy, siliceous, thermic, Grossarenic Peluderts	5.8	0.8	1.0
Harkey silt	Coarse silty, mixed (calcareous), thermic, Typic Torrifluvents	7.8	1.0	14.3

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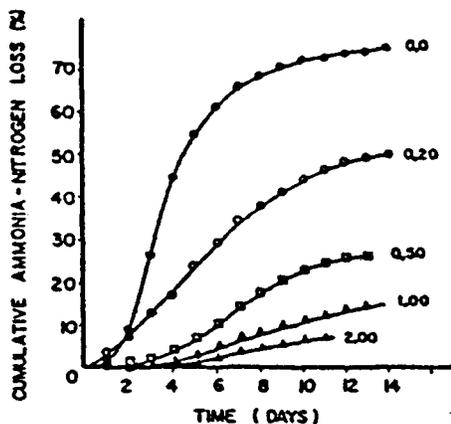


Fig. 1—Cumulative ammonia losses from urea (550 kg N/ha) surface applied to Harkey silt at 32°C as affected by varying soluble Ca/urea-N ratios.

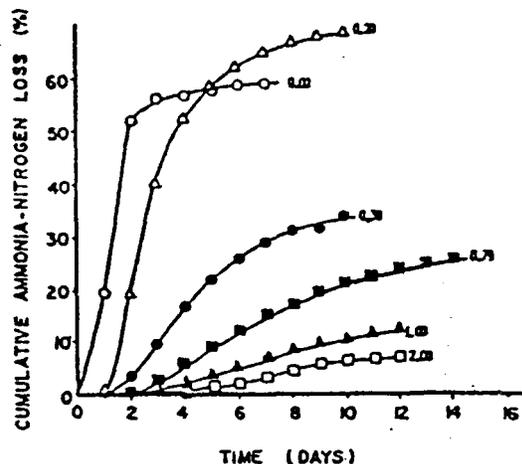


Fig. 2—Cumulative ammonia losses from urea (550 kg N/ha) surface applied to Darco fs at 32°C as affected by varying soluble Ca/urea-N ratios.

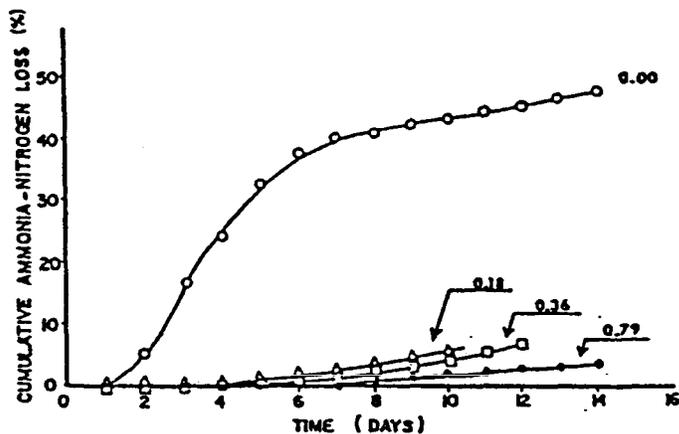


Fig. 3—Cumulative ammonia losses from urea (550 kg N/ha) surface applied to Beaumont c at 32°C as affected by varying soluble Ca/urea-N ratios.

ding CaCl₂ to supply 0, 0.25, and 0.50 eq Ca to 1.0 eq urea-N (550 Kg N/ha) to the sand. In addition, AS received 1.5 eq of Ca to 1.0 eq N. No additional Ca was added to Ca(NO₃)₂ or to the no N check soil. The N and Ca salts were added as solutions to the entire soil surface. Sudangrass was harvested 9 times by clipping at a height of 25 cm when it was 60 to 90 cm tall. At termination of the experiment, the soil was leached with water or KCl to extract residual NO₃-N and NH₄-N. Plant roots were collected on a 0.50-mm sieve and tops and roots analyzed for total N content. The N removed from the check soil was the sum of plant content (tops and roots) and that extracted as NH₄-N and NO₃-N. Use of N by sudangrass was estimated as follows:

$$\text{N recovery (\%)} = \frac{\text{N uptake with applied NH}_4\text{-N} - \text{uptake with no N}}{\text{N recovered with Ca(NO}_3)_2 - \text{uptake with no N}} \times 100$$

RESULTS

Laboratory Studies

Urea alone produced a rapid loss of NH₃, totaling 75% of N applied on Harkey silt (Fig. 1). The addition of 0.20 eq Ca to 1.0 eq urea significantly reduced the initial rate and total loss of NH₃ ($P=0.01$). The total loss was about 50% of the applied N. Increasing Ca/urea-N eq ratio to 0.5, 1.0, and 2.0 significantly decreased the initial and total NH₃ loss to 25, 14, and 6%, respectively, of the applied N ($P=0.01$).

The rate of NH₃ loss from urea alone was extremely rapid from Darco fs (Fig. 2): 20% of applied N the first day, with a final loss of about 60% in 4 days. Addition of 0.20 eq Ca did not reduce initial rate or total NH₃ loss. Then NH₃-N loss at 0.39, 0.79, 1.00, and 2.00 eq Ca to 1.0 eq N was 32, 23, 10, and 5%, respectively, of applied N ($P=0.05$).

Addition of small amounts of Ca eliminated NH₃ loss from urea for 4 to 7 days from Beaumont c, a strongly acid soil (Fig. 3). The greatest loss of NH₃-N occurred at 0.18 eq Ca (about 5% of applied N), but was not significantly different from 0.79 eq Ca.

Urea applied without supplemental Ca to Harkey silt decreased KCl-extractable soil Ca in the top 2.5 cm of soil by 26% of equivalent N added which was equivalent to all available Ca in the top 6.7 mm of soil. Calcium a 0.20 eq resulted in the precipitation of 100% of applied Ca but an increase to 1.0 eq Ca resulted in the precipitation of only 21% of applied Ca.

Use of 0.56 eq Ca with 1.0 eq AS on Harkey silt (Fig. 4) reduced NH₃ losses from 70 to 39% of applied N ($P=0.01$). With an equivalent Ca/N ratio of 1, additional reduction in NH₃ loss seemed to occur but it was not statistically different. Losses from AN with both 0.56 and 1.0 eq Ca decreased from 38 to 18% of applied NH₃-N for both Ca levels ($P=0.01$).

Soil pH dropped rapidly from 8.0 to 6.4 with 25.8 meq Ca (equivalent to 550 kg N/ha) when added to Harkey silt paste (26.6 g soil + 13.3 g H₂O) (Fig. 5). The pH value with pure AC was 9.0 but gradually decreased to 6.0 with an approximate Ca/N ratio of 1. All the Ca was precipitated by AC if the Ca/N ratio was < 1.

Greenhouse Studies

Absorption of N by sudangrass without Ca addition was as follows: urea, 31%; NH₄Cl, 53%; and AS, 20% of added N (Table 2). Addition of Ca at the Ca/urea-N eq ratio of 0.25 increased plant absorption to 89% of applied N, while a ratio of 0.50 further increased N absorption to 94%.

With AS, a Ca/N eq ratio of 1.5 resulted in total N values comparable to those with 0.25 and 0.50 Ca/urea-N ratios.

Table 2—Recovery of surface-applied N by sudangrass from a calcareous sand. The soil was fertilized at 550 kg N/ha in the presence of varying amounts of Ca as CaCl₂.

Nitrogen source	Ca/N ratio	Total dry plant weight	N in grass		Extractable soil N	Relative values†	
			Forage	Roots		N recovery	NH ₃ loss*
			% of applied N				
CO(NH ₂) ₂	0	97.0	22.9	12.1	-	31.1	68.9a
CO(NH ₂) ₂	0.25	167.3	53.5	17.6	-	89.0	11.0b
CO(NH ₂) ₂	0.50	181.2	58.7	19.0	-	94.0	6.0b
NH ₄ Cl	0	111.6	37.0	12.5	-	52.6	47.5c
(NH ₄) ₂ SO ₄	0	95.3	17.8	9.6	-	19.9	80.3a
(NH ₄) ₂ SO ₄	1.5‡	-	-	-	80.1	95.2	4.8b
Ca(NO ₃) ₂	0	189.2	66.0	15.6	-	100.0	0
Check†		56.3					

* Data followed by different letters are significantly different at the 5% level.

† Check N recovery substrated from each value; equal to 14.1% of applied N.

‡ Plants were killed by the salinity of the fertilizer mixture.

DISCUSSION

Laboratory Studies

Calcareous Harkey silt has a pH buffer system regulated by the presence of CaCO₃. The native pH of soil, 7.8 to 8.3, is high enough to cause considerable NH₃-N loss. This is demonstrated by the NH₃ loss from AN alone (Fig. 4); however, reduction in NH₃ loss with AN in the presence of Ca is a result of soil pH depression. Calcium added with AS reduced NH₃ loss probably by reducing both AC production and soil pH (Fig. 4). Higher NH₃ loss from AS may result from the use of two separate solutions possibly permitting unequal surface concentrations of the two compounds. The same trend was evident for AC surface applied with Ca (data not presented).

The pH of Harkey silt was reduced to 6.5 when Ca(NO₃)₂ was added alone at the chemical equivalency of 550 kg NH₃-N/ha (6). Subsequent addition of an equivalent amount of AC reduced the pH to 5.6. Ammonium nitrate added without AC at the same chemical equivalent reduced soil pH to only 6.7. The presence of soluble Ca with AN has allowed the additional pH decline from 6.7 to 5.6. Data in Fig. 5 show a pH of 6.4 after 3 days. The pH depression found with 1.0 eq Ca may be more than needed to reduce NH₃ losses. Economically, one will add the lowest quantity of Ca necessary to reduce NH₃ losses to a predetermined acceptable level.

Reduction in NH₃ loss also is dependent on CEC of the soil (3). Exchangeable H, Al, Ca, and Mg will all reduce NH₃ loss by reacting with CO₂ directly or indirectly. The effect of CEC is best seen in the initial rates of NH₃ loss since the native pH of these soils was greatly different. Initial losses were greatest with the Darco fs, intermediate with Harkey silt, and lowest with Beaumont c. Total loss of NH₃ will probably depend on total amount of Ca added plus exchangeable Ca and Mg and soil acidity. The temporary acidic pH of Harkey silt produced by Ca is caused by inhibition of the Ca(OH)₂-CaCO₃ buffer system (6). Additional pH reduction occurs with formation of NH₄Cl or AN; the pH approaches that of a saturated equilibrium solution of NH₄Cl or AN.

Adding Ca to Darco fs (CEC of 1 meq/100 g) did not

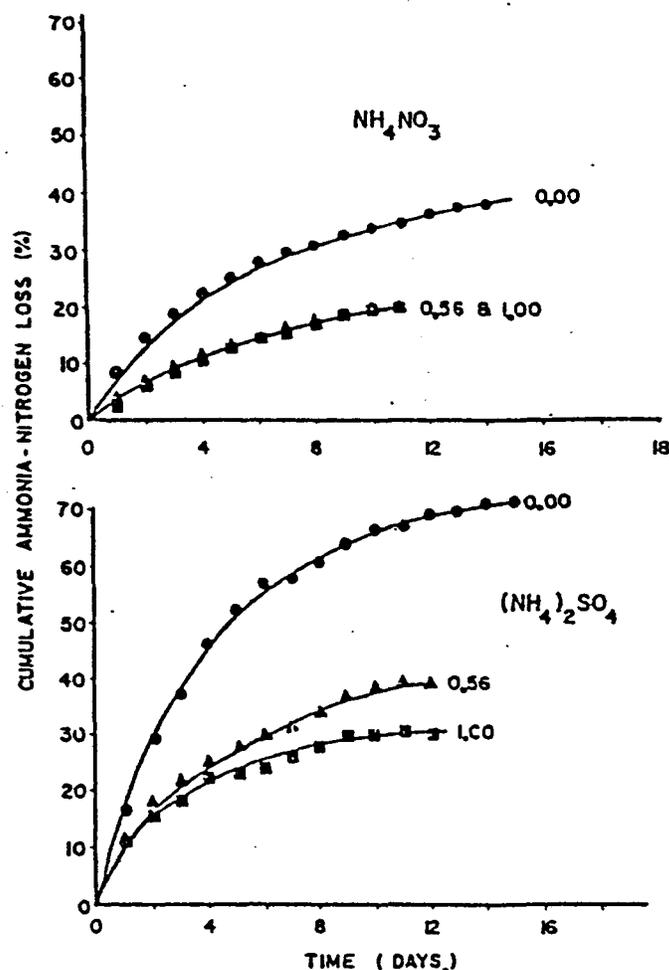


Fig. 4—Cumulative ammonia losses from AN or AS (550 kg NH₃-N/ha) surface applied to Harkey silt at 32°C as affected by varying soluble Ca/urea-N ratios.

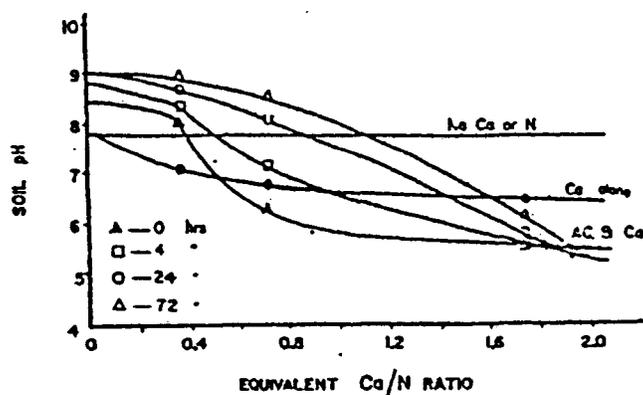


Fig. 5—Soil pH values of Harkey silt as affected by different Ca/N ratios. Soil sample was top 3 mm soil (26.6 g) containing (NH₄)₂CO₃·H₂O and Ca(NO₃)₂·4H₂O.

replace more than 1 meq/100 g of acidic H and Al. Adsorbed Ca + Mg is also < 1 meq/100 g. Hydrolysis of urea caused a rapid pH increase, resulting in rapid NH₃ volatilization in the first 1 to 2 days. A 1:1 (Ca/N) equivalent rate was required to reduce NH₃ loss to levels found at much lower Ca additions with the same fertilizer on other soils. A calcareous system was established as soon as the inherent and produced acidity was neutralized (6). The subsequent reaction is similar to

that found with Ca in calcareous Harkey silt. The rapidly diminishing NH_3 loss with additional Ca corresponds to the increased formation of NH_4Cl and AN in the calcareous system discussed previously. Ammonia loss occurring after the permanent precipitation of Ca is determined by CaCO_3 , controlled pH of the surface soil.

Urea surface applied alone to Harkey silt resulted in a 26% loss of extractable Ca in the top 2.5 cm of soil (equal to all extractable Ca to a depth of 6.7 mm). Apparently, hydrolyzed urea effectively precipitated surrounding Ca and Mg. Increasing Ca content rapidly reduced total NH_3 losses because of continuing decreases in soil pH values (Fig. 5). Increasing Ca content does not necessarily increase amount of Ca precipitated but it does continue to decrease the pH (6). At the higher rates of Ca, the loss of the C in urea may occur partially through the formation of CO_2 rather than the consumption of Ca to form CaCO_3 .

In the absence of AS soil pH gradually decreased with each increasing amount of Ca added (Fig. 6). Presence of AC with the Ca resulted in higher pH values than found with untreated native soil with Ca/N ratios of < 1. Increasing Ca content with a fixed amount of AC gradually decreased the soil pH. One equivalent of Ca in the presence of AC, however, resulted in reduction of soil pH at least 0.5 units lower than occurred with Ca alone. Urea will slowly hydrolyze to AC and results in a high Ca/AC ratio. With equivalent Ca and its associated pH depression only 21% of the Ca appears as CaCO_3 . This ratio of Ca/N approaches the maximum depressive effect on NH_3 loss.

Greenhouse Study

Nitrogen recovery by sudangrass indicates that the additions of small amounts of Ca greatly reduced NH_3 losses from urea applied to the surface of calcareous sands. Urea without Ca resulted in plant uptake of only 31% of applied N, whereas the other ratios of Ca/N increased plant uptake to > 89%. The smallest amount of Ca applied was adequate to substantially eliminate NH_3 loss from urea. Larger amounts of Ca were unnecessary. Soil conditions for NH_3 loss were deliberately made maximal to test effects of added Ca under adverse conditions. Field conditions may make this NH_3 loss-repression system even more effective. Greenhouse losses of NH_3 were much less than those measured in the laboratory under extreme conditions. It is possible that

urea hydrolyzed more slowly at lower temperatures, which increases the effectiveness of Ca. Conditions which favor reduced urea hydrolysis may somehow render Ca more effective, possibly venting more C from urea to the atmosphere as CO_2 .

Uptake of N by sudangrass from NH_4Cl alone was much higher than from urea or AS. Loss of NH_3 from NH_4Cl depends strictly on soil pH. Ammonium chloride applied on the surface of a calcareous soil will produce a slow but potentially high NH_3 -N loss. Previous work (4) with AN showed a loss of approximately 50% of the applied NH_3 -N. Soil fertilized with NH_4Cl resulted in loss of 48% N as NH_3 .

Sudangrass absorbed 20% of the N applied as AS, suggesting an approximate 80% NH_3 -N loss. This is larger than for urea, but is in reasonable agreement with laboratory data for NH_3 loss from AS on calcareous sands (3). Addition of a large amount of Ca with AS resulted in the same amount of N available to the plant as was absorbed from $\text{Ca}(\text{NO}_3)_2$.

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