AP42 Section:	9.2.1
Background Ch	2
Reference:	9
Title:	L. B. Fenn and D. E. Kissel, "Ammonia volatilization from surface applications of ammonia compounds on calcareous soils. II. Effects of temperature and rate of ammonium nitrogen application," *Soil Sci. Soc. Am. Proc.*, 38:606-610, 1974.

Ammonia Volatilization from Surface Applications of Ammonium Compounds on Calcareous Soils: II. Effects of Temperature and Rate of Ammonium Nitrogen Application[1]

L. B. FENN AND D. E. KISSEL[2]

ABSTRACT

The effects of temperature and rate of application on NH_3-N volatilization from NH_4^+ salts applied to the surface of a calcareous soil were investigated in the laboratory. Total NH_3-N losses were only slightly influenced by temperature over a broad range of NH_4^+-N application rates with a precipitate forming NH_4^+ compound such as $(NH_4)_2SO_4$ in a calcareous soil. The rates of NH_3-N loss were highly influenced by temperature. High temperatures increased the initial rates of NH_3-N loss although they were proportionally reduced at later stages. The lowest temperature resulted in the lowest initial NH_3-N loss rate but became highest for the last 76 hours. Total ammonia nitrogen losses were dependent on the rate of NH_4^+-N application. The quantity of NH_3-N loss varied from 19 to 50% of the applied NH_4^+-N at 33 to 550 kg NH_4^+-N/ha, respectively.

The increasing temperature increased losses of NH_3-N from NH_4NO_3 which does not form precipitates with $CaCO_3$ or appreciable $(NH_4)_2CO_3$. In 100 hours, NH_4NO_3 lost 14, 18, and 26% of the applied NH_4^+-N at 12, 22, and 32C, respectively. Both the total 100-hour NH_3-N losses and rates of NH_3-N loss were increased by increased temperatures; however, the percent of NH_3-N volatilized was unaffected by rates of NH_4^+-N application.

Ammonium sulfate losses from a noncalcareous Wilson clay loam buffered to the pH of the calcareous soil produced NH_3-N losses equivalent to NH_4NO_3 at 12C and lower than NH_4NO_3 at 32C. Ammonia nitrogen losses, both total NH_3-N and rates of NH_3-N loss, were similar to losses of NH_4NO_3 from the calcareous soils. Therefore in the calcareous Houston Black clay the NH_3-N loss caused by reaction of $(NH_4)_2SO_4$ with $CaCO_3$ ranged from 0 to 70 or 80%.

Regression equations were developed that predict NH_3-N losses at certain temperatures, time, and rate of NH_4^+-N application.

Additional Index Words: $(NH_4)_2CO_3$ formation, NH_3-N loss model, NH_3 volatilization, N fertilizer efficiency.

MANY FACTORS affect ammonia (NH_3) volatilization from soil (3). Temperature is related directly to NH_3-N loss. Martin and Chapman (4) studied NH_3-N volatilization from neutral, alkaline and one slightly calcareous soil and observed a moisture temperature interaction. A moisture level of 25% of field capacity and temperatures of 21, 38, and 65C produced NH_3-N losses of 27, 55, and 53% of the applied ammonium nitrogen (NH_4^+-N), respectively. Moisture levels of 75 and 100% of field capacity at 65C increased losses of 100% of applied N. Wahhab et al (5) reported that a temperature increase from 30 to 45C increased NH_3-N loss from $(NH_4)_2SO_4$ by 185% in sandy soils.

Rates of NH_4^+-N application are reported to have little influence on the percent NH_3-N lost. Martin and Chapman (4) reported that higher NH_4^+-N application rates increased total NH_3-N losses but loss percentages remained unchanged. Chao and Kroontje (1) reported no change in percent NH_3-N lost at several NH_4^+-N application rates on noncalcareous soils. Wahhab et al. (5) found that the percentage loss of NH_4^+-N increased from 15 to 25% with NH_4^+-N application rates of 550, 1,100, and 2,200 kg/ha. They did not indicate the presence of free $CaCO_3$ in their soil, but a pH of 8.3 and the use of irrigation suggest some may have been present.

Fenn and Kissel (2) have demonstrated unique differences in NH_3-N losses from various ammonium chemicals in a calcareous soil. Certain ammonium compounds like $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ react with $CaCO_3$ causing formation of $(NH_4)_2CO_3$; however, compounds like NH_4NO_3 are unreactive in this respect. The NH_3-N loss from a reaction between $(NH_4)_2SO_4$ and $CaCO_3$ should be influenced by the NH_4^+-N application rate since slightly soluble $CaSO_4$ is formed. Loss of water from the soil should increase $CaSO_4$ precipitation (2). The increased $CaSO_4$ precipitation should produce more $(NH_4)_2CO_3$ and increase the quantity of NH_3-N lost. The objectives of this study were to investigate the effects of temperature and rates of application of surface applied ammonium compounds on NH_3 volatilization on a Houston Black clay and Wilson clay loam.

MATERIALS AND METHODS

The experimental apparatus used has been described previously (2). All work was conducted in a ±1C constant temperature room at 12, 22, and 32C. In addition, two studies were conducted with diurnal temperature variations of 10 to 22C and 21 to 32C.

Houston Black clay and a Wilson clay loam were used in the experiments. The properties and treatment preparation for the Houston Black clay have been described previously (2). Wilson clay loam is a noncalcareous soil to which 10% KH_2PO_4, K_2HPO_4 was added as a buffer. This produced a soil with an initial pH of 7.5 and a surface pH of 7.0 in the top 6.4 mm of soil after the addition of 550 kg NH_4^+-N/ha as $(NH_4)_2SO_4$ or NH_4NO_3. Soil moisture was approximately 63% of field capacity.

Three nitrogen sources, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, and NH_4NO_3 were applied to the soil surface at 33, 66, 110, 275, and 550 kg NH_4^+-N/ha. All experiments were terminated 100 hours after fertilizer application due to cessation of major NH_3 losses.

The statistical method used for determining the accumulated NH_3-N loss equations was a nonlinear polynomial regression analysis.

A general equation for the polynomial regression is:

[1] Contribution from Texas Agr. Exp. Sta., Texas A&M Univ., College Station, Texas 77843, in cooperation with the ARS/USDA, Temple, Texas. Received 26 Nov. 1973. Approved 26 March 1974.

[2] Assistant Professor and Associate Professor, respectively, Texas Agr. Exp. Sta., Temple, Texas 76501. Senior Author now at Texas A&M Univ. Agr. Res. Center, El Paso, Texas 79927.

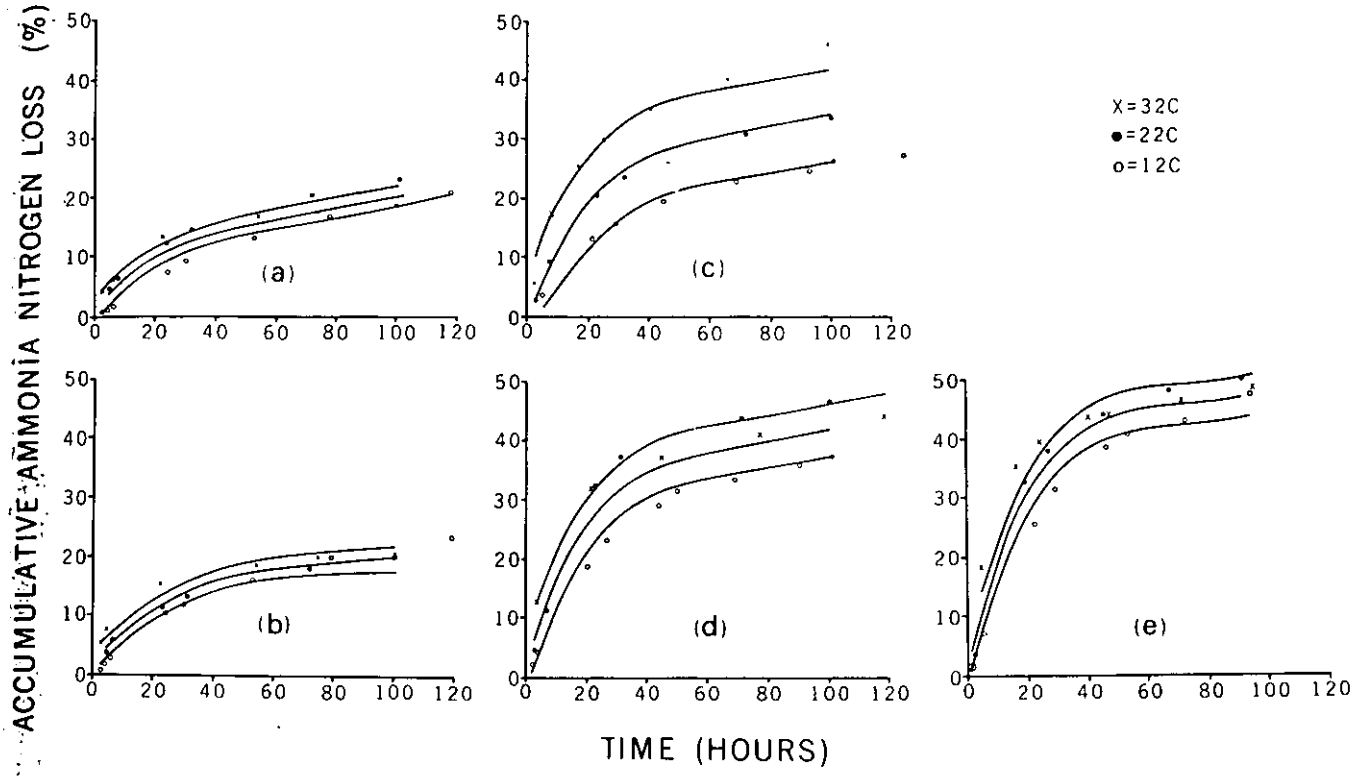

Fig. 1—Actual and predicted NH_3-N loss from several NH_4^+-N application rates on a Houston Black clay in relation to temperature. Nitrogen was applied at: (*a*) 33 kg NH_4^+-N/ha as $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$, (*b*) 66, (*c*) 100, (*d*) 275, and (*e*) 550 to the soil surface.

$$X = a + b_1t + c_1T + d_1U + b_2t^2 + c_2T^2 + d_2U^2 + b_3t^3 + c_3T^3 + d_3U^3 \ldots \text{ et. cetera.,}$$

where X is the percentage of applied NH_4^+-N lost as NH_3-N, a is the intercept, b, c, and d are determined coefficients, t is time in hours, T is temperature in °C, and U is NH_4^+-N application rate in kg/ha.

RESULTS AND DISCUSSION

Influence of Temperature on Total Ammonia Nitrogen Loss in Houston Black Clay

The influence of temperature on NH_3-N volatilization from surface applications of ammonium compounds can be divided into two categories: (i) compounds that form precipitates in calcareous soils (e.g., $(NH_4)_2SO_4$) and (ii) compounds that do not form precipitates in a calcareous soil (e.g., NH_4NO_3).

Precipitate Forming Ammonium Compounds

Total loss of NH_3-N from $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ at 33 and 66 kg N/ha changed little with a 20C increase in temperature (Figs. 1-a, 1-b). The total NH_3-N losses were 19 to 23% at 33 and 66 kg NH_4^+-N/ha, respectively, for 12, 22, and 32C. The actual data points would indicate no temperature effect at these lowest NH_4^+-N application rates. A response to temperature was evident at 110 kg NH_4^+-N/ha where total NH_3-N losses were 26, 33, and 45% of applied N at 12, 22, and 32C, respectively. This temperature induced NH_3-N loss was increased 73% on a relative basis by increasing the temperature from 12 to 32C. Figure 1d contains data for 275 kg NH_4^+-N/ha where a slightly lower NH_3-N loss existed at 12C than 22 and 32C. The total NH_3-N losses were 38, 46, and 43%, respectively. Total NH_3-N losses at 550 kg NH_4^+-N/ha were approximately 49% of the applied N at all three temperatures.

Nonprecipitate Forming Ammonium Compounds

Temperature was an important factor affecting total NH_3-N volatilization from NH_4NO_3. An increase in temperature from 12 to 32C produced a relative increase in total NH_3-N loss of 86% or an actual increase from 14 to 26% of applied NH_4^+-N (Fig. 2). Wahhab et al. (5) found a 185% increase in NH_3-N loss with a 15C temperature increase when working with $(NH_4)_2SO_4$ in a sand. This was possibly a result of low cation exchange capacity. The total NH_3-N loss for NH_4NO_3 at all rates of NH_4^+-N application was 14, 18, and 26% at 12, 22, and 32C, respectively. A comparison of NH_4NO_3 with $(NH_4)_2SO_4$ at 33 and 66 kg NH_4^+-N/ha showed nearly identical NH_3-N losses. The total percent NH_3-N loss from NH_4NO_3, unlike the precipitate forming compounds, was not increased at higher NH_4^+-N application rates. The effect of temperature on percent NH_3-N losses from NH_4NO_3 was unchanged over the entire range of application rates at each temperature.

The rates of NH_3-N loss from NH_4NO_3 were similar to the precipitate forming compounds when applied at 66 kg NH_4^+-N/ha or less. At higher rates of NH_4^+-N application, the rates of NH_3-N loss during the initial 30 hours were

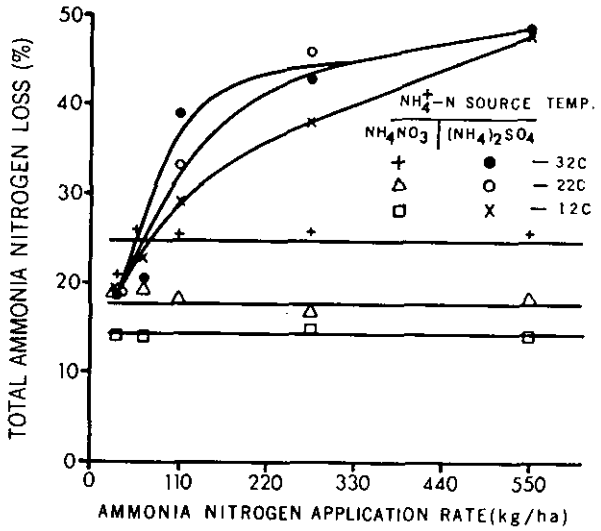

Fig. 2—Total ammonia nitrogen losses from surface applications of $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$ and NH_4NO_3 on Houston Black clay at different temperatures and NH_4^+-N application rates.

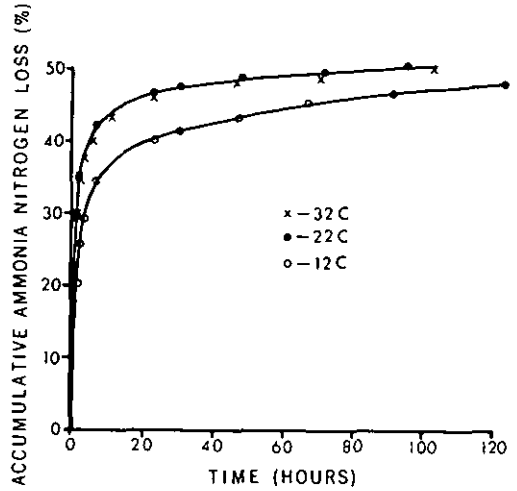

Fig. 3—Temperature effects on accumulative ammonia nitrogen volatilization losses with $(NH_4)_2CO_3$ surface applied to Houston Black clay. Nitrogen applied at 550 kg NH_4^+-N/ha.

much higher for the precipitate forming compounds (Fig. 1). From 40 to 100 hours, the rates of NH_3-N loss were slightly greater from NH_4NO_3. Ammonia nitrogen losses beyond 100 hours would produce some additional NH_3-N losses for NH_4NO_3 but very little for $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$.

The differences in both total and rate of NH_3-N loss as affected by temperature and rate of NH_4^+-N application were due to the difference in the type of reaction with soil $CaCO_3$ (2). Losses of NH_3-N are greatly enhanced with compounds such as $(NH_4)_2SO_4$, which form a calcium precipitate and $(NH_4)_2CO_3$ in calcareous soils. Losses of NH_3-N from $(NH_4)_2CO_3$ are limited, since $(NH_4)_2CO_3$ applied at 550 kg NH_4^+-N/ha lost only 50% of the applied N (Fig. 3). Total NH_3-N loss with $(NH_4)_2CO_3$ was only slightly sensitive to temperature, a fact also observed with the total NH_3-N loss from $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ (Figs. 1, 2). The initial rates of NH_3-N loss from $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ were considerably lower than for applied $(NH_4)_2CO_3$ (Figs. 1-e, 3, 5). Temperature controls the rate of reaction of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ with $CaCO_3$ and the rate of $(NH_4)_2CO_3$ formation, therefore, the initial NH_3-N loss rates should be lower. The rates of NH_3-N loss for $(NH_4)_2SO_4$ at various temperatures were highest initially at 32C but dropped to the lowest rates within 24 hours (Fig. 5). The lower temperatures exhibited the lowest initial NH_3-N loss rates but soon exceeded those of the higher temperatures which accounted for the reduced temperature influence on total NH_3-N losses.

Influence of Temperature on Ammonia Losses in a Noncalcareous Soil

The NH_3-N losses from NH_4NO_3 and $(NH_4)_2SO_4$ in Houston Black clay and Wilson clay loam + 10% KH_2PO_4-K_2HPO_4 can be compared in Fig. 1-e and 6. The KH_2PO_4-K_2HPO_4 was added to the noncalcareous Wilson clay loam to maintain a pH similar to calcareous Houston Black clay when NH_4^+ compounds were added at 550 kg NH_4^+-N/ha.

The NH_3-N loss rates and 100 hour total NH_3-N losses from Wilson clay loam were essentially identical for both NH_4NO_3 and $(NH_4)_2SO_4$ at 12C. Rates of NH_3-N loss and total NH_3-N losses from NH_4NO_3 were similar from both soils. However, losses of NH_3-N from $(NH_4)_2SO_4$ in Houston Black clay at 12C were higher than in Wilson clay loam. In addition, $(NH_4)_2SO_4$ exhibited greater temperature response from 12 to 32C in the Wilson clay loam than in Houston Black clay. Wilson clay loam at 32C with $(NH_4)_2SO_4$ had a total NH_3-N loss 100% greater than at 12C but there was only a slight difference in the Houston Black clay. The difference in the Houston Black clay from that in the Wilson clay loam was attributed to the formation of $(NH_4)_2CO_3$ in the calcareous soil, which increased NH_3-N loss at 12C to equal the total loss at 22 and 32C. Lack of $CaCO_3$ in Wilson clay loam and retention of the approximate soil pH demonstrated that $(NH_4)_2SO_4$ reacted only to soil pH similar to NH_4NO_3 when $(NH_4)_2CO_3$ formation was not possible. At 32C, even less NH_3-N was lost from $(NH_4)_2SO_4$ than NH_4NO_3 in the buffered Wilson clay loam. Measurement of CO_2 evolution in a calcareous soil revealed that essentially no $(NH_4)_2CO_3$ was formed with NH_4NO_3 whereas high levels of CO_2 were measured after application of $(NH_4)_2SO_4$. These results indicate that differences in NH_3-N loss from the nonprecipitate forming and precipitate forming NH_4 compound in the calcareous Houston Black clay can be attributed to $(NH_4)_2CO_3$ formation. The extent of NH_3-N loss attributable to $(NH_4)_2CO_3$ formation ranges from 0 to 70 or 80% at 12C and to 50 or 60% at 32C.

Equations Relating NH_3-N Loss with Temperature and NH_4^+-N Application Rates

Equations for Variable Temperatures at Fixed Application Rates

Characteristics of NH_3-N loss were closely related to temperature. The data were fitted into a family of curves to obtain a predictive NH_3-N loss equation for any temperature. The analytical approach used did not direct the curves through the origin, and therefore, seriously affects the cal-

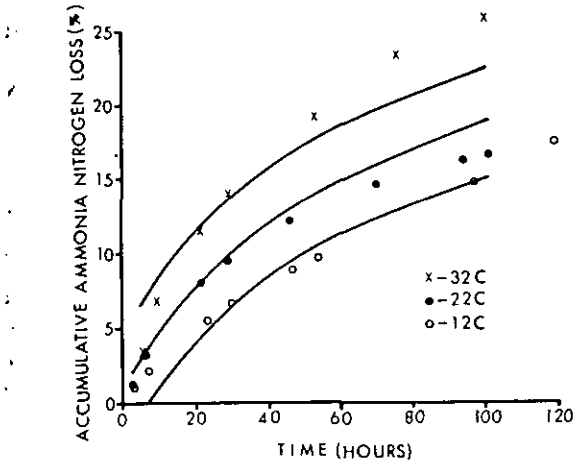

Fig. 4—Predicted temperature effects on the accumulative NH_3-N losses from surface applications of NH_4NO_3 at all NH_4^+-N application rates on Houston Black clay.

culated values for the first 4 to 6 hours. The most practical use of this information would be for times beyond 4 to 6 hours. The general equation is presented in the materials and methods section. Its use for temperature does not include the term U, which is the NH_4^+-N application rate in kg/ha. The correlation coefficients (R^2) for the general temperature equations at all application rates were from 0.95 to 0.98 (Table 1). The best fit determination revealed that time, t, had to be raised to the fourth power to obtain the best fit and temperature, T, had no influence on the correlation coefficient beyond its first power. The curves represented in Figs. 1 a, b, c, d, e, and 4 are a predicted family of curves from the developed equation (Table 1). The greatest deviations from actual data for NH_3-N losses occurred during the first 4 to 6 hours and near 100 hours. The prediction error from 0 to 6 hours may approach 100%, but NH_3-N loss predictions are excellent from 5 to 90 hours. Increased NH_3-N loss prediction error occurred at 100 hours but was usually less than 10%. This discrepancy is introduced by grouping the observed data as a family of curves rather than calculating each equation separately. Diurnal temperature variations from 10 to 22C and 21 to 32C indicated that the highest temperature encountered during any 24-hour period best predicted the total NH_3-N lost at 110 and 550 kg NH_4^+-N/ha. Total NH_3-N losses were stimulated by diurnal temperature fluctuations.

Table 1—Regression equations for NH_3-N loss from NH_4^+-N applications to the surface of a Houston Black clay

Chemical	Application rate	Regression equations*	Correlation coefficient
	kg NH_4^+-N/ha		R^2
$(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$	33	$X = -2.84 + 0.60t + 0.19T - 0.0097t^2 + 7.71 \times 10^{-5} t^3 - 2.16 \times 10^{-7} t^4$	0.95
	66	$X = -0.8 + 0.45t + 16T - 0.0021t^2 - 316 \times 10^{-5} t^3 + 2.95 \times 10^{-7} t^4$	0.98
	110	$X = -16.9 + 1.32t + 0.78T - 0.022t^2 + 0.00017t^3 - 4.64 \times 10^{-7} t^4$	0.98
	275	$X = -7.12 + 1.65t + 0.45T - 0.030t^2 + 2.49 \times 10^{-4} t^3 - 7.51 \times 10^{-7} t^4$	0.96
	550	$X = -5.3 + 2.0t + 0.35T - 0.036t^2 + 0.00028t^3 - 7.7 \times 10^{-7} t^4$	0.97
NH_4NO_3	33 to 550	$X = -6.57 + 0.35t + 0.36T + 0.19t^2 - 5.9 \times 10^{-6} t^3 + 7.3 \times 10^{-8} t^4$	0.96

* t = time, T = temperature, X = %NH_3-N loss.

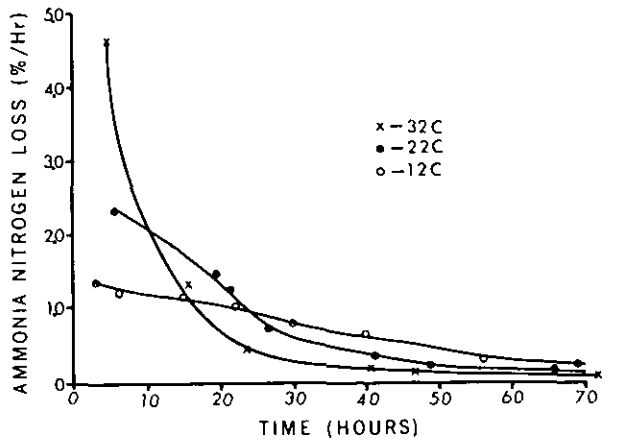

Fig. 5—Temperature effects on NH_3-N volatilization rates of a 550 kg NH_4^+-N/ha application rate of $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$. Nitrogen was applied to the surface of a Houston Black clay.

Equations for Variable NH_4^+-N Application Rates and Temperatures

Ammonium nitrate showed no NH_4^+-N application rate influence on NH_3-N loss, therefore, the equation developed for temperature would be of general use at all NH_4^+-N application rates on Houston Black clay or similar soil. The regression equation for temperature with the precipitate forming NH_4^+ compounds was expanded to include variable NH_4^+-N application rates. The term U, application rate in kg/ha, produces an equation of wide general applicability. Its computed form is:

$$X = -18.44 + 1.24t + 0.42T + 0.091U - 0.021t^2 + 1.68 \times 10^{-4}t^3 - 4.71 \times 10^{-7}t^4 - 8.97 \times 10^{-5}U^2$$ with an R^2 of 0.98.

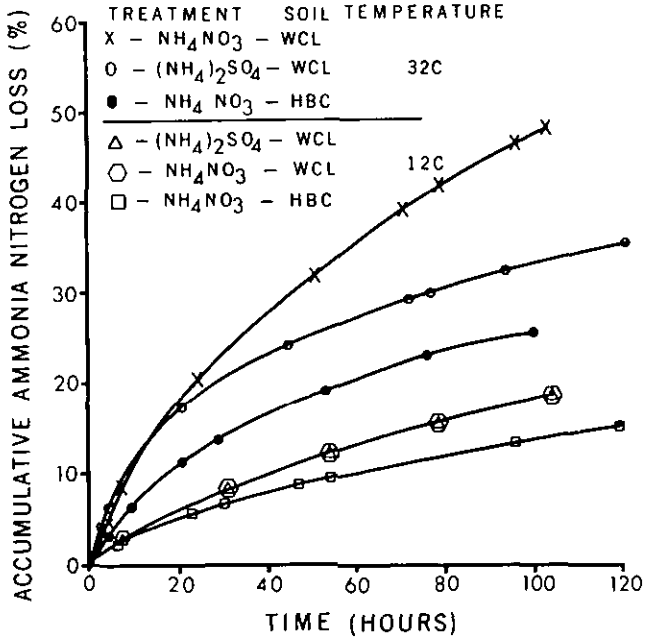

Fig. 6—Temperature effects on NH_3-N losses with NH_4NO_3 and $(NH_4)_2SO_4$ in the presence and absence of $CaCO_3$. Ammonium nitrogen was applied at 550 kg/ha to surface of Houston Black clay and Wilson clay loam.

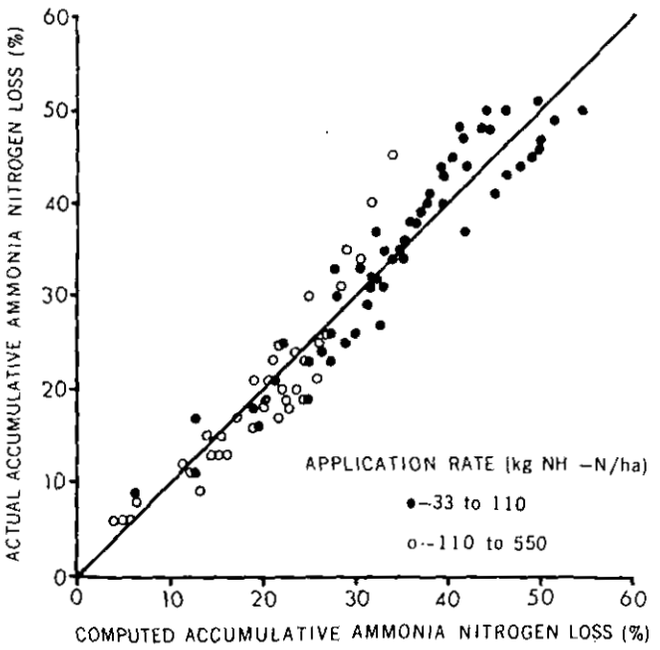

Fig. 7—A comparison of projected and actual data points for NH_3-N loss equations embodying time, temperature, and rate of NH_4^+-N application.

The equation has an intercept of —18.44 that eliminates the predictive use of this equation during the first 4 to 6 hours as discussed previously. If the equation for $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$ is divided into two segments the R_2 values can be greatly increased. The segment from 33 to 110 kg NH_4^+-N/ha is:

$$X = -5.20 + 0.71t + 0.36T - 0.17U - 0.0089t^2 + 4.08 \times 10^{-5}t^3 - 5.30 \times 10^{-9}t^4 + 0.0021U^2$$

with an $R^2 = 0.90$. The segment from 110 to 550 kg NH_4^+-N/ha is:

$$X = -21.52 + 1.67t + 0.53T + 0.56U - 0.029t^2 + 2.2 \times 10^{-4}t^3 - 6.15 \times 10^{-7}t^4 - 4.39 \times 10^{-5}U^2$$

with an R^2 of 0.95. A plot of the actual vs. calculated data is shown in Fig. 7. The restrictions on these equations are those of the experiment, namely, a soil similar to Houston Black clay with a relatively high $CaCO_3$ content and use of time beyond 6 hours.

SUMMARY AND CONCLUSIONS

The effect of temperature on total NH_3-N loss depends on the presence or absence of $CaCO_3$ in the soil and the type of NH_4^+ compound. Ammonia nitrogen losses from NH_4^+ compounds that reacted with $CaCO_3$ were influenced moderately by temperature changes. The influence of temperature on total NH_3-N loss was greatest at 110 kg NH_4^+-N/ha where NH_3-N losses increased 73% between 12 and 32C. A distinct temperature effect was evident in the NH_3-N loss rates. The lowest temperature, 12C, produced the lowest NH_3-N loss rates for the first day and highest loss rates for the remaining 76 hours. Conversely, the highest temperature, 32C, produced the highest first day NH_3-N loss rates and lowest NH_3-N loss rates for the following 76 hours.

Ammonium nitrate did not react with $CaCO_3$ and responded differently to change in temperature and NH_4^+-N application rates. The percent NH_3-N losses were not influenced by NH_4^+-N application rates but were influenced by temperature. Total NH_3-N losses and NH_3-N loss rates were both greater at the higher temperatures. A temperature increase from 12 to 32C increased the total NH_3-N loss by 86% and the rates of NH_3-N loss by essentially the same amount throughout the 100-hour period.

The addition of $(NH_4)_2SO_4$ to a buffered Wilson clay loam with the same pH as the calcareous Houston Black clay produced NH_3-N losses similar to NH_4NO_3 at 12C but less at 32C. Therefore, it was estimated that a maximum of 70 to 80% of the total NH_3-N loss from precipitate-forming ammonium compounds was due to the formation and decomposition of $(NH_4)_2CO_3$ and not directly related to the initial soil pH. The decomposition of $(NH_4)_2CO_3$ to NH_4^+-OH and CO_2 (2) has the effect of increasing the surface soil pH and thereby exerts an additional influence on NH_3-N loss. The similarity of the NH_3-N losses from all ammonium compounds, which form relatively insoluble precipitates, suggest either a similarity in amount of $(NH_4)_2CO_3$ formed or that other soil properties limit the extent of NH_3 loss.

Several general equations for prediction of accumulative NH_3-N loss for different temperatures and NH_4^+-N application rates have been developed. The correlation coefficients (R^2) for variable temperatures at fixed NH_4^+-N application rates ranged from 0.95 to 0.98 with the greatest NH_3-N loss deviations occuring in the first 4 to 6 hours and near 100 hours. An equation was developed that included variable NH_4^+ application rates for precipitate-forming NH_4^+ compounds. A regression correlation coefficient of 0.89 was obtained at rates of NH_4^+-N application from 33 to 550 kg NH_4^+-N/ha. Correlation coefficients improved to 0.90 and 0.95, respectively, when two equations were used for 33 to 110 and 110 to 550 kg NH_4^+-N/ha application rates. The nonprecipitate-forming compound, NH_4NO_3, did not respond to NH_4^+ application rates; therefore, one equation was applicable at all NH_4^+-N application rates.

LITERATURE CITED

1. Chao, T. T., and W. Kroontje. 1964. Relationships between ammonia volatilization, ammonia concentration and water evaporation. Soil Sci. Soc. Amer. Proc. 28:393–395.
2. Fenn, L. B., and D. E. Kissel. 1973. Ammonia volatilization from surface application of ammonium compounds on calcareous soils. I. General theory. Soil Sci. Soc. Amer. Proc. 37:855–859.
3. Harmsen, G. W., and G. J. Kolenbrander. 1965. Soil inorganic nitrogen. *In* W. V. Bartholomew and F. F. Clark. (ed.) Soil nitrogen. Agronomy 10:43–92. Amer. Soc. Agron., Madison, Wis.
4. Martin, J. P., and H. D. Chapman. 1951. Volatilization of ammonia from surface fertilized soils. Soil Sci. 71:25–34.
5. Wahhab, A., M. S. Randhawa, and S. Q. Alam. 1956. Loss of ammonia from ammonium sulfate under different conditions when applied to soils. Soil Sci. 84:249–255.