

DIVISION S-4—SOIL FERTILITY AND PLANT NUTRITION

Ammonia Volatilization from Surface-Applied Urea: Effect of Hydrogen Ion Buffering Capacity¹

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ABSTRACT

The influence of soil pH and soil cation exchange capacity on ammonia volatilization from surface applied ammoniacal nitrogen has been reported in previous studies. Since the hydrolysis of urea-containing N fertilizers causes an increase in alkalinity, a soil's inherent H⁺ buffering capacity (defined as the soil's total acidity, comprised of exchangeable acidity plus non-exchangeable, titratable acidity), should exert a dominant influence on the maximum soil pH at the site of urea fertilizer application. The objective of this study was to demonstrate the importance of a soil's H⁺ buffering capacity in affecting NH₃ volatilization from surface-applied urea. The H⁺ buffering capacity of two soils was increased by adding hydroxy-Al polymers to one soil, and weak and strong acid cation exchange resins to the other soil. Care was taken to keep cation exchange capacity and initial pH close to the same on amended and unamended (control) soils. Urea was surface-applied to amended and unamended soils and ammonia volatilization and soil surface pH were measured. The increase of H⁺ buffering capacity of soils was found to reduce soil surface pH and NH₃ volatilization after application of urea. It is concluded from this work that H⁺ buffering capacity of a soil is a better indicator of NH₃ loss potential than a soil's initial pH.

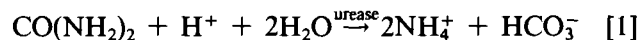
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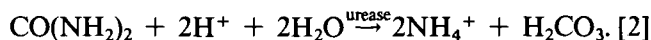
WHEN UREA OR urea-containing fertilizers are applied to the surface of a soil, urea is hydrolyzed by the enzyme urease. The products of urea hydrolysis are NH₄⁺ and one or more inorganic carbon species. In a soil of near neutral pH, HCO₃⁻ will be the pre-

dominant carbon species from urea hydrolysis although some H₂CO₃ (CO₂) and small amounts of CO₃²⁻ also will result in the soil solution.

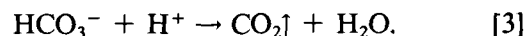
The resultant pH from urea hydrolysis in most soils would range from 7 to 9. In this pH range, the urea hydrolysis reaction can be represented as



or during the initial stages of urea hydrolysis on very acid soils (<pH 6.3), as



The HCO₃⁻ produced in Eq. [1] may undergo further reaction with another H⁺ as CO₂ loss proceeds and the system attempts to maintain chemical equilibrium,

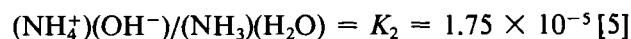


The net result of these reactions is the consumption of H⁺. Considering the completed urea hydrolysis and loss of CO₂, 2H⁺ are consumed for each mole of urea hydrolyzed.

As a result of this H⁺ ion consumption, soil pH increases. As soil pH rises, the proportion of ammoniacal nitrogen in the form of NH₃ becomes larger and volatilization of NH₃ can occur. DuPlessis and Kroontje (1964) showed that an increase in OH⁻ concentration of a soil would favor a shift to NH₃ in the reaction



For dilute solutions



Thus, an increase in soil solution pH causes a subsequent increase in the NH₃ concentration as well, increasing the potential for NH₃ volatilization. For example, at pH 6.0, 7.0, and 8.0 the percent of ammoniacal nitrogen in the form of NH₃ is 0.026, 0.26, and 2.6, respectively.

The soils' ability to resist an increase in pH during

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urea hydrolysis therefore should influence the amount of NH_3 loss. A soil with more "H⁺ supplying ability" (hereafter referred to as "H⁺ buffering capacity") than another soil should tend to have less potential for ammonia volatilization provided all other factors are equal.

Soils are buffered against both a decrease and increase in pH to some degree. Therefore, soil buffering capacity can be approached in two different manners. Avnimelech and Laher (1977) and Vlek and Stumpe (1978) both described the significance of a soil's buffering capacity against a decrease in soil pH (primarily by CaCO_3) after application of ammoniacal nitrogen fertilizers. Avnimelech and Laher (1977) found that, for the same pH, more NH_3 was lost with an increase in buffer capacity. Vlek and Stumpe (1978) stated that "the ammonia volatilization capacity of aqueous systems is dependent on the buffering capacity of the system. If present, CaCO_3 can provide the necessary alkalinity to support the NH_3 volatilization process."

Conversely, soils also are buffered against an increase in OH^- concentration. If an acid soil is well buffered against an increase in OH^- concentration, ammoniacal nitrogen will be more likely to remain in the NH_4^+ form, and not be susceptible to volatilization as NH_3 .

The buffering capacity of a soil against an increase in pH depends upon the soil's total acidity comprised of exchangeable acidity plus non-exchangeable titratable acidity. Usually, a large component of a soil's total acidity is that associated with the "layer silicate-sesquioxide complex" (Coleman and Thomas, 1967) resulting from the clay mineral in association with positively charged and nonexchangeable sesquioxides of aluminum and iron. These sesquioxides carry a net positive charge and can hydrolyze to form H^+ ions, which resist an increase in pH upon addition of a base. A discussion of these forms of acidity in soils is presented by Jackson (1963) and Coleman and Thomas (1967).

Hsu and Bates (1964) found that positively charged aluminum sesquioxides or hydroxy-aluminum polymers could be added to a clay, becoming fixed in the clay interlayers of vermiculite. The same type of polymer fixation was found in pure montmorillonite clays by Coleman et al., (1964).

The objective of this study was to demonstrate the effect of soil H⁺ buffering against an increase in pH on NH_3 volatilization from surface applied urea.

MATERIALS AND METHODS

Enhancement of the native soil buffering was achieved by two methods in two separate experiments:

- 1) The addition of hydroxy-aluminum polymers carrying a net positive charge to a silt loam soil; and
- 2) The addition of cation exchange resins to a silt loam soil in such a manner that soil buffering capacity could be varied without affecting cation exchange capacity.

Experiment 1

A sample of Smolan silt loam soil (fine, montmorillonitic, mesic Pachic Argiustolls) was obtained from the North Agronomy Farm at Kansas State Univ., Manhattan, KS. The soil was air dried, then ground through a flail grinder

to pass through a 2-mm sieve. The soil was stored at ambient temperature in the lab in an airtight container.

The soil was divided into two equal samples with one sample amended as described below. A hydroxy-aluminum polymer was prepared by adding 100 mL of 1 M AlCl_3 to approximately 2.5 L distilled H_2O in a commercial blender. To this solution 7 g of dry CaO were slowly added while blending. The resulting hydroxy-aluminum polymer could be represented as $[\text{Al}(\text{OH})_{2.6}^{+0.4}]_x$. After complete mixing, 500 g of air dry soil were added and mixed for 60 s. The total supplementation to the soil was 80 mmols ("H⁺") kg^{-1} soil. "H⁺" refers to potential acidity that can be produced by hydrolysis prior to complete neutralization of the polymer to $\text{Al}(\text{OH})_3$.

The soil suspension was transferred to a Buchner funnel under suction containing Whatman no. 2 filter paper. The soil was leached with distilled-deionized H_2O until no precipitate formed when AgNO_3 crystals were added to the leachate. This was to insure complete removal of any excess Ca^{2+} and Cl^- . The moist soil was transferred to an evaporating dish and dried at 30°C, then reground to pass through a 2-mm sieve and stored in an airtight container.

Buffer curves of the native soil (native Smolan) and the soil with increased H⁺ buffering capacity (amended Smolan) were determined by means of a serial titration. Ten grams of each air-dried soil were placed in 150-mL Erlenmeyer flasks. Seventy-five milliliters of distilled H_2O was added to the flask, along with an aliquot of standard NaOH . The flasks were stoppered and shaken for 2 h on a reciprocating shaker. After 2 h the suspensions were allowed to settle and pH measurements were made of the supernatant liquid (Fig. 1).

Plexiglas chambers of the type described by Hargrove and Kissel (1979) were used in the study to measure NH_3 volatilization. Soils of the native and amended types were moistened to 70% of the gravimetric soil water content at 3.33×10^{-2} MPa, then packed into the chambers at a bulk density of 1.5 Mg m^{-3} . An airspace of approximately 1 cm was left between the soil surface and the lid of the chambers. After packing with soil, urea was applied uniformly to the soil surface in finely ground crystalline form at rates equivalent to 56 and 224 kg N ha^{-1} . Each soil type/application rate treatment was duplicated. An unduplicated, nonfertilized check of each soil type also was included.

Compressed air was passed through a 0.05M H_2SO_4 scrubber, a humidifying column and a manifold prior to entry into the chamber. A Dwyer Visi-Float air flowmeter, model VFB68BV, was mounted ahead of the manifold to continuously monitor the air flow rate through the chambers. The flow rate was maintained at 15 chamber volumes $\text{chamber}^{-1} \text{ min}^{-1}$. Air flowing out of the chambers was passed through a 0.5M H_2SO_4 trapping flask. Ammonia trapped in the flask was determined periodically by a steam distillation procedure (Bremner and Keeney, 1965).

Soil water content in the chambers was maintained by adding water on a daily basis. The chambers were weighed,

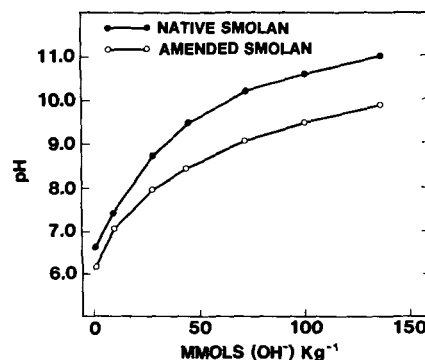


Fig. 1—Buffer curves for native and amended Smolan, Exp. 1.

and any deficit from the original weight was considered to be moisture loss. The majority of the water added to the chambers was injected below the soil surface with a hypodermic syringe in order to prevent leaching. A small amount of water was misted onto the surface as well.

Periodic measurements of the soil surface pH were made using a Fisher "MicroProbe" combination pH electrode and an Orion digital pH meter, Model 601 A.

Small samples of the soil in the chambers were periodically removed and analyzed for urea and $\text{NH}_4\text{-N}$ content. The samples were extracted according to techniques outlined by Douglas and Bremner (1970) and analyzed according to the method described by Keeney and Bremner (1967). Prior to the initiation of the study, urease activity of the two soils used was determined by the colorimetric technique outlined by Zantua and Bremner (1975). These steps were taken to insure that the urease activity of the Smolan soil was not significantly affected by the procedure used to increase buffering capacity.

The soil surface pH curves as a function of time were developed using a nonlinear regression procedure available as part of the SAS package (Goodnight, 1979). A model was selected which best approximated the curves described by the data. The nonlinear procedure then produced least-squares estimates of the model parameters for each soil-application rate curve. The model used was:

$$\text{pH} = (A + BT + CT^2)/(D + T^2)$$

where A , B , C and D are empirical parameters generated for each curve, and T is time in days. The parameters for each curve were tested and found to be significantly different from each other at the 0.05 level of significance.

Experiment 2

Two artificial cation exchange resins were used to adjust the buffering and cation exchange properties of a Eudora silt loam soil (coarse-silty, mixed, mesic Fluventic Hapludolls) from the Ashland Agronomy Farm at Manhattan, KS. The soil was dried and sieved as in Exp. 1. Bio-Rex 70³, a weak acid acrylic polymer with carboxylic acid exchange sites provided H^+ buffering. Dowex 50 W-X12,³ a strongly acidic styrene-divinylbenzene with sulfonic acid exchange sites, provided nonbuffered cation exchange.

The weak acid resin was first H^+ saturated using the procedure recommended by the manufacturer (equilibration with concentrated HCl, repeated once). The resin then was rinsed six times with 0.01 M KCl to remove any free acid until the pH reached 3. Finally, the resin was titrated with 0.1 M KOH to a pH of 6.5, at which the resin was approximately 60% H^+ -saturated.

The strong acid resin (Dowex 50W-X12) was saturated with K^+ by shaking with 2 M KCl for 2 h and decanting the

³ Product of Bio-Rad Labs, Richmond, CA.

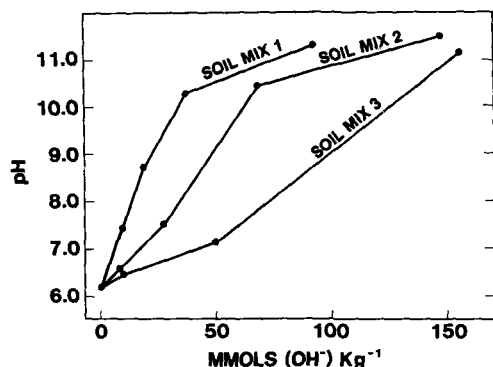


Fig. 2—Buffer curves for soil-exchange resin mixes, Exp. 2.

supernatant liquid, repeating this procedure two times. Excess Cl^- was removed by rinsing with distilled water until the supernatant was judged Cl^- free, as determined by the lack of a precipitate upon addition of AgNO_3 to the supernatant. Finally, a few drops of weak HCl were added to adjust the pH to 6.5. After cation saturation, the resins were dried overnight in an oven at 80°C.

The prepared resins were mixed with dry soil in the necessary quantities to obtain three different soil-resin mixtures, all with a cation exchange capacity of 280 mmols (+) kg^{-1} and a pH of 6.5

Soil Mix 1 = 4.69 g strong acid resin + 95.3 g soil.

Soil Mix 2 = 0.51 g weak acid resin + 3.82 g strong acid resin + 95.7 g soil.

Soil Mix 3 = 1.48 g weak acid resin + 2.18 g strong acid resin + 96.3 g soil.

The H^+ buffering capacity of the soil-cation exchange resin mixtures was measured by a serial titration using 0.1 M KOH as the titrant with 10 g of the soil-resin mixtures suspended in 75 mL 0.05 M KCl solution. The stated buffering capacity of each mixture was defined as the mmols of base needed to raise the pH of the mixture to 8.5.

The cation exchange capacity was determined on the soil and resins by suspending with 0.5 M CaCl_2 , washing two times with 0.5 M CaOAc (pH 7.8), once again with 0.5 M CaCl_2 , and washing two times with ethyl alcohol, and then up to three times with methyl alcohol until a negative test for Cl^- was found with AgNO_3 . All shaking times were 15 min. The weight of soil was 2 g and resin weights were 0.5 g. The solution volumes were 50 mL. The Ca^{2+} saturated soil or resin was extracted with 0.4 M BaCl_2 and the exchanged Ca^{2+} determined by atomic absorption spectrometry.

The Eudora silt loam soil used had an original CEC (at pH 7.8) of 63 mmols (+) kg^{-1} , a buffering capacity of 17 mmols ("H⁺") kg^{-1} , and a pH of 6.3. Bio-Rex 70 had a CEC of 8500 mmols (+) kg^{-1} , and Dowex 50 W-X12 had a CEC of 5000 mmols (+) kg^{-1} . All soil-resin mixtures had a CEC of 280 mmols (+) kg^{-1} and a pH approximately equal to 6.5. Buffering capacities were 17, 41, and 86 mmols ("H⁺") kg^{-1} respectively for soil mixes 1, 2, and 3. Buffer curves for these soil mixes are shown in Fig. 2.

Water was added to the soil-resin mixtures to obtain a gravimetric water content of 0.20 g g^{-1} . Each soil mixture was packed into two volatilization chambers, and finely ground urea crystals were applied to the surface at a rate equivalent to 112 kg N ha^{-1} . The remainder of the experimental setup, including maintenance of water content, col-

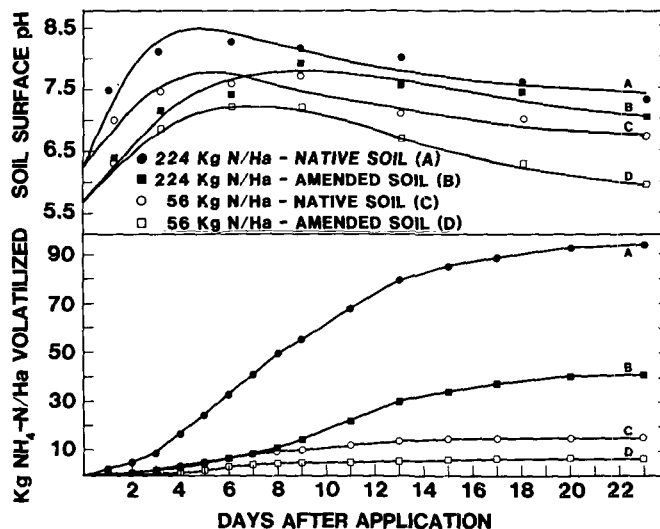


Fig. 3—Soil surface pH and cumulative $\text{NH}_4^+\text{-N}$ loss, Exp. 1.

lection of evolved NH_3 , and monitoring of soil surface pH and urea hydrolysis rate, was the same as in Exp. 1.

Soil surface pH curves as a function of time were developed in the same manner as for Exp. 1 using nonlinear curve fitting procedures.

RESULTS AND DISCUSSION

Experiment 1

The cumulative NH_3 loss and soil surface pH with time after urea application are shown in Fig. 3. Actual soil surface pH and NH_3 loss values measured are indicated by data points in Fig. 3. Best fit curves are shown by the line. By 23 d after urea application to the soil surface at 224 kg N ha⁻¹, the cumulative loss of NH_3 was 94 kg N ha⁻¹ (42% of the applied N) on the native soil, while only 40 kg N ha⁻¹ (18% of the applied N) was lost from the amended soil. At the lower rate of application (56 kg N ha⁻¹), the cumulative loss of NH_3 also was greater from the native soil (16 kg N ha⁻¹) than from the amended soil (7 kg N ha⁻¹).

The total NH_3 lost by 23 d and the rates of NH_3 loss during the experiment corresponded closely to the soil surface pH in the respective treatments. By 23 d after application, the soil surface pH values were ranked in the same order as the amount of ammonia that had been lost by that time. For example, the native Smolan receiving 224 kg N ha⁻¹ had lost 94 kg N ha⁻¹ by the end of the experiment and had a surface pH of 7.4 while the lowest pH (5.9) and the smallest loss (7.5 kg N ha⁻¹) occurred on the amended Smolan that had received 56 kg N ha⁻¹. The other two treatments were intermediate and ranked in order as well.

It also was observed that the maximum rate of ammonia loss generally corresponded to the maximum soil surface pH. This can be seen by comparing the native and amended soil at the 224 kg N ha⁻¹ rate. The maximum rate of ammonia loss occurred from 5 to 8 d after application on the native Smolan, the time when soil surface pH was near its highest value of around 8.4. On the amended Smolan, the maximum rate of ammonia loss occurred somewhat later, between 9 and 13 d after application. The maximum soil surface pH of 7.8 occurred near the beginning of the maximum rate phase on that soil.

The amount of urea hydrolysis during Exp. 1 is given in Table 1. Overall, urea hydrolysis was quite rapid. By 2 d after application, about 70% of the urea had been hydrolyzed and by 6 d over 90% of the urea had been hydrolyzed. All but a fraction of 1% of the applied urea had been hydrolyzed in all treatments at the end of 14 d. The rate of addition of ammoniacal

nitrogen and carbon species to the soil solution from urea hydrolysis would have become almost negligible at some point between 6 and 14 d after application, when almost all of the urea has hydrolyzed. The time required for complete urea hydrolysis corresponded closely to the time when the pH of the soil solution began to decline, indicating that NH_3 was being volatilized faster than it was being added to the soil solution by hydrolysis. It should be emphasized that the rate of urea hydrolysis was not slowed by the amendment process used to add more H^+ buffering capacity to the soil (Table 1). Particularly, at the 224 kg N ha⁻¹ rate, the hydrolysis rates appeared to be identical in the native and amended Smolan soil. Since hydrolysis rates were the same at the high N rate, the reduced pH and the longer time to reach the maximum pH in the amended soil was apparently due to the additional H^+ buffering capacity in the amended soil. More H^+ buffering in that soil would allow less of the ammoniacal N to become NH_3 and thus reduce the potential for volatilization.

The amount of extra H^+ -buffering in the amended soil can be obtained from the buffer curves in Fig. 1. When the buffer curves for the two soils are compared, it can be shown graphically that almost 50% more base is required to reach a pH of 8.5 in the amended Smolan than in the native Smolan (i.e., the amended Smolan had 50% more acidity).

It should be pointed out that although the amended Smolan had 50% more acidity than the native Smolan, the initial pH was slightly higher in the native Smolan which, in turn, also could influence the amount of ammonia loss (Ernst and Massey, 1960). Because of the difficulty in attaining identical pH values with the amended and native soils, an experiment was carried out to evaluate different levels of H^+ buffering using another procedure.

Experiment 2

In Exp. 2, differences in the amount and kind of cation exchange resin mixed with Eudora soil allowed a greater range in H^+ buffering capacity and also allowed all soil/resin mixtures to have the same initial pH and cation exchange capacity.

The cumulative ammonia loss and soil surface pH with time after urea application are shown in Fig. 4. Ammonia loss and soil surface pH again were influenced very much by the amount of H^+ buffering of the soil mixtures. Soil mix 1 had only the acidity from the soil itself since the resins added were saturated with exchangeable K^+ only. Approximately 11 kg N ha⁻¹ was lost as ammonia by 16 d after application from soil mix 1. Soil mix 2 and soil mix 3 lost considerably less NH_3 by 16 d; 2.5 kg N ha⁻¹ and 0.7 kg N ha⁻¹, respectively.

As in Exp. 1, the maximum soil surface pH values agreed well with the rates of ammonia loss and the total ammonia lost from each of the soil mixes. The maximum rate of ammonia loss from soil mix 1 occurred at the same time as the maximum soil surface pH during the fifth day after urea application. The soil surface pH at that time was ≈ 8.7 .

The maximum rates of ammonia loss from soil mixes 2 and 3 occurred about the same time (day 5).

Table 1—Cumulative amount of urea hydrolyzed during Exp. 1.

Days after application	Applied urea-N hydrolyzed					
	56 Kg N Ha ⁻¹			224 Kg N Ha ⁻¹		
	Native	Amended	CV	Native	Amended	CV
	%					
2	60.2	79.0	17.9	75.9	77.9	9.0
6	98.4	100.0	1.6	90.6	87.0	7.7
14	100.0	100.0	--	100.0	99.5	0.3

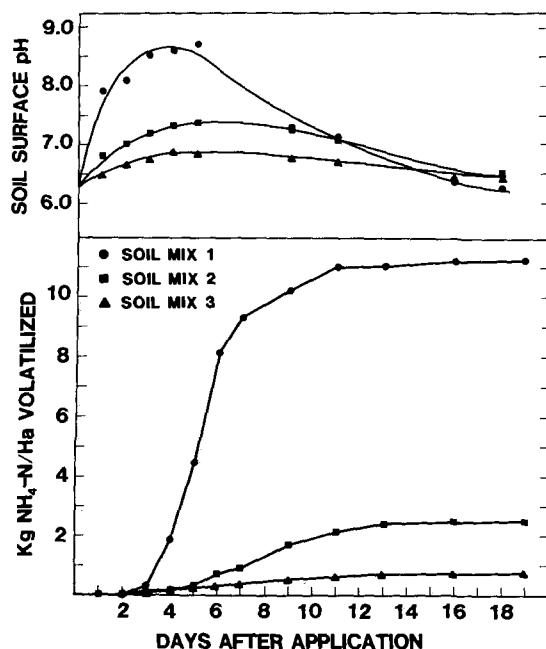


Fig. 4—Soil surface pH and cumulative NH_4^+ -N loss, Exp. 2.

The maximum rates of loss from these mixes were difficult to determine exactly since losses were quite low. Maximum soil surface pH values also were considerably less for soil mixes 2 and 3—about 7.4 and 6.9, respectively. Clearly, the additional H^+ buffering in soil mixes 2 and 3 did not allow the soil surface pH to rise as high. The amount of H^+ buffering to a pH of 8.5 was inversely proportional to the ammonia loss. Buffering was 14, 35, and 74 mmols of H^+ kg^{-1} for soil mixes 1, 2, and 3, respectively. It should be emphasized again that the CEC and initial pH were the same in all three soil mixes and only the amount of buffering from soil acidity varied between the soil mixes.

The urea hydrolysis rate was approximately the same in all three soil mixes (as would be expected since the amounts of resin were small and about the same in all mixes) and was quite fast. Three days after application, 73% of the applied urea had been hydrolyzed and 10 d after application, more than 99% of the urea had been hydrolyzed. The soil surface pH began to decline after 5 d in all treatments. The decline in soil surface pH after 5 d was due to the rate of loss of NH_3 by volatilization being greater than the rate of addition of NH_3 by hydrolysis after that time.

General Discussion

It has been demonstrated previously that NH_3 volatilization from surface-applied urea generally will be more severe from soils of high pH than from soils of low pH. Ernst and Massey (1960) showed that with each successive rate of lime application to an acid soil (and successively increasing soil pH) NH_3 volatiliza-

tion became progressively more severe. Such data may be misinterpreted, when generalized over a range of soil types, to mean that a soil's initial pH has a direct influence on NH_3 volatilization. Other factors also must be considered.

Our data indicate that the amount of H^+ buffering capacity between a soil's initial pH and a pH of around 7.5 would be more directly related to the expected NH_3 loss than a soil's initial pH. When urea is applied to the soil surface, NH_3 volatilization probably will not be economically serious unless the soil surface pH rises above 7.5. In order for the surface layer of an acid or neutral pH soil to reach pH 7.5 or above, the capability of the soil to provide H^+ must be low or the H^+ released from the soil in that pH range must be neutralized by other chemical reactions. With more H^+ present in the soil (more H^+ buffering capacity), extra H^+ ions are available for the urea hydrolysis step (Eq. [2]) and the $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2\uparrow$ reaction (Eq. [3]). The result is a smaller increase in soil surface pH and less NH_4^+ dissociation to $\text{NH}_3 + \text{H}^+$. Consequently, the potential for NH_3 volatilization is decreased with increased H^+ buffering capacity.

REFERENCES

- Avnimelech, Yoram, and Malka Laher. 1977. Ammonia volatilization from soils: Equilibrium considerations. *Soil Sci. Soc. Am. J.* 41:1080-1084.
- Bremner, J.M., and D.R. Keeney. 1965. Steam distillation methods for determination of ammonium, nitrate and nitrite. *Anal. Chem. Acta.* 32:485-495.
- Coleman, N.T., G.W. Thomas, F.H. LeRoux, and G. Bredell. 1964. Salt exchangeable and titratable acidity in Bentonite-Sesquioxide mixtures. *Soil Sci. Soc. Am. Proc.* 28:35-37.
- Coleman, N.T., and G.W. Thomas. 1967. The basic chemistry of soil acidity. In R.W. Pearson and F. Adams (ed.) *Soil Acidity and Liming*. Agronomy 12:1-41. Am. Soc. of Agron., Madison, WI.
- Douglas, L.A., and J.M. Bremner. 1970. Extraction and colorimetric determination of urea in soils. *Soil Sci. Soc. Am. Proc.* 34:859-862.
- DuPlessis, M.C.F., and W. Kroontje. 1964. The relationship between pH and ammonia equilibria in soil. *Soil Sci. Soc. Am. Proc.* 28:751-754.
- Ernst, J.W., and H.F. Massey. 1960. The effects of several factors on volatilization of ammonia formed from urea in the soil. *Soil Sci. Soc. Am. Proc.* 24:87-90.
- Goodnight, James H. 1979. NLIN Procedure. In J.T. Helwig and K.A. Council (ed.) *SAS Users Guide*, 1979 edition. SAS Institute, Inc., Cary, NC.
- Hargrove, W.L., and D.E. Kissel. 1979. Ammonia volatilization from surface application of urea in the field and laboratory. *Soil Sci. Soc. Am. J.* 43:359-363.
- Hsu, P.H., and T.F. Bates. 1964. Fixation of hydroxy-aluminum polymers by vermiculite. *Soil Sci. Soc. Am. Proc.* 28:763-769.
- Jackson, M.L. 1963. Aluminum bonding in soils: A unifying principle in soil science. *Soil Sci. Soc. Am. Proc.* 27:1-10.
- Keeney, D.R., and J.M. Bremner. 1967. Determination and isotope-ratio analysis of different forms of nitrogen in soils: 7. Urea. *Soil Sci. Soc. Am. Proc.* 31:317-321.
- Vlek, P.L.G., and J.M. Stumpe. 1978. Effect of solution chemistry and environmental conditions on ammonia volatilization losses from aqueous systems. *Soil Sci. Soc. Am. J.* 42:416-421.
- Zantua, M.I., and J.M. Bremner. 1975. Comparisons of methods of assaying urease activity in soils. *Soil Biol. Biochem.* 7:291-295.