



In Vitro Evaluation of Coatings to Control Ammonia Volatilization from Surface-Applied Urea

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ABSTRACT

Ammonia (NH_3) volatilization from surface-applied N fertilizers containing urea can be substantial if environmental conditions are favorable. Physically coating urea with sulfate salts and urease inhibitor may reduce NH_3 volatilization and supply plant available S. The objectives of this study were to quantify in vitro N loss from surface-applied urea; and measure the rate and total N volatilization loss from urea coated with calcium sulfate, potassium sulfate, alone and in combination with the urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT). Six trials, lasting 14 d, were conducted using a laboratory system at 26°C, 1.00 L min^{-1} air flow, 44.6 mg N kg^{-1} air-dried soil, and 100 mL of 0.02 M phosphoric acid to recover volatilized NH_3 . Cumulative NH_3 loss ranged from 33.9 to 37.2% of the applied N in all trials. Initial NH_3 volatilization losses were delayed by calcium and potassium sulfate coatings alone. The inhibitor NBPT reduced cumulative NH_3 losses to 17.9 to 24.7% of applied N and delayed NH_3 volatilization for 96 h after N application when applied at the 0.08% w/w application rate in trials I to IV. In trials V and VI, applying NBPT at 0.02% w/w reduced cumulative NH_3 volatilization from 35.6 and 35.1% to 25.4 and 24.1%, respectively. In both trials, no difference in cumulative NH_3 loss was observed when NBPT rates exceeded 0.04%. The inhibitor NBPT had the greatest influence on NH_3 volatilization losses in these studies, though the K_2SO_4 coated urea also reduced NH_3 volatilization and supplies a small amount of S for crop growth.

UREA FERTILIZER SUPPLIES N to a majority of agricultural systems worldwide. With the increasing need for more efficient nutrient management strategies, there has been extensive research conducted to reduce the inefficiencies associated with urea. The major inefficiency of urea arises from volatilization of NH_3 during the hydrolysis of urea by urease, an enzyme found ubiquitously throughout agricultural systems (Krajewska, 2009). Urease catalyzes the reaction that converts urea to carbamate and ammonium. The carbamate molecule decomposes into bicarbonate and ammonium (Ciurli et al., 1999). The bicarbonate ion increases the soil pH converting ammonium to NH_3 (Ciurli et al., 1999; Kissel et al., 2008; Krajewska, 2009). Once urea left on the soil surface is converted to NH_3 , N is lost through volatilization. Nitrogen losses from urea through volatilization can be as great as 70% of the applied fertilizer N, with losses of 35 to 50% of applied fertilizer N in laboratory and field studies commonly reported under favorable environmental conditions (Antisari et al., 1996; Bayrakli, 1990; Beyrouthy et al., 1988; Carmona et al., 1990; Christianson et al., 1990, 1995). Ammonia volatilization loss of N contributes to a relatively low nitrogen use efficiency

(NUE) of agronomic systems, which have been estimated about 33% worldwide (Raun and Johnson, 1999).

Urea hydrolysis raises soil pH adjacent to urea granules, inhibiting nitrification, resulting in excess NH_3 and conditions favoring NH_3 volatilization. Surface application of urea without reducing or delaying urea hydrolysis reaction will result in a high pH zone from NH_3 on the soil surface. Urease activity varies with soil characteristics such as soil texture, moisture, temperature, crop residue, and organic carbon (Antisari et al., 1996; Bremner and Douglas, 1973; Carmona et al., 1990; Krajewska, 2009; Rawluk et al., 2001; Sanz-Cobena et al., 2008). Soil urease is unique compared to ureases derived from living organisms in that it is more stable and persistent in the soil environment. The enzyme urease accumulates in soil systems and can be adsorbed to soil mineral particles and humic substances (Kiss and Simihaijan, 2002). This adsorption inhibits the ability of microorganisms to metabolize urease allowing for excess amounts to build within the soil with the result that more than enough urease to rapidly hydrolyze fertilizer urea exists in most soils.

Multiple control measures can be implemented to prevent N loss as NH_3 volatilization from agricultural systems. Growers typically try to apply urea-based N fertilizers before a rainfall event to ensure movement of urea into the soil profile, or they incorporate urea into the soil. Both management strategies are extremely effective in preventing NH_3 volatilization from urea. However, many times growers do not have the luxury of waiting for rain or irrigation to apply nutrients because they must ensure that nutrients are applied so that plant growth is not limited by N. To do this, farmers may apply urea when rain is not in the immediate future, which can potentially lead to volatilization losses of N. Alternative approaches incorporate

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Abbreviations: NBPT, N-(n-butyl) thiophosphoric triamide; NH_3 , ammonia; NUE, nitrogen use efficiency.

urea using banded applications next to the plant rows or use urease inhibitors to reduce and delay urea hydrolysis. This creates a window of time after urea application in which volatilization losses are low with the anticipation that timely rainfall will move the urea into the soil.

Many studies have been conducted to find the most effective urease inhibitor but few have produced commercially viable options for controlling NH_3 volatilization (Kiss and Simihaian, 2002). The urease inhibitor, NBPT, has been found to be the most effective in controlling NH_3 volatilization (Byrnes and Amberger, 1989; Chai and Bremner, 1987; Watson, 2005). The NBPT is degraded in soil to N-(n-butyl) phosphoric triamide (NBPTO) which is a competitive inhibitor of urease. Competitive inhibitors bind directly to the active site of the enzyme, thus competing with the substrate (urea in the case of urea N fertilizers) at the enzyme active site. During field and laboratory studies NBPT has successfully decreased urea hydrolysis in varying soil types and tillage systems. Carmona et al. (1990) reported a reduction in N losses through NH_3 volatilization from 52% in uncoated urea to only 14.7% using 0.05% NBPT on a weight basis. Byrnes and Amberger (1989) showed similar results with the N loss of 73.4% in a simulated flooded soil using untreated urea with only 34.7% loss of applied N when treated with NBPT. Antisari et al. (1996) found that the magnitude of reduction in NH_3 volatilization varied from soil to soil and concluded different rates of NBPT may be needed for different soil types. This supports the evidence of changing urease activity with changing soil characteristics previously mentioned.

Until recently, Agrotain (Koch Agronomic Services, Wichita, KS) was the only commercially available source of NBPT being widely marketed. Weyerhaeuser Co. (Federal Way, WA) and Brooks Whitehurst Associates Inc. (New Bern, NC) have developed a different solvent system (Trade Name Arborite Ag) to adhere NBPT to the surface of urea granules. The NBPT solvent system developed by Weyerhaeuser and Brooks Whitehurst Associates Inc. can also be used as a binder to attach physical coatings (i.e., calcium sulfate and potassium sulfate) to the surface of urea granules alone, or in combination with the urease inhibitor, NBPT. This technology has the potential to supply various nutrients and adjust nutrient blends for selected regions or cropping systems because the coatings are applied at the fertilizer blend plant before application.

The objectives of this experiment were: (i) quantify NH_3 volatilization losses from surface applied urea under controlled laboratory conditions favoring volatilization; (ii) measure the rate and total N volatilization loss from uncoated urea and urea coated with calcium sulfate, potassium sulfate, and with or without NBPT incorporated into the sulfur-coatings, and (iii) measure the effect of NBPT application rate on NH_3 volatilization losses from granular urea.

MATERIAL AND METHODS

General

The study consisted of six trials to quantify the reduction, if any, in NH_3 volatilization from physical and chemical coatings applied to granular urea. Each trial was conducted in the laboratory using the NH_3 volatilization system described by Woodward et al. (2011). The NH_3 volatilization measurement

system consisted of three temperature controlled cabinets, each containing six individual soil chambers. Each soil chamber was filled with 500 g of air-dried soil limed to a pH of 6.5 to 6.7. During all trials, air flow rates through the soil chambers were controlled at 1.00 L min^{-1} and temperatures were maintained at 26°C . The headspace in the chambers during the trials was on average 0.43 L resulting in 2.33 exchange volumes per minute. Moisture laden air was used to sweep NH_3 vapors from the soil chambers (Woodward et al., 2011).

Nitrogen was applied at the rate of $44.6 \text{ mg N kg}^{-1}$ air dry soil, N application rate approximating 100 kg N ha^{-1} , for all fertilizer treatments. All urea fertilizers were sieved to pass an 8 mesh sieve and retained on a 10 mesh sieve. This ensured uniformity of granule size and more accurate treatment weights. Five to six granules were equally spaced on the surface of the soil in each chamber to achieve the desired N rate.

The soil used was the A horizon from a fine-loamy, mixed, active, mesic Ultic Hapludalf (Wheeling silt loam). Soil was air-dried and passed through a 2-mm sieve. Physical and chemical characteristics of the soil are in Table 1. Before each trial the soil was limed with calcium oxide (CaO) at a rate of $0.7 \text{ g CaO kg}^{-1}$ air dried soil to adjust the pH to 6.5 to 6.7 (Table 1). After liming, the soil was weighed for each individual chamber and 65 mL of deionized water were added to each chamber and thoroughly mixed to ensure consistent moisture throughout the soil within the chamber. The addition of water raised the soil moisture content to approximately two-thirds of field capacity ($\sim 14\%$) (Table 1). This ensured adequate soil moisture to dissolve urea granules and provide conditions for volatilization. Once the moisture equilibrated throughout the soil, the chamber was placed inside the specified temperature controlled cabinet for 24 h to equilibrate the moistened soil to 26°C . After equilibration, the fertilizer granules were placed on the moistened soil surface of each chamber.

Acid traps containing 100 mL of 0.02 M ortho-phosphoric acid captured volatilized NH_3 in the air stream flowing over the soil surface, and acid traps were changed at 1, 3, 6, 9, 12, 24, 48, 72, 96, 120, 144, 168, 216, 264, 312, and 336 h (2 wk) after initiation of each trial. Acid traps were weighed and total volume of solution calculated using the density of 0.02 M phosphoric acid at 25°C . Ammonical N concentration in the acid traps was determined colorimetrically using a Lachat QuickChem Automated Ion Analyzer (Lachat Instruments, Loveland, CO). Ammonia captured from the soil without N fertilization (check) was averaged and subtracted from other acid trap totals at each sampling interval for individual trials. Ammonia levels in the acid traps from the soil checks ranged from 0.05 to 0.25 mg N captured over the duration of a 2-wk trial, and these levels did not fluctuate from trial to trial.

Upon completion of each trial the soil from each chamber was immediately air-dried in a greenhouse for 24 h. Air-dried

Table 1. Soil pH and physical characteristics for the Wheeling silt loam soil used in all NH_3 volatilization trials

Soil	pH	Moisture	Sand	Silt	Clay	Carbon
		%				
Wheeling silt loam	6.6–6.7	~14 (2/3 F.C.†)	44.2	50.2	5.6	2.33

† F.C. denotes field capacity determined by the pressure plate apparatus at -33330.0 Pa ($-1/3 \text{ bar}$) (Cassell and Nielsen, 1998).

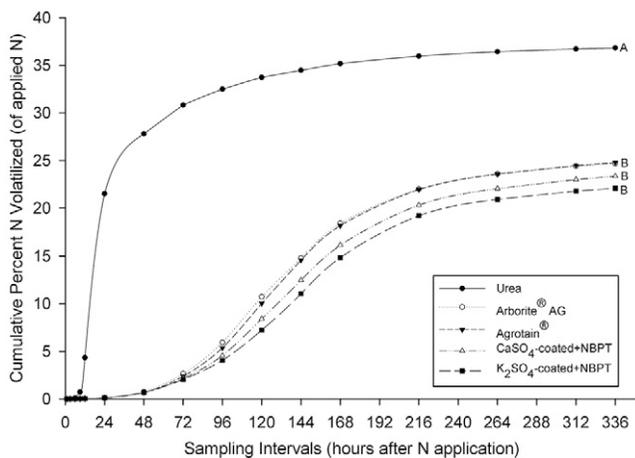


Fig. 1. Cumulative N loss (percent of applied) as NH₃ from granular urea treated with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) and CaSO₄ and K₂SO₄ physical coatings during Trial I. Different letters to the right of the volatility curves indicate significantly different cumulative N loss between treatments at $\alpha = 0.05$.

soil was extracted with 2 M KCl to determine ammonium and nitrate concentrations. Concentrations of ammonium and nitrate were determined colorimetrically using the Lachat QuickChem Automated Ion Analyzer (Lachat Instruments, Loveland, CO). The soil nitrate, soil ammonium, and the NH₃ in the acid traps were used to calculate the mass balance system N recovery (Woodward et al., 2011). The average percentage of urea-N hydrolyzed over all chambers during each trial in this study ranged from 96.3 to 99.7% of the applied N with average standard deviations ranging from 2.2 to 3.1% of applied N. This high recovery of applied N over all chambers indicated that urea hydrolysis was nearly complete over the 2-wk trials.

All trials were analyzed as randomized complete block designs with repeated measurements. Blocks were individual cabinets with treatments randomized among each chamber within each cabinet, totaling three replications for each treatment. Each trial was analyzed separately using e ANOVA with the Proc Mixed model in SAS (SAS Institute, 2009).

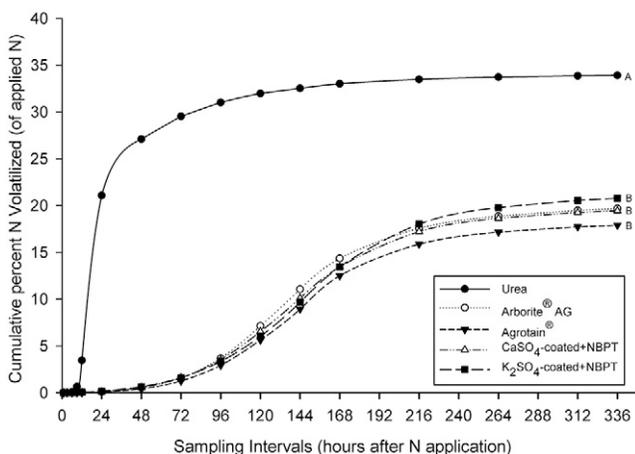


Fig. 2. Cumulative N loss (percent of applied) as NH₃ from granular urea treated with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) and CaSO₄ and K₂SO₄ physical coatings during Trial II. Different letters to the right of the volatility curves indicate significantly different cumulative N loss between treatments at $\alpha = 0.05$.

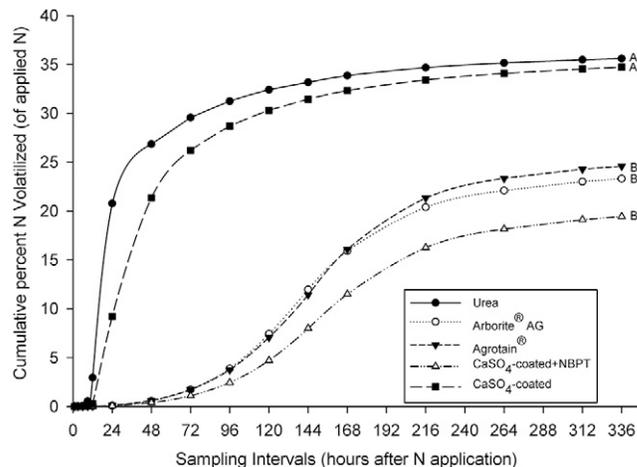


Fig. 3. Cumulative N loss (percent of applied) as NH₃ from granular urea coated with CaSO₄ alone and in conjunction with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) during Trial III. Different letters to the right of the volatility curves indicate significantly different cumulative N loss between treatments at $\alpha = 0.05$.

Least significant difference (LSD) mean separation was used to determine treatment differences in cumulative N captured in acid traps at $\alpha = 0.05$ (Fig. 1–6). Significant differences in percent NH₃ losses within sampling intervals are discussed in the text and data for sampling intervals where no differences were found are not shown. Maximum loss rates were calculated by dividing the percent NH₃ lost during a sampling interval by the duration (hours) of the sampling intervals.

Trial I and II

Trial I and II consisted of four different coating treatments on granular urea, urea, and a “check” Wheeling silt loam to which no N was applied, totaling six treatments (Table 2). The urea treatment in Trial I and II served as the N fertilization control treatment. The urease inhibitor, NBPT was applied to the granular urea using two different solvent systems to bind the molecules of NBPT to the granule. The inhibitor was applied at the North American Industry standard rate of 0.08% w/w. The

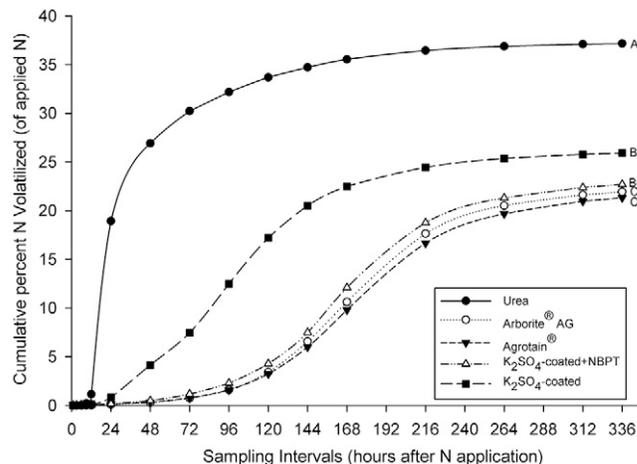


Fig. 4. Cumulative N loss (percent of applied) as NH₃ from granular urea coated with K₂SO₄ alone and in conjunction with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) during Trial IV. Different letters to the right of the volatility curves indicate significantly different cumulative N loss between treatments at $\alpha = 0.05$.

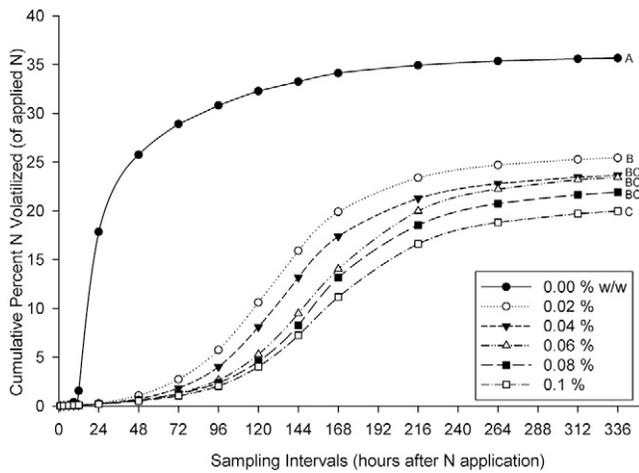


Fig. 5. Cumulative N loss (percent of applied) as NH₃ from granular urea treated with varying rates of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) during Trial V. Different letters to the right of the volatility curves indicate significantly different cumulative N loss between treatments at $\alpha = 0.05$.

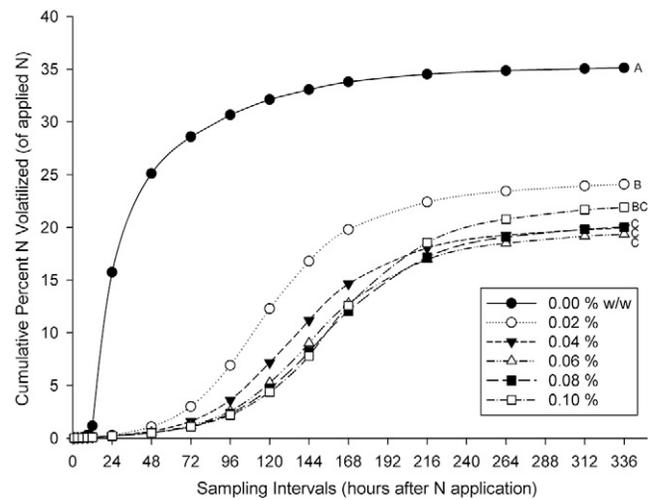


Fig. 6. Cumulative N loss (percent of applied) as NH₃ from granular urea treated with varying rates of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) during Trial VI. Different letters to the right of the volatility curves indicate significantly different cumulative N loss between treatments at $\alpha = 0.05$.

first method to bind the inhibitor to urea is the commercially available formulation, Agrotain (Agrotain-coated urea). The second method is a new solvent system technology under the trade name, Arborite Ag. Using Arborite Ag two physical coatings were applied in conjunction with NBPT to urea. Calcium sulfate (-325 mesh) (CaSO₄-coated+NBPT) and potassium sulfate (-50 mesh) (K₂SO₄-coated+NBPT) were applied in a powder form to urea resulting in fertilizers with the analyses of 39.9-0-0-3.0 S and 36.6-0-7.4-3.2 S, respectively. All coatings were prepared by Brooks Whitehurst Associates Inc. laboratories, developer of the Arborite Ag technology.

Trials III and IV

Trials III and IV differentiate the impact of the physical coatings from the urease inhibitor, NBPT. Treatments in Trial III were noncoated urea, Agrotain-coated urea, Arborite Ag urea, and the check. The last two treatments in this trial are the CaSO₄-coated urea, with and without the NBPT. In Trial IV the first four treatments remain the same as in Trial III; however the last two treatments were K₂SO₄-coated urea, with and without NBPT. The calcium and potassium sulfate coated urea without NBPT used the same solvent system of Arborite Ag but without NBPT.

Table 2. Treatment descriptions for Trials I, II, III, and IV.

Coating	Fertilizer analysis (N-P-K-S)	Trial I	Trial II	Trial III	Trial IV
Check		L	L	L	L
Urea	46-0-0-0	L	L	L	L
Arborite Ag	45.9-0-0-0	L	L	L	L
Agrotain	45.8-0-0-0	L	L	L	L
CaSO ₄ -coated+NBPT†	39.9-0-0-3	L	L	L	
CaSO ₄ -coated	39.9-0-0-3			L	
K ₂ SO ₄ -coated+NBPT†	36.6-0-7.4-3.2	L	L		L
K ₂ SO ₄ -coated	36.6-0-7.4-3.2				L

† Potassium and calcium physical coatings received the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) in the form of Arborite Ag.

Trials V and VI

Trial V and VI assessed the application rate of NBPT applied to the urea granule. Six rates of NBPT, on a percent by weight basis, were used during this trial being 0.00, 0.02, 0.04, 0.06, 0.08, and 0.1%. The Arborite Ag binder was used as the carrier to coat the urea granules with the different concentrations of NBPT during this trial.

RESULTS AND DISCUSSION

Trials I and II

Trials I and II were conducted to compare urea to coated urea containing NBPT from Agrotain and Arborite Ag as well as physically coated urea with Arborite Ag. Ammonia losses were negligible from N treatments for 1 to 6 h after N application. At 9 h after fertilizer application NH₃ volatilization from urea was greater than the coated treatments in Trials I (0.7%) and II (0.6%). This loss was not significant for Trial I due to slightly larger variation, standard error of 0.3%, compared to a standard error for Trial II of 0.2%. From 12 to 72 h NH₃ volatilization at each sampling interval was significantly greater from urea than the coated urea products for both Trials I and II. The greatest loss of N from urea came between 12 and 24 h after application with losses of 17.2% (1.4% of applied N h⁻¹) and 17.6% (1.5% of applied N h⁻¹) of applied N for Trials I and II, respectively. The NH₃ loss from 12 to 24 h equaled 46.7 and 51.9% of the total NH₃ loss during the 2-wk period for Trials I and II, respectively. Ammonia loss, within sampling intervals, from urea decreased from 24 to 336 h after urea application and was significantly lower than that of the coated treatments from 96 to 264 h in both Trials I and II.

Cumulative NH₃ volatilization N losses from urea plateau beyond 96 h after application, and cumulative N loss was 36.8 and 33.9% of applied N for Trials I and II, respectively (Fig. 1 and 2). Cumulative N loss for noncoated urea was significantly higher than all NBPT-coated materials for Trials I and II, but none of the coating treatments differed in cumulative N loss (Fig. 1 and 2). The coated materials slowed NH₃ volatilization

losses out to 96 h after N application (Fig. 1 and 2). For the inhibitor only coatings, Agrotain and Arborite Ag, cumulative NH_3 loss as well as ammonia loss at each sampling interval did not differ for Trial I (Fig. 1). Ammonia losses from Agrotain and Arborite Ag were greatest from 96 to 120 h with a maximum NH_3 loss rate of 0.20 and 0.19% of the applied N h^{-1} during Trial I. Losses during Trial II for Arborite Ag were greatest from 120 to 144 h (0.16% of applied N h^{-1}) whereas Agrotain did not reach a maximum NH_3 loss rate until 168 h (0.15% of applied N h^{-1}). Agrotain had significantly lower NH_3 loss at the 120 h (2.7% of applied N) and 144 h (3.3% of applied N) sampling intervals than Arborite Ag (3.5% of applied N at 120 h and 3.9% of applied N at 144 h) during Trial II. These two sampling intervals during Trial II were the only sampling intervals throughout Trials I to IV where Agrotain and Arborite Ag were found to be significantly different (Fig. 1–4). In all trials, cumulative N loss at the end of the 2-wk sampling period from Agrotain and Arborite Ag were similar.

The CaSO_4 -coated+NBPT and K_2SO_4 -coated+NBPT reached a maximum NH_3 loss rate from 120 to 144 h with maximum NH_3 loss rates of 0.17% and 0.16% of applied N h^{-1} during Trial I. The CaSO_4 -coated+NBPT treatment lost significantly lower amounts of ammonia at the 96 h (2.4% of applied N) than Arborite Ag (3.3% of applied N) as well as being significantly lower at 120 h (3.9% of applied N) than Agrotain (4.7% of applied N) and Arborite AG (4.8% of applied N) during Trial I. The K_2SO_4 -coated+NBPT treatment lost significantly less NH_3 at 96 (2.0% of applied N) and 120 h (3.2% of applied N) than Arborite AG (3.3% of applied N at 96 h and 4.8% of applied N at 120 h) and Agrotain (3.0% at 96 h of applied N and 4.7% of applied N at 120 h), during Trial I. The CaSO_4 -coated+NBPT and K_2SO_4 -coated+NBPT treatments were not statistically different during any sampling interval during Trial I.

During Trial II, the CaSO_4 -coated+NBPT treatment reached a maximum NH_3 loss rate from 120 to 144 h with an NH_3 loss rate of 0.15% of the applied N h^{-1} , while the K_2SO_4 -coated+NBPT treatment reached a maximum NH_3 loss rate of 0.16% of the applied N h^{-1} from 144 to 168 h. However, the CaSO_4 -coated+NBPT treatment was only significantly different from Arborite Ag during the 216 h sampling interval with NH_3 losses of 3.8 and 3.2% of applied N, respectively. The K_2SO_4 -coated+NBPT treatment had significantly lower ammonia loss (2.7% of applied N) than Arborite AG (3.5% of applied N) at 120 h, but ammonia losses for K_2SO_4 -coated+NBPT (4.6% of applied N) were significantly higher than Arborite AG (3.2% of applied N) at 216 h. The physically coated treatments did not differ from Agrotain at any sampling interval during Trial II.

Cumulative N loss did not differ between CaSO_4 -coated+NBPT, K_2SO_4 -coated+NBPT, Agrotain and Arborite Ag (Fig. 1 and 2). Cumulative N loss for CaSO_4 -coated+NBPT, K_2SO_4 -coated+NBPT, Agrotain and Arborite Ag ranged from 22.1 to 24.8% and 17.9 to 20.8% for Trials I and II, respectively. Physically coating the urea granule did not significantly decrease the amount of ammonia loss beyond that of the inhibitor, NBPT alone over the 2-wk trial period.

Trials III and IV

Trial III was designed to determine the effect on NH_3 volatilization when urea was coated with CaSO_4 alone compared to products using the inhibitor NBPT alone, or in combination with the CaSO_4 coating. Ammonia volatilization from noncoated urea was similar to Trials I and II with the peak NH_3 loss occurring at the 24 h sampling interval, 17.8% of applied N. When CaSO_4 was applied to urea granules, NH_3 volatilization was delayed 24 h and the maximum NH_3 loss rate was 0.74% of applied N h^{-1} with a total of 8.9% of the applied N being lost by the 24 h sampling interval. The hourly NH_3 loss rate with CaSO_4 -coated urea reached a maximum during the same sampling interval as urea alone (1.5% of applied N h^{-1}) but the physical coating reduced the ammonia loss rate by 50% during the sampling interval. Ammonia loss from CaSO_4 -coated urea was 12.1, 4.9, and 2.5% of applied N at 48, 72, and 96 h, respectively. Ammonia losses for CaSO_4 -coated urea were significantly higher than for urea (6.1, 2.7, and 1.7% of the applied N) over the same sampling intervals. Ammonia losses were the same for CaSO_4 -coated urea and urea alone beyond 96 h after N application. The higher losses of N from CaSO_4 -coated urea resulted in cumulative losses that were the same as urea at the conclusion of Trial IV (Fig. 3)

The CaSO_4 -coated+NBPT treatment significantly reduced NH_3 losses during the 96, 120, and 144 h sampling intervals with (1.3, 2.3, 3.3% of the applied N) compared to Arborite Ag (2.1, 3.6, and 4.6% of the applied N). The CaSO_4 -coated+NBPT (2.3, 3.3, and 3.5% of the applied N) significantly reduced ammonia losses compared to Agrotain during the 120, 144, and 168 h sampling intervals (3.3, 4.4, and 4.6% of the applied N). The maximum NH_3 loss rates for the coatings containing NBPT occurred at 144 h for Arborite Ag (0.19% of the applied N h^{-1}) and 168 h for Agrotain (0.19% of the applied N h^{-1}) and CaSO_4 -coated+NBPT (0.15% of the applied N h^{-1}). Coatings containing NBPT continue to volatilize significantly higher amounts of NH_3 within sampling intervals until 264 h (11 d) after N application. The higher levels of NH_3 loss at later sampling intervals indicated that urea hydrolysis was still occurring at 264 h when NBPT was used. The higher losses of NH_3 were due to the delayed urea hydrolysis with NBPT indicated by lower ammonia loss from 0 to 96 h and low concentrations of urea left at the soil surface due to the rapid hydrolysis of urea without NBPT. However, NH_3 loss was the same among all treatments within the sampling intervals from 312 to 336 h. All coatings that received NBPT had significantly lower cumulative N loss than urea applied without NBPT (Fig. 3). When NBPT was applied with and without the CaSO_4 coating cumulative NH_3 volatilization losses were 24.6, 23.3, and 19.4% for Agrotain, Arborite Ag, and CaSO_4 -coated+NBPT, respectively (Fig. 3).

Trial IV was identical in treatment design as Trial III with K_2SO_4 replacing CaSO_4 as the physical coating. Noncoated urea released NH_3 within 9 h after N application and reached a maximum rate of NH_3 volatilization 24 h after application with 17.8% (1.5% of the applied N h^{-1}) of the N being lost from 12 to 24 h (Fig. 4). When urea was coated with K_2SO_4 , NH_3 volatilization was delayed until 24 h with 0.7% of the applied N lost. Ammonia loss from the K_2SO_4 -coated urea was 3.3% of the applied N at 48 h and was significantly lower than 8.0%

loss from urea. Ammonia loss from K_2SO_4 -coated urea was significantly higher than from urea at 72 to 216 h. However, the maximum NH_3 loss rate of 1.4% of the applied $N\ h^{-1}$ for urea occurred from 12 to 24 h where the maximum NH_3 loss rate for K_2SO_4 -coated urea was 0.21% of the applied $N\ h^{-1}$ from 72 to 96 h. The K_2SO_4 -coating delayed NH_3 loss for 48 h, reduced the maximum rate of NH_3 loss by 0.9% of the applied $N\ h^{-1}$, and also delayed the time to reach maximum NH_3 loss for 3 d (Fig. 4).

The K_2SO_4 -coated urea lost significantly greater amounts of NH_3 than coatings containing NBPT from 24 to 120 h during Trial IV. Maximum NH_3 loss rates for the coatings containing NBPT occurred from 144 to 168 h and were 0.17, 0.16, and 0.19% of the applied $N\ h^{-1}$, corresponding to 4.1, 3.8, and 4.6% of the applied N for Arborite Ag, Agrotain, and K_2SO_4 -coated+NBPT (Fig. 4). Ammonia losses from coatings containing NBPT were higher than K_2SO_4 -coated urea from 168 to 312 h. The higher NH_3 loss with NBPT at later sampling intervals is evidence that the inhibitor delayed urea hydrolysis up to 13 d after N application.

Cumulative NH_3 volatilization by 120 h was under 5% of the applied N when NBPT was applied and no differences among treatments receiving NBPT were seen until 168 h after N application when Agrotain differed from K_2SO_4 -coated+NBPT (Fig. 4). The K_2SO_4 -coated urea did delay and significantly decrease the cumulative N lost from NH_3 volatilization (Fig. 4).

Nitrogen loss was lower with the K_2SO_4 -coating, than urea alone; however, NBPT further decreased NH_3 volatilization compared to K_2SO_4 alone (Fig. 4). It has been postulated that alkali and alkaline earth metals may displace calcium from cation exchange sites, resulting in calcium reacting with bicarbonate produced during urea hydrolysis creating a precipitate (Fenn et al., 1982). The reaction, known as the "Fenn reaction", minimizes the pH increase around the zone of high urea concentration and decreases the amount of NH_3 gas formed (Fenn et al., 1982; Kiss and Simihaian, 2002). The reduction in NH_3 volatilization during the K_2SO_4 and $CaSO_4$ trials is most likely due to the reduced pH in the urea concentrated zone after dissolution. The greater effect observed for potassium sulfate is believed attributable its greater solubility in water ($11.1\ g\ 100\ mL^{-1}$ at $20^\circ C$) vs. the solubility of calcium sulfate ($0.21\ g\ 100\ mL^{-1}$ at $20^\circ C$). Observations during the trial revealed that a shell of $CaSO_4$ was left on the soil surface after the 2-wk trial while there were no physical remains of K_2SO_4 . Bayrakli (1990) found that phosphogypsum decreased NH_3 volatilization when mixed into the soil with urea. The results from this study indicate that calcium sulfate and potassium sulfate (Fig. 3 and 4) alone did delay NH_3 volatilization initially, and in the case of potassium sulfate (Fig. 4) decreased cumulative NH_3 volatilization when applied as a coating to urea granules.

Trials V and VI

Trials V and VI were conducted to ascertain the effectiveness of NBPT at different rates using the new binding technology Arborite Ag. When no inhibitor was applied to the urea granules, the NH_3 volatilization rate again peaked at 24 h with an NH_3 loss rate 1.4 and 1.2% of the applied $N\ h^{-1}$ in Trials V and VI, respectively. Ammonia volatilization did not differ as NBPT rate increased from 0.02 to 0.1% for the first

48 h in Trial V and the first 24 h in Trial VI. During the 48 h sampling in Trial VI the 0.02% NBPT treatment lost 0.81% of the applied N and was significantly higher than NBPT levels of 0.06, 0.08, and 0.1% with losses of 0.33, 0.31, and 0.30% of the applied N. The 0.02% NBPT rate reached a maximum NH_3 loss rate of 0.22% of the applied $N\ h^{-1}$ (5.35% total N loss) at 144 h during Trial V and 0.22% of the applied $N\ h^{-1}$ (5.38% total N loss) at 120 h during Trial VI. The 0.04% reached maximum NH_3 loss rates at 144 h in both Trials V and VI with rates of 0.21 (5.11% total N loss) and 0.17% of the applied $N\ h^{-1}$ (4.06% total N loss). The three higher NBPT rates (0.06, 0.08, and 0.1%) all showed maximum NH_3 loss rates at 168 h during Trials V and VI. The addition of NBPT to the urea granule delayed the maximum NH_3 loss rate with each addition of NBPT up to 0.06%. At NBPT rates of 0.08 and 0.1% no additional effects were seen in NH_3 volatilization control compared to the 0.06% NBPT rate.

As the rate of NBPT increased, NH_3 volatilization decreased in both Trials V and VI. At NBPT rates of 0.02% w/w cumulative NH_3 volatilization decreased from 35.6 and 35.1% to 25.4 and 24.1% for Trials V and VI, respectively. However, for NBPT rates ranging from 0.04 to 0.1% cumulative NH_3 volatilization losses ranged from 23.6 to 19.4% with no differences in either Trials V or VI (Fig. 5 and 6). When NBPT was applied at rates equal to or above 0.06% NH_3 volatilization remained below 5% of applied N until 120 h after N application (Fig. 5 and 6). By applying more NBPT, NH_3 volatilization was delayed an extra 48 h over the 0.02% NBPT rate, however, cumulative volatilization did not differ between the 0.04 and 0.1% NBPT rates. This delay in N loss could allow for a more flexible time frame for N application in comparison to trying to match rainfall events and N application to a smaller time window.

SUMMARY AND CONCLUSION

Ammonia volatilization (32–35% total N loss) from urea during the six trials was similar in total N loss to other laboratory trials (Antisari et al., 1996; Carmona et al., 1990; Rawluk et al., 2001). Urea reached a maximum volatilization rate from 12 to 24 h after N application when conditions were favorable for volatilization. The inhibitor NBPT delayed NH_3 volatilization in all trials; however reduction in NH_3 volatilization was not as great as in previous research (Rawluk et al., 2001). The higher NH_3 volatilization with NBPT treatment in our studies compared to other studies in the literature may be due to diffusion away from the zone of NBPT in other studies, because of higher soil moisture contents. The conditions of our trials may allow greater interaction of the urea granules with soil urease resulting in higher rates of NH_3 volatilization. Urease inhibitors do not stop urea hydrolysis, but their use allows for the urea in the soil solution to diffuse into a greater volume of soil minimizing the pH increase and the resulting NH_3 volatilization.

The physical coatings did not have an additive effect in controlling NH_3 volatilization when applied with NBPT. Though when applied alone the physical coatings did delay ammonia volatilization for 24 h. This supports other research cited by Kiss and Simihaian (2002) which reported that alkali and alkaline earth metals may reduce NH_3 volatilization. The physical coatings

tested in this trial allow for S, in the form of CaSO_4 or K_2SO_4 , to be applied with N which may be useful in many regions. However, the low solubility of CaSO_4 may limit its effectiveness for NH_3 volatilization control. By coating the urea with the aforementioned physical coatings the need for a plant available N and S fertilizer could be met. However, applying a coating to urea adds additional cost as well as lowers the N content of urea. The additional cost associated with CaSO_4 and K_2SO_4 coated urea may be offset by the value of S and K in the coating.

Increasing NBPT rates decreased NH_3 volatilization in the initial hours after application, but cumulative N loss from the 0.04 to 0.1% rates did not differ significantly. The inhibitor NBPT is a very efficient urease inhibitor and rates as low as 0.02% w/w, NBPT can decrease NH_3 volatilization. At NBPT rates of 0.04 to 0.1% w/w NH_3 volatilization was delayed an extra 48 h which could be beneficial. Our data indicate that 0.04 to 0.06% NBPT produce the same total NH_3 volatilization control under laboratory conditions, as the North American industry standard rate of 0.08% NBPT. Further research is needed to confirm these findings and determine optimum NBPT rates for field conditions; and to determine how NBPT in combination with various physical coatings can be most effectively used to increase N use efficiency of urea fertilizers in agronomic crop production.

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