

EFFICACY OF UREASE AND NITRIFICATION INHIBITORS IN REDUCING AMMONIA VOLATILIZATION FROM UREA AND UAN IN HIGH-pH SOILS

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SUMMARY

Urea-based fertilizers (urea and urea ammonium nitrate (UAN)) are susceptible to losses that reduce fertilizer efficiency and economic benefit. Urease and nitrification inhibitors can reduce nitrogen (N) losses due to volatilization, thereby improving fertilizer efficiency. The objective of this study was to evaluate the efficacy of new formulations of Active AgriScience inhibitor products, which cost lower than existing commercial inhibitors, such as Agrotain. Ammonia volatilization was measured for 14 d after banded and broadcast application of inhibitor-treated and check urea-based fertilizers. Residual soil N was measured at the end of the study. Results showed that all inhibitor treatments lowered ammonia volatilization from urea and UAN treatments. When compared with Agrotain, 18% ARM U and Active Stabilizer applied at the rate of 1.5 L per 1000 kg of UAN (1.5 AS) produced similar results for cumulative ammonia volatilization and percentage reduction in volatilization in UAN treatments. Similarly, cumulative ammonia volatilization and percentage reduction in ammonia volatilization from urea treated with 18% ARM U, 30% ARM U and Active Stabilizer applied at the rate of 2.4 L per 1000 kg of urea (2.4 AS) were similar to those for Agrotain-treated urea. Incorporation of fertilizer (shallow banding) significantly reduced ammonia volatilization losses. Soil residual ammonium-N was greater under banded urea than broadcast urea treatments. Nitrate-N concentrations in Agrotain, 30% ARM U, Active Stabilizer PLUS applied at the rate of 1.8 L per 1000 kg of urea (1.8 ASP), and Active Stabilizer applied at the rate of 1.8 L per 1000 kg of urea (1.8 AS) treatments were significantly higher than those in the untreated urea treatment. Reduced N losses from inhibitor treatments could potentially translate to increased yields. The treatment of UAN and urea with urease inhibitor with and without nitrification inhibitor reduced ammonia volatilization, with some Active AgriScience products showing similar efficacy to Agrotain despite their lower concentration of the active ingredient, NBPT.

INTRODUCTION

Nitrogen (N) is one of the most limiting nutrients in soil and affects crop production (Malhi et al., 2001). Globally, urea is the most common synthetic N fertilizer used to meet crop N requirements and improve yield (Cantarella et al., 2008). Urea fertilizer is the preferred N fertilizer for most farmers due to its ease of application, high N content and low-cost (Li et al., 2015). Despite the several benefits of urea, a significant percentage of N is lost through processes such as ammonia volatilization, leaching, denitrification, and immobilization when urea is applied to soil (Malhi et al., 2001). These losses translate to a reduction in fertilizer efficiency and may lead to ground-and surface water contamination (Riley et al., 2001; Xu et al., 2013; Cantarella et al., 2018). Ammonia volatilization is a significant pathway for N loss from surface applied urea-based fertilizers (Rochette et al., 2013) and may result in losses of up to 40% of applied N under high temperature and humid conditions (Cantarella et al., 2003). Volatilization losses of 64% of applied N have been

reported for broadcast urea compared with 31% from soils receiving banded urea under no-till (Rochette et al., 2009a). High temperature and high pH are factors that increase ammonia volatilization from urea (Liu et al., 2019). Ammonia loss from urea has been reported even under low temperatures (Perin et al., 2020). To address the loss of N from urea-based fertilizers (urea and urea ammonium nitrate (UAN)) and achieve the desired economic benefit of fertilizer application, researchers recommend best nutrient management practices such as the 4R principle (Right rate, Right time, Right placement, and Right source) (Davidson et al., 2016).

Fertilizer placement in the soil influences N loss from organic and inorganic fertilizers (Rochette et al., 2009a; Drury et al., 2017; Woodley et al., 2018). Broadcasting urea-based fertilizers on the soil surface increases the susceptibility to ammonia volatilization losses, especially in high pH and moist soils (Wang et al., 2004; Rochette et al., 2013; Perin et al., 2020). Fertilizer incorporation soon after application and banding have been shown to reduce ammonia volatilization and are often recommended to reduce N loss. Placing urea in bands reduced ammonia volatilization losses by 50% compared to surface application (Rochette et al., 2009a). The deeper the fertilizer placement, the lower the volatilization losses; for example, Rochette et al. (2013) reported a 7% cm^{-1} decrease in ammonia volatilization when urea granules were incorporated. In contrast to these studies, higher ammonia emissions from banded relative to broadcast urea have also been observed (Rochette et al., 2009b). Thus, combining incorporation/banding with the use of urease and nitrification may be a better strategy to reduce N loss and increase fertilizer efficiency (Drury et al., 2017).

Urease and nitrification inhibitors are recent technologies adopted to increase fertilizer efficiency by reducing losses through volatilization, denitrification, and nitrate leaching. Urease inhibitors (UI) reduce ammonia volatilization by inhibiting the ability of the urease enzyme to catalyze urea hydrolysis, with the advantage of keeping N in a stable and non-volatile form (Silva et al., 2017; Sigurdarson et al., 2018). Nitrification inhibitors (NI), on the other hand, work by temporarily delaying the conversion of ammonium to nitrate, thus retaining the fertilizer in the ammonium form while reducing losses through denitrification or nitrate leaching (Ruser and Schulz, 2015; Wang et al., 2020).

Currently, there are inhibitor products containing both urease and nitrification inhibitors aimed at concurrently reducing urea hydrolysis and inhibiting nitrification, thereby improving the economic benefit of fertilizers (Soares et al., 2012). These products contain double inhibitors (DI) and could potentially improve crop yields. Results on the effect of the combination of UIs and NIs on ammonia volatilization are inconsistent. While some researchers reported no difference between UIs and DIs (Lasisi et al., 2019), others reported an increase in volatilization with the addition of DIs (Zaman et al., 2008; Soares et al., 2012). It is of interest to evaluate the effect of the addition of nitrification inhibitor (DMPP) to NBPT on ammonia volatilization in our study.

New formulations of UI and DIs from Active AgriScience are sold at lower cost compared to other commercial inhibitors and could potentially reduce volatilization at rates comparable to those of the other inhibitors on the market. The Active AgriScience products also contain lower rates of UIs and NIs in comparison to their counterparts. To increase the marketability of the inhibitor products by Active Agriscience and increase consumer awareness, it is important to evaluate the

efficacy of these products in lowering ammonia volatilization. Therefore, the objective of this study was to evaluate the efficacies of a range of products from Active Agriscience containing NBPT only or NBPT plus DMPP (DI) on ammonia volatilization from surface and banded applications of urea and UAN.

METHODS

The soil used for this growth room study was collected from a farm in Roseisle, MB and had a high pH and low OM and N contents. The trial was set up to maximize ammonia volatilization by selecting soil with high pH, low organic matter and low moisture. The characteristics of the soil are listed in Table 1. The experimental layout was a completely randomized design in which factorial combinations of treatments were replicated 4 times. UAN treatments consisted of untreated UAN, UAN plus Active Stabilizer (containing NBPT only) and Active Stabilizer PLUS (NBPT + DMPP) at rates of 1, 1.5 and 2 L per 1000 kg UAN (1 AS, 1.5 AS, 2 AS, 1 ASP, 1.5 ASP, and 2 ASP respectively), ARM U (18% NBPT) (18% ARM U), ARM U (30% NBPT) (30% ARM U), Arm U Advanced and a commercial inhibitor, Agrotain Advanced 1.0 (Agrotain). The same treatments were used for urea, but with different rates of AS and ASP: 1.2, 1.8 and 2.4 L per 1000 kg urea (1.2 AS, 1.8 AS, 2.4 AS, 1.2 ASP, 1.8 ASP, and 2.4 ASP, respectively).

Table 1: Selected characteristics of soil used in this study

Soil property	Values
Soil pH	7.9 ± 0.09
Electrical conductivity (ds m ⁻¹)	0.28 ± 0.02
Field capacity (g kg ⁻¹)	260
Organic matter (%)	2.4 ± 0.1
CEC (meq/100g)	11.3 ± 0.4
Soil type	Sand
Sand %	89.3 ± 0.9
Silt %	7.3 ± 0.9
Clay %	3.4 ± 0
N (mg kg ⁻¹)	15.7 ± 0.5
P (mg kg ⁻¹)	23.3 ± 0.5
K (mg kg ⁻¹)	213.3 ± 18
S (mg kg ⁻¹)	5 ± 0.8
Ca (mg kg ⁻¹)	1767 ± 47
Mg (mg kg ⁻¹)	223 ± 12
Na (mg kg ⁻¹)	11.3 ± 0.9

Ammonia volatilization was measured using the static chamber method (Grant et al., 1996; Jantalia et al, 2012; Lasisi et al., 2019). Briefly, soil was packed into cylindrical polyvinyl chloride (PVC) columns (0.15 m id. and 0.25 m height) to a height of 7 cm and a bulk density of 1.1 metric tons m⁻³. Water was added to the soils in the column to achieve a moisture content of 60% of field capacity. After soil-water equilibration, fertilizer treatments were applied either on the soil surface (broadcast) or in a band 2 cm below the soil surface (banded) to supply an equivalent of 120 kg N ha⁻¹. After treatment application, columns were fitted with two acid charged foam discs (1M

phosphoric acid + 4% glycerol). The inner foam disc was placed 5 cm above the soil surface to trap volatilized ammonia (NH₃) while the upper foam disc was placed 5 cm below the top of the column to reduce contamination by atmospheric ammonia. Experimental units were kept under controlled conditions (30 °C; 50% relative humidity; 16 h photoperiod) for the duration of the study. Soil temperature measured every sampling day averaged 30.3°C. The inner foam disc was sampled at 1, 2, 4, 7, and 14 d after fertilizer application. On each sampling day, the inner foam was collected from each unit and replaced with a fresh acid-soaked foam disc. Ammonia trapped in the foam disc was extracted using 250 mL of 2 M KCl solution, and concentration of the ammonium in the extract was determined colorometrically. At the end of the 14-d study, soil in from each column was thoroughly mixed, air-dried, ground, and analyzed for residual ammonium-N and nitrate-N. Results were used to calculate ammonia volatilization:

$$\text{NH}_3\text{-N (kg ha}^{-1}\text{)} = \left(\frac{\text{Extractant (mL)} + \text{absorbent in disc (mL)} \times \text{NH}_3 \text{ (mg N mL}^{-1}\text{)}}{\text{Area of chamber (ha)} \times 10^6} \right) \quad (\text{Lasisi et al. 2019})$$

Percent reduction in ammonia volatilization was calculated as the ratio of the difference between cumulative NH₃-N volatilized from untreated and treated fertilizer to cumulative NH₃-N from untreated fertilizer.

RESULTS

Daily volatilization losses

Ammonia volatilization in untreated urea and UAN peaked on Day 2 for banded and broadcast placements (Fig. 1.1 and 1.2). Peak volatilization for untreated UAN was lower than that for urea, probably due to the lower urea N content (Peng et al., 2015; Lasisi et al., 2019). When inhibitor-treated urea was surface-applied (broadcast), ammonia volatilization peaked on Day 4 for 1.2 AS, 1.2 ASP, 1.8 AS, 1.8 ASP, 2.4 ASP, 30% ARM U, Agrotain and ARM U Advanced, indicating a delay in the time to maximum volatilization loss. Maximum volatilization was further delayed for 2.4 AS, 18% ARM U as peak volatilization occurred 7 d after treatment application.

The volatilization losses of ammonia on Day 1 from all broadcast UAN treatments except 1.8 AS were surprisingly high. The high losses were likely due to a short burst of rapid release of ammonium-N from UAN after contact with the warm soil surface (Rochette et al., 2009b). Peak ammonia volatilization for UAN broadcast treatments occurred on Day 4 for all rates of Active Stabilizer treatments, 30% ARM U, ARM U Advanced, and Agrotain. Maximum volatilization loss was recorded on Day 7 for 1 ASP, 1.5 ASP, 2 ASP and 18% ARM U. In comparison to AS, ASP treatments delayed ammonium volatilization by 3 days in broadcast UAN treatments. The NI in ASP could have offset the inhibitory action of NBPT (Lasisi et al., 2020a), thus delaying the inhibitory effect until Day 7. Similar to our results, other studies have shown a one-day delay in peak volatilization when DCD was added to urea + NBPT (Soares et al., 2012; Zaman et al., 2008).

For banded urea treatments, peak ammonia volatilization occurred on Day 4 for 1.2 AS, 1.2 ASP, 1.8 AS, 18% ARM U, 2.4 AS, 2.4 ASP, 30% ARM U, Agrotain and ARM U Advanced. ASP applied at the rate of 1.8 L/1000 kg (1.8 ASP) delayed peak volatilization until Day 7. Maximum

volatilization occurred on Day 4 for UAN treated with 1 ASP, all rates of active stabilizer treatments, 30 % ARM U and ARM U Advanced. Similar to broadcast application, 1.5 ASP, 2 ASP and 18% ARM U delayed peak volatilization until Day 7. Ammonia volatilization peaked on Day 1 for Agrotain-treated UAN. Inhibitor products have been shown to delay volatilization by up to 14 d (Lasisi et al., 2019).

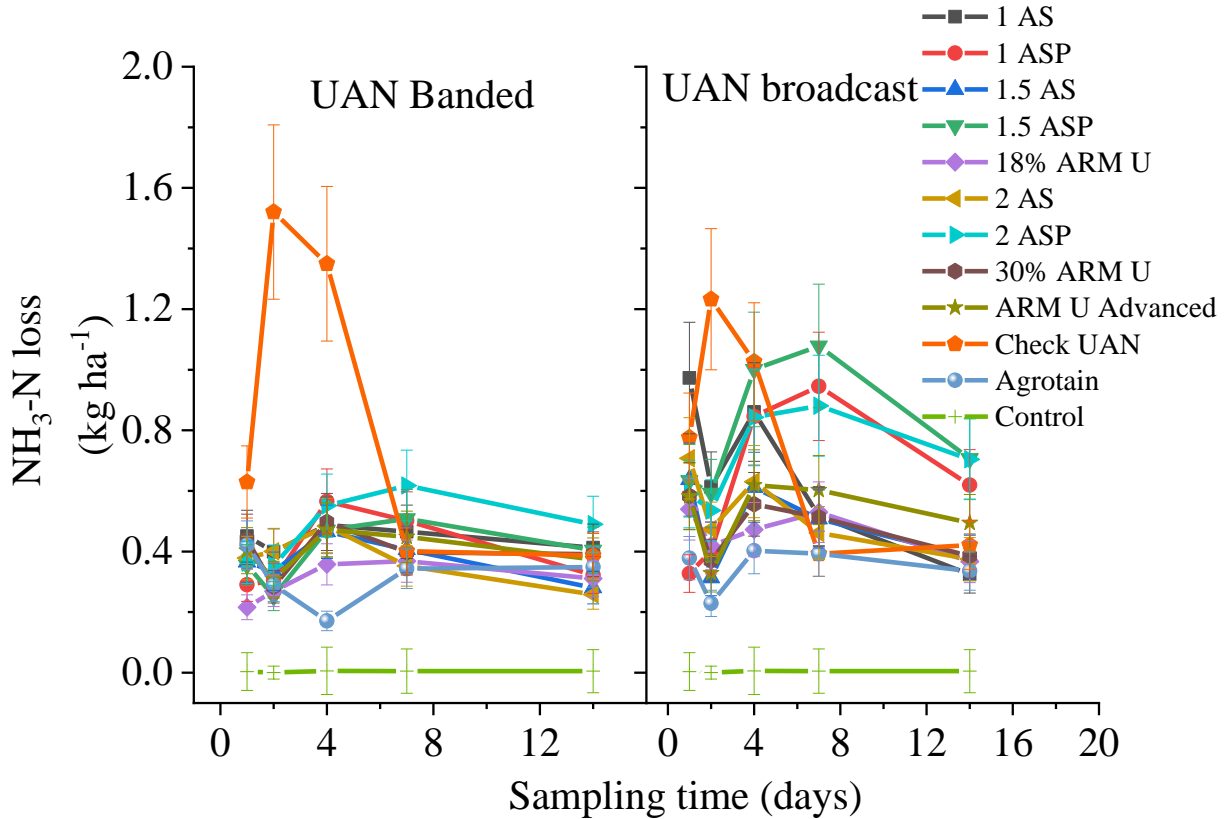


Figure 1.1. Urease and nitrification inhibitor effects on ammonia volatilization loss following broadcast and banded application of UAN. Error bars represent standard errors of the mean (SEM) (n = 4).

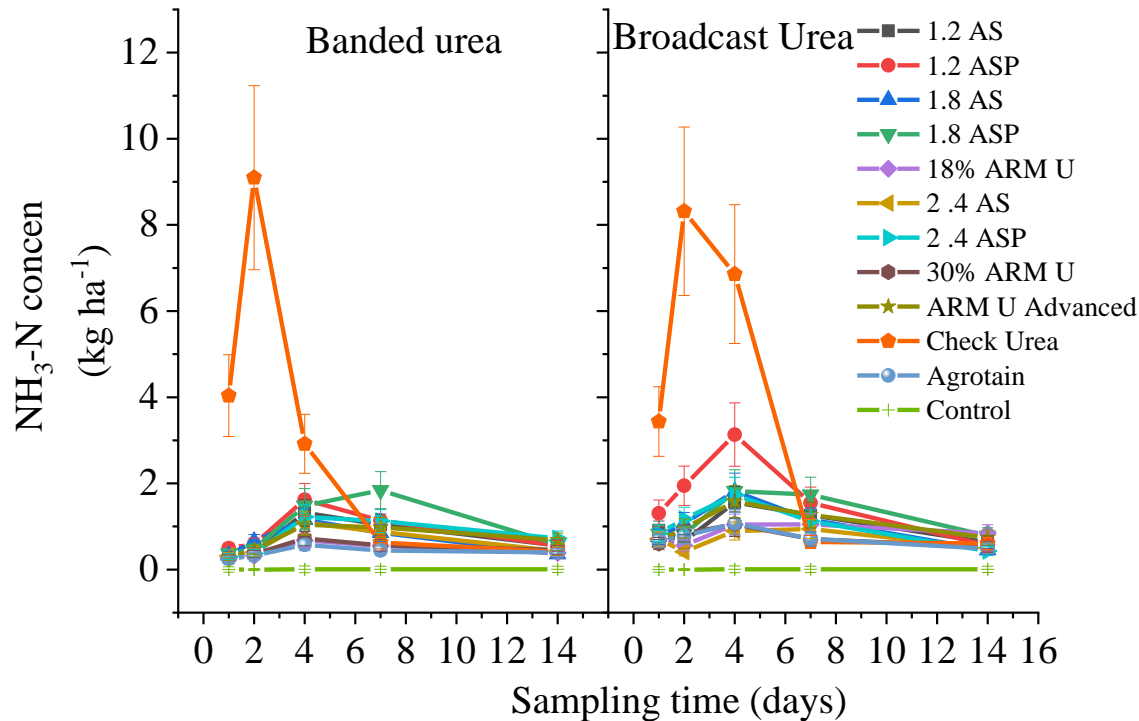


Figure 1.2. Urease and nitrification inhibitor effects on ammonia volatilization loss following broadcast and banded application of urea. Error bars represent standard errors of the mean (SEM) (n = 4).

Cumulative ammonia volatilization and percent reduction in volatilization

Cumulative volatilization loss from UAN ranged from 0.4 – 3.3 kg ha⁻¹, corresponding to 0.3 – 3% of applied N and 1.1 – 19 kg ha⁻¹ (1 – 16% applied N) for urea treatments (Table 2). There was a significant treatment and placement effect on ammonia volatilization for both sources of N (Table 2). Averaged across placements, the greatest cumulative NH₃-N loss was from untreated UAN at 3 kg ha⁻¹ (~3% of applied N) and urea at 18 kg ha⁻¹ (15% of applied N) (Figs. 2). Cumulative volatilization losses were lowest for UAN and urea treated with Agrotain. This was expected as the Agrotain, due to its recommended application rate and percent NBPT content, contained more UI than all other products. In UAN treatments, cumulative loss from untreated UAN was similar to that from 1 AS, 1 ASP, 1.5 ASP, and 2 ASP (Fig. 2). Cumulative volatilization loss from Agrotain treated UAN was statistically similar to losses from 18% ARM U and 1.5 AS.

Inhibitor treatments reduced cumulative ammonia volatilization loss from UAN by 29 to 81% and from urea by 62% - 94% (Table 2). Averaged across both placements, there was a significant treatment effect on ammonia volatilizations (Table 2). Agrotain reduced ammonia volatilization from UAN by 84% and performed better than 1 AS, 1ASP, 1.5 ASP, 2 AS, 2ASP, 30% ARM U

and ARM U Advanced (Figure 3). Agrotain performance was comparable to those of 18% ARM U (71%) and 1.5 AS (65%), indicating similar efficacies of these new formulations and the commercial inhibitor (Agrotain). For urea treatments, Agrotain, 30% ARM U, 18% ARM U and 2.4 AS produced statistically similar reductions in $\text{NH}_3\text{-N}$ loss (91, 90, 88, and 87 %, respectively) (Figure 3). It is noteworthy that the percentage reduction in ammonia volatilization losses from urea treatments without DMPP increased with increasing concentration of NBPT. The lowest reduction was in the lowest rate of ASP (1.2 ASP). Interestingly, for ASP treatments, the percentage reduction in $\text{NH}_3\text{-N}$ loss increased as the application rate increased. Although ammonia losses have been shown to increase with increasing concentration of NI (Soares et al., 2012), in the current study, ammonia volatilization from urea decreased with an increase in NI. As the inhibitor application rate increased, both NBPT and DMPP concentrations increased; therefore, the resultant decrease in ammonia emissions could be due to higher NBPT concentrations at higher application rates.

Overall, ammonia emissions from AS treatments were significantly lower than those from ASP treatments; thus the percentage reduction in ammonia loss was significantly greater for all AS treatments regardless of N source. This result corroborates previous reports of a reduction in the efficacy of UIs with the addition of NIs (Soares et al., 2012; Frame, 2017).

Fertilizer placement influenced ammonia volatilization across all treatments. For both urea and UAN, cumulative ammonia loss was greater for broadcast than banded placement, while percentage reduction in volatilization was greater for banded than broadcast placement. A combination of fertilizer incorporation and the use of inhibitors could be a good nutrient management strategy for urea-based fertilizers, as previously demonstrated in a study combining fertilizer injection and the use of UI and NI (Drury et al., 2017).

Table 2: Treatment effects on cumulative ammonia volatilization from urea and UAN.

Treatment	Cumulative ammonia volatilization (kg ha ⁻¹)		Reduction in volatilization (%)	
	UAN	Urea	UAN	Urea
Placement				
Banded	0.95b	2.57b	72.71a	86.58a
Broadcast	1.78a	4.59a	49.73b	78.21b
Inhibitor × placement				
Banded				
1 AS	1.17	2.58	64.52	84.03
1 ASP	1.57	4.57	53.21	72.24
1.5 AS	0.78	2.98	75.29	86.45
1.5 ASP	0.84	3.41	75.09	79.19
18% ARM U	0.47	1.15	84.27	92.45
2 AS	0.80	2.04	74.79	87.13
2 ASP	1.32	2.69	63.31	83.31
30% ARM U	1.0	1.27	69.77	91.71
ARM U advanced	0.94	2.56	70.89	84.03
Check-untreated	3.34	16.59	-	-
Agrotain	0.41	1.14	86	93.96
Broadcast				
1 AS	2.24	3.92	39.65	78.78
1 ASP	2.13	7.38	46.34	61.91
1.5 AS	1.39	6.21	60.29	67.74
1.5 ASP	2.73	4.75	34.76	75.02
18% ARM U	1.68	3.37	53.19	82.01
2 AS	1.58	2.42	55.73	86.76
2 ASP	2.62	5.69	28.77	70.55
30% ARM U	1.63	2.38	54.84	87.09
ARM U advanced	2.08	4.50	38.61	76.23
Check-untreated	2.79	19.17	-	-
Agrotain	0.62	2.65	81.61	85.76
			<i>P</i> value	
Inhibitor	<0.0001	<0.0001	<0.0001	<0.0001
Placement	<0.0001	<0.0001	<0.0001	<0.0001
Inhibitor × placement	0.15	0.06	0.10	0.08

Means followed by the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$)

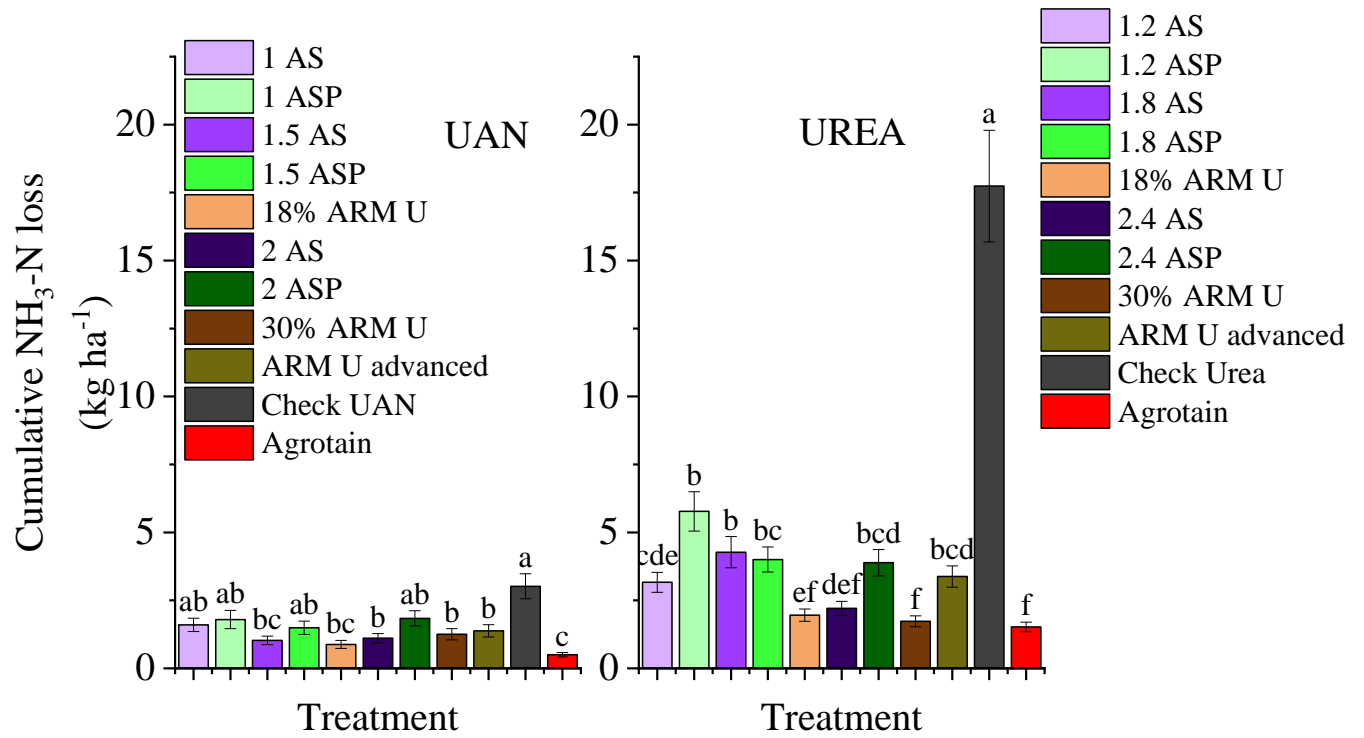


Fig 2 Cumulative ammonia volatilization losses from UAN and urea treatments. Error bars represent standard errors of the mean (SEM) (n = 4). Bars with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$).

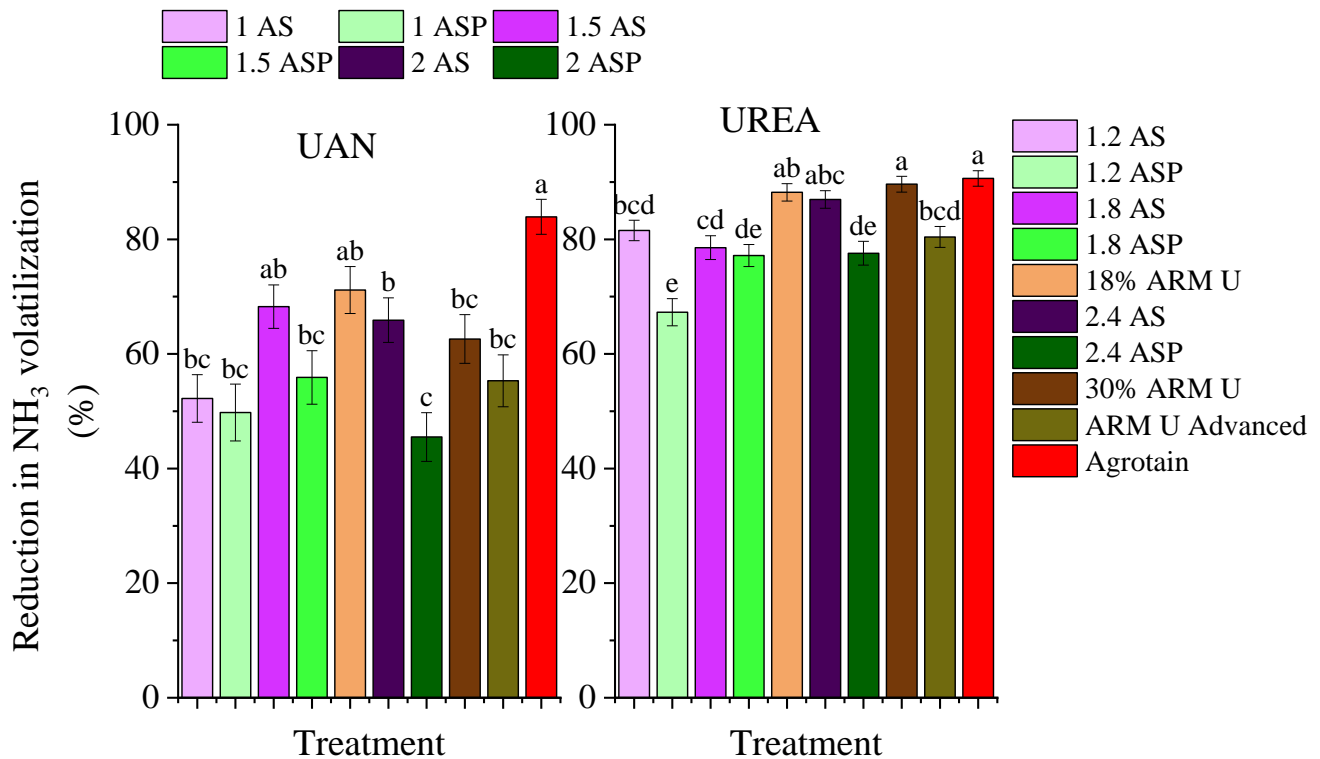


Figure 3 Percent reduction in ammonia volatilization from inhibitor-treated UAN and urea. Error bars represent standard errors of the mean (SEM) (n = 4). Bars with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$).

Residual soil N concentration

Inhibitor treatment of UAN had no significant effect on ammonium-N and nitrate-N concentration. Interestingly, fertilizer placement influenced residual ammonium-N concentration for urea treatments, with ammonium-N concentration greater for banded urea treatments than broadcast treatments. Inhibitor treatment of urea significantly influenced residual nitrate-N concentration (Table 3). Residual nitrate-N concentration was lowest for untreated urea and highest for 30% ARM U-treated urea (Table 3). Residual soil N concentrations for all inhibitor treatments were statistically similar for urea. The highest residual N concentration was expected for 30% ARM U and Agrotain because both had the highest concentration of NBPT, and nitrification was not inhibited with the addition of NI (Frame, 2017). The reduced N loss from inhibitor treatment could potentially translate to improved crop yields and an added return on investment.

Table 3: Inhibitor treatment effect on soil residual N at the end of the 14-d study.

Treatment	Ammonium N (mg kg ⁻¹)		Nitrate- N (mg kg ⁻¹)	
	UAN	Urea	UAN	Urea
Control	4.2	4.2	31.4	31.4c
1 AS	10.36	13.30	144.5	155.38 ab
1 ASP	15.88	9.67	164.25	154.25 ab
1.5 AS	10.55	9.81	152.25	178.5 a
1.5 ASP	15.33	12.27	150.62	172.75 a
18% ARM U	8.81	9.77	147.75	133.25 ab
2 AS	9.59	10.06	151	146.5 ab
2 ASP	16.11	11.91	141.5	135.6 ab
30% ARM U	12.89	10.43	180.25	176.5a
ARM U				
Advanced	16.88	12.51	153.37	143.5ab
Check-				
untreated	13.04	14.47	137.62	109.69b
Agrotain	16.23	8.37	146.25	163.5a
Application				
Banded	13.90	13.3902a	155.36	154.82
Broadcast	12.58	8.893b	148.16	148.71
			<i>P</i> value	
Inhibitor	0.10	0.89	0.05	0.0001
Application	0.64	0.03	0.37	0.61
Inhibitor × application	0.8629	0.61	0.61	0.13

Means followed by the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$).

CONCLUSION

Total ammonia volatilization losses (percent of applied N) from untreated UAN averaged 2.7% for banded placement and 2.3% for surface broadcast placement. Corresponding losses for urea were 13.8% and 16%, respectively. Shallow banding of urea and UAN in combination with the use of inhibitors significantly reduced cumulative ammonia volatilization and improved the percentage reduction in ammonia loss. Active Stabilizer treatments with NBPT only (AS) performed better than double inhibitors (ASP). The effectiveness of 18% ARM U, 30% ARM U and 2.4 AS in reducing ammonia volatilization from urea was comparable to that of Agrotain. For UAN, 18% ARM U and 1.5 AS performed similarly to Agrotain. Active AgriScience products were as effective as Agrotain, despite their lower concentration of NBPT per kg of fertilizer. We conclude that products from Active AgriScience can be used to lower ammonia emission from

applied urea, thus limiting N loss and increasing fertilizer use efficiencies. Lower dosage rates for the products relative other products such as Agrotain will likely make them more economical.

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