

Efficacy of a new *N*-(*n*-butyl) thiophosphoric triamide formulation in reducing ammonia volatilization from urea-based fertilizers

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Abstract: *N*-(*n*-Butyl)thiophosphoric triamide (NBPT) has been reported to reduce ammonia volatilization from surface-applied urea and urea ammonium nitrate (UAN). A new NBPT formulation (ARM UTM, 18% NBPT) that contains a polymer allowing for lower application rate of NBPT was evaluated for its efficacy relative to Agrotain[®] (30% NBPT) and Arborite[®] (24% NBPT). Trials consisted of (i) a greenhouse study that compared two rates of ARM U-treated urea (360 and 540 mg NBPT kg⁻¹ urea) with Arborite- or Agrotain-treated urea (480 and 600 mg NBPT kg⁻¹ urea, respectively) and (ii) a field study that compared urea and UAN treated with either ARM U (360 mg NBPT kg⁻¹ urea) or Agrotain (600 mg NBPT kg⁻¹ urea) at two sites. Static chambers fitted with acid-charged discs were used to measure ammonia volatilization at six or seven dates over 28 d. In the greenhouse study, ammonia volatilization was reduced by 96% with either ARM U or Agrotain and 95% with Arborite. In the field study, ARM U and Agrotain reduced ammonia volatilization from urea by 80% and 66%, respectively, across sites. Similarly, ammonia volatilization from UAN was reduced by 46% and 60% with ARM U and Agrotain, respectively. Despite the lower NBPT application rates with ARM U, ammonia reduction by ARM U, Agrotain, and Arborite was not significantly different. The addition of ARM U to urea and UAN enabled lower application rate of NBPT without compromising its efficacy.

Key words: urea, ammonia volatilization, *N*-(*n*-butyl)thiophosphoric triamide, ARM UTM.

Résumé : Il semble que le *N*-(*n*-butyl)triamide de l'acide thiophosphorique (NBPT) réduise la volatilisation de l'ammoniac après l'application en surface d'urée ou de nitrate d'ammonium et d'urée (NAU). Les auteurs ont évalué une nouvelle formule de NBPT (ARM U^{MC}, 18 % de NBPT) contenant un polymère qui autorise un taux d'application plus faible et ont comparé son efficacité relative à celle d'Agrotain[®] (30 % de NBPT) et d'Arborite[®] (24 % de NBPT). Les essais se sont déroulés comme suit : i) étude en serre comparant deux taux d'application d'urée traitée avec de l'ARM U (360 et 540 mg de NBPT par kg d'urée) à l'urée conditionnée avec Arborite ou Agrotain (480 et 600 mg de NBPT par kg d'urée, respectivement); ii) essai au champ comparant l'urée et le NAU conditionnés avec de l'ARM U (360 mg de NBPT par kg d'urée) ou de l'Agrotain (600 mg de NBPT par kg d'urée) à deux endroits. Les auteurs ont utilisé des chambres statiques avec disque saturé d'acide pour jauger la volatilisation de l'ammoniac à six ou sept dates au cours d'une période de 28 jours. Lors de l'étude en serre, ARM-U et Agrotain ont réduit la volatilisation de l'ammoniac de 96 %, comparativement à 95 % pour Arborite. Sur le terrain, ARM U et Agrotain ont respectivement diminué la volatilisation de l'ammoniac de 80 % et de 66 %, aux deux endroits. La quantité d'ammoniac qui s'évapore après l'application de NAU a elle aussi diminué de 46 % avec ARM-U et de 60 % avec Agrotain. Malgré la plus faible quantité de NBPT appliquée, ARM U diminue presque autant le volume d'ammoniac se volatilisant qu'Agrotain et Arborite. L'addition d'ARM U à l'urée et au NAU permet de diminuer la quantité de NBPT appliquée sans que l'efficacité du traitement en souffre. [Traduit par la Rédaction]

Mots-clés : urée, volatilisation de l'ammoniac, *N*-(*n*-butyl)triamide de l'acide thiophosphorique, ARM U^{MC}.

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Introduction

Urea and urea ammonium nitrate (UAN) are urea-based nitrogen (N) fertilizers that are commonly used to supply N to crops. Urea is the most widely used N fertilizer in most agricultural systems due to its ease of application, high N content, and relatively low cost (Behera et al. 2013; Li et al. 2015). However, the potential for substantial N loss as a result of ammonia volatilization can reduce the N use efficiency of urea-based fertilizers. Ammonia volatilization from urea-based fertilizers occurs during the hydrolysis of urea $[(\text{NH}_2)_2\text{CO}]$ to ammonium and carbonate ions in the presence of urease enzyme which increases soil pH around the urea granules (Bremner 1995; Chien et al. 2009; Soares et al. 2012). The high soil pH caused by urea hydrolysis favours the conversion of ammonium to ammonia, thereby increasing the risk of ammonia volatilization. The predominantly calcareous soils with neutral to alkaline pH on the Canadian prairies (Michalyna et al. 1988) increase the potential of ammonia volatilization from urea-based fertilizers.

The magnitude of ammonia volatilization from urea-based fertilizers depends on several factors including soil pH, texture, organic matter, moisture, temperature, relative humidity, and wind intensity (Chien et al. 2009; Cabrera et al. 2010). For example, soils with high sand content and low organic matter generally have greater ammonia volatilization than those with low sand content and high organic matter (Carmona et al. 1990; Watson et al. 1994). In addition, ammonia volatilization increases as soil temperature increases (Yan et al. 2016) especially in a moist soil. This is because an increase in temperature increases the rate of urea hydrolysis with a greater risk of ammonia volatilization. In addition to soil and environment factors, methods of measurement influence the magnitude of ammonia volatilization. Static chamber method has been reported to underestimate ammonia volatilization when compared with dynamic methods such as wind tunnel and micrometeorological methods (Smith et al. 2007; Miola et al. 2015). The reasons for the underestimation with static chambers include ammonia gradient and wind restriction across the soil surface. Despite the limitations with the static chamber method, it is still commonly used in many studies because (i) it is relatively cheap to construct; (ii) it requires little logistics compared with wind tunnel; (iii) it allows for ease of several treatments comparison; and (iv) it allows for easy replications.

Nitrogen losses due to ammonia volatilization can be greater than 35% of applied N (Rawluk et al. 2001; Cai et al. 2002; Soares et al. 2012) when conditions are favourable. The consequence of these losses is a reduction in crop N use efficiency of urea-based fertilizers. In addition to its negative agronomic consequence, the volatilized ammonia can react with acidic gases in the

atmosphere to form droplets of ammonium salt that are detrimental to human health (Sheppard et al. 2010).

To mitigate ammonia volatilization from urea-based fertilizers, farmers are advised to incorporate surface-applied urea-based fertilizers immediately after application. The incorporation practice should position urea granules at least 5 cm below the surface; otherwise ammonia loss may result if conditions are favourable for volatilization (Rochette et al. 2013). Immediate irrigation or rainfall greater than 14.6 mm after fertilization has been reported to reduce ammonia volatilization by moving urea molecules beneath the soil surface (Holcomb et al. 2011). However, due to constraints such as labour and time shortage, immediate incorporation of urea-based fertilizers is not usually feasible. Several products have been developed and tested over the years to reduce ammonia volatilization from urea-based fertilizers (Chien et al. 2009). The most studied of these products is a urease inhibitor whose active ingredient is *N*-(*n*-butyl)thiophosphoric triamide (NBPT) (Watson et al. 2008; Chien et al. 2009). The NBPT slows down urea hydrolysis by being rapidly transformed into its oxygen analogue *N*-(*n*-butyl)phosphoric triamide, which then competes with the urease enzyme for active sites on urea (Christianson et al. 1990; Creason et al. 1990). The use of NBPT provides an opportunity to change the source of N fertilizer in agreement with the “4R nutrient stewardship” of using the right source at the right time, at the right rate in a right placement (Johnston and Bruulsema 2014). Recent meta-analyses and reviews have shown that treating urea with NBPT reduced ammonia volatilization from surface-applied urea-based fertilizers across different soil properties and environmental conditions (Pan et al. 2016; Silva et al. 2017; Cantarella et al. 2018). The reduction relative to untreated urea may exceed 70% during the first 7 d of fertilization when ammonia volatilization from urea is at a maximum (Rawluk et al. 2001; Engel et al. 2011; Soares et al. 2012).

In recent years, several formulations of NBPT such as Agrotain[®] (Koch Agronomic Services LLC, Wichita, KS, USA), Arborite[®] (Weyerhaeuser Co., Olympia, WA, USA), N-Veil[®] (Innvictis Crop Care LLC, Loveland, CO, USA), and Nitrain[™] (Loveland Product Inc., Dorchester, ON, Canada) have been developed to reduce ammonia volatilization from urea-based fertilizers. Each formulation has unique qualities that have bearing on its efficacy (Sanders 2007; Franzen et al. 2011; Goos 2013; Peng et al. 2015). A new formulation of NBPT is ARM U[™] with 18% NBPT that was developed by Active AgriScience Inc. (Abbotsford, BC, Canada). The unique attributes and proprietary formulations of ARM U[™] include (i) the presence of polymers that enable uniform coverage of urea granules, thereby enabling lower application rate of NBPT per kilogram of urea and (ii) low-temperature fluidity that allows for easy handling at temperature as low as $-15\text{ }^{\circ}\text{C}$ without

Table 1. Characteristics of Dezwood, Carman, and High Bluff soils at 0–15 cm.

| Soil property | Greenhouse | Field | |
|---|----------------------------|------------------------|------------------------|
| | Dezwood | Carman | High Bluff |
| Soil order | Orthic Dark Grey Chernozem | Orthic Black Chernozem | Gleyed Cumulic Regosol |
| Soil series | Dezwood | Hibsin | High Bluff |
| Soil pH ^a | 7.4 | 5.8 | 7.7 |
| Electrical conductivity ^a (µS m ⁻¹) | 453 | 191 | 465 |
| Organic matter ^b (g kg ⁻¹) | 40 | 39 | 47 |
| Volumetric water content at field capacity ^c (m ³ m ⁻³) | 0.35 | 0.28 | 0.37 |
| Bulk density ^d (Mg m ⁻³) | 1.1 | 1.2 | 1.2 |
| Soil type ^e | Loam | Sandy loam | Loam |
| Sand content (g kg ⁻¹) | 465 | 680 | 450 |
| Silt content (g kg ⁻¹) | 318 | 120 | 310 |
| Clay content (g kg ⁻¹) | 217 | 200 | 240 |

^aHendershot and Lalande 2008 (1:1 soil:water suspension).

^bWalkley and Black 1934.

^cCassel and Nielsen 1986.

^dHao et al. 2008.

^eGee and Bauder 1986.

freezing. We are not aware of any study that has tested the efficacy of ARM U™ formulation in reducing ammonia volatilization from urea-based fertilizers. The objective of this study was to evaluate the efficacy of ARM U in reducing ammonia volatilization from surface-applied urea-based fertilizers in comparison to Agrotain (30% NBPT) and Arborite (24% NBPT) under greenhouse and field conditions. We hypothesized that ARM U with a lower rate of NBPT application would have similar effectiveness in reducing ammonia volatilization compared to Agrotain or Arborite with higher rate of NBPT application, thereby improving the efficiency of NBPT application.

Materials and Methods

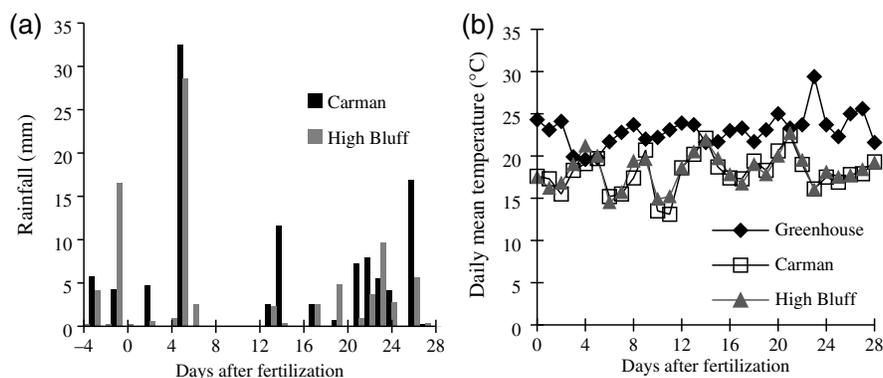
Greenhouse study: soil description, treatment applications, and experimental design

The Dezwood soil used for this study was an Orthic Dark Grey Chernozem in the Canadian soil classification system (Langman 1986), which is comparable to Boralfic Boroll in the USDA classification system and to Greyzem in the WRB/FAO classification system (Agriculture and Agri-Food Canada 2013). The soil properties are presented in Table 1.

Treatments consisted of urea treated with ARM U applied at a rate of 2 L per 1000 kg urea (360 mg NBPT kg⁻¹ urea, UR_{ARM}), urea treated with ARM U applied at a rate of 3 L per 1000 kg urea (540 mg NBPT kg⁻¹ urea, UR_{ARM2}), urea treated with Agrotain applied at a rate of 2 L per 1000 kg urea (600 mg NBPT kg⁻¹ urea, UR_{AG}), urea treated with Arborite applied at a rate of 2 L per 1000 kg urea (480 mg NBPT kg⁻¹ urea, UR_{AB}), and untreated urea (UR). These treatments were set up as a randomized complete block design with four replications.

Ammonia volatilization was measured with white polyvinyl chloride cylindrical static chambers (0.20 m in height by 0.15 m internal diameter) following a method described by Grant et al. (1996) and Jantalia et al. (2012). The chambers were sealed at the bottom with flat plastic plates. This was followed by filling the chamber with air-dried and sieved (<2 mm) soil up to 0.05 m height from the bottom at a bulk density of 1.1 Mg m⁻³. The soils in the chambers were moistened to 75% field capacity, covered with paper plates and allowed to stand for 24 h in the greenhouse for the soil and water to equilibrate. Twenty-four hours after wetting, treatments were surface-applied to the centre of the chamber to provide a rate of 100 kg N ha⁻¹ based on the surface area of the chamber. Agrotain and Arborite were sourced from a farm input dealer, whereas ARM U was sourced directly from its manufacturer. Urea was coated with inhibitor a day before application by spraying 1 kg of urea in a jar with appropriate volume of inhibitor (2 or 3 mL). The urea in the jar was immediately mixed vigorously to ensure thorough and uniform coating of the urea with the inhibitors. Despite the low inhibitor volume to urea quantity ratio, coating urea with the inhibitors was relatively uniform across the NBPT formulations. As claimed by the manufacturer, NBPT formulations are designed to allow enough time for coating even at a lower rate (volume) before they dry off.

Immediately after treatment application, two acid-charged polyfoam discs (upper and lower discs) of 0.025 m thick and 0.16 m diameter were fitted into the chambers to absorb ammonia. The discs were designed to tightly fit into the chambers and reduce air exchange with outside air. The discs were charged by washing in 0.001 mol L⁻¹ H₂SO₄ solution twice. The H₂SO₄ washed

Fig. 1. Daily (a) rainfall and (b) mean air temperature in the greenhouse and field.


discs were then immersed twice in glycerol – phosphoric acid solution (40 mL 14.7 mol L⁻¹ H₃PO₄ and 50 mL of glycerol in 1 L of de-ionized water). The prepared charged discs were wrung to reduce the amount of solution in them and transferred through an air-tight bag to the greenhouse where they were fitted into the chambers. The lower discs were fitted at 0.05 m above the surface of the treated soils to trap volatilized ammonia, whereas the upper discs were fitted at 0.02 m below the top of the chambers to prevent atmospheric ammonia contamination of lower discs.

Field study: site description, treatment applications, and experimental design

A complementary field study was conducted at two sites seeded to canola (*Brassica napus* L. 'LibertyLink') in the spring of 2016. The two sites were Carman (latitude 49°29'6"N, longitude 98°02'2"W, and 239 m a.s.l.) and High Bluff (latitude 50°01'2"N, longitude 98°08'9"W, and 227 m a.s.l.). The soil at Carman was an Orthic Black Chernozem in the Canadian soil classification system (Mills and Haluschak 1993), which is comparable to a Udic Boroll Mollisol in the USDA classification system and a Chernozem in the WRB/FAO classification system (Agriculture and Agri-Food Canada 2013). The soil at High Bluff is a Gleyed Cumulic Regosol (Michalyne and Smith 1972), which is comparable to an Entisol in the USDA classification system and a Regosol in the WRB/FAO classification system (Agriculture and Agri-Food Canada 2013). The properties of the soils (0–15 cm) at the two sites are shown in Table 1.

The treatments for the field study consisted of two sources of N (urea and UAN, 28–0–0) and two sources of urease inhibitors (ARM U and Agrotain) to give the following seven treatments: UR_{ARM}; UR_{AG}; UAN with either ARM U (360 mg NBPT kg⁻¹ urea, UAN_{ARM}) or Agrotain (600 mg NBPT kg⁻¹ urea, UAN_{AG}) at a rate of 1 L per 1000 L UAN; UR; UAN; and a control with no N amendment. Urea granule was coated with inhibitor as described above. The UAN was treated with inhibitor by adding 10 mL of inhibitor to 10 L of UAN in a jug. The UAN was then thoroughly mixed.

Chambers (0.20 m in height by 0.15 m internal diameter) were installed to a depth of 0.05 m at the Northwest corner of each 5 m × 3 m plot in a randomized complete block design. Seedlings as well as crop residues within the internal area of the chambers were removed. Rainfall events from 1 to 3 d before fertilization at both sites provided sufficient water to keep the soil moist for treatment application (Fig. 1). Treatment application followed the same method and rate (100 kg N ha⁻¹) described for the greenhouse study. The UAN was applied to the soil surface with a pipette. Disc preparation and fitting followed the same procedure that was described for the greenhouse study. Chambers were covered with puck board sheets positioned at about 0.30 m aboveground level to prevent rainfall from falling directly into the chamber but still permit air circulation above chambers.

Ammonia measurement

Discs were sampled and replaced with newly prepared discs on 1, 2, 4, 7, 14, 21, and 28 d after fertilization in the greenhouse and field studies (except no sampling on 1 d in the field). The lower discs were placed directly in a zip-lock bag of known weight for ammonium extraction. In the greenhouse study, soil moisture was maintained at 75% field capacity by weighing chambers and adding water around the interior chamber edges after sampling events on 4, 7, 14, and 21 d (Franzen et al. 2011). In the field study, water was not added to the chambers after sampling or after rainfall. However, the initially moist soil condition within the chamber and possible lateral and upward movement of water within the chamber following rainfall events provided a moist soil condition necessary for hydrolysis. Daily mean temperature in the greenhouse was monitored with Watchdog 2000 series weather station (model 2900ET; Spectrum Technologies Inc., Aurora, IL, USA). For the field study, daily rainfall and temperature data were collected from nearest Environment Canada weather station during the sampling periods.

In the laboratory, each ziplock bag containing disc was weighed to calculate the amount of absorbing solution

trapped in the foam disc. The ammonia trapped in the discs was extracted with 250 mL of 0.5 mol L⁻¹ KCl solution. Ammonium concentration in the KCl extract was

determined colorimetrically using an AQ2 Discrete Analyzer (SEAL Analytical Inc., Mequon, WI, USA). Ammonia volatilization loss was calculated as follows:

$$\text{NH}_3 \text{ loss (kg N ha}^{-1}\text{)} = \frac{(\text{Extractant (mL)} + \text{absorbent in disc (mL)}) \times \text{NH}_3 \text{ (mg N mL}^{-1}\text{)}}{\text{Area of chamber (ha)} \times 10^6}$$

Cumulative ammonia volatilization loss was calculated by summing ammonia losses between the sampling periods. Total ammonia volatilization was calculated as sum of ammonia volatilization during the sampling periods. Percentage ammonia volatilization was calculated as a ratio of ammonia loss to total N applied. Percentage reduction of ammonia volatilization from urea and UAN treated with inhibitors was calculated as a percentage of ammonia volatilization in untreated urea and UAN, respectively.

Statistical analysis

Analysis of variance (ANOVA) was conducted with PROC GLIMMIX (SAS Institute, Inc. 2014; version 9.4) for repeated measure analysis to determine the significant of fertilizer treatments, time, and fertilizer treatment × time interaction on daily ammonia volatilization. Covariance structures that accounted for the unequal sampling intervals were compared, and the one with lowest Akaike's information criterion was used for the model (Littell et al. 2006). Fertilizer treatment and time were fixed effects, whereas block (replicate) was a random effect. Because most losses occurred during the first 7 d after fertilization in untreated urea and UAN and after the first 7 d in urea and UAN treated with urease inhibitors (Rochette et al. 2009; Soares et al. 2012), cumulative ammonia volatilization were analyzed at three time intervals (0–7 d, 7–28 d, and 0–28 d) with PROC GLIMMIX in which fertilizer treatment is a fixed effect, and block (replicate) is a random effect. Prior to PROC GLIMMIX, data were checked for the assumption of normal distribution with PROC UNIVARIATE (Shapiro–Wilk's test). Data that were not normally distributed were specified for lognormal transformation in the model. Percentage reduction of ammonia volatilization by the inhibitors was also compared using PROC GLIMMIX (beta distribution) in which fertilizer treatment was a fixed effect, and block (replicate) was a random effect. The Fisher's protected least significant difference procedure at 0.05 alpha level was used for the comparison of treatment means.

Results

Greenhouse study

Daily mean air temperature in the greenhouse ranged from 19.6 to 29.4 °C (Fig. 1). Addition of water to the chambers from 4 d helped to keep the soil moist

throughout the sampling periods for biological activities to proceed.

Repeated measure ANOVA for ammonia volatilization showed that there was significant ($P < 0.0001$) fertilizer treatment by time interaction. Ammonia volatilization was significantly greater in untreated urea than the inhibitor-treated urea on 1, 2, 4, 7, and 14 d (except UR_{AB} on 14 d), whereas there were no significant differences between untreated and inhibitor-treated urea on 21 and 28 d (Fig. 2). Ammonia volatilization peaked on 4 d in untreated urea (15.8 kg N ha⁻¹), whereas the peak of ammonia volatilization was delayed until 14 d in urea treated with urease inhibitors (0.3–0.7 kg N ha⁻¹; Fig. 2 “inset”). Daily ammonia volatilization was not significantly different among the urea treated with inhibitors except on 7 and 14 d when UR_{AB} had significantly greater volatilization than UR_{ARM2} (Fig. 2 “inset”).

Cumulative ammonia volatilization was significantly greater in UR than in other treatments by 7 d when UR had lost a cumulative of 21.6 kg N ha⁻¹ compared with a loss of less than 0.5 kg N ha⁻¹ in urea treated with inhibitors (Table 2). The addition of ARM U, Agrotain, and Arborite to urea reduced ammonia volatilization by at least 98% at the end of 7 d. Cumulative ammonia volatilization was not significantly different between the two rates of ARM U by 7 d (Table 2). Similarly, cumulative ammonia volatilization from UR_{ARM}, UR_{ARM2}, UR_{AG}, and UR_{AB} was not significantly different after 7 d (Table 2). Cumulative ammonia volatilization from 7 to 28 d was not significantly different among the treatments except between UR and UR_{ARM2} where UR_{ARM2} had significantly lower cumulative ammonia volatilization than UR (Table 2).

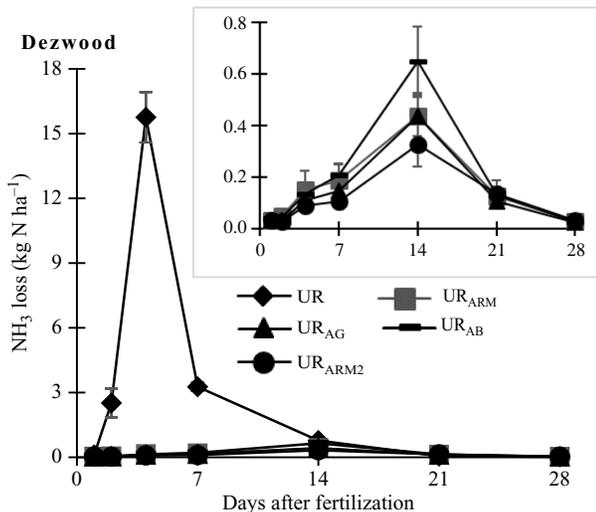
At the end of 28 d, total ammonia volatilization was significantly greater in untreated urea than in NBPT-treated urea. Untreated urea lost a total of 22.5% of applied N by the end of 28 d, whereas UR_{ARM} and UR_{ARM2} lost 0.8% and 1.0% of applied N, respectively, and UR_{AG} and UR_{AB} lost 0.9%–1.2% of applied N, respectively (Table 2). Total ammonia volatilization was not significantly different between UR_{ARM} and UR_{ARM2} (Table 2). Total ammonia volatilization from UR_{ARM}, UR_{AG}, and UR_{AB} that contained the same volume of formulation but different concentrations of NBPT were not significantly different from one another. At the end of 28 d, ammonia volatilization reduction was not significantly affected ($P = 0.3249$) by the concentrations of NBPT or types of formulations (Table 2). Ammonia losses from

Table 2. Effect of urease inhibitors on cumulative ammonia volatilization and percentage reduction of ammonia volatilization from surface-applied urea in the greenhouse.

| Treatments | 0–7 d (kg N ha ⁻¹) | 7–14 d (kg N ha ⁻¹) | 0–28 d (kg N ha ⁻¹) | Reduction (%) |
|--------------------|--------------------------------|---------------------------------|---------------------------------|---------------|
| UR | 21.6a | 0.9a | 22.5a | — |
| UR _{ARM} | 0.4b | 0.6ab | 1.0bc | 96a |
| UR _{AG} | 0.3b | 0.6ab | 0.9bc | 96a |
| UR _{AB} | 0.4b | 0.8ab | 1.2b | 95a |
| UR _{ARM2} | 0.3b | 0.5b | 0.8c | 96a |
| ANOVA | <0.0001 | 0.1729 | <0.0001 | 0.3249 |

Note: Means with different lowercase letters within a column are significantly different at $P < 0.05$ as determined by Fisher's least significant difference mean separation. UR, untreated urea; UR_{ARM}, urea treated with ARM U applied at a rate of 2 L per 1000 kg urea; UR_{AG}, urea treated with Agrotain applied at a rate of 2 L per 1000 kg urea; UR_{AB}, urea treated with Arborite applied at a rate of 2 L per 1000 kg urea; UR_{ARM2}, urea treated with ARM U applied at a rate of 3 L per 1000 kg urea; ANOVA, analysis of variance.

Fig. 2. Daily ammonia volatilization between sampling days following surface application of urea with and without urease inhibitors in the greenhouse. The inset graph contains results from all treatments except untreated urea. UR, untreated urea; UR_{ARM}, urea treated with ARM U applied at a rate of 2 L per 1000 kg urea; UR_{ARM2}, urea treated with ARM U applied at a rate of 3 L per 1000 kg urea; UR_{AG}, urea treated with Agrotain; UR_{AB}, urea treated with Arborite.



urea were reduced by 96%, 96%, and 95% with ARM U, Agrotain, and Arborite, respectively.

Field study

Daily mean temperature and rainfall were similar between Carman and High Bluff during the sampling period (Fig. 1). Daily mean air temperatures ranged from 13.1 to 22.4 °C at Carman and from 15.2 to 22.7 °C at High Bluff. Daily rainfall ranged from 0 to 33 mm at Carman and from 0 to 29 mm at High Bluff. At both sites, the largest amount of precipitation was received on 5 d.

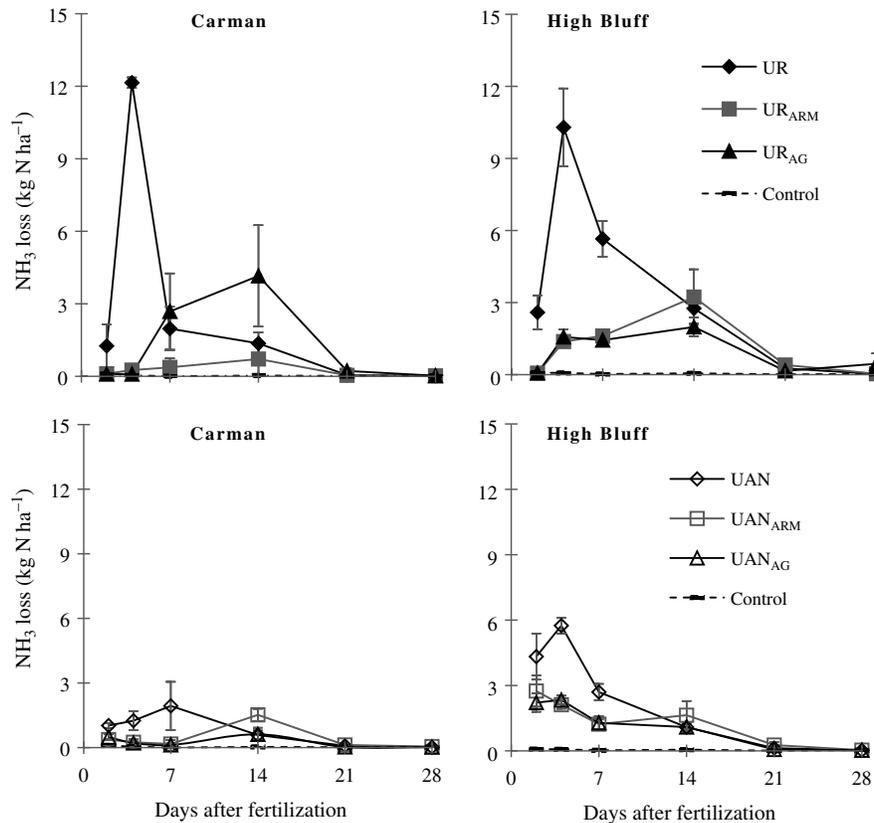
There was a significant treatment by time interaction ($P < 0.0001$) for ammonia volatilization at both sites.

Expectedly, daily ammonia volatilization was significantly smaller in control plots without N amendment at each site throughout the sampling period (Fig. 3). Ammonia volatilization peaked on 4 d in untreated urea at each site and on 4 and 7 d in untreated UAN at High Bluff and Carman, respectively (Fig. 3). At Carman, the peak of ammonia volatilization occurred at 14 d for urea and UAN treated with inhibitors. At High Bluff, peak ammonia volatilization occurred at 7 and 14 d for UAN and urea treated with inhibitors, respectively (Fig. 3).

Cumulative ammonia volatilization by 7 d from UR was 15.4 kg N ha⁻¹ at Carman and 18.5 kg N ha⁻¹ at High Bluff, whereas it was 0.7 and 2.9 kg N ha⁻¹ in UR_{ARM} and UR_{AG}, respectively, at Carman and 3.1 kg N ha⁻¹ in both UR_{ARM} and UR_{AG} at High Bluff (Table 3). Cumulative ammonia volatilization from untreated UAN by 7 d was 4.2 kg N ha⁻¹ at Carman and 12.8 kg N ha⁻¹ at High Bluff, whereas it was 0.8 kg N ha⁻¹ from both UAN_{ARM} and UAN_{AG} at Carman and 6.1 and 5.8 kg N ha⁻¹ from UAN_{ARM} and UAN_{AG}, respectively, at High Bluff (Table 3). Cumulative ammonia volatilization from UR_{ARM}, UAN_{ARM}, and UAN_{AG} at High Bluff was at least four times the cumulative ammonia volatilization at Carman by 7 d. Cumulative ammonia volatilization in urea and UAN treated with ARM U was not significantly different from cumulative ammonia volatilization in their corresponding urea and UAN treated with Agrotain at each site (Table 3). When averaged across sites, ARM U and Agrotain reduced ammonia volatilization by 89% and 82%, respectively, in urea and 59% and 61%, respectively, in UAN by 7 d.

Cumulative ammonia volatilization was significantly different among the treatments during 7–28 d period at each site (Table 3). At Carman, significant difference exists among the N-amended treatments. However, the significant difference at High Bluff was due to the significantly low cumulative ammonia volatilization in control treatment with no N amendment and not due to the differences in N-amended treatments. Cumulative ammonia volatilization during the 7–28 d period

Fig. 3. Daily ammonia volatilization between sampling days following surface application of urea (upper graphs) and urea ammonium nitrate (UAN) (lower graphs) treated with and without urease inhibitors in the field. UR, untreated urea; UR_{ARM}, urea treated with ARM U; UR_{AG}, urea treated with Agrotain; UAN_{ARM}, UAN treated with ARM U; UAN_{AG}, UAN treated with Agrotain.



from UR_{ARM} and UR_{AG} was not significantly different from UR at each site (Table 3). Similarly, cumulative ammonia volatilization from UAN_{ARM} and UAN_{AG} was not significantly different from the cumulative ammonia volatilization in UAN during the 7–28 d period at each site (Table 3).

Total ammonia volatilization (0–28 d) was significantly greater from UR than from the other treatments at Carman and High Bluff (Table 3). Total ammonia volatilization in UR was 16.8% of applied N at Carman and 21.6% of applied N at High Bluff. Total ammonia volatilization from UR_{ARM} and UR_{AG} was 1.5% and 7.3% of applied N, respectively, at Carman, whereas total ammonia volatilization was 6.7% and 5.7% of applied N from UR_{ARM} and UR_{AG}, respectively, at High Bluff (Table 3). Total ammonia volatilization in untreated UAN was 4.9% of applied N at Carman and 14.0% of applied N at High Bluff. The corresponding values for UAN_{ARM} and UAN_{AG} were 2.5% and 1.5% of applied N, respectively, at Carman and 8.0% and 7.0% of applied N, respectively, at High Bluff (Table 3). Based on the proportion of urea-N fraction, untreated UAN lost 1.3 times more ammonia than untreated urea at High Bluff and 1.7 times less ammonia than untreated urea at

Carman. Total ammonia volatilization from UR_{ARM} and UAN_{ARM} was not significantly different from total ammonia volatilization in the corresponding UR_{AG} and UAN_{AG} at each site. Total ammonia volatilization from urea and UAN treated with urease inhibitors was generally greater at High Bluff than at Carman except in UR_{AG}. At the end of 28 d, ammonia volatilization reduction by ARM U and Agrotain was not significantly different on urea ($P = 0.0777$) and UAN ($P = 0.2911$) at Carman (Table 3). Similarly, ammonia volatilization reduction by ARM U and Agrotain was not significantly different on urea ($P = 0.5631$) and UAN ($P = 0.4405$) at High Bluff (Table 3). ARM U and Agrotain significantly reduced ammonia volatilization from urea by 57%–91% at Carman and 69%–74% at High Bluff and from UAN by 49%–69% at Carman and 42%–50% at High Bluff (Table 3).

Discussion

The pattern of daily ammonia fluxes in the field was similar to greenhouse especially at Carman. The minimal amount of ammonia losses by 1 d in the greenhouse was because even under favourable conditions, hydrolysis of urea to ammonium carbonate takes about 2 d

Table 3. Effect of urease inhibitors on cumulative ammonia volatilization and percentage reduction of ammonia volatilization from surface-applied urea and urea ammonium nitrate (UAN) in the field.

| Treatments | 0–7 d (kg N ha ⁻¹) | 7–14 d (kg N ha ⁻¹) | 0–28 d (kg N ha ⁻¹) | Reduction (%) |
|--------------------|--------------------------------|---------------------------------|---------------------------------|---------------|
| Carman | | | | |
| UR | 15.4a | 1.4ab | 16.8a | — |
| UR _{ARM} | 0.7c | 0.8ab | 1.5cd | 91a |
| UR _{AG} | 2.9bc | 4.4a | 7.3bc | 57ab |
| UAN | 4.2b | 0.7b | 4.9b | — |
| UAN _{ARM} | 0.8c | 1.7ab | 2.5bcd | 49b |
| UAN _{AG} | 0.8c | 0.7b | 1.5d | 69ab |
| Control | 0.1d | 0.1c | 0.2e | — |
| ANOVA | <0.0001 | 0.0030 | <0.0001 | 0.1991 |
| High Bluff | | | | |
| UR | 18.5a | 3.0a | 21.6a | — |
| UR _{ARM} | 3.1c | 3.7a | 6.7c | 69ab |
| UR _{AG} | 3.1c | 2.6a | 5.7c | 74a |
| UAN | 12.8a | 1.2a | 14.0b | — |
| UAN _{ARM} | 6.1b | 1.9a | 8.0c | 42c |
| UAN _{AG} | 5.8b | 1.2a | 7.0c | 50bc |
| Control | 0.2d | 0.1b | 0.3d | — |
| ANOVA | <0.0001 | <0.0001 | <0.0001 | 0.0203 |

Note: Means with different lowercase letters within a column are significantly different at $P < 0.05$ as determined by Fisher's least significant difference mean separation. UR, untreated urea; UR_{ARM}, urea treated with ARM U; UR_{AG}, urea treated with Agrotain; UAN_{ARM}, UAN treated with ARM U; UAN_{AG}, UAN treated with Agrotain; ANOVA, analysis of variance.

(Cantarella et al. 2008; Behera et al. 2013). Logistics and minimal ammonia losses on 1 d in the greenhouse contributed to lack of sampling on 1 d in the field. Ammonia volatilization measured on 2 d in the field did not suggest that large amount of ammonia losses occurred on 1 d in urea treatments. In the UAN treatments, ammonia volatilization on 2 d was relatively high when compared with the total ammonia volatilization especially at High Bluff (32%–34% of total ammonia losses). The relatively high ammonia volatilization at High Bluff on 2 d was similar to the study of Woodley et al. (2018) that found 33% and ~50% of the total ammonia volatilization from surface-applied UAN to have occurred within 1 and 2 d, respectively. Peak ammonia volatilization from untreated urea in the greenhouse and field trials were similar to other studies (Rawluk et al. 2001; Cantarella et al. 2008; Rochette et al. 2009) that showed that most of the ammonia volatilization in untreated urea occurred between 2 and 5 d. The lower peak of ammonia volatilization in untreated UAN compared with untreated urea may be due to lower urea-N fraction in UAN. The lower peak from untreated UAN relative to untreated urea, however, contradicts with the findings reported by Viero et al. (2014) where peak ammonia volatilization in untreated UAN was found to be similar or greater than peak ammonia volatilization of untreated urea. In addition, some of the volatilized ammonia from UAN during the early sampling days will be from the ammonium fraction of the UAN, which is prone to be lost as ammonia on neutral to alkaline soils. The pattern of ammonia losses from

urea treated with and without urease inhibitors were similar in the greenhouse and field. Although the amount of losses from urea treated with urease inhibitors was smaller in the greenhouse than in the field, the amount of losses from untreated urea was greater in the greenhouse than in the field. The period of peak ammonia volatilization in urea and UAN treated with urease inhibitors showed that the hydrolysis of urea was delayed beyond 7 d with the addition of urease inhibitors, which thereafter resulted in a significant overall reduction in ammonia volatilization. The time of maximum losses of ammonia in urea and UAN treated with urease inhibitors in our study was similar to previous studies that showed most of the ammonia volatilization from urea treated with urease inhibitor occurred after 7 d (Rawluk et al. 2001; Zaman and Blennerhassett 2010; Engel et al. 2011; Viero et al. 2014). The amount of ammonia volatilization from urea and UAN treated with urease inhibitors after 7 d shows clearly that the inhibitory action of these urease inhibitor decreases with time. The delayed hydrolysis of urea and UAN treated with urease inhibitors may extend the period of ammonia volatilization from urea and UAN beyond 14 d because urea hydrolysis may not have been completed. Engel et al. (2011) measured as much as 50% of applied urea from NBPT-treated urea after 20 d due to insufficient precipitation, whereas urea concentration was very small in untreated urea. This implies that ammonia volatilization from urea treated with inhibitor may be appreciable after 7 d depending on environmental conditions. Cantarella et al. (2008) found

that ammonia volatilization from urea treated with urease inhibitor was similar to ammonia volatilization from untreated urea in a dry environment. They attributed the similarity in ammonia volatilization between the urea treated with and without urease inhibitor in a dry condition to insufficient rainfall needed to incorporate the remaining urea into the soil after the effective period of urease inhibitor. Although rainfall or irrigation events can help to mitigate ammonia volatilization from urea and UAN treated with inhibitor, the amount of rainfall or irrigation may affect the magnitude of ammonia volatilization, as inadequate rainfall may exacerbate ammonia volatilization. Holcomb et al. (2011) observed that rainfall or irrigation event that is less than 7.6 mm did not significantly reduce ammonia volatilization from surface-applied urea. Under field condition or open chamber condition without the plexiglass that was used in this study, the amount of rainfall (32.5 mm at Carman and 28.6 mm at High Bluff) on 5 d was sufficient to move the urea below the soil surface where ammonia volatilization will be significantly reduced. As such, most of the losses in urea and UAN treated with inhibitor in the field study would have been avoided by the rain event, whereas the losses from the untreated urea and UAN would still be large, as much of the volatilization occurred before the rainfall event. In addition, under field condition without a chamber, the canopy from canola leaves may provide conditions that would reduce ammonia volatilization from unhydrolyzed urea during the later days of sampling (Sommer and Olesen 2000). However, this would not have any effect on ammonia volatilization from untreated urea as most of the losses had occurred before the leaves were large enough to provide such canopy.

The magnitude of ammonia volatilization depends on soil and environmental conditions (Rachhpal-Singh and Nye 1986; Kissel et al. 2004; Behera et al. 2013). For example, higher ammonia volatilization from urea and UAN treated with and without inhibitors at High Bluff than at Carman during the first 7 d would have been due to its higher soil moisture as result of greater water-holding capacity of loam over sandy loam following precipitation that occurred before fertilizer application. In addition, higher ammonia volatilization at High Bluff than at Carman might be due to its higher soil pH, which promoted ammonia volatilization by shifting the equilibrium between ammonium and ammonia in favour of ammonia. The greater total ammonia volatilization from untreated UAN than untreated urea based upon urea-N composition at High Bluff was probably due to the ammonium fractions of the UAN on an alkaline soil. The lack of water addition to the chambers after rain events (to move some urea downward as it is in an open-field condition) might have overestimated the ammonia volatilization from urea and UAN treated with urease inhibitors in this study. However, this overestimation due to lack of water addition might have been partly compensated for by underestimation of the losses due to

chamber enclosure and reduced wind movement in the chamber (Harper 2005; Smith et al. 2007; Miola et al. 2015). The magnitude of ammonia volatilization in our greenhouse and field studies is, however, lower than the ammonia volatilization measured in studies (Frame et al. 2012; Soares et al. 2012) that allowed air exchange between the chambers and the environment. The lower magnitude of ammonia volatilization in our studies agreed with the result of Smith et al. (2007) that found static chamber method to underestimate ammonia volatilization by 95%–99% after 6 d of manure application when compared with dynamic methods. However, the underestimation by static chamber method was reported to decrease with an increase in the duration of measurement (Miola et al. 2015). Miola et al. (2015) reported that the underestimation by static chamber method decreased from 74% by 1 d to 23% by 22 d. The lack of significant difference in total ammonia volatilization between UR_{ARM} (360 mg NBPT kg⁻¹ urea) and UR_{ARM2} (540 mg NBPT kg⁻¹ urea) and among UR_{ARM}, UR_{AG} (600 mg NBPT kg⁻¹ urea), and UR_{AB} (480 mg NBPT kg⁻¹ urea) despite different concentrations of NBPT kg⁻¹ urea in the greenhouse showed that NBPT effectively reduced ammonia volatilization from urea even at lower concentration. The lack of differences in ammonia volatilization among the different concentrations of NBPT in our study is in agreement with Watson et al. (2008) that compared ammonia volatilization from different concentrations of NBPT and found no significant benefit at concentrations greater than 250 mg NBPT kg⁻¹ urea. In addition, Frame et al. (2012) that compared ammonia volatilization from different rates of NBPT (200, 400, 600, and 800 mg NBPT kg⁻¹ urea) found no significant benefit of additional NBPT above 200 mg NBPT kg⁻¹ urea.

Conclusion

Coating urea or mixing UAN fertilizers with urease inhibitors will not only delay ammonia volatilization from urea-based fertilizers, it will also significantly reduce ammonia volatilization. The most effective period for NBPT was during the 0–7 d when ammonia volatilization from urea and UAN was the greatest. Ammonia volatilization was reduced by 69%–96% when urea was coated with ARM U and by 42%–49% when UAN was mixed with ARM U during 28 d period. The greenhouse and field studies showed that a lower rate of NBPT with ARM U (360 mg NBPT kg⁻¹ urea) was as effective as a higher rate of NBPT with Agrotain (600 mg NBPT kg⁻¹ urea). The new formulation, ARM U, has the same efficacy as other available products. Our study corroborated earlier study that optimum ammonium reduction can be achieved with low concentration of NBPT even though all NBPT concentrations used in this study were greater than the earlier established optimum rates (250 mg NBPT kg⁻¹ urea). Also, addition of ARM U to urea and UAN enabled lower application rate of NBPT without compromising its

efficacy. In the future, studies will be conducted to see if the reduced ammonia volatilization by urease inhibitor can be used to bridge nitrogen use efficiency gap between fall and spring applied urea-based fertilizers.

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