# Rice Response and Ammonia Volatilization from Experimental Zinc Sulfate-Coated Ureas Containing Urease Inhibitors

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*Authors' contributions*

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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## ABSTRACT

Laboratory studies have shown that treating urea with low concentration of NBPT prior to coating can minimize ammonia loss. There is limited field research on the ammonia volatility potential of nutrient-coated urea fertilizers containing urease inhibitors. A two-year study was conducted to determine the ammonia loss and rice response to surface-broadcast urea, urea treated with N-(n-butyl) thiophosphoric triamide (NBPT), and five formulations of experimental zinc sulfate-coated urea (ZSCU) fertilizers with or without urease inhibitors. The ammonia volatilization and yield trials were analyzed as randomized complete block design. The nitrogen (N) treatments for the ammonia

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loss trial were applied at a rate of 134 kg N ha$^{-1}$ and ammonia loss was monitored for 15 days using a semi-open static chamber. A yield trial was set up adjacent to the ammonia loss trial with N applied at 67 kg N ha$^{-1}$ and134 kg N ha$^{-1}$. In 2014, ammonia loss from urea (15.4%) was greater than ZSCU fertilizer with NBPT and urea treated with 0.9 g kg$^{-1}$ NBPT (2.6 – 10.0%). The ammonia loss from urea (23.5%) in 2015 was greater than the other N treatments (4.1 – 18.4%). Among the various formulations of experimental ZSCU fertilizers, only the ones where urea was treated with 0.6 g kg$^{-1}$ NBPT prior to coating with 1.7 g B kg$^{-1}$ and ZnSO$_4$ were effective in reducing cumulative ammonia loss as urea treated with 0.9 g kg$^{-1}$ NBPT. The N treatments did not increase grain yield when compared to urea in 2014. In 2015, the NBPT-treated urea had greater grain yields than the other N treatments, which were not different from each other. Application of urea treated with 0.6 g kg$^{-1}$ NBPT prior to coating with 1.7 g B kg$^{-1}$ and ZnSO$_4$ is a reliable alternative to reduce ammonia loss from urea.

## ABBREVIATIONS

*ZSCU : zinc sulfate-coated urea;*
*ZnSO$_4$ : zinc sulfate;*
*NBPT : N-(n-butyl) thiophosphoric triamide*

## 1. INTRODUCTION

Urea is the most commonly used N fertilizer because of its economic advantage compared to other N fertilizer sources [1,2]. Surface applied urea is susceptible to ammonia volatilization when compared to the other N sources [3]. Surface-applied urea is hydrolyzed by the urease enzyme to ammonium at a favorable moisture and temperature condition [4,5]. Urea hydrolysis leads to an increase in soil pH that facilitates the production of ammonia from ammonium in upland condition. Soil properties, prevailing environmental conditions, and management practices dictate the rate of ammonia volatilization from surface-broadcast urea [5]. In a delayed-flood rice production system, urea is typically surface broadcast at the 4- to 5-leaf stage of rice development followed by the establishment of a permanent flood [6]. Ammonia volatilization has been documented to account for 7 – 33% of total N loss from surface broadcast urea in delayed-flood rice production [3,7,8]. Reducing ammonia volatilization can minimize economic loss and environmental damage [9,10].

Ammonia volatilization from surface applied urea can be minimized by treating urea with urease inhibitors or physically coating urea to temporarily halt urea hydrolysis [11]. N-(n-butyl) thiophosphoric triamide is a urease inhibitor that has consistently been effective in inhibiting urease activity and subsequently, reducing ammonia volatilization across a wide range of soils and cropping systems [12]. Treating urea with NBPT has been reported to reduce ammonia volatilization losses by 50 – 80% and increase grain yield in the delayed flood rice production system in the southern USA [7,13]. However, treating urea with NBPT at the recommended rate can be expensive for commercial rice producers. There are efforts to develop less expensive fertilizers that are made up of urea treated with low NBPT concentration and then coated with nutrients that can simultaneously minimize ammonia volatilization and correct other nutritional deficiencies often encountered in crop production [14]. Urea coated with a B compounds can inhibit urease activity and subsequently, reduce ammonia volatilization [15-17]. Benini et al. (2004) proposed that B compounds such as boric acid (H$_3$BO$_3$) inhibit urease activity as a result of competitive inhibition of the urease enzyme.

Nutrient-coated urea fertilizer and polymer-coated urea fertilizers have been reported to minimize ammonia volatilization in field studies [18,19]. However, the effect of polymer- and nutrient-coated urea fertilizers on ammonia volatilization are inconsistent across cropping systems and soil types [20], suggesting that the use of coated urea fertilizers may be unreliable as the sole approach in minimizing ammonia volatilization. Zinc (Zn) deficiency is a common nutrient deficiency in flooded rice production; therefore, Zn fertilizers are often used in rice production in the southern USA [21]. Zinc is able to inhibit urease activity by reacting with the sulfhydryl group of urease enzyme [22]. Producers stand to gain if a cost-effective fertilizer that can simultaneously reduce ammonia volatilization and supply Zn becomes commercially available.

Most field trials that have evaluated ammonia volatilization in the southern USA have focused on either NBPT or a polymer coating. Several formulations of experimental $ZnSO_4$-coated urea fertilizers have recently been developed (Brooks Whitehurst Associates Inc., New Bern, NC). Laboratory studies have shown that these experimental fertilizers, particularly, when urea was treated with low concentration of NBPT prior to coating with B and $ZnSO_4$ is as effective in reducing ammonia volatilization as urea treated with NBPT at the recommended rate [23]. However, it's very important to evaluate how these experimental fertilizers perform under field conditions. The objectives of this study were therefore (1) to quantify ammonia volatilization losses from surface-applied experimental ZSCU fertilizers and (2) to evaluate the effect of these experimental fertilizers on grain yield in a drill-seeded, delayed flood rice production system.

## 2. MATERIALS AND METHODS

### 2.1 Study Site

Ammonia volatilization and yield trials were carried out for two years (2014 – 2015) at the H. Rouse Caffey Rice Research Station, near Crowley, LA (N 30° 14.840' W 92° 21.196). The fields for both years were managed in a rice-fallow rotation for over 30 years. The study site has a humid subtropical climate with an average annual air temperature and rainfall of 20°C and 1524 mm, respectively. The soil at the study site was a Crowley silt loam (Fine, smectitic, thermic Typic Albaqualfs) [24]. Soil samples were collected from the surface soil to a depth of 15 cm for both years. The soils were air dried, sieved through a 2-mm sieve, and analyzed for selected chemical and physical properties. Soil pH was analyzed in a 1:1 soil to water ratio [25]. Organic matter was determined using the Wakley-Black method [26]. Nutrients were determined using the Mehlich III soil test extraction [27]. Elemental concentrations in the extract were measured using inductively coupled plasma atomic emission spectroscopy [28]. Mean values of selected soil properties are reported in Table 1.

### 2.2 Ammonia Volatilization Trial

Five formulations of the experimental ZSCU fertilizers were compared with urea and urea treated with the recommended NBPT rate of 0.9 g $kg^{-1}$ (NBPT-treated urea). The experimental ZSCU fertilizers were provided by Brooks Whitehurst Associates Inc. The five experimental fertilizers include $ZnSO_4$-coating alone (ZU); B and $ZnSO_4$-coating ($ZB^L$); B and $ZnSO_4$-coating ($ZB^H$); B, NBPT, and $ZnSO_4$-coating ($ZN^L$); B, NBPT, and $ZnSO_4$-coating ($ZN^L$). The concentration of B in experimental fertilizers with superscript L and H was 1.0 and 1.7 g B $kg^{-1}$, respectively. For $ZN^L$ and $ZN^L$ fertilizers, urea granules were first treated with NBPT prior to the B and $ZnSO_4$ coating. The NBPT concentration in $ZN^L$ and $ZN^H$ was 0.3 and 0.6 g $kg^{-1}$ in 2014 and 2015, respectively. Laboratory studies have shown that urea treated with low concentrations of NBPT (0.3 – 0.5 g $kg^{-1}$) reduced ammonia volatilization [14,29] and hence the concentration of NBPT in the experimental ZSCU fertilizers used in 2014 was 0.3 g $kg^{-1}$. Based on the results from 2014 trial, the NBPT concentration in the experimental ZSCU fertilizers was increased from 0.3 to 0.6 g $kg^{-1}$ in 2015. All the experimental ZSCU fertilizers contained 390 g N $kg^{-1}$, 54 g $P_2O_5$ $kg^{-1}$, 11 g S $kg^{-1}$, and 20 g Zn $kg^{-1}$. Control plots with no N fertilizer were included in trial to normalize the volatilization data. The rice variety used in 2014 and 2015 was CL152 and CL111, respectively. Rice was drill-seeded at 359 seed $m^2$ to a depth of 1.27 cm on March 13, 2014 and March 19, 2015 with an Almaco heavy-duty grain drill (Almaco, Iowa) equipped with double-disk openers. Each plot was 1.24 m wide by 4.88 m long and consisted of seven rows spaced at 20 cm apart. Phosphorus fertilizer was surface broadcast at planting at a rate of 67 kg $P_2O_5$ $ha^{-1}$ using triple super phosphate (0-46-0). Potassium was surface broadcast at planting as potash (0-0-60) at a rate of 67 kg $K_2O$ $ha^{-1}$.

**Table 1. Chemical properties of soil from study sites in 2014 and 2015.**

| | | | | Mehlich III extractable nutrient levels | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Year | pH | OM[†] | P | K | Ca | Mg | S | Na | Zn |
| | | g $kg^{-1}$ | -----------------------------mg $kg^{-1}$----------------------------- | | | | | | |
| 2014 | 7.40 | 14.4 | 6.7 | 55.2 | 1595 | 265 | 9.1 | 58.7 | 4.6 |
| 2015 | 7.61 | 15.0 | 26.0 | 76.0 | 1641 | 231 | 6.7 | 111.0 | 9.0 |

[†]*OM, Organic matter*

Ammonia volatilization losses were monitored using the semi-open, static chamber method [3,8]. The chambers were constructed using 14 cm (diameter) by 60 cm (height) transparent Plexiglas cylinders. Two (2014) or three (2015) tubes were installed in the middle drill-row within experimental plots. Each tube contained two rice seedlings. The air temperature inside and outside the tube was measured using HOBO Pendant Temp/Alarm 8K data loggers (Onset Computer Corporation, Bourne, MA). The N treatments were surface applied at a rate of 134 kg N ha$^{-1}$ into each tube by hand at the 4- to 5-leaf stage of development. A 2.54 cm thick circular polyurethane foam sponge treated with 0.73 M H$_3$PO$_4$ and 33% glycerol was tightly placed in each chamber 28 cm above the soil surface to capture volatilized ammonia from fertilizer and soil. A second treated sponge was placed flush with the top of the chamber, 15.2 cm above the first sponge, to absorb atmospheric ammonia. A cross section of PVC pipe was fixed on top of the chambers and then covered with nineteen-liter buckets to allow air circulation and to protect the chambers from rain. The sponges were replaced 1, 3, 5, 7, 9, 11, and 15 days after N fertilizer application. Once removed, the sponges were placed in Ziploc bags and transported to the laboratory for extraction and analysis. Fields were flooded 10 days after N fertilizer application and maintained until physiological maturity. Ammonium was extracted from the sponges with 2 M KCl. The ammonium concentration from the extract was determined with an automated QuikChem® 8500 Series 2 flow injection analyzer using the salicylate-hypochlorite method (QuikChem® Method 12-107-06-2-H, Lachat Instrument, Loveland, CO). Standard agronomic and pest management practices were utilized during the growing season based on state recommendations [30].

### 2.3 Yield Trial

Yield trial was conducted at the same time as the ammonia volatilization trial on adjacent plots. In addition to the N treatments evaluated for ammonia volatilization, a urea:ZnSO$_4$ blend was included in the yield trial, where an equivalent amount of Zn was added to urea based on the amount of Zn supplied by experimental fertilizer. The N treatments for the yield trial were applied at two N rates, 67 and 134 kg N ha$^{-1}$. Control plots with no N fertilizer were included in the yield trial. Individual rice plots were harvested using a Wintersteiger Delta Combine (Wintersteiger, Inc., Salt Lake City, UT 84116-2876) equipped with a

HM800 Harvest Master Grain Gauge system (Juniper Systems, Inc., Logan, UT, USA). Rough grain yield was adjusted to a moisture content of 120 g kg$^{-1}$.

### 2.4 Statistical Analysis

The ammonia volatilization and yield trials were analyzed as randomized complete block design with a repeated measurement design for ammonia volatilization. The data was analyzed using the PROC Mixed procedure in SAS 9.4 [31]. The Tukey's HSD mean separation procedure was used determined differences.

## 3. RESULTS

### 3.1 Weather Conditions

The cumulative rainfall during the 2014 field trial (13 March – 6 August) was 671 mm. Rainfall between N fertilizer application and permanent flood establishment in 2014 was 18 mm (Fig. 1a). During the 2015 field trial, 9 March – 28 July, the total rainfall was 787 mm and the amount of rainfall collected between fertilizer application and permanent flood establishment was 0.5 mm (Fig. 1b). The average air temperature inside the ammonia volatilization chambers was 25 and 27°C in 2014 and 2015, respectively for 15 days. The average daily air temperature in the ammonia volatilization tubes was comparable to the air temperature outside the tubes except for the first sampling day each year (Fig. 1a and b). In 2014, the air temperatures inside the ammonia volatilization tubes were lower compared to the outside air temperature within the first day after N fertilizer application. However, the air temperature inside the ammonia volatilization tubes was warmer than the outside air temperature in 2015 (Fig. 1a and b).

### 3.2 Ammonia Volatilization

Ammonia losses from N treatments were negligible a day after N fertilizer application in 2014. The peak daily ammonia loss for urea (4.5%) occurred on the fifth sampling time and was higher than the other N treatments (1.0 – 3.7%) with the exception of ZB$^L$ (4.6%). Application of NBPT-treated urea delayed the time to reach peak ammonia loss by 4 days when compared with urea. Daily ammonia losses varied significantly among N treatments at sampling times during periods of peak ammonia losses (5 – 9 days after N fertilizer application); however, differences were not observed at the
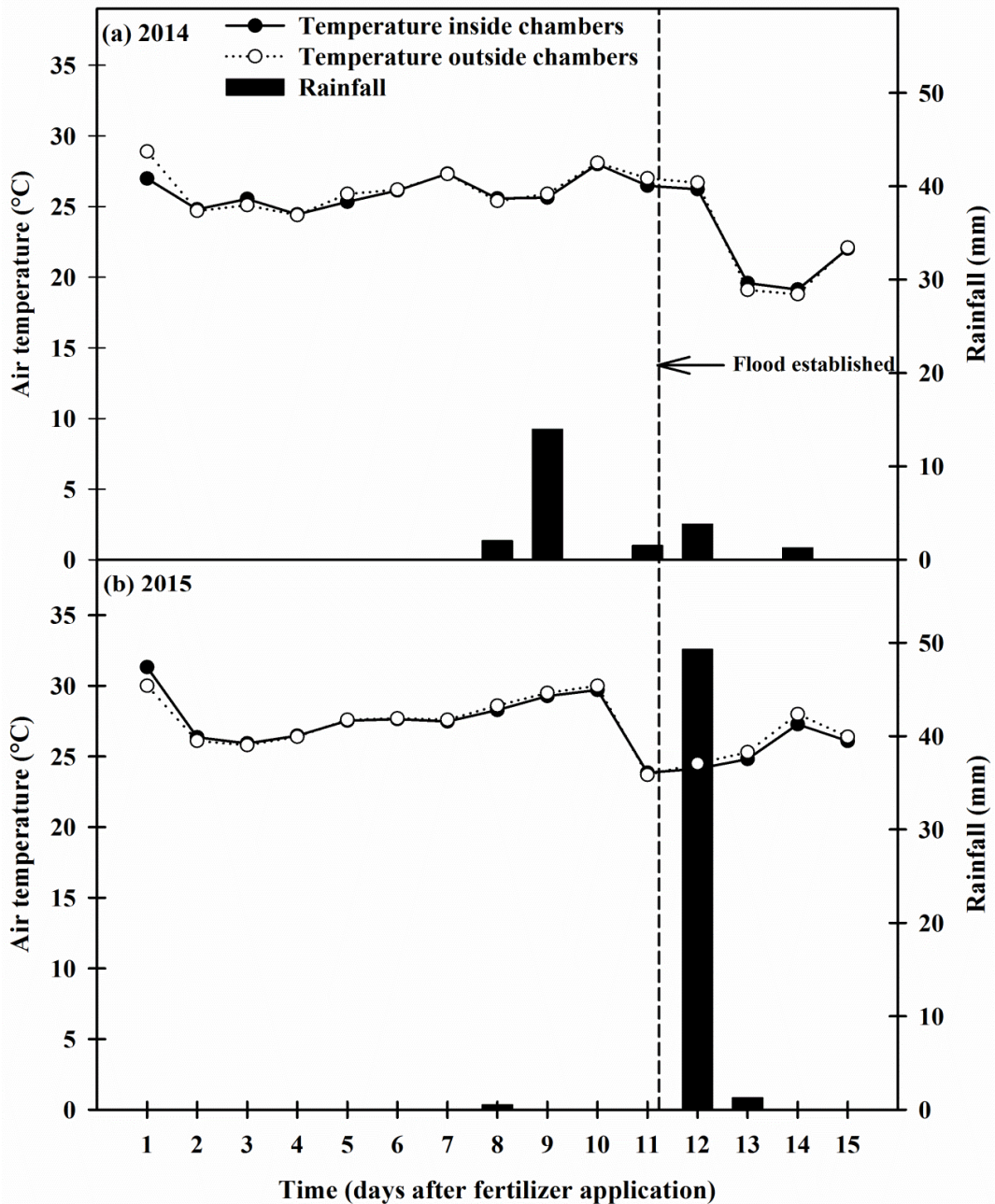
**Fig. 1. Rainfall and air temperature during the 15-day ammonia volatilization study in 2014 and 2015**

remaining sampling times. Only three experimental ZSCU fertilizers (ZU, ZB[H], and ZN[H]) volatilized lower ammonia than urea on the same sampling time during the period of peak ammonia loss. All the three experimental ZSCU fertilizers had lower ammonia loss than urea on the fifth day after N fertilizer application; but only

ZN[H] had lower ammonia loss than urea on the seventh day. Ammonia loss was similar among the experimental ZSCU fertilizers regardless of sampling time. Ammonia loss at each sampling interval during periods of peak ammonia losses was significantly greater for urea (3.4 – 4.5%) than NBPT-treated urea (0.07 – 1.0%). The

NBPT-treated urea had lower ammonia loss than the experimental ZSCU fertilizers 7 days after N fertilizer application. Cumulative ammonia loss from all the N treatments showed gradual increase with time until permanent flood was established on day 11 days after N fertilizer application (Fig. 2b). Cumulative ammonia loss from urea (15.4%) was similar to ZU (12.7%) and ZB^L (12.8%). Among the experimental ZSCU fertilizers, ZB^L (8.5%) had the least cumulative ammonia loss which was similar to ZB^L (10.0%) and ZN^L (10.6%). Cumulative ammonia loss from

NBPT-treated urea (2.6%) was significantly lower than the other N treatments (Fig. 2b).

In contrast to 2014, there was substantial ammonia loss from all the N treatments on the first sampling day except for the NBPT-treated urea in 2015 (Fig. 2c). The peak ammonia loss from urea in 2015 occurred on the third day after N fertilizer application. Only the NBPT-treated urea delayed the time to reach peak daily ammonia loss; however, the peak daily ammonia loss was higher for urea (15.3%) than the other N
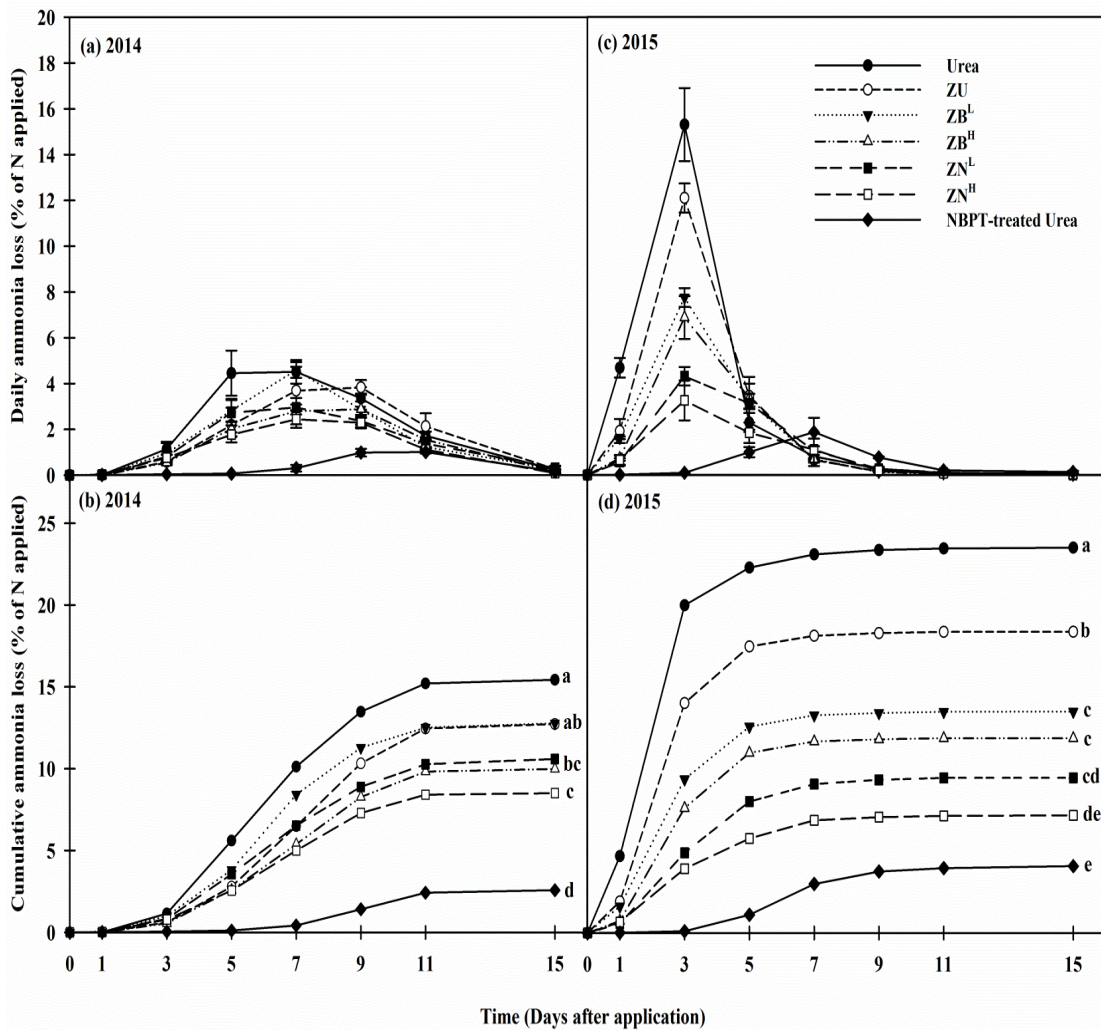


**Fig. 2. Daily and cumulative ammonia volatilization from urea, with NBPT-treated urea, and various formulations of zinc sulfate coated urea (ZSCU) fertilizers during a 15-day study in 2014 and 2015. †ZU, ZnSO$_4$-coating alone; ZB$^L$, 1.0 g B kg$^{-1}$ and ZnSO$_4$-coating; ZB$^H$, 1.7 g B kg$^{-1}$ and ZnSO$_4$-coating; ZN$^L$, 1.0 g B kg$^{-1}$, NBPT, and ZnSO$_4$-coating; ZN$^L$, 1.0 g B kg$^{-1}$, NBPT, and ZnSO$_4$-coating. The NBPT concentration in ZN$^L$ and ZN$^H$ was 0.3 and 0.6 g kg$^{-1}$ in 2014 and 2015, respectively. Urea was treated with 0.9 g kg$^{-1}$ NBPT for the NBPT-treated urea treatment.**
*Means followed by the same letters are not significantly different within each graph*

treatments (1.9 – 12.1%). Daily ammonia loss differed among N treatments on the first and third day after N fertilizer application. On the first day, urea had higher ammonia loss than the other N treatments. Among the experimental ZSCU fertilizers, ammonia loss from ZU was only comparable to $ZB^L$ but greater $ZB^H$, $ZUN^L$, and $ZUN^H$ treatments (Fig. 2c). The NBPT-treated urea volatilized the least ammonia loss which was lower than the urea and experimental ZSCU fertilizers. On the third day, ammonia loss from urea (15.3%) was similar to ZU (12.1%) but greater than the other N treatments. There was no difference in ammonia loss between $ZB^L$ (7.8%) and $ZB^H$ (6.9%) or $ZN^L$ (4.3%) and $ZN^H$ (3.3%). Cumulative ammonia loss for urea and experimental ZSCU fertilizers increased rapidly within the first 5 days after N fertilizer application and plateaued by day 7. Cumulative ammonia loss from urea (23.5%) was significantly greater than the other N treatments (Fig. 2d). The ZU (18.4%) treatment had higher cumulative ammonia loss that the other experimental ZSCU fertilizers and NBPT-treated urea. The $ZB^H$ (11.9%), $ZN^L$ (9.5%), and $ZN^H$ (7.2%) treatments had similar cumulative ammonia losses. Among the experimental ZSCU fertilizers, only $ZN^H$ treatment volatilized similar cumulative ammonia as the NBPT-treated urea (Fig. 2d).

### 3.3 Grain Yield

The grain yield from the control plots in 2014 was 7,538 kg ha$^{-1}$. Grain yield differed between the N treatments at the 67 kg N ha$^{-1}$ rate, but similar among the N treatments at 134 kg N ha$^{-1}$ rate in 2014 (Table 2). In 2014, the highest grain yield at the 67 kg N ha$^{-1}$ rate was observed in plots fertilized with urea (10,424 kg ha$^{-1}$) which was similar to Urea:ZnSO$_4$, $ZB^L$, $ZB^H$, $ZN^H$, and NBPT-treated urea (Table 2). Differences were not observed among the experimental ZSCU fertilizers at the 67 kg N ha$^{-1}$ rate. The grain yield from unfertilized N plots in 2015 was 4,047 kg ha$^{-1}$ (Table 2). Grain yield varied among N treatments at the 67 and 134 kg N ha$^{-1}$ rates in 2015. Grain yield for urea at 67 kg N ha$^{-1}$ rate was 5,753 kg ha$^{-1}$. Experimental ZSCU fertilizers (5,965 – 6,694 kg ha$^{-1}$) did not improve grain yield over urea; however, NBPT-treated urea at 67 kg N ha$^{-1}$ significantly increased grain yields by 38% when compared to urea in 2015 (Table 2). The NBPT-treated urea out yielded all the experimental ZSCU fertilizers at the 67 kg N ha$^{-1}$ rate. Grain yield from urea at the 134 kg N ha$^{-1}$ rate was similar to urea:ZnSO$_4$, ZU, and $ZN^L$ treatments. Grain yield differed among experimental ZSCU fertilizers where ZU treatment had the lowest yield and was similar to only $ZN^L$. At the 134 kg N ha$^{-1}$ rate, with NBPT-treated urea produced significantly higher yields than the other N sources and increased grain yield by 46% when compared with urea.

## 4. DISCUSSION

Results of this work support previous studies that the N source and environmental conditions at fertilizer application can influence ammonia volatilization losses [13,32]. The cumulative ammonia loss from urea in 2014 was 45% lower than in 2015 trial was 8.1%. The air temperature

**Table 2. Nitrogen treatment effect on grain yield at the 67 and 134 kg N ha$^{-1}$ application rates in 2014 and 2015**

| N treatments [†] | 2014 | | 2015 | |
|---|---|---|---|---|
| | 67 kg N ha$^{-1}$ | 134 kg N ha$^{-1}$ | 67 kg N ha$^{-1}$ | 134 kg N ha$^{-1}$ |
| | ------------------------------------kg ha$^{-1}$-------------------------------- | | | |
| Control | 7538 | | 4047 | |
| Urea | 10424 a | 11110 a | 5753 b | 7217 d |
| Urea:ZnSO$_4$ | 10122 ab | 10180 a | 5778 b | 7377 cd |
| ZU | 8625 b | 10797 a | 6162 b | 7041 d |
| $ZB^L$ | 8768 ab | 10880 a | 5965 b | 8115 bc |
| $ZB^H$ | 9826 ab | 10167 a | 6298 b | 8609 b |
| $ZN^L$ | 8629 b | 10445 a | 6316 b | 7868 b-d |
| $ZN^H$ | 10238 ab | 10795 a | 6408 b | 8351 b |
| NBPT-treated urea | 9757 ab | 10633 a | 7949 a | 10563 a |

[†]*ZU, ZnSO$_4$-coating alone; $ZB^L$, 1.0 g B kg$^{-1}$ and ZnSO$_4$-coating; $ZB^H$, 1.7 g B kg$^{-1}$ and ZnSO$_4$-coating; $ZN^L$, 1.0 g B kg$^{-1}$, NBPT, and ZnSO$_4$-coating; $ZN^L$, 1.0 g B kg$^{-1}$, NBPT, and ZnSO$_4$-coating. The NBPT concentration in $ZN^L$ and $ZN^H$ was 0.3 and 0.6 g kg$^{-1}$ in 2014 and 2015, respectively. Urea was treated with 0.9 g kg$^{-1}$ NBPT for the NBPT-treated urea treatment.*
*Means followed by the same letters within a column are not significantly different.*

between N fertilizer application and the first sampling time may partly account for the difference in cumulative ammonia losses between the two years [33,34]. Laboratory studies by Wahl et al. (2006), showed that the solubility of urea increased from 1.1 to 1.3 g g$^{-1}$ when air temperature increase from 20 to 30 °C. The air temperature between N fertilizer application and the first sampling time was 26 and 31°C in 2014 and 2015, respectively (Fig. 1b). The warmer air temperature in 2015 caused rapid urea dissolution and hence, the peak ammonia loss occurred within the first 3 days after N application in 2015. In contrast, peak ammonia loss in 2014 was delayed until 5 to 9 days after N fertilizer application. The rapid ammonia loss with the first three days resulted in a higher cumulative ammonia loss in 2015 than 2014.

The ZSCU fertilizer with physical coating alone had similar ammonia loss as urea in 2014. Similarly, in a laboratory studies, Hawke and Baldock (2010) found that ZSCU fertilizer was not effective in reducing ammonia loss cumulative ammonia loss from urea (7.9%) applied on a calcareous sandy loam. In 2015, the physical coating alone provided ammonia volatility control in comparison to urea (23.5%). The result in 2015 is consistent with a laboratory study that reported reduction in ammonia loss from $K_2SO_4$-coated urea [14]. The study was conducted on a silt loam soil and the ammonia losses from urea were greater than 30% of the total N applied. The inconsistency in performance highlights the claim that the physical coating alone may not be a reliable approach to reducing ammonia volatilization in drill seeded delayed rice production [20]. The results from current and previous studies suggest that physically coating urea with nutrient may be effective in reducing ammonia volatilization in conditions where urea is susceptible to higher ammonia loss.

There was no difference in cumulative ammonia loss between the experimental ZSCU fertilizers containing either 1.0 g B kg$^{-1}$ or 1.7 g B kg$^{-1}$ in both year. It is worth noting that the cumulative ammonia loss from the lower rate (1.0 g B kg$^{-1}$) was similar to urea in 2014. For the ZSCU fertilizer with 1.7 g B kg$^{-1}$, cumulative ammonia loss was significantly lower than urea irrespective of the year, giving credence to the inhibitory effect of B on ammonia loss documented in previous studies [15,16]. According to [15] ammonia volatilization from urea treated with 1%

boric acid was 21 and 54% lower than NBPT-treated urea and urea, respectively. Benini et al. (2004) proposed that B compounds such as boric acid ($H_3BO_3$) inhibit urease activity as a result of competitive inhibition of the urease enzyme. The urease enzyme required for urea hydrolysis has bi-nuclear nickel (Ni) ions required for activation urea and water molecules [35]. The boric acid has topologically similar binding of urea to the Ni ions, thereby temporarily taking the place of urease enzyme and slowing urea hydrolysis. The slow urea hydrolysis prevents rapid conversion of ammonium to ammonia and subsequently minimizing ammonia volatilization [17].

The cumulative ammonia loss from ZSCU fertilizers with either 1.0 g B kg$^{-1}$ or 1.7 g B kg$^{-1}$ and NBPT were similar regardless of ammonia loss and were effective in reducing cumulative ammonia loss in 2014 and 2015. This result is consistent with previous studies where combining NBPT with physical coating reduced ammonia loss [14,23]. The ZSCU fertilizer containing 1.7 g B kg$^{-1}$ and 0.6 g kg$^{-1}$ NBPT was equally as effective in minimizing ammonia volatilization as urea treated with 0.9 g kg$^{-1}$ NBPT. This experimental fertilizer could be useful in reducing ammonia loss particularly in acid soils where the efficacy of NBPT has been reported to be less effective [4,23].

Application of NBPT-treated urea resulted in the lowest ammonia loss in 2014 and 2015. This result is in agreement with other studies that reported reduced ammonia loss from NBPT-treated urea fertilizer in a drill-seeded delayed flood rice production system [7,8]. Treating urea with NBPT slows urea hydrolysis due to its similar fit in the binding site of the urease enzyme and, thus, temporarily avoids the rapid increase in soil pH which serves as a catalyst for increasing the rate of ammonia volatilization [35-37].

The grain yield data from the control plots suggest that N was not a yield-limiting nutrient in 2014. Sufficient N availability in soil and rainfall events following N fertilizer application may partly explain the lack of difference in grain yield among N treatment in 2014. The average grain yield (7,538 kg ha$^{-1}$) from the control plot in 2014 was higher than typically reported [7]. Nitrogen strongly influences plant growth and development, thus, the relatively high grain yield from control plot suggests that the soil may have supplied sufficient N to counteract any N loss via ammonia volatilization and other N loss

processes. There were two rainfall events (18.0 mm) within the first 9 days after the application of fertilizer in 2014 (Fig. 1a). The rainfall may have incorporated fertilizer granules, suppressed ammonia loss, and improved plant available N. Holcomb et al. (2011) reported that the application of 14.6 mm of water after urea application can significantly decrease ammonia loss. Grain yield response to ZSCU fertilizer has been documented in Zn-deficient rice fields [38,39]. In current study, Zn was not limiting in both years as soil test results were greater than sufficiency level of 2.2 mg kg$^{-1}$ recommended for rice production in Louisiana (Table 1). Previous study suggests that B is not a yield-limiting factor in drill-seeded delay flood rice production system in the southern USA, as such the boron in the experimental fertilizers were not expected to influence grain yield [40]. Grain yield from plots fertilized with urea were similar to the NBPT-treated urea and the experimental ZSCU fertilizers in 2014. Fields fertilized with NBPT-treated urea have been reported to produce similar grain yield as urea in rice fields in southern USA [8]. In 2015, grain yield was similar between urea and the experimental ZSCU fertilizers; however, NBPT-treated urea had greater the other N treatments. The results from the yield study in 2015 support previous studies that indicated that NBPT-treated urea can significantly increase grain yield in comparison to urea fertilizers under conditions where N is limiting [13]. The lack of significant difference in grain yield between urea and ZSCU fertilizers in 2015 may be partly attributed to loss of physical coating during fertilizer application. During fertilizer application, some of the coatings appeared to stick to the fertilizer applicator which left the urea exposed with no protection and susceptible to ammonia volatilization losses.

## 5. CONCLUSION

This study evaluated different formulations of experimental zinc sulfate-coated urea fertilizers as a reliable means of reducing ammonia volatilization and improving rice productivity in a drill-seeded, delayed rice production system. The cumulative ammonia loss from urea was 15.4% and 23.5% in 2014 and 2015, respectively. Among the various formulations of experimental ZSCU fertilizers, only those containing 1.7 g B kg$^{-1}$ and 0.6 g kg$^{-1}$ had similar ammonia loss as urea treated with 0.9 g NBPT kg$^{-1}$. Application of the ZSCU fertilizers did not increase grain yield regardless of the growing season.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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