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# Mitigation of ammonia volatilization with application of urease and nitrification inhibitors from summer maize at the Loess Plateau

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## ABSTRACT

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Field experiments were conducted at three sites: Yangling (YL); Zhouzhi-1 (ZH-1) and Zhouzhi-2 (ZH-2) of the Loess Plateau during summer maize crop, to investigate the effectiveness of N-(n-butyl) thiophosphoric triamide (NBPT) and NBPT + dicyandiamide (DCD) with urea on reducing $NH_3$ volatilization from different soils under different environmental conditions. Four treatments including control (no N), N-220 kg/ha, N-220 + NBPT and N-220 + NBPT + DCD were applied in two splits through the band placement method. Total $NH_3$-N loss observed were 65.8, 40.5 and 20.1 $NH_3$-N kg/ha (accounting for 29.9, 18.4 and 9.2% of N applied) from urea for YL, ZH-1 and ZH-2, respectively. The application of NBPT and NBPT + DCD significantly reduced $NH_3$ volatilization by 80–93% and 75–90%, respectively. The meteorologic factors such as precipitation, air temperature and wind speed significantly affected $NH_3$ volatilization. These results suggested that the amendment of urea with NBPT and NBPT + DCD have potential to mitigate $NH_3$-N losses from alkaline soils in the Loess Plateau.

**Keywords**: urea hydrolysis; nitrogen stabilizers; vented chamber; mineral-N changes; *Zea mays* L.

Ammonia ($NH_3$) volatilization is a significant nitrogen (N) loss pathway for urea in calcareous and alkaline soils (Sommer et al. 2004, Soares et al. 2012). Globally, the $NH_3$ volatilization loss had increased up to 64% from N fertilization, equal to 20–70% of the total farmland N loss (Pan et al. 2016). Besides the economic loss to farmers, $NH_3$ volatilization loss may have detrimental effects to ecosystem including acidification in terrestrial systems, eutrophication of aquatic systems and decline in biodiversity (Zaman et al. 2009). Furthermore, $NH_3$ also contributes to global warming by reacting with nitric acid and sulfuric acid in the atmosphere, and also contributes to secondary aerosols, haze pollution and poses a considerable threat to human health (Liu et al. 2013).

Urease inhibitor (UI) could reduce the $NH_3$ volatilization by slowdown of the urea hydrolysis in soils (Abalos et al. 2012). Among the various types of UIs, N-(n-butyl) thiophosphoric triamide

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(NBPT) was widely used and was highly effective in reducing $NH_3$ emission (Zaman et al. 2009, Sanz-Cobena et al. 2011). Dicyandiamide (DCD) is a well-known nitrification inhibitor used in combination with NBPT and has been more effective in reduction of N losses from urea fertilization (Zaman and Nguyen 2012). Apart from reducing $NH_3$ emission, NBPT and DCD have been effective in minimizing other N losses like $N_2O$ emission and nitrate leaching into surface and ground water, thereby improving N use efficiency (Soares et al. 2012).

Air temperature, wind speed, time and the amount of rainfall or irrigation also have effect on $NH_3$ loss (Sanz-Cobena et al. 2011, Li et al. 2015, 2017). Soils in the Loess Plateau are calcareous and have pH higher than 7.5 (Li et al. 2017), which supports $NH_3$ volatilization. Considering the importance of reducing $NH_3$ volatilization, field experiments were conducted with hypothesis that NBPT and combined use of NBPT with DCD would be effective in reducing N losses via $NH_3$ volatilization under different soil physico-chemical properties and climatic factors.

## MATERIAL AND METHODS

**Site description**. Field experiments were carried out on maize in summer 2016 at three different sites in two counties (Yangling, Zhouzhi), Shaanxi, the south edge of the Loess Plateau, China, with warm-temperate sub-humid continental monsoon climate. Approximately 65–80% of precipitation were recorded between July and September. The soil at Yangling (34°17'N, 108°04'E) was classified as Eum-Orthic Anthrosol (Udic Haplustalf in the USDA system). Other sites were located at the Yujiahe catchment area (34°9'N, 108°12'E) of the Zhouzhi County and the soil was classified as a cinnamon soil (Udic Haplustalf in the USDA system). The soil characteristics of top layer (0–20 cm) of all three selected fields are mentioned in Table 1.

**Experimental design**. Four treatments: control (no fertilizer); N-220 kg/ha; N-220 + NBPT; and N-220 + NBPT + DCD were arranged in a randomized block design with three replications. Treatments were applied in two top-dressings, 70% 25 days after sowing and 30% 24 days after fertilization, by band placement method 8 ± 1 cm deep near the plant rows and covered by soil (Zhao et al. 2016). The rates of NBPT and DCD were 1% and 10%, respectively on the w/w basis of N.

Soil temperature was measured at different depths (5, 10, 15, 20 and 25 cm) by using right-angled thermometers (Yang et al. 2015). Climatic measurements like daily mean air temperature, air humidity, wind speed and precipitation were recorded from the local meteorological stations near the study sites.

**Analytical procedures**. Soil pH and electrical conductivity (EC) were tested by 1:2.5 and 1:5 soil-water ratio, respectively. Total N and soil organic carbon (SOC) were analyzed by micro-Kjeldahl digestion and soil wet digestion with $H_2SO_4$-$K_2Cr_2O_7$ method, respectively (Zhang et al. 2017). Soil particle size distribution (sand, silt and clay (%)) was determined by Master sizer 2000E (Malvern, UK) laser diffractometer (Sochan et al. 2012). Soil urease activity (UA) was determined by taking 5 g of soil using 10% urea substrate solution, and incubated at 37°C for 24 h (Tabatabai 1994). A sub-sample of 5 g fresh soil (oven dry-equal) was extracted with 50 mL of 1 mol/L KCl solution for $NH_4^+$-N and $NO_3^-$-N concentration. Soil moisture content was measured by the oven-drying method at 105°C.

Table 1. Chemical and physical properties of three different experimental sites

| Parameter | Yangling | Zhouzhi-1 | Zhouzhi-2 |
|---|---|---|---|
| pH | 8.02 ± 0.02 | 7.96 ± 0.02 | 8.01 ± 0.01 |
| SOC (g/kg) | 11.9 ± 0.19 | 5.8 ± 0.82 | 6.1 ± 0.08 |
| Total N (g/kg) | 0.73 ± 0.01 | 0.35 ± 0.05 | 0.31 ± 0.03 |
| $NH_4^+$-N (mg/kg) | 5.1 ± 0.85 | 4.1 ± 1.13 | 3.4 ± 0.14 |
| $NO_3^-$-N (mg/kg) | 23.9 ± 0.55 | 22.8 ± 0.20 | 2.6 ± 0.49 |
| Available P (mg/kg) | 35.5 ± 1.80 | 16.7 ± 0.11 | 17.3 ± 0.95 |
| Available K (mg/kg) | 265.9 ± 2.58 | 100.0 ± 3.56 | 104.42 ± 1.0 |
| EC (µS/cm) | 168.6 ± 3.78 | 167.4 ± 2.9 | 134.3 ± 1.83 |
| Urease activity (N mg/kg/h) | 9.7 ± 0.88 | 2.4 ± 0.35 | 1.0 ± 0.21 |
| Soil texture class | Silt loam | Loam | Silt clay loam |
| **Particle size distribution** | | | |
| Sand (%) | 18.4 ± 1.25 | 31.6 ± 0.47 | 15.5 ± 1.17 |
| Silt (%) | 56.6 ± 0.62 | 47.9 ± 0.82 | 54.4 ± 0.54 |
| Clay (%) | 25.0 ± 0.75 | 20.5 ± 1.22 | 30.1 ± 0.75 |

Values are the means ± standard error (*n* = 3). SOC – soil organic carbon; EC – electrical conductivity

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Vented chamber method was used to measure $NH_3$ volatilization (Yang et al. 2015). Chambers were made of polyvinyl chloride (PVC) pipe (height 25 cm and internal diameter 15 cm) inserted 3 cm deep into the soil. Four wooden sticks for supporting the rain roof (30 × 30 $cm^2$ of PVC) were placed 5 cm above the top of cylinder to shed rainfall. Two sponges as $NH_3$ absorbers soaked with 20 mL (bottom) and 10 mL (top) of 50 mL/L phosphoric acid ($H_3PO_4$) + 40 mL/L ($C_3H_8O$) glycerol solution to trap ammonia were placed inside the cylinder. Only bottom sponges (5 cm above soil surface) were used for analysis, while top sponges were placed 5 cm overhead the bottom sponge for eliminating atmospheric $NH_3$. Sponges were extracted with 50 mL of 1 mol/L KCl solution and analysed by using the UV2400 ultraviolet-visible spectrophotometer (Shanghai UNICO Instrument Co., Ltd, Shanghai, China). Two vented chambers were randomly installed at 5 ± 1 cm soil depth in each plot besides two plants, over the fertilized row just after fertilization (Martins et al. 2015).

**Calculations and statistical analysis**. Relative $NH_3$ volatilization rate (kg N/ha/day) was calculated using formula:

$$R_{AV} = \frac{M}{(A \times D)} \times 10^{-2} \qquad (1)$$

Where: $R_{AV}$ – $NH_3$ volatilization rate (kg N/ha/day); M – $NH_3$-N collected using the PVC chamber (mg); A – cross-sectional area of PVC ($m^2$); D – sampling interval (day). The cumulative $NH_3$ volatilization rate was determined as the sum of daily $NH_3$ emission rates.

The emission factor (EF, %) of $NH_3$-N emission and reduction efficiency (RE) of NBPT were calculated by using formulas:

$$EF = \frac{(NH_3 \text{ loss from fertilized} - NH_3 \text{ loss from control})}{\text{Applied N}} \times 100 \qquad (2)$$

$$RE = \frac{(NH_3 \text{ loss from fertilized} - NH_3 \text{ loss from N amended})}{NH_3 \text{ loss from N source}} \times 100 \qquad (3)$$

Data were evaluated by the analysis of variance (ANOVA) and the means were compared using the least significant difference (*LSD*) at a $P < 0.05$ level. Graphs were prepared using Sigma plot 10.0 (San Jose, USA).

## RESULTS

**Climatic and soil conditions**. First rainfall occurred (7.4 mm and 32 mm) at Zhouzhi on days

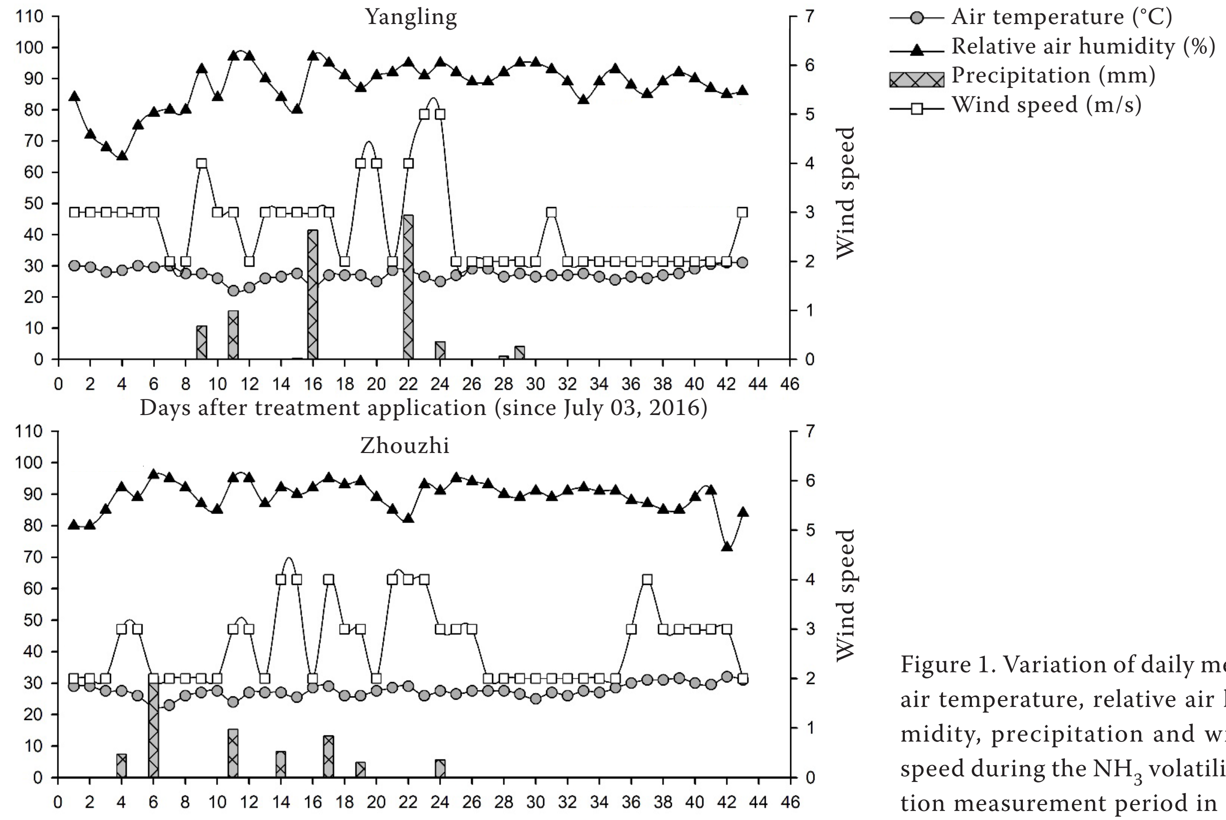

Figure 1. Variation of daily mean air temperature, relative air humidity, precipitation and wind speed during the $NH_3$ volatilization measurement period in the Yangling and Zhouzhi sites

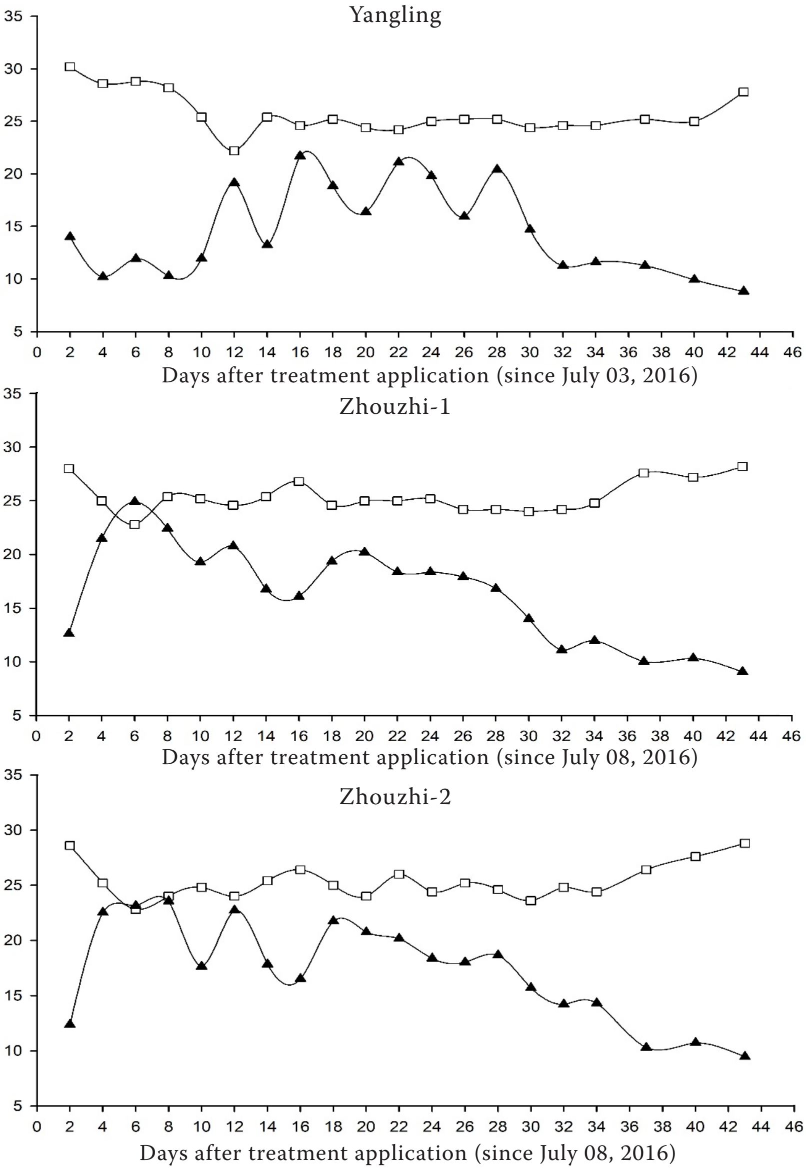

Figure 2. Variation in the mean soil temperature in the soil 0–25 cm layer, and the soil moisture content in the 0–20 cm soil layer during the $NH_3$ volatilization measurement period of three different sites

4 and 6 and at Yangling (10.7 mm and 15 mm) on days 9 and 11 after fertilization (Figure 1). Mean soil moisture contents varied intensely: 14.6, 16.7 and 17.4% and the differences in mean soil temperature during the first week were 28.9, 25.3 and 25.1°C for YL, ZH-1 and ZH-2 fields, respectively (Figure 2).

**Changes in mineral N**. At YL site, the concentration of $NH_4^+$-N dramatically increased and peaked (108 and 92.3 mg/kg) on days 10 and 6, $NO_3^-$-N (158.8 and 120.3 mg/kg) on days 14 and 10 after the first and second top-dressing of urea, respectively. At ZH-1 and ZH-2, the concentration of $NH_4^+$-N peaked on day 10 (90.7 and 66 mg/kg) and on day 14 (86.6 and 55 mg/kg) after the first and second urea fertilization, respectively. $NO_3^-$-N concentration significantly increased (100.7 and 135.5 mg/kg) on day 14 accordingly. The use of NBPT and NBPT + DCD significantly reduced $NH_4^+$-N and $NO_3^-$-N concentration across all fields (Figure 3).

**Daily $NH_3$ volatilization**. Daily $NH_3$ volatilization was measured at the maize crop over a 43-day period during summer across all sites in 2016 (Figure 4). At YL, a significant loss of $NH_3$ from urea rapidly showed up on day 2 and peaked (11.6 $NH_3$-N kg/ha/day) on day 6 and then dropped steadily. At the ZH-1 and ZH-2, the substantial loss of $NH_3$ from urea slowly showed up on day 8 because of two rainfall events that occurred on day 4 and 6, sharply peaked (10.5 and 6.6 $NH_3$-N kg/ha/day) on day 14 and slowly declined, respectively. After the second fertilization, the $NH_3$ volatilization re-

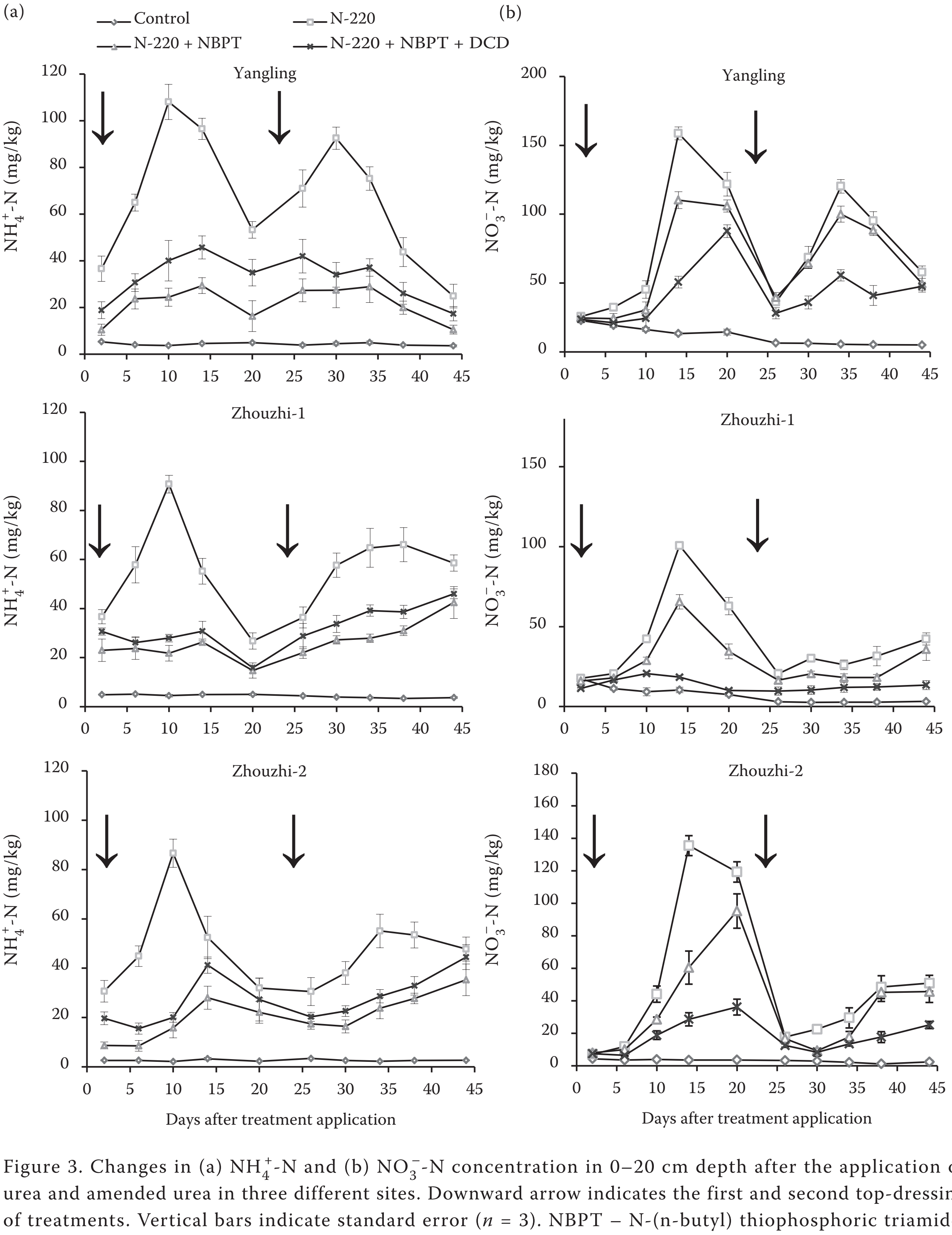

Figure 3. Changes in (a) $NH_4^+$-N and (b) $NO_3^-$-N concentration in 0–20 cm depth after the application of urea and amended urea in three different sites. Downward arrow indicates the first and second top-dressing of treatments. Vertical bars indicate standard error (*n* = 3). NBPT – N-(n-butyl) thiophosphoric triamide; DCD – dicyandiamide

mained lower and peaked on day 28 across all fields (Figure 4). However, the application of NBPT and NBPT + DCD significantly reduced the hydrolysis process and mitigated N losses compared to urea.

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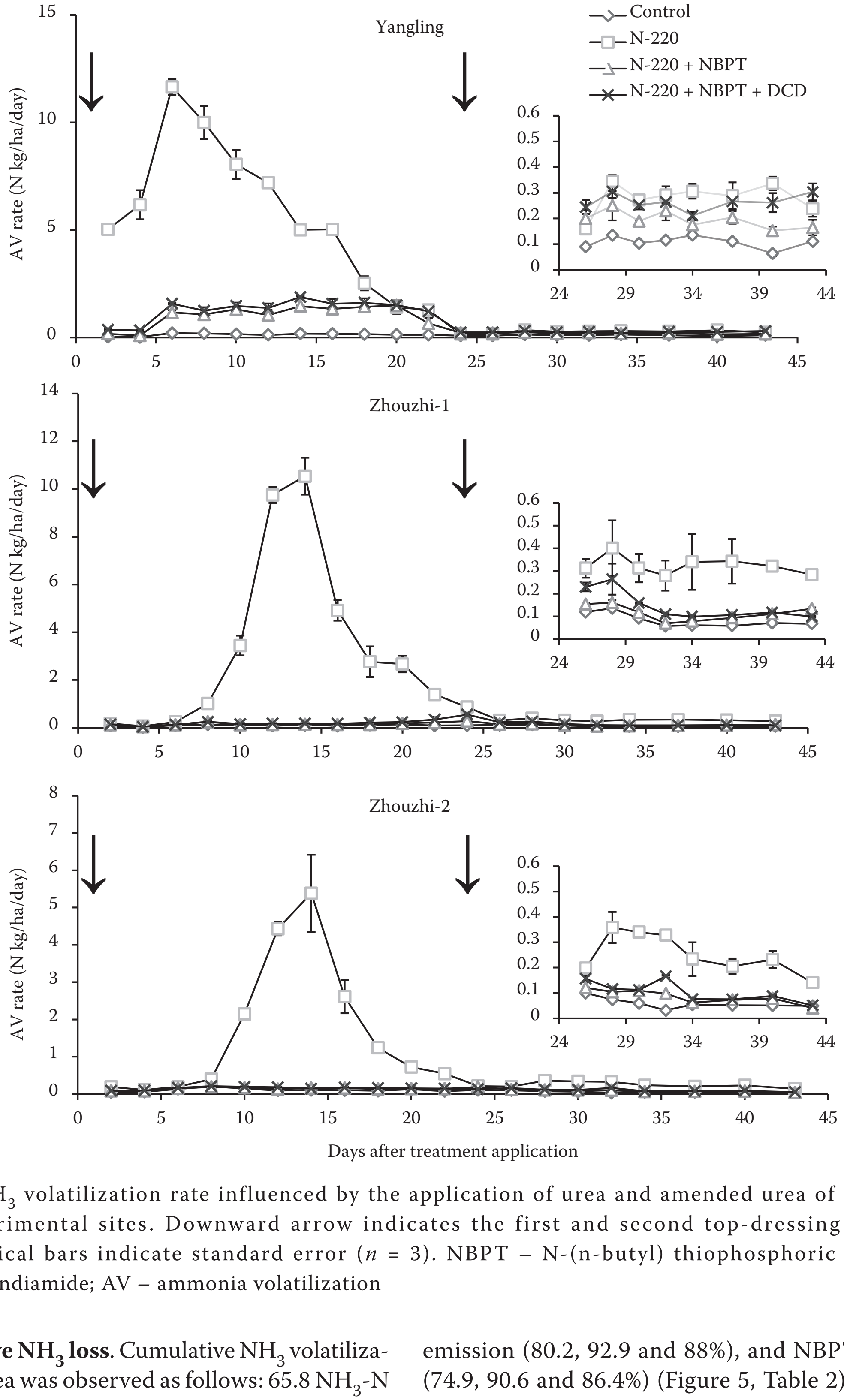

Figure 4. $NH_3$ volatilization rate influenced by the application of urea and amended urea of three different experimental sites. Downward arrow indicates the first and second top-dressing of treatments. Vertical bars indicate standard error (*n* = 3). NBPT – N-(n-butyl) thiophosphoric triamide; DCD – dicyandiamide; AV – ammonia volatilization

**Cumulative $NH_3$ loss**. Cumulative $NH_3$ volatilization from urea was observed as follows: 65.8 $NH_3$-N kg/ha (29.9% of N applied), 40.5 $NH_3$-N kg/ha (18.4% of N applied) and 20.1 $NH_3$-N kg/ha (9.2% of N applied) in YL, ZH-1 and ZH-2 sites, respectively. The urea amended with NBPT significantly reduced $NH_3$ emission (80.2, 92.9 and 88%), and NBPT + DCD (74.9, 90.6 and 86.4%) (Figure 5, Table 2). Overall, the effect of amended urea in decreasing $NH_3$ loss is a clear evidence of significantly lower emission factor of N + NBPT and N + NBPT + DCD, than that of urea across all sites (Table 2).

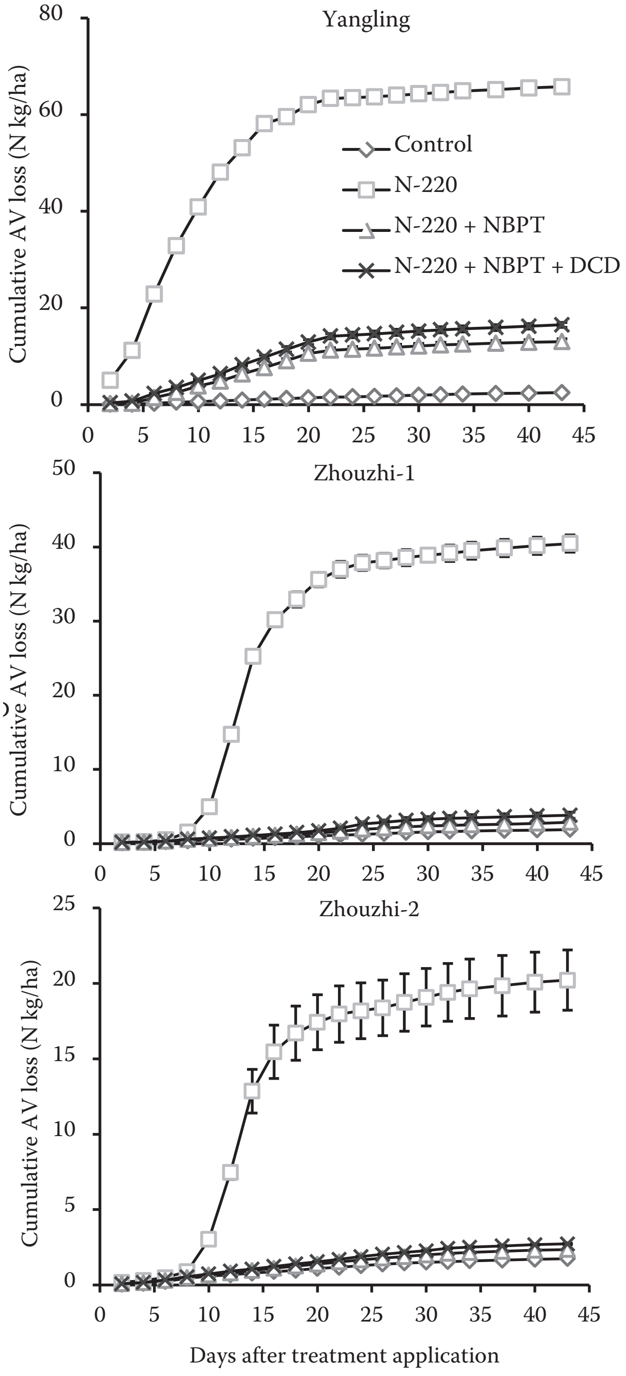

Figure 5. Cumulative $NH_3$ volatilization loss after the application of urea and amended urea in three different experimental sites. Vertical bars indicate standard error ($n = 3$). NBPT – N-(n-butyl) thiophosphoric triamide; DCD – dicyandiamide; AV – ammonia volatilization

## DISCUSSION

**$NH_3$ volatilization loss**. Cumulative $NH_3$ losses from urea ranged between 9.2–29.9% of N applied across all sites, which was related to high soil $NH_4^+$-N and $NO_3^-$-N concentration compared to other treatments (Abalos et al. 2012). Similar $NH_3$ losses were obtained from clay loam (5–30%) and loam (30%) soils (Sanz-Cobena et al. 2011, Suter et al. 2013). However, cumulative $NH_3$ losses ranged between 10–36% of applied N from conventional urea in calcareous loamy and silty textured soils (Li et al. 2017). In addition, $NH_3$ volatilization from urea ranged between 28–37% of applied N under laboratory conditions (Soares et al. 2012). However, cumulative $NH_3$ loss was 11–25% with winter wheat crop reported in other studies (Ni et al. 2014, Li et al. 2015). Obviously, $NH_3$ volatilization is a main N loss pathway for urea in calcareous and alkaline soils.

The sharp increase in $NH_3$ volatilization was observed in early days after fertilization at YL, which might be due to rapid urea hydrolysis by urease enzymes activity (Shang et al. 2014) and initial soil moisture began to dry rapidly (Tian et al. 2015). The rate of $NH_3$ volatilization in the second top dressing was observed relatively very low across all fields (Figure 4). That was due to the lower amount of fertilization (30%), and possibly the plant N uptake was higher because of peak vegetative growth stage and higher leaf canopy (Sommer et al. 2004).

**Effect of inhibitors on $NH_3$ volatilization**. The inclusion of NBPT with urea slowdowned hydrolysis and formation of $NH_4^+$-N, and resulted in reduced $NH_3$ volatilization (80–93%, Suter et al. 2013). $NH_3$ reduction in New Zealand averaged 29–93% at different concentrations of NBPT (Saggar et al. 2013). Moreover, our observations are higher than the results (58–77%) of previous studies related to NBPT (Sanz-Cobena et al. 2011, Abalos et al. 2012). Li et al. (2017) reported that the application of Limus (a mixture of NBPT and NPPT) reduced 84% of $NH_3$ volatilization. Furthermore, the combined use of NBPT + DCD also decreased $NH_4^+$-N concentration, and $NH_3$ volatilization of 75% to 90% is better than the results of previous studies (Zaman et al. 2009, Soares et al. 2012). The addition of DCD with NBPT showed no significant increase in $NH_3$ volatilization (Soares et al. 2012, Ni et al. 2014). Overall, our findings indicate that the application of NBPT and/or combination of NBPT + DCD with urea could be a mitigating tool for reduction of $NH_3$ emission under agro-ecological conditions.

**Factors affecting $NH_3$ loss**. The dynamics of $NH_3$ volatilization were generally determined

Table 2. Cumulative $NH_3$-N emission (kg/ha), $NH_3$-N loss (% of applied N), emission factor of $NH_3$-N and the reduction efficiency of inhibitors of three different sites

| Site | Treatment | $NH_3$-N emission (kg/ha) | $NH_3$-N loss (% of N applied) | Emission factor | Reduction efficiency |
|---|---|---|---|---|---|
| | | | | (%) | |
| Yangling | control | $2.5 \pm 0.10^{d}$ | – | – | – |
| | N-220 | $65.8 \pm 1.33^{a}$ | $29.9 \pm 0.60^{a}$ | $28.8 \pm 0.60^{a}$ | – |
| | N + NBPT | $13.2 \pm 0.58^{c}$ | $5.9 \pm 0.26^{b}$ | $4.8 \pm 0.26^{b}$ | $80.2 \pm 0.89^{a}$ |
| | N + NBPT + DCD | $16.5 \pm 0.52^{b}$ | $7.5 \pm 0.24^{b}$ | $6.4 \pm 0.24^{b}$ | $74.9 \pm 0.79^{a}$ |
| Zhouzhi-1 | control | $1.9 \pm 0.05^{b}$ | – | – | – |
| | N-220 | $40.5 \pm 1.16^{a}$ | $18.4 \pm 0.53^{a}$ | $17.5 \pm 0.53^{a}$ | – |
| | N + NBPT | $2.9 \pm 0.05^{b}$ | $1.3 \pm 0.02^{b}$ | $0.4 \pm 0.01^{b}$ | $92.9 \pm 0.13^{a}$ |
| | N + NBPT + DCD | $3.8 \pm 0.42^{b}$ | $1.7 \pm 0.19^{b}$ | $0.9 \pm 0.17^{b}$ | $90.6 \pm 1.03^{a}$ |
| Zhouzhi-2 | control | $1.8 \pm 0.06^{b}$ | – | – | – |
| | N-220 | $20.1 \pm 2.00^{a}$ | $9.2 \pm 0.91^{a}$ | $8.4 \pm 0.93^{a}$ | – |
| | N + NBPT | $2.4 \pm 0.07^{b}$ | $1.1 \pm 0.03^{b}$ | $0.3 \pm 0.06^{b}$ | $88.0 \pm 0.35^{a}$ |
| | N + NBPT + DCD | $2.7 \pm 0.04^{b}$ | $1.2 \pm 0.02^{b}$ | $0.5 \pm 0.05^{b}$ | $86.4 \pm 0.21^{b}$ |

Different letters in a column mean a significant difference applying ANOVA least significant difference (*LSD*) test at $P < 0.05$. Values are the means ± standard error ($n = 3$). NBPT – N-(n-butyl) thiophosphoric triamide; DCD – dicyandiamide

by the weather conditions of area such as precipitation, wind speed and air temperature after urea application (Li et al. 2017). The timing of the rainfall event influenced the peak emission rate and successive reduction of $NH_3$ volatilization, which was probably because of rainfall had dispersed urea into the soil. Our results are related to the previously reported studies, showing that the addition of water or rainfall event (≥ 7 mm) decreased $NH_3$ volatilization rate (Sanz-Cobena et al. 2011, Ni et al. 2014).

The rate of $NH_3$ volatilization was influenced by an increase in air temperature and increased urea hydrolysis leading to high $NH_3$ emission (Li et al. 2017). The variation in wind speed, especially during the first week, strongly affected the rate of $NH_3$ volatilization. Increased $NH_3$ volatilization rate could be associated with high wind speed due to an increased pressure gradient of $NH_3$ emission between soil and atmosphere (Sanz-Cobena et al. 2011). $NH_3$ volatilization losses strongly depended on the weather conditions (rainfall, wind speed and temperature) of the experimental site (Li et al. 2015).

Consequently, high $NH_3$ volatilization could be explained by the higher UA in the YL soil (9.7 mg N kg/h) than the ZH-1 and ZH-2 soil (2.4 and 1.0 mg N kg/h). Furthermore, it was reported that high soil UA has a close relationship with the rate of $NH_3$ volatilization (Zhao et al. 2016, Li et al. 2017). High initial mineral N and total N content also might be the reasons of higher $NH_3$ volatilization (Li et al. 2015). In addition, Yang et al. (2015) reported that $NH_3$ loss was intensely related to soil mineral N content.

The magnitude of $NH_3$ volatilization was affected by the variation in moisture content (Sommer et al. 2004). High soil temperature probably increased the microbial activity and hydrolysis process of urea fertilizer increased the $NH_3$ volatilization (Yang et al. 2015). Results of the current study demonstrate that $NH_3$ volatilization rate is strongly dependent on the variation of climatic conditions, physicochemical properties of soil, soil temperature and moisture content.

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