Field Crops Research 212 (2017) 73–81

Contents lists available at ScienceDirect

Field Crops Research

journal homepage: www.elsevier.com/locate/fcr

Performance of matrix-based slow-release urea in reducing nitrogen loss and improving maize yields and profits

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ARTICLE INFO

Keywords:
Corn
Zea mays L.
Bentonite
Polyacrylamide
Low cost

ABSTRACT

To reduce N loss in field crop production, application of slow-release fertilizers with acceptable cost is a possible option. Matrix-based urea is a novel, low-cost, slow-release urea developed in the past 10 years. However, there is little consensus about the effects of matrix-based urea on N loss, field maize yields, N use efficiency and profitability. The current study aimed to (i) determine the effects of matrix-based urea on N loss, maize yields, and N use efficiency and elucidate the possible mechanisms; and (ii) assess whether the profitability is acceptable to maize growers. A 2-year field experiment was conducted during 2015–2016 following a randomized block design with three treatments: control test (CK, without urea application), common urea treatment (CU, 195 kg N ha^{-1}) and matrix-based urea treatment (MU, 195 kg N ha^{-1}). Additionally, two laboratory tests were conducted to assess N leaching and ammonia emission from matrix-based urea. The results showed that due to increases in grain number per ear and 1000-grain weight, grain yields with MU were 6.3 and 14.7% greater than those with CU in 2015 and 2016, respectively. Agronomic efficiency (AE) and apparent recovery efficiency (ARE) were greater with MU than with CU. Greater grain yield, biomass, AE, and ARE with MU were attributed to better plant development, i.e., greater plant height, leaf area, root area, chlorophyll concentration, carotenoid concentration, nitrate reductase activity, and glutamine synthetase activity. Better plant development with MU was related to greater available N in the 0–20-cm top soil layers, due to decreased N leaching and ammonia emission. The profitability of maize production with MU was 118.7 and 176.0 USD ha^{-1} greater than with CU in 2015 and 2016, respectively. Overall, matrix-based urea performs well at reducing N loss and improving maize yields, AE, ARE, and profitability, and is thus suitable for application in field maize production.

1. Introduction

N is an essential element for crop growth. Rational application of N fertilizer enhances food security. During the last 3 decades, application of N fertilizers in China has doubled to increase crop yield in order to feed the increasing population (Liu et al., 2013). Urea is the most widely used N fertilizer, partly due to its high N content (46.4%) and relatively low cost (Ni et al., 2013). For example, urea accounts for more than 50% of N fertilizer consumption in China (Li et al., 2015). However, common urea (CU) applied in soils carries the risk of N leaching and ammonia emission (Yang et al., 2015b; Zhang et al., 2013), leading to economic loss and environmental pollution (Geng et al., 2015; Ju et al., 2009). How to reduce N loss has become a focus of worldwide concern.

Application of slow- or controlled-release urea is a possible option to alleviate N loss (Grant et al., 2012; Zhang et al., 2009). Slow- or controlled-release urea mainly reduces N loss via the functional materials added to urea or the polymerization of urea (Li et al., 2015; Ni et al., 2013; Yamamoto et al., 2016). For instance, stabilized urea amended with a nitrification inhibitor or urease inhibitor such as N-(*n*-butyl)thiophosphoric triamide (NBPT), polyphenol, and pomegranate fruit powder, reduces ammonia emission and increases fertilizer N retention (Chagas et al., 2016; Kiran and Patra, 2003; Li et al., 2015; Sabahi et al., 2017); while coated urea, such as polyethylene-coated urea and sulfur-coated urea, reduces the N release rate via the functional materials coated on the surface of urea granules (Gao et al., 2015; Ni et al., 2013). However, the cost of slow- or controlled-release urea is high, limiting its application in field crop production (Naz and Sulaiman, 2016; Ni et al., 2013; Zheng et al., 2016). Furthermore, some coated materials, such as polyethylene, carry a risk of pollution, while the production of some eco-friendly plant nitrification or urease inhibitors struggle to meet the huge demand for fertilizer production.

It is necessary to develop slow- or controlled-release urea, which is produced with eco-friendly materials with ample supply, and can

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http://dx.doi.org/10.1016/j.fcr.2017.07.005
Received 29 April 2017; Received in revised form 6 July 2017; Accepted 7 July 2017
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reduce N loss with acceptable cost. Matrix-based fertilizer (MF) is a novel, low-cost, slow-release fertilizer. MFs mainly consist of matrix-based urea (MU) and matrix-based compound fertilizer, which are produced based on similar mechanisms and matrix materials (Bai et al., 2017; Ni et al., 2013). MU reduces N loss via the functional materials added to urea granules (Golbashy et al., 2017; Ni et al., 2013; Qin et al., 2012). The functional materials mainly consist of silicate minerals (such as bentonite, attapulgite, and montmorillonite) and organic polymers (such as polyacrylamide) (Golbashy et al., 2017; Qin et al., 2012; Xiang et al., 2014; Zhang et al., 2009). The performance of silicate minerals is highly dependent on their dispersion capacity. Natural silicate minerals tend to aggregate with each other, leading to low dispersion capacity (Chen and Shu, 2012; Xiang et al., 2014). Hence, natural silicate minerals are usually modified using physical and chemical methods (such as high-energy electron beam irradiation and sodium-activation conversion) to enhance their dispersion capacity (Qin et al., 2012; Xiang et al., 2014).

MF is a novel slow-release fertilizer developed in the past 10 years, and mainly consists of MU and matrix-based compound fertilizer (Bai et al., 2017; Chen and Shu, 2012; Golbashy et al., 2017; Ni et al., 2013; Qin et al., 2012). To date, MF has mainly been produced and applied in seven provinces in China, with Xinlianxin being the largest producer (Fig. 1). MF is produced with eco-friendly silicate minerals and organic polymers. Ni et al. (2013) found that MU has a three-dimensional lattice structure and a lower specific surface area than CU, which is partly responsible for its lower N release rate. Cai et al. (2014) reported MF forms a micro-nano network in soils, which can adsorb nutrients via hydrogen bonds, surface tension, viscous force, and molecular force. Golbashy et al. (2017) also reported that MU has a good slow-release behavior. The effects of MF on field crop yields have been tested in some studies (Bai et al., 2017; Liu et al., 2016; Xu et al., 2014; Zhou et al., 2016). Although slow-release fertilizers are beneficial to crop production, their actual effects are highly affected by field conditions, such as various meteorological conditions in different growing seasons (Grant et al., 2012; Guo et al., 2016). Therefore, the effects of MFs on crop yields should be tested via field experiments conducted in multiple seasons or environments. To determine whether MU is suitable for field maize production, we need detailed information about its effects and mechanisms on grain yields, as well as whether the profitability is acceptable.

Previous studies have provided valuable information about the production of MU and the effects of MU on crop yields. However, most field experiments have focused on crop yield performance, with little explanation about possible mechanisms; while most laboratory experiments have focused on the chemical process or microscopic characterization, without field crop validation. We conducted a 2-year field experiment and two laboratory trials with the following objectives: (i) to investigate the effects of MU on N loss, field maize yields, and N use efficiency, and elucidate the possible mechanisms; and (ii) to assess whether the profits from MU application are acceptable to maize growers.

Fig. 1. Major producers of matrix-based fertilizers in China.

2. Materials and methods

2.1. Site and materials

A 2-year field experiment was conducted during 2015 (Jun 20–Sep 21) and 2016 (Jun 23–Sep 23) maize growing seasons under rain-fed conditions. The study site (31°53′55″ N, 117°10′22″ E; 27 m above sea level) was located on the experimental farm of Hefei Institutes of Physical Science, Chinese Academy of Sciences, China. During the 2015 and 2016 seasons, the mean air temperature was 27.4 and 27.3 °C, and rainfall totaled 465.3 and 369.4 mm, respectively. The soil was classified as a yellow clunamon soil, with selected properties of the top soil layer (0–20 cm) as: sand (20–2000 μm) 9.4%, silt (2–20 μm) 41.8%, clay (< 2 μm) 48.8%, organic C 10.4 g kg^{-1}, total N 0.96 g kg^{-1}, pH (soil:water, 1:2.5) 6.3, field capacity 26.8%. Prior to the current study, a maize (*Zea mays* L.) – winter wheat (*Triticum aestivum* L.) rotation had been used for 2 years without fertilization and irrigation. The maize cultivar was *Zea mays* L. 'Fengnuo476'.

N fertilizer was CU (46.6% N) and MU (43.2% N, Xinlianxin Co., Ltd., Henan); P fertilizer was single super phosphate (16% P_2O_5, Luke Co., Ltd., Shandong); K fertilizer was potassium sulfate (50% K_2O, Hongsifang Co., Ltd., Anhui). The MU was produced by adding matrix materials to urea with the tower granulation method. The matrix materials were a mixture of modified bentonite and organic polymer (Ni et al., 2013). Briefly, oven-dried matrix materials (particle diameter: 0.05–0.07 mm) were sprayed into molten urea (at about 130–135 °C) at a proportion of 5%. The mixture of molten urea and matrix materials was then sprayed into a high tower to produce MU granules. The MU granules that fell to the bottom of the tower were sieved (granules with diameter of 2.50–2.80 mm) and then packed with waterproof bags. MU granules were similar to CU granules, but with lower transparency (Fig. 2b–c). Powder of matrix material, CU, and MU were all white or light gray (Fig. 2d–f). When soaked in water, matrix material formed aggregates (Fig. 2h and j), and the aggregates were partly broken when washed several times with water (Fig. 2k and m). CU dissolved rapidly when washed with water, with a small quantity of urea crystals left (Fig. 2l). In contrast, MU formed aggregates of urea and matrix material, which inhibited the dissolution of urea, with a considerable amount of urea crystals left (Fig. 2m–n).

2.2. Experimental design

2.2.1. Field experiment

The field experiment consisted of three treatments, i.e., the CK, CU treatment, and MU treatment. Treatments were arranged in a randomized block design with three replicates. Each plot was 5 × 10 m^2 with 1.5-m gaps between blocks. In both CU and MU treatments, urea was applied at 195 kg N ha^{-1}. In all treatments, P fertilizer was applied at 45 kg P_2O_5 ha^{-1} and K fertilizer at 45 kg K_2O ha^{-1}. All fertilizers were applied as a basal fertilization before sowing maize. Fertilizers were broadcast and then incorporated into 0–20-cm soil layers. Then, maize was sown to a 5-cm depth with a 30-cm spacing between plants in each planting row. There was a 40-cm spacing between planting rows. No side-dressing or irrigation was applied during the maize growing seasons. Between maize growing seasons, winter wheat was planted without irrigation and fertilization.

2.2.2. Leaching experiment

The leaching experiment consisted of two urea treatments, i.e., CU treatment and MU treatment. A leaching tube (diameter 3.2 cm; height 14.5 cm) was filled with 60 g oven-dried quartz sand (0.25–0.42 mm), then urea granules equivalent to 0.93 g N were added, and thereafter covered with another 60 g oven-dried quartz sand. Distilled water was pumped into the leaching tube using a peristaltic pump at 90 rpm. Leaching samples were collected 12 times, 25 mL each. Each treatment was tested with five replicates.

2.2.3. Ammonia emission experiment

The ammonia emission experiment consisted of three treatments, i.e., the CK, CU treatment, and MU treatment. An emission chamber (diameter 15 cm; height 22 cm; volume 4 L) was filled with 800 g air-dried soil (< 2 mm) and 240 mL distilled water; 24-h later, urea granules equivalent to 2.32 g N were broadcast on the soil surface, then covered with 200 g air-dried soil, and thereafter 60 mL distilled water was added. The emission chambers were then incubated at 25 °C. Ammonia emission samples were collected with the acid trapping method. Briefly, gas was pumped into the emission chamber with a gas pump during 02:00–02:20, 08:00–08:20, 14:00–14:20, and 20:00–20:20 every day, and ammonia from each emission chamber was

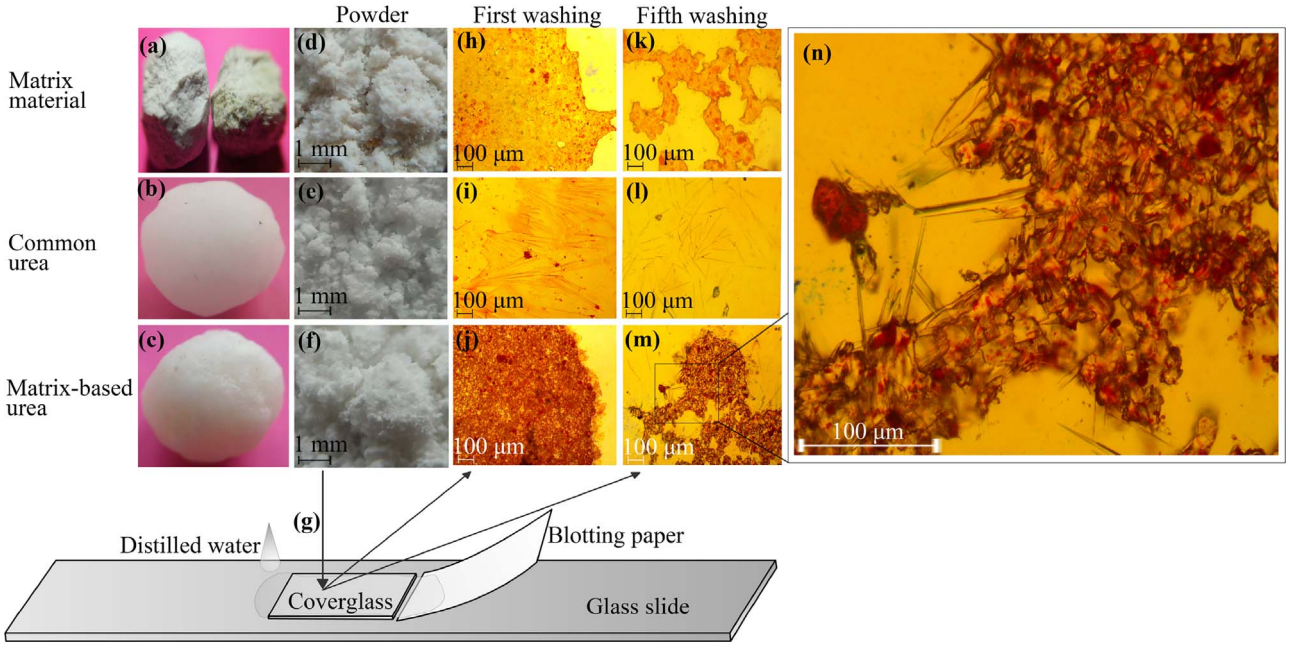


Fig. 2. Microscopic characterization of slow-release mechanisms of matrix-based urea. (a) matrix material minerals; (b–c) granules of common urea and matrix-based urea; (d–f) powder; (g) microscopic test (each powder was stained with 1 mg mL^{-1} methyl red, then washed five times with distilled water, and air-dried for observation); (h–j) micrograph after the first washing; (k–n) micrograph after the fifth washing.

trapped with 100 mL 20 g L^{-1} boric acid in a trapping chamber (diameter 7 cm; height 10 cm; volume 0.4 L). Emission samples were collected every 3 days until the 30th day after incubation. Each treatment was tested with five replicates.

2.3. Sampling and lab analysis

Grain yield and biomass were determined by harvesting the entire plot, excluding border rows, at maturity. Subsamples of grains and stalks were oven-dried at 105 °C for 30 min and then at 80 °C for 72 h to determine moisture (Yao et al., 2007). Oven-dried subsamples were ground and pass through a 0.15-mm sieve, and used for N analysis. The total N concentration of grains and stalks was determined using a continuous flow analyzer (AA3, Bran + Luebbe, Germany) after wet digestion with H_2SO_4-H_2O_2 (Kalra, 1998). Grain and stalk yields (kg ha^{-1}) were multiplied by the grain and stalk N concentration (mg N kg^{-1}), respectively, to calculate plant N accumulation (kg N ha^{-1}), as described by Salvagiotti et al. (2009). Twenty ears were randomly collected from each plot and grain number per ear was determined. The 1000-grain weight was determined using an automatic seed-counting system (Tuopu Co., Ltd., Zhejiang) with three replicates.

Ten plants were collected from each treatment at the silking stage and plant height, leaf area, and root area were measured. Plant height was determined with a ruler. Leaf area was measured using the WinFOLIA leaf analysis system, while root area was measured using the WinRHIZO root analysis system (Regent Co., Ltd, Canada). Five ear leaves were collected from each plot, cut into pieces, and mixed thoroughly to provide a single sample for the determination of chlorophyll *a*, chlorophyll *b*, carotenoid, nitrate reductase (NR), and glutamine synthetase (GS). Concentrations of chlorophyll *a*, chlorophyll *b*, and carotenoid were measured as described by Feng et al. (2009). The activity of NR and GS was measured as described by Sinha et al. (2015).

Five soil cores from the 0–20 cm soil layer were collected (in a W shape) from each plot, and then bulked to provide a single sample to analyze the concentration of available N (Stroud et al., 2010). Briefly, a 20 g soil sample was extracted with 200 mL 1 M KCl solution, and available N ($=NH_4^+ - N + NO_3^- - N$) in the extracts was then measured using a continuous flow analyzer (AA3, Bran + Luebbe, Germany) as described by Yang et al. (2015b). Urea-N in leaching samples was determined using a spectrophotometer (Lambda 35, PerkinElmer Co., Ltd., US) as described by Ni et al. (2013). The N in emission samples was measured using the titration method with 0.005 M H_2SO_4 as described by Han et al. (2014).

2.4. Calculations and statistical analyses

Agronomic efficiency and apparent recovery efficiency were given as (Fageria et al., 2014):

$$AE = (GY_{urea} - GY_{ck})/NAR, \quad (1)$$

$$ARE = (NA_{urea} - NA_{ck})/NAR, \quad (2)$$

where *AE* is agronomic efficiency (kg kg^{-1} N); GY_{urea} is grain yield in the urea-fertilized treatment (kg ha^{-1}); GY_{ck} is grain yield in CK (kg ha^{-1}); *NAR* is N application rate (kg N ha^{-1}); *ARE* is apparent recovery efficiency (%); NA_{urea} is N accumulation in the urea-fertilized treatment (kg N ha^{-1}); NA_{ck} is N accumulation in CK (kg N ha^{-1}).

N leaching ratio was calculated as:

$$NLR = N_{leaching}/N_{urea} \times 100\%, \quad (3)$$

where *NLR* is N leaching ratio (%); $N_{leaching}$ is the N content in leaching sample (g N); N_{urea} is the N content in applied urea, i.e., 0.93 g N.

Ammonia emission from applied urea was given as:

$$E_{urea} = E_{treat} - E_{ck}, \quad (4)$$

where E_{urea} is ammonia emission from applied urea (mg N); E_{treat} is ammonia emission in urea treatment (mg N); E_{ck} is ammonia emission in CK (mg N).

Ammonia emission ratio was calculated as:

$$ER = E_{urea}/N_{urea} \times 100\%, \quad (5)$$

where *ER* is the ammonia emission ratio (%); E_{urea} is ammonia emission from applied urea (mg N); N_{urea} is the N content in applied urea, i.e., 2.32 g N.

A first-order kinetic model was used to describe the characteristics of N leaching and ammonia emission as (Zhang et al., 2009):

$$N_t = N_o\ (1 - e^{-bx}), \quad (6)$$

where N_t is the cumulative N leaching ratio or cumulative ammonia emission ratio (%); N_o is the maximum cumulative N leaching ratio or cumulative ammonia emission ratio (%); b is the coefficient of the N leaching ratio or ammonia emission ratio; *x* is the leaching sequence number (1–12) or emission sampling sequence number (1–10).

Urea cost, maize income, and net profit were calculated as (Guo et al., 2017):

$$U_{cost} = U_{input} \times U_{price}, \quad (7)$$

$$M_{income} = M_{yield} \times M_{price}, \quad (8)$$

$$NP = M_{income} - U_{cost} - O_{cost}, \quad (9)$$

where U_{cost} is urea cost (USD ha^{-1}); U_{input} is urea input (kg N ha^{-1}); U_{price} is urea price (USD kg^{-1} N); M_{income} is maize income (USD ha^{-1}); M_{yield} is maize yield (kg ha^{-1}); M_{price} is maize price (USD kg^{-1}); *NP* is net profit (USD ha^{-1}); O_{cost} is other costs besides urea cost (USD ha^{-1}), i.e., costs from seeds, P fertilizer, K fertilizer, and field management. The value of O_{cost} is not discussed, since it was the same with the CU and MU treatments.

Profit increment with MU compared with CU was given as (Guo et al., 2017):

$$PI = (M_{income,MU} - U_{cost,MU} - O_{cost}) - (M_{income,CU} - U_{cost,CU} - O_{cost}), \quad (10)$$

$$PI = (M_{income,MU} - U_{cost,MU}) - (M_{income,CU} - U_{cost,CU}), \quad (11)$$

where *PI* is the profit increment with MU compared with CU (USD ha^{-1}); $M_{income,MU}$ is maize income in MU (USD ha^{-1}); $U_{cost,MU}$ is urea cost in MU (USD ha^{-1}); $M_{income,CU}$ is maize income in CU (USD ha^{-1}); $U_{cost,CU}$ is urea cost in CU (USD ha^{-1}).

Means were compared using the least significant difference (LSD) test ($\alpha = 0.05$) with SAS 9.1 (SAS Institute Inc., NC, US).

3. Results

3.1. Grain yield and biomass

Compared with CU and CK, MU increased grain yield, grain number per ear, 1000-grain weight, and biomass (Table 1). During 2015, grain yield in MU was 6.3 and 48.9%, grain number per ear in MU was 3.7 and 20.4%, 1000-grain weight in MU was 2.6 and 23.8%, and biomass in MU was 12.6 and 58.5% greater than in CU and CK, respectively. During 2016, grain yield in MU was 14.7 and 65.8%, grain number per ear in MU was 8.5 and 37.5%, 1000-grain weight in MU was 5.9 and 20.9%, and biomass in MU was 15.7 and 69.9% greater than in CU and CK, respectively (Table 1).

3.2. Agronomic efficiency and apparent recovery efficiency

Compared with CU, MU increased agronomic efficiency (AE) and apparent recovery efficiency (ARE) (Table 2). During 2015, AE and ARE were 22.9 and 33.9% greater in MU than in CU, respectively. During 2016, AE and ARE were 48.2 and 34.9% greater in MU than in CU,

Table 1
Effects of matrix-based urea on grain yield (14% moisture), grain number per ear, 1000-grain weight (14% moisture), and biomass. CK represents the control test without urea application. Values are mean ± standard deviation (SD; $n = 3$). Means with the same letters in the same column and season are not significantly different ($P > 0.05$).

Growing season	Treatment	Grain yield (kg ha^{-1})	Grain number per ear	1000-grain weight (g)	Biomass (kg ha^{-1})
2015	CK	5846 ± 519 ^{b}	380.7 ± 20.0 ^{b}	161.6 ± 14.0 ^{b}	10604 ± 456 ^{b}
	Common urea	8189 ± 287 ^{a}	441.9 ± 20.8 ^{a}	195.0 ± 6.8 ^{a}	14931 ± 2370 ^{a}
	Matrix-based urea	8703 ± 221 ^{a}	458.2 ± 29.5 ^{a}	200.0 ± 7.7 ^{a}	16806 ± 1746 ^{a}
2016	CK	4158 ± 177 ^{c}	305.4 ± 34.7 ^{b}	163.0 ± 7.1 ^{b}	9292 ± 282 ^{c}
	Common urea	6007 ± 283 ^{b}	387.0 ± 31.4 ^{a}	186.1 ± 13.4 ^{a}	13651 ± 104 ^{b}
	Matrix-based urea	6892 ± 179 ^{a}	419.8 ± 12.7 ^{a}	197.1 ± 11.3 ^{a}	15790 ± 49 ^{a}

Table 2
Effects of matrix-based urea on agronomic efficiency and apparent recovery efficiency. Values are mean ± SD ($n = 3$). Means with the same letters in the same column and season are not significantly different ($P > 0.05$).

Growing season	Treatment	Agronomic efficiency (kg kg^{-1} N)	Apparent recovery efficiency (%)
2015	Common urea	10.5 ± 1.1 ^{a}	25.4 ± 2.8 ^{b}
	Matrix-based urea	12.9 ± 1.3 ^{a}	34.0 ± 2.7 ^{a}
2016	Common urea	8.3 ± 0.5 ^{b}	24.1 ± 0.5 ^{b}
	Matrix-based urea	12.3 ± 0.6 ^{a}	32.5 ± 0.4 ^{a}

respectively (Table 2).

3.3. Morphological and physiological traits

3.3.1. Plant height, leaf area and root area

Compared with CU and CK, MU increased plant height, leaf area, and root area (Fig. 3). During 2015, plant height in MU was 10.5 and 32.9%, leaf area in MU was 2.5 and 93.8%, and root area in MU was 1.2 and 81.0% greater than in CU and CK, respectively. During 2016, plant height in MU was 18.1 and 47.0%, leaf area in MU was 11.7 and 87.0%, and root area in MU was 11.5 and 83.9% greater than in CU and CK, respectively (Fig. 3).

3.3.2. Concentrations of chlorophyll and carotenoid

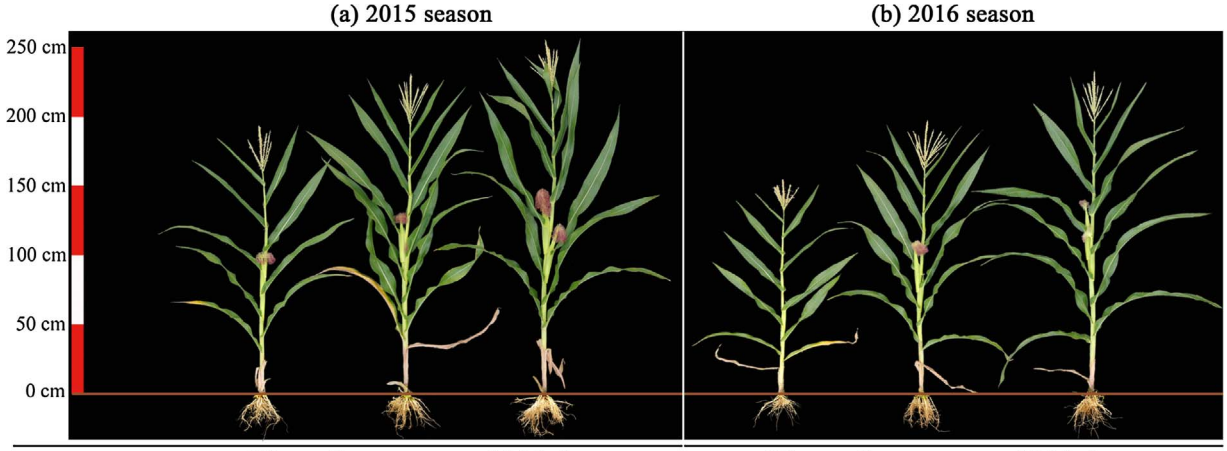
Compared with CU and CK, MU increased the concentrations of chlorophyll *a*, chlorophyll *b*, and carotenoid in ear leaves (Table 3). During 2015, chlorophyll *a* in MU was 38.7 and 79.9%, chlorophyll *b* in MU was 27.3 and 72.5%, and carotenoid in MU was 108.0 and 264.1% greater than in CU and CK, respectively. During 2016, chlorophyll *a* in MU was 19.8 and 158.2%, chlorophyll *b* in MU was 30.3 and 99.0%, and carotenoid in MU was 3.4 and 108.5% greater than in CU and CK, respectively (Table 3).

Table 3
Effects of matrix-based urea on chlorophyll *a*, chlorophyll *b*, and carotenoid concentration in ear leaves. CK represents the control test without urea application. Values are mean ± SD ($n = 3$). Means with the same letters in the same column and season are not significantly different ($P > 0.05$).

Growing season	Urea treatment	Chlorophyll *a* (mg g^{-1} FW)	Chlorophyll *b* (mg g^{-1} FW)	Carotenoid (mg g^{-1} FW)
2015	CK	0.914 ± 0.120 ^{b}	0.211 ± 0.070 ^{a}	0.064 ± 0.030 ^{b}
	Common urea	1.185 ± 0.199 ^{b}	0.286 ± 0.076 ^{a}	0.112 ± 0.045 ^{b}
	Matrix-based urea	1.644 ± 0.126 ^{a}	0.364 ± 0.114 ^{a}	0.233 ± 0.015 ^{a}
2016	CK	0.627 ± 0.016 ^{c}	0.203 ± 0.029 ^{c}	0.130 ± 0.017 ^{b}
	Common urea	1.351 ± 0.019 ^{b}	0.310 ± 0.017 ^{b}	0.262 ± 0.007 ^{a}
	Matrix-based urea	1.619 ± 0.018 ^{a}	0.404 ± 0.004 ^{a}	0.271 ± 0.012 ^{a}

3.3.3. Activity of nitrate reductase and glutamine synthetase

Compared with CU and CK, MU increased the activity of NR and GS in ear leaves (Table 4). During 2015, NR activity in MU was 29.3 and 73.6%, and GS activity in MU was 18.6 and 79.8% greater than in CU and CK, respectively ($P < 0.05$). During 2016, NR activity in MU was



	CK	Common urea	Matrix-base urea	CK	Common urea	Matrix-base urea
Plant height (cm)	192.4 c	231.5 b	255.7 a	154.4 c	192.2 b	226.9 a
Leaf area (cm^2 plant^{-1})	3052 b	5773 a	5915 a	2883 c	4829 b	5392 a
Root area (cm^2 plant^{-1})	282.5 b	505.1 a	511.3 a	302.1 b	498.2 a	555.5 a

Fig. 3. Effects of matrix-based urea on plant height, leaf area, and root area at the silking stage during the 2015 (humid) and 2016 (dry) seasons. CK represents the control test without urea application. Means with the same letters in the same season are not significantly different ($n = 10$, $P > 0.05$).

Table 4
Effects of matrix-based urea on the activity of nitrate reductase and glutamine synthetase in ear leaves. CK represents the control test without urea application. Values are mean ± SD (n = 3). Means with the same letters in the same column and season are not significantly different (P > 0.05).

Growing season	Treatment	Nitrate reductase (μg NO_2^- g^{-1} FW h^{-1})	Glutamine synthetase (A_{540} mg^{-1} protein h^{-1})
2015	CK	17.8 ± 1.0 ^{c}	12.4 ± 0.6 ^{c}
	Common urea	23.9 ± 3.8 ^{b}	18.8 ± 0.4 ^{b}
	Matrix-based urea	30.9 ± 2.1 ^{a}	22.3 ± 1.0 ^{a}
2016	CK	14.4 ± 0.3 ^{c}	13.0 ± 0.5 ^{c}
	Common urea	20.7 ± 0.3 ^{b}	18.1 ± 0.3 ^{b}
	Matrix-based urea	27.2 ± 0.3 ^{a}	21.6 ± 1.4 ^{a}

31.4 and 88.9%, and GS activity in MU was 19.3 and 66.2% greater than in CU and CK, respectively (P < 0.05) (Table 4).

3.4. N availability in soil

Compared with CU and CK, MU increased the available N concentration in the 0–20-cm top soil layer (Table 5). During 2015, the available N concentration in MU was 9.3 and 32.9% greater than in CU and CK, respectively (P < 0.05). During 2016, the available N concentration in MU was 21.3 and 40.6% greater than in CU and CK, respectively (P < 0.05) (Table 5).

3.5. N leaching and ammonia emission

3.5.1. N leaching

Differences in leaching were observed between CU and MU (Fig. 4). At the first leaching, the N leaching ratio (NLR) with CU (80.3%) was greater than that with MU (24.3%). At the second leaching, the NLR was similar with CU (16.9%) and MU (14.9%); however, the cumulative NLR with CU reached 97.2%, while that with MU was only 39.2%. From the third to the twelfth leaching, the NLR with MU (1.6–8.4%) was consistently greater than that with CU (0–1.0%), and the cumulative NLR with MU increased from 47.6 to 79.8%, while that with CU remained stable (from 98.2 to 98.4%) (Fig. 4).

The cumulative N leaching ratio under both urea treatments was described by a first-order kinetic model (P < 0.0001). The model showed that the maximum cumulative N leaching ratio in MU (79.3%) was lower than that in CU (98.5%), while the coefficient of N leaching ratio in MU (0.30) was also lower than that in CU (1.73) (Fig. 4b).

3.5.2. Ammonia emission

Differences in ammonia emission were observed between CU and MU (Fig. 5). At 1–18 days after application (DAP), the ammonia emission ratio (ER) with CU (0.5–4.6%) was consistently greater than that with MU (0.4–3.0%). At 18 DAP, the cumulative ER with CU reached 10.7%, while that with MU was 7.4%. At 19–30 DAP, the ER with MU (0.10–0.29%) was greater than that with CU (0.01–0.28%). At 30 DAP, the cumulative ER with CU reached 11.2%, while that with MU was 8.1% (Fig. 5).

Table 5
Effects of matrix-based urea on the available N concentration (mg N kg^{-1}) in the 0–20-cm top soil layer at the silking stage. CK represents the control test without urea application. Values are mean ± SD (n = 3). Means with the same letters in the same season are not significantly different (P > 0.05).

Treatment	2015 season	2016 season
CK	15.8 ± 0.5 ^{c}	14.6 ± 0.6 ^{c}
Common urea	19.2 ± 0.5 ^{b}	16.9 ± 0.6 ^{b}
Matrix-based urea	21.0 ± 0.9 ^{a}	20.5 ± 0.4 ^{a}

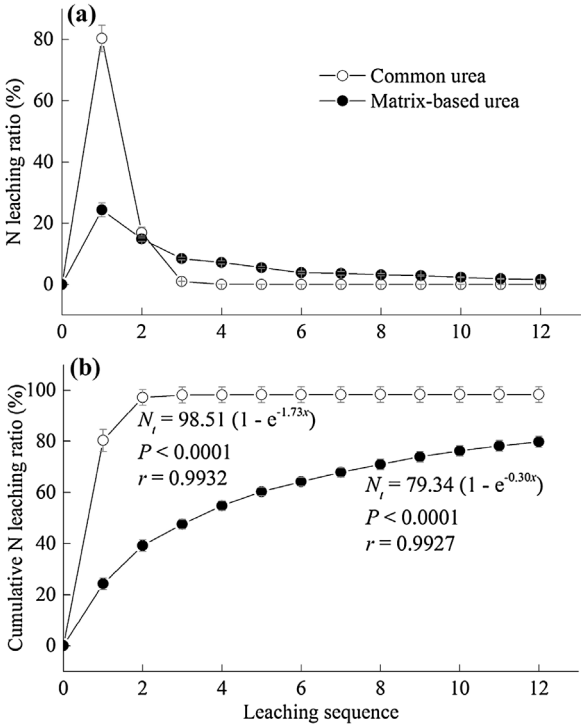


Fig. 4. Characterization of N leaching with common urea and matrix-based urea. Each treatment was leached 12 times (25 mL each time) with distilled water. Error bars represent the standard deviation (n = 5). N leaching ratio = N in leaching sample/N in applied urea * 100%, where, N in applied urea is 0.93 g N. The cumulative N leaching ratio was described by a first-order kinetic model as: $N_t = N_o$ (1–e^{-bx}), where, N_t is the cumulative N leaching ratio (%); N_o is the maximum cumulative N leaching ratio (%); b is the coefficient of N leaching ratio; x is the leaching sequence number (1–12).

The cumulative ammonia emission ratio under both urea treatments was described by a first-order kinetic model (P < 0.0001). The model showed that the maximum cumulative ammonia emission ratio with MU (8.1%) was lower than that with CU (11.3%), while the coefficient of ammonia emission ratio with MU (0.42) was also lower than that with CU (0.47) (Fig. 5b).

3.6. Profits from matrix-based urea application

Application of MU increased maize production profitability compared with CU (Table 6). The urea cost in MU increased by 30.6 and 30.2 USD ha^{-1}, and the maize income in MU increased by 149.3 and 206.2 USD ha^{-1} compared with CU during 2015 and 2016, respectively. Hence, application of MU increased profits by 118.7 and 176.0 USD ha^{-1} compared with CU during 2015 and 2016, respectively (Table 6).

4. Discussion

4.1. Grain yield, biomass, agronomic efficiency, and apparent recovery efficiency

The findings of the current study confirmed the higher positive effects of MU on maize yields, biomass, agronomic efficiency, and apparent recovery efficiency compared with CU (Tables 1 and 2). Based on the results shown in Tables 3–5, it can be concluded that MU improved the availability of mineral N in soil during the advanced growth stages (silking) of maize, and improved the N nutrition status in maize plants. Furthermore, increasing N availability at advanced growth stages was associated with lower N availability at early stages when the

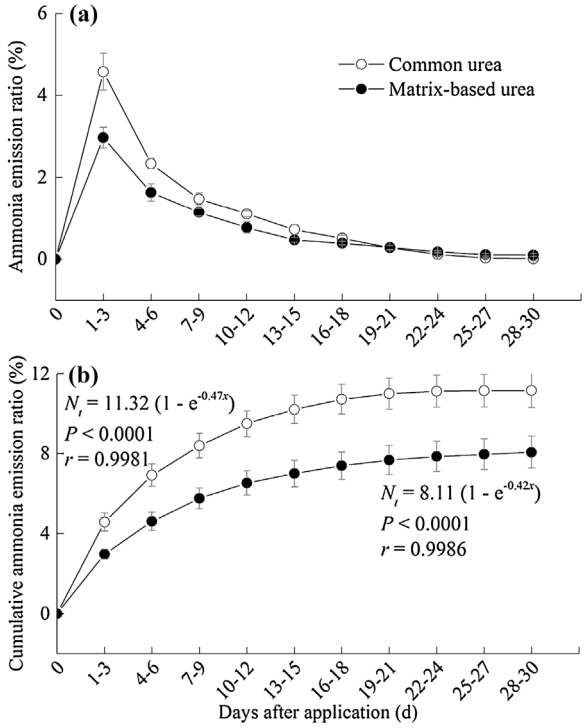


Fig. 5. Characterization of ammonia emission from common urea and matrix-based urea. Each treatment was measured 10 times at a 3-day interval. Error bars represent the standard deviation (n = 5). Ammonia emission ratio = N in the emission sample/N in applied urea * 100%, where, N in applied urea is 2.32 g N. The cumulative ammonia emission ratio was described by a first-order kinetic model as: $N_t = N_o\ (1–e^{-bx})$, where, N_t is the cumulative ammonia emission ratio (%); N_o is the maximum cumulative ammonia emission ratio (%); b is the coefficient of ammonia emission ratio; x is the emission sampling sequence number (1–10).

N need of the plants was low. In other words, MU as a N slow-release fertilizer synchronized the N supply with the crop N demand. Additionally, the positive effect of polyacrylamide matrix on the stability of soil structure and its effects on reducing phosphorus losses were also responsible for higher grain yield and biomass (Jiang et al., 2010; Mamedov et al., 2010). Similarly, Sun et al. (2015) and Zhou et al. (2016) reported that maize yield with MU treatment was 9.9–13.7% greater than with CU treatment. Jiang et al. (2016) and Zhou et al. (2016) reported that maize biomass with MF treatment was 6–13% greater than with CF treatment. Zhou et al. (2016) found that maize agronomic efficiency was 29–175% greater in MU than in CU, while maize apparent recovery efficiency was 64–104% greater in MU than in CU. It should be noted that the effects of MU on grain yields are also comparable with those of controlled-release urea (CRU), which increased grain yields by 6–26% compared with CU (Gao et al., 2015; Geng et al., 2015; Zheng et al., 2016).

4.2. Morphological and physiological traits, N availability, and N losses

Better plant development is responsible for greater maize yields and biomass with MU treatment (Fig. 3). Application of MU increased maize height and leaf area (Fig. 3). Similarly, Bai et al. (2017) and Sun et al. (2015) found that MF increased maize height by 1.3% and wheat height by 1.1–5.8% compared with common fertilizer (CF). Jiang et al. (2016) found that the leaf area of maize with MF treatment was 19.6% greater than with CF treatment. Greater plant height and leaf area with MU treatment favored maize growth, partly due to a higher ability to gain solar radiation for photosynthesis (Bai et al., 2017; Jiang et al., 2016). As maize root development was highly dependent on N supply (Li et al., 2016), differences in N release characteristics between MU and CU led to variations in maize root morphology (Fig. 3). MU increased the maize root area compared with CU (Fig. 3), which was beneficial to the uptake of water and nutrients. Furthermore, MU increased the concentration of chlorophyll and carotenoid in ear leaves (Table 3), and this was partly responsible for the greater biomass observed (Pagani and Echeverria, 2011). Moreover, MU enhanced N assimilation in maize plants (Table 4), which was beneficial to protein synthesis and favored plant growth (Geng et al., 2016). MU also improved reproductive growth in maize, i.e., MU resulted in greater grain number per ear and 1000-grain weight, which was responsible for the greater grain yield observed (Table 1). Jiang et al. (2016) and Sun et al. (2015) also reported that MF increased grain number per ear by 0.8–8.6% and 1000-grain weight by 7.5–12.3%, which was responsible for increases in maize yield. Bai et al. (2017) found that MF increased grain number per ear and 1000-grain weight, and thus, increased wheat yield.

Better plant development with the MU treatment is attributed to greater available N concentration in the top soil layers (Table 5), as a result of the lower risk of N leaching and ammonia emission (Figs. 4 and 5). Chen and Shu (2012) and Liu et al. (2016) also reported that the application of MF reduced N runoff and leaching by 20–50%, decreased ammonia emission by 17–32%, and thus increased soil available N concentrations. Lower N loss in MU is mainly due to the slow release of urea from matrix (Cai et al., 2014; Golbashy et al., 2017; Ni et al., 2013; Yamamoto et al., 2016) or due to the positive effect of polyacrylamide matrix on the aggregation and structure stability of soils (Jiang et al., 2010; Mamedov et al., 2010). A laboratory test revealed that matrix material and urea formed aggregates, which were beneficial for reducing N loss against water washing (Fig. 2). However, since the aggregates were partly broken when washed with water (Fig. 2), the performance of MU in reducing N loss was weaker than that of CRU. For example, cumulative ammonia emission under MU treatment was 72% of that under CU treatment (Fig. 5), while ammonia emission under CRU treatment was approximately 10% of that under CU treatment (Yang et al., 2013). Notably, although reducing the N release rate increases fertilizer N retention, the N release rate should not be overly reduced (Chagas et al., 2016; Li et al., 2015). For example, application of some CRUs led to yield loss, partly due to the delay in N release from CRU granules, which was unable to meet crop requirements during early growth stages (Grant et al., 2012; Zhou et al., 2016). In the

Table 6
Profit increments with matrix-based urea (MU) compared with common urea (CU). Urea cost = urea price * urea input, where, urea input is 195 kg N ha^{-1} in both treatments. Maize income = maize yield * maize price. Difference = value in MU – value in CU. Urea price and maize price were obtained from local distributors. Profit increment with MU compared with CU = difference of maize income – difference of urea cost.

Growing season	Treatment	Urea price (USD kg^{-1} N)	Urea cost (USD ha^{-1})	Maize yield (kg ha^{-1})	Maize price (USD kg^{-1})	Maize income (USD ha^{-1})	Maize income minus urea cost (USD ha^{-1})
2015	CU	0.517	100.8	8189.4	0.291	2383.1	2282.3
	MU	0.674	131.4	8703.6	0.291	2532.4	2401.0
	Difference		30.6			149.3	118.7
2016	CU	0.502	97.9	6007.0	0.233	1399.6	1301.8
	MU	0.657	128.1	6892.0	0.233	1605.8	1477.7
	Difference		30.2			206.2	176.0

current study, N leaching and ammonia emission under MU were estimated based on the results of laboratory experiments, and thus, field factors were not taken into consideration. Since N loss is related to field factors, such as soil moisture and soil temperature (Yang et al., 2015a), further studies conducted under field conditions are needed for a better understanding of N loss from MU.

4.3. Profits from matrix-based fertilizer application

Slow- or controlled-release urea has not been widely applied in field crop production, largely due to the high price, which is unacceptable to farmers (Naz and Sulaiman, 2016; Ni et al., 2013; Zheng et al., 2016). Therefore, although MU performed well at improving maize yields (Table 1), profitability is also of interest. Unlike materials used to coat some controlled-release fertilizers (CRFs), the silicate minerals in MFs are of lower cost (Golbashy et al., 2017). Compared with CU, the production of MU increased costs by about 4.4–7.3 USD t^{-1}, while that of CRU increased costs by 29–290 USD t^{-1} (Ni et al., 2013). Although the cost of MU is lower than that of CRU, it is still higher than that of CU (Table 6). The profitability of MU treatment should be at least equal to that in CU treatment. Our findings showed that although the cost of urea in MU treatment was approximately 30 USD ha^{-1} greater than that in CU treatment, maize income with the MU treatment was much higher than that with the CU treatment. Hence, application of MU increased profits compared with CU, especially in the dry season in 2016 (by 176 USD ha^{-1}) (Table 6). Chen and Shu (2012) and Xu et al. (2014) also found that application of MF increased profits from wheat production by 83–274 USD ha^{-1} compared with CF treatments. Overall, application of MU resulted in higher profits than application of CU, and thus, the relatively higher cost of MU will not limit its application in field crop production.

There are two ways to further reduce the high cost of slow- or controlled-release urea: (i) decreasing the application rate and (ii) applying a mixture of CU and slow- or controlled-release urea. Sun et al. (2015) found that reducing the application rate of MU by 20% produced the same maize yield as application of 100% CU. Liu et al. (2016) reported that MF applied at 77% of the local recommended fertilization dose was beneficial to wheat production, with lower N loss and greater wheat yield. Geng et al. (2015) reported that reducing the application rate of CRU by 30% produced the same rice yield as the application of 100% CU. Zheng et al. (2016) found that combining CU and CRU increased crop yields and decreased fertilizer cost. In the current study, MU performed well at increasing profit when applied at the same rate as CU (Table 6). For more cost-effective application strategies, further studies are needed to investigate the effects of MU on maize profit, when applied at lower rates or combined with CU.

It should be noted that MF is a novel slow-release fertilizer developed in the past 10 years. Although MF performs well at improving crop growth (Bai et al., 2017; Jiang et al., 2016; Liu et al., 2016; Xu et al., 2014) and reducing N loss (Chen and Shu, 2012; Liu et al., 2016; Zhou et al., 2016), and has been produced and applied in seven provinces in China (Fig. 1), there are no widely accepted criteria for MF. In contrast, the international standard for controlled-release fertilizer has been published (ISO 18644:2016), which will promote its development and application. To promote the development of MF, further studies are necessary to develop widely accepted criteria.

5. Conclusions

Due to aggregates formed in MU treatment, N loss via leaching and ammonia emission was reduced. Therefore, the available N in the top soil layers was greater with MU than with CU treatment. With greater soil available N, morphological traits such as plant height, leaf area, and root area increased with MU, while physiological traits, such as the concentration of chlorophyll and carotenoid, and the activity of NR and GS, were improved with MU. Grain number per ear and 1000-grain weight were also improved with MU, leading to greater grain yields, especially during the 2016 season when rainfall was limited. Agronomic efficiency (AE) and apparent recovery efficiency (ARE) were greater with MU than with CU. The profitability of maize production with MU was > 110 USD ha^{-1} greater than that with CU. Since MU reduced N loss and improved maize yields, AE, ARE, and profit, it is suitable for application in field maize production.

Acknowledgements

This study were supported by the National Natural Science Foundation of China (31601828), the National Key Research and Development Program of China (2017YFD0301302), and the Science and Technology Service Network Initiative of Chinese Academy of Sciences (KFJ-STS-QYZD-020, KFJ-STS-ZDTP-002). We appreciate the reviewers' comments and we thank Prof. Mancai Guo, Fengzhu Zou, Yingzhou Liu, Xianyong Meng, and Bentang Su for their help with statistical analyses.

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