Chemical Speciation & Bioavailability

ISSN: 0954-2299 (Print) 2047-6523 (Online) Journal homepage: https://www.tandfonline.com/loi/tcsb20

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To cite this article: Xiaojing Yu, Xiaofei Tian, Yanyan Lu, Zhiguang Liu, Yanle Guo, Jianqiu Chen, Chengliang Li, Min Zhang & Yongshan Wan (2018) Combined effects of straw-derived biochar and bio-based polymer-coated urea on nitrogen use efficiency and cotton yield, Chemical Speciation & Bioavailability, 30:1, 112-122, DOI: 10.1080/09542299.2018.1518730

To link to this article: https://doi.org/10.1080/09542299.2018.1518730

CHEMICAL SPECIATION & BIOAVAILABILITY
2018, VOL. 30, NO. 1, 112–122
https://doi.org/10.1080/09542299.2018.1518730

Combined effects of straw-derived biochar and bio-based polymer-coated urea on nitrogen use efficiency and cotton yield

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ABSTRACT
The interactive effects of straw-derived biochar and bio-based polymer-coated urea (BPCU) was examined with a pot experiment conducted in 2014 and 2015. Using a split-plot design, the main plot factor was the form of straw use and the sub-plot factor was the type of N fertilizer. The soil inorganic nitrogen (N), organic carbon and lint yield of biochar treatments were significantly higher than for straw treatments. Meanwhile, the BPCU treatments enhanced nitrogen use efficiency (NUE) and yield over urea treatments. Biochar combined with BPCU resulted in the highest lint yield, 14.3–108.2% increasing over the other treatments, with NUE 27.1–63.5% increased. We attributed this superior performance to the interactive effects between BPCU's controlled supply of N according to cotton's N requirements and biochar's functionalities in enhancing soil quality. Thus, the application of biochar and BPCU is a sustainable strategy to improve soil quality and increase cotton yield.

ARTICLE HISTORY
Received 7 July 2018
Accepted 27 August 2018

KEYWORDS
Biochar; straw; slow release fertilizer; Nitrogen use efficiency; cotton

1 Introduction

Straw is an important biological resource in agricultural production systems. Incorporation of crop straw into the soil has been widely recommended for sustaining soil organic matter and improving crop productivity [1]. However, ample results also indicated that incorporation of crop straw into the soil can significantly increase CH_4 emissions [2]. Moreover, soil microbes are prone to absorb N from the soil when straw is biologically decomposed, thus contributing to N deficiency in the early growth period [3]. Alternative and sustainable ways of using straw for soil management are needed to enhance soil quality while increasing crop yield.

Biochar is a carbon-rich material that is pyrolyzed from agricultural residues at moderately high temperatures. Because of its large specific surface area and rich functional groups, biochar has been widely recognized as a soil amendment with great benefit of improving soil quality. Adding biochar to croplands has also been proposed worldwide as a technically sound strategy to increase soil organic carbon stocks as part of climate change mitigation in agriculture [4–6]. This practice may also change soil N dynamics by altered transformation rates [7], thereby reducing N loss through runoff and leaching and increasing N availability to plants [8–10]. Many studies were conducted to examine the effect of biochar applications on soil fertility and crop yields [11,12]. The literature generally indicates that the effect of biochar application varied with the type of biochar applied, the experimental conditions such as the soil, crop, irrigation practices, and the length of biochar application. Very few studies were conducted to examine the effects of different fertilizers on the benefits of biochar application.

It is well known that controlled-release urea (CRU) synchronizes N release with crop N requirement [13], thereby enhancing crop yields and N-use efficiency [14,15]. However, the high manufacturing cost of CRUs has limited their use in most crops. The development of low-cost, renewable and biodegradable controlled-release fertilizer coatings will help improve N-use efficiency (NUE) and reduce the cost associated with CRU application. After a few years of study, we developed a new N fertilizer known as bio-based polymer-coated urea fertilizer (BPCU) [16], which is relatively inexpensive, biodegradable, and has a high N-use efficiency. However, the interactive effects between BPCU and biochar applications on soil properties and crop yield have not been reported.

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Supplementary data for this article can be accessed here.

In this study, we examined the combined effects of BPCU and cotton straw-derived biochar applications on N supply patterns, soil quality, as well as cotton growth and yield with a 2 years pot experiment under controlled conditions. The experiment employed a split-plot design, consisting of a main plot factor, which was the form of straw use (without straw or its biochar application, C0; straw application, straw; straw derived biochar application, biochar), and a sub-plot factor, the type of N fertilizer (without N fertilization, N0; uncoated urea, Urea; BPCU). We hypothesized that the N release characteristics of BPCU correspond well to the N requirements while biochar application increases soil nutrient status, and consequently, the combined effects of BPCU and biochar increases cotton yield and NUE significantly. The objectives of the study were (1) to determine changes in soil N contents and leaf chlorophyll fluorescence during cotton growth of different treatments; and (2) to study the combined effects of biochar and BPCU on NUE and cotton yield. These results will provide the needed scientific basis for innovations in fertilization technology to ensure that N fertilizer is efficiently used in cotton production while providing new directions for effective utilization of straw.

2 Materials and methods

2.1 *Experimental sites and materials*

The experiments were carried out in two cotton growth seasons (2014 and 2015) at the New Fertilizer Experiment Station of Shandong Agricultural University in Northeast China (36°20′N, 117°13′E). Cotton (*Gossypium hirsutum cv. Lu Yanmian 28*) was grown in clay pots (height of 0.50 m, top diameter of 0.50 m, and bottom diameter of 0.40 m). To allow drainage, a hole was placed at the bottom of each pot, and a plastic pallet was placed beneath the pots to prevent water loss. The soil, a Typic Hapludalf, according to the USDA classification, was collected from the adjacent cotton farmland. The soil texture was sandy loam with 56.97% sand, 31.05% silt, and 11.98% clay. The soil properties were as follows: pH value, 7.5; organic matter concentration, 7.6 g kg^{-1}; total N concentration, 0.8 g kg^{-1}; NO_3^-–N concentration, 17.7 mg kg^{-1}; NH_4^+–N concentration, 5.4 mg kg^{-1}; and available P and K concentrations, 27.1 and 94.2 mg kg^{-1}, respectively. The climate of the experimental area is temperate and monsoonal, and the weather data are presented in Supplementary Figure 1.

Cotton straw, collected from the field at the Shandong Agricultural University, was chopped and dried at 105°C for 24 h. Straw samples were milled and sieved to pass through a 0.25 mm mesh for analysis. The total C, N, P and K contents of the straw were 386.1, 5.4, 2.5 and 6.1 g kg^{-1}, respectively. Dried cotton straw was used for biochar production, which was conducted at a temperature of 450°C with a residence time of 2 h under oxygen-limited conditions (in N_2 atmosphere) followed by cooling to room temperature for 24 h. This process converted 36.5% of the straw mass to biochar. The biochar was sieved to 2 mm prior to use and analysis.

To achieve an identical BPCU (bio-based polymer-coated urea) with a release rate synchronized with cotton growth, the BPCU (40% N) used in this study was coated with liquefied cotton straw [16,17] and epoxy resin [18,19]. The total weight of the LCS (liquefied cotton straw) and epoxy resin coating accounted for 7.5% wt (6.0% of the LCS and 1.5% of the epoxy resin) of the urea fertilizer. The release longevity of N from BPCU in 25°C water was 3 months (Figure 1). The conventional fertilizer included urea (46% N), calcium superphosphate (14% P_2O_5) and potassium sulfate (50% K_2O) as N, P and K, respectively.

2.2 *Experimental design*

The experiment was set up as three complete blocks with a repetitive factorial split design in 2014 and 2015. The main plot factor was the form of straw use (without straw or its biochar application, C0; straw application, straw; straw derived biochar application, biochar), and the sub-plot factor was the type of N fertilizer (without N fertilization, N0; uncoated urea, Urea; bio-based polymer-coated urea, BPCU). All fertilizers were applied before the seeds were sown, and all plots received a basal application of 3.04–2.04–3.08 g N-P_2O_5-K_2O pot^{-1} and conducted with triple replicates and ranked in a randomized block design. To ensure that the nutrient content of the treatments was consistent, 160 g of straw or 75 g of biochar was applied; detailed information about the nutrients added with the straw or biochar is shown in Table 1.

All fertilizers and biochar (or straw) were homogeneously mixed with 30 kg of soil (dry-weight basis, 1-cm sieved). The mixture was packed into each pot before the seeds were sown. The pots were placed in a netted shed, allowing them to be exposed to the outside air temperature and environment. Five cotton seeds were directly planted into each pot, and seedlings were thinned to one per pot when they generally had three true leaves. All treatments were performed with the same field management; insect control and other agricultural measures were utilized as needed. After the cotton was harvested in 2014, all pots were moved indoors and the same procedure was followed for 2015.

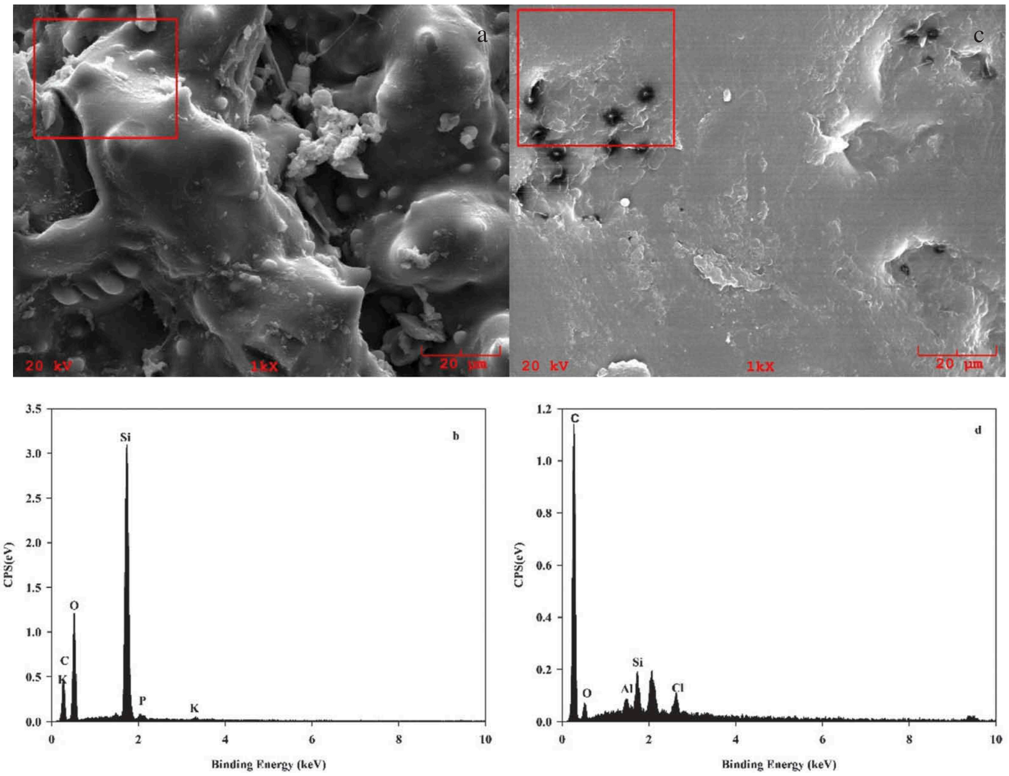

Figure 1. SEM/EDX analysis of BPCU and biochar: (a) SEM image of BPCU, (b) EDX spectrum of the square region inside the image of BPCU, (c) SEM image of biochar, (d) EDX spectrum of the square region inside the image of biochar.

Table 1. Nutrients application with fertilizer biochar/straw.

Type	Amounts (g pot^{-1})	C (g pot^{-1})	N (g pot^{-1})	P (g pot^{-1})	K (g pot^{-1})
straw	160.00	61.76	0.86	0.39	0.98
biochar	75.00	62.50	0.99	0.36	1.03

2.3 *Sampling and measurement*

In the 2015 experiment, soil samples were collected using a drill at the seeding stage, first-bloom stage, full boll-setting stage, initial boll-opening stage and full boll-opening stage on days 30, 56, 80, 120 and 150 after fertilization. Soil samples from three random points of each pot were mixed as a composite sample, of which 50 g were stored, and the remaining soil samples were refilled into the soil pores. The concentrations of NO_3^--N and NH_4^+-N (extraction with 0.01 M $CaCl_2$) of fresh soil samples were analysed in extract supernatant within 48 h after collection using an AA3-A001-02E Auto-Analyzer (Bran-Luebbe, Germany). The remaining soil sample was air-dried, ground and sieved through 2.0 mm and 0.25 mm sieves, respectively. The 2.0 mm soil samples were used for measuring soil pH, available P and available K contents while the 0.25 mm soil samples for measuring the organic C and total N contents.

The organic C content of the soil was measured using a total carbon analyser (Vario TOC, Elementar, Germany), and total N content was measured by the Kjeldahl digestion method. Soil pH was analysed at a 1:5 (w:v) ratio of soil to distilled water without CO_2 using a pH meter (PB-10, Sartorius AG, Germany). The soil-available K content was measured using the CH_3COONH_4 extraction method with a flame photometer. The soil-available P content was determined using the Olsen-P method based on the extraction of air-dried soil with 0.5 M $NaHCO_3$ at pH 8.5. The chlorophyll content (SPAD value) of the cotton function leaves was measured with a chlorophyll meter (SPAD-502; Minolta, Tokyo, Japan) when soil sampling was conducted at the seeding stage, first bloom stage, full boll setting stage, initial boll-opening stage and maturity stage in the days of 30, 56, 80, 120 and 150 after fertilization in 2015.

2.4 *Characterization of biochar and BPCU*

The specific surface area of biochar was determined using the Brunauer-Emmett-Teller (BET) method, and the cumulative volume of the pores and the pore-size distribution were analysed according to the N_2

adsorption data using the Barrett-Joyner-Halenda (BJH) method. A JSM-6360LV scanning electron microscope (SEM, JEOL) equipped with an X-ray energy dispersive X-ray spectrometer (EDX, Oxford) was used for morphological survey and elemental identification of the surface of biochar and BPCU. The FTIR spectra of biochar and BPCU coating were recorded on a Nicolet 380 Fourier transform infrared spectrometer. The N-release rates of BPCU in 25°C water was determined by the method of the 'National Standard of the People's Republic of China-Slow Release Fertilizer' [20]. The cumulative N release rates in soil conditions were measured using a weight loss method [21].

2.5 *Yield and N-use efficiency*

To measure cotton yield, each plant was manually harvested. All open bolls (>2 cm in diameter) were recorded as the number of bolls and sampled to measure the lint percentage. To calculate the biomass accumulation of different parts of the plant, fallen leaves and bolls were also collected from the initial-bloom stage onward. After all the cotton was harvested, the plants were separated into roots, branches, leaves, boll walls, fibres, and seeds and then oven-dried to a constant weight, and ground to pass through a 0.25 mm sieve. The plant samples were then digested with H_2SO_4 and H_2O_2 for determination of total plant N concentrations using the micro-Kjeldahl procedure [22]. The N uptake by plant was calculated from the N concentrations of the various plant parts. The total apparent N-use efficiency (NUE) was calculated with the following formula [23]:

$$\mathrm{NUE}(\%) = \frac{\text{N uptake in N treatment} - \text{N uptake in no N fertilizertreatment}}{\text{total applied fertilizer N in the N treatment}} \times 100\%$$

2.6 *Statistical analyses*

Analyses of variance and mean separation tests (Duncan's multiple range test, $p < 5\%$) were performed using Statistical Analysis System (SAS) version 9.2 (SAS Institute Cary, NC, USA, 2010).

3 Results

3.1 *Characteristics of biochar and BPCU*

The basic properties of the biochar were as follows: pH (H_2O), 10.3; CEC, 40.1 cmol kg^{-1}. The total C, N, P, K, Ca, and Mg contents were 890.5, 7.2, 4.3, 15.2, 3.20, and 1.13 g kg^{-1}, respectively. The SEM/EDX results indicated that the biochar was heterogeneous with a rough surface (Figure 1(a)), consisting of C, N, O, Si, K, and P elements (Figure 1(b)). The FTIR spectrum of biochar suggested that the biochar contained rich functional groups such as carboxyl and hydroxyl (Supplementary Figure 2). The specific surface area of the straw biochar was 255.50 m^2 g^{-1}. Biochar N_2 adsorption/desorption isotherms indicated that the biochar had a wide range of pores, mostly in nano-sizes (Supplementary Figure 3).

N release curves for BPCU under the laboratory condition (in water at 25°C) showed a linear release pattern from 0–50 days, accelerated from 50–90 days, and then decelerated from 90–150 days (Figure 2(a)). Under the soil condition, the N-release rate of BPCU was similar to that in the laboratory, low in the seeding stage (Figure 2(b)), accelerated from the squaring stage to the initial boll-opening stage, and finally slowed down during the harvest stage. These N release characteristics correspond well to the N requirements of cotton growth. Slight change in release rate in the soil was possibly due to the increased temperature and precipitation (Supplementary Figure 1). In the harvest stage, the N-release rate of BPCU reached 94.6%.

Satisfactory release patterns of BPCU were indicative of the effectiveness of the bio-based polymer coating derived from straw. The SEM image of BPCU revealed that the coating had a dense and relatively smooth surface along with tiny depressions, which facilitated initial release of N during the seeding

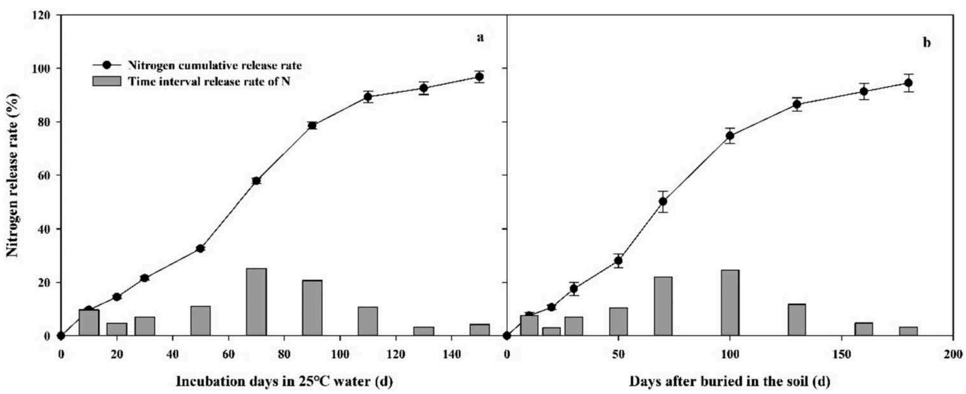

Figure 2. Time interval and accumulative release rate curves of controlled release urea in mesh bags buried in 25°C water (a) and the soil (b).

stage (Figure 1(c)). The EDX spectrum showed that the BPCU coating consist of C, O, Si, Cl and Al elements (Figure 1(d)). The bio-based nature of coating was further confirmed by the FTIR spectrum, which showed multiple functional groups of the material (Supplementary Figure 2).

3.2 *Effects on soil nutrients*

The form of straw use and the type of N fertilizer had a significant effect on the contents of soil inorganic N (NO_3^-N and NH_4^+-N) (Figure 3 and Supplementary Table 1). The contents of soil inorganic N without N fertilization treatments, including CK, straw and biochar treatment, were lowest in all growth stages, following the order of biochar>CK>straw. With different type of N fertilizer, biochar addition increased soil NO_3^-N contents relative to straw treatments, especially in the seeding stage. With the same form of straw, the NO_3^-N and NH_4^+-N contents were higher in the Urea treatments than in the BPCU treatments at the seeding stage. However, the opposite trend was observed after the bloom stage (except for the straw application treatments), indicating that a relatively steady N supply was provided by BPCU during the entire growing season, especially when combined with biochar application.

The contents of soil organic C and total N were considerably affected by the forms of N fertilizer and straw applied, and the pH values and C/N were affected by the types of carbon source (Table 2). With the same type of N fertilizer (Urea, BPCU), organic C of biochar treatments were remarkably higher than for straw treatments. With the same form of straw used, there was no significant difference in soil organic C between BPCU treatments and Urea treatments. The soil organic C of biochar combined with BPCU (biochar+BPCU) treatment was the highest (10.82 g kg^{-1}).

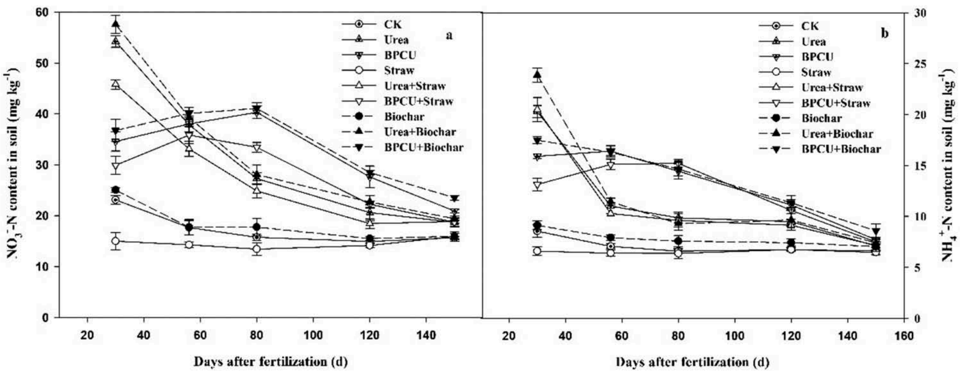

Figure 3. Changes of soil NO_3^-N (a) and NH_4^+-N (b) content during cotton growth.

Table 2. Chemical analyses of soil at the cotton harvest stage in 2015.

Treatment	Organic carbon (g kg^{-1})	Total N (g kg^{-1})	C/N	pH	Available P (mg kg^{-1})	Available K (mg kg^{-1})
Types of carbon sources						
C0	7.70 c	0.96 b	8.04 c	7.53 b	29.23 a	95.25 b
straws	8.81 b	0.97 b	9.11 b	7.52 b	29.32 a	97.39 ab
biochars	10.72 a	0.99 a	10.89 a	7.58 a	27.95 a	99.59 a
Types of nitrogen fertilizers						
N0	8.89 b	0.94 c	9.51 a	7.55 a	29.21 a	98.35 a
Ureas	9.07 ab	0.97 b	9.31 a	7.54 a	28.75 a	97.37 a
BPCUs	9.27 a	1.00 a	9.22 a	7.55 a	28.54 a	96.51 a
Carbon sources +Nitrogen fertilizers interaction						
CK	7.55 d	0.93 d	8.09 d	7.53 bc	29.64 a	97.74 ab
Urea	7.68 d	0.96 cd	8.03d	7.53 bc	29.26 a	95.27 ab
BPCU	7.88 d	0.98 bc	8.02 d	7.53 bc	28.80 a	92.75 b
straw	8.55 c	0.94 d	9.13 c	7.52 bc	29.84 a	97.51 ab
straw+Urea	8.79 bc	0.97 bc	9.04 c	7.51 c	29.07 a	96.70 ab
straw+BPCU	9.11 b	1.00b	9.15 c	7.54 bc	29.05 a	97.96 ab
biochar	10.58 a	0.94 d	11.3 a	7.61 a	28.16 a	99.81 ab
biochar+Urea	10.76 a	0.99 bc	10.87 ab	7.57 ab	27.93 a	100.13 a
biochar+BPCU	10.82 a	1.03 a	10.49 b	7.57 ab	27.77 a	98.83 ab
Source of variance						
C	<0.0001	0.0115	<0.0001	0.0002	0.2942	0.0726
N	0.0173	<0.0001	0.1450	0.3561	0.7634	0.5687
C × N Interaction	0.7742	0.1865	0.1687	0.1677	0.9988	0.7149

N0, without N fertilization, including CK, straw and biochar; Ureas, including Urea, straw+Urea and biochar+Urea; BPCU (bio-based polymer-coated urea), BPCUs, including BPCU, straw+BPCU, biochar+BPCU; C0, without straw or biochar addition, including CK, Urea and BPCU; straws, including straw, straw+Urea, straw+Biochar; biochars, including biochar, biochar+Urea, biochar+BPCU. Means followed by a same lowercase letter in the same column are not significantly different by Duncan's test ($p < 0.05$).

Within straw and biochar treatments, total N of BPCU treatments was higher than that of Urea treatments. There was no significant difference between biochar treatments and straw treatments, under different types of N fertilizer. The total N of biochar +BPCU treatment was the highest (1.03 g kg^{-1}). Within BPCU treatments, the total N of biochar +BPCU treatment was remarkably higher than for straw+BPCU. Within biochar treatments, the total N of biochar+BPCU treatment was significantly higher than for biochar+Urea. However, within straw treatments, the total N of straw+BPCU treatment was not significantly different from that of straw+Urea. In particular, biochar treatments caused a remarkable increase in soil pH compared with straw treatments. Although both the biochar and straw applications increased the soil-available K content, there was no significant difference in soil-available K contents between the BPCU and Urea treatments within the same straw use form. No significant difference in available P content was observed between treatments.

3.3 *Cotton growth and N-use efficiency*

Treatment effects on SPAD values varied with growth stages with peaks occurring largely 80–120 days after fertilization (Figure 4). While the SPAD value of the only straw application treatment was the lowest throughout all the growth stages, and during the squaring stage, SPAD value of biochar treatments was consistently higher than for the corresponding straw treatments. Meanwhile, the SPAD value of the BPCU treatments was higher than for the Urea treatments after the first-bloom stage. The combined biochar+BPCU treatment exhibited higher SPAD values in the last two growth stages (initial ball opening and maturity) than for all other treatments.

The lint yield was mainly influenced by the forms of fertilizer and straw use and their interactions

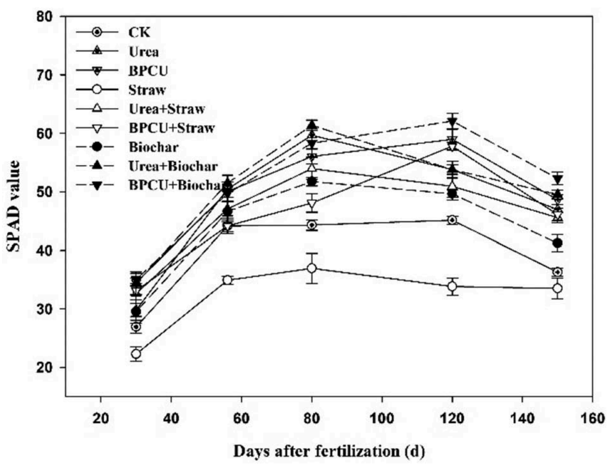

Figure 4. Changes of SPAD value during cotton growth.

(Table 3). Within the same type of Urea or BPCU, the boll number of biochar treatments was higher than for the straw treatments by 11.8–16.7% and 32.3–33.3% in 2014 and 2015. Within the same form of straw used, the boll number of BPCU treatments and Urea treatments was not significantly different in 2014 and 2015, except for biochar treatments in 2015. The different effects between years were probably because of different rainfall and temperature during the cotton growth period (in Supplementary Figure 1).

Within the same type of Urea or BPCU, the boll weight of biochar treatments was not significantly different from that of straw treatments. Similarly, within the same form of straw used, the boll weight of BPCU treatments and Urea treatments were not significantly different. However, the boll number and boll weight of biochar+BPCU treatment were the highest among all treatments. Lint percentage remained at 44.0% to 46.0% in all treatments. Within the same type of Urea or BPCU, the lint yield of the biochar treatments was higher than for the straw treatments by 13.7–16.0% and 37.5–39.9% in 2014 and 2015. The lint yield was significantly enhanced by biochar and N fertilization, especially under the combined application of biochar and BPCU treatment, which had 14.3–108.2% increase over the other treatments in 2014 and 2015.

For the same type of straw or biochar, the biomass of the BPCU treatments increased by 0.8–2.3% and 5.2–6.6% over that of the Urea treatments, in 2014 and 2015 (Table 4). Biochar+BPCU treatment's biomass caused 5.2–78.4% increase in 2014 and 2015 compared with the other treatments. Within the same type of Urea or BPCU, the boll number of biochar treatments was higher than for the straw treatments by 11.8–16.7% and 32.3–33.3% in 2014 and 2015.

Furthermore, within the same type of straw or biochar, the N-use efficiency (NUE) of the BPCU treatments increased significantly by 7.9–28.6% in 2014 and 14.0–54.6% in 2015, over that of the Urea treatments. Meanwhile, the NUE of the biochar application treatments was 23.1–30.6% higher than that of the straw treatments. The biochar+BPCU treatment achieved the highest NUE among all treatments, reaching up to 59.0–65.8%, which was equivalent to 27.1–63.5% increase over that of N fertilization treatments in 2014 and 2015 (Table 4).

4 Discussion

4.1 *Effects of biochar*

Biochar possesses excellent physical properties and nutrient regulation functionalities to promote plant growth and increase crop productivity [24]. The

Table 3. Yield and yield components of cotton with different treatments.

Treatment	2014				2015			
	Bolls (No plant^{-1})	Boll weight (g)	Lint percentage (%)	Lint yield (g plant^{-1})	Bolls (No plant^{-1})	Boll weight (g)	Lint percentage (%)	Lint yield (g plant^{-1})
Types of carbon sources								
C0	11.00 b	5.19 b	44.52 a	25.41 b	11.00b	5.33 a	44.92 a	26.50 b
straws	10.11 c	5.22 b	44.57 a	23.67 c	10.89 b	5.50 a	45.38 a	27.25 b
biochars	12.22 a	6.00 a	44.53 a	30.54 a	13.33 a	5.52 a	45.49 a	33.75 a
Types of nitrogen fertilizers								
N0	9.67 b	4.98 b	44.35 a	21.41 c	9.44 c	5.16 b	44.63 a	21.7 c
Ureas	11.78 a	5.38 a	44.63 a	28.21 b	12.22 b	5.51 ab	45.83 a	30.88 b
BPCUs	11.89 a	5.65 a	44.64 a	30.01 a	13.56 a	5.68 a	45.33 ab	34.92 a
Carbon sources +Nitrogen fertilizers interaction								
CK	10.00 e	4.89 cd	44.62 a	21.8 f	9.67 ef	4.96 b	44.45 b	21.34 e
Urea	11.33 cd	5.16 bcd	44.41 a	25.78 de	10.67 de	5.52 ab	45.29 ab	26.65 d
BPCU	11.67 bc	5.52 abc	44.51 a	28.65 c	12.67 c	5.53 ab	45.02 ab	31.52 c
straw	8.67 f	4.69 d	44.03 a	17.90 g	8.67 f	5.22 ab	45.03 ab	20.37 e
straw+Urea	11.33 cd	5.42 abc	44.81 a	27.53e	12.00 cd	5.56 ab	45.72 ab	30.54 c
straw+BPCU	10.33 de	5.54 ab	44.87 a	25.58 e	12.00 cd	5.71 a	45.38 ab	30.83 c
biochar	10.33 de	5.35 abc	44.39 a	24.53 e	10.00 ef	5.29 ab	44.39 b	23.39 e
biochar +Urea	12.67 ab	5.54 ab	44.66 a	31.31 b	14.00 b	5.46 ab	46.47 a	35.44 b
biochar +BPCU	13.67 a	5.89 a	44.54 a	35.79 a	16.00 a	5.82 a	45.60 ab	42.40 a
Source of variance								
C	<0.0001	0.0115	0.9701	<0.0001	<0.0001	0.8058	0.5085	<0.0001
N	<0.0001	<0.0001	0.3840	<0.0001	<0.0001	0.0284	0.0942	<0.0001
C × N Interaction	0.0863	0.1865	0.4172	0.0012	0.0294	0.9040	0.8135	0.0044

N0, without N fertilization, including CK, straw and biochar; Ureas, including Urea, straw+Urea and biochar+Urea; BPCU (bio-based polymer-coated urea), BPCUs, including BPCU, straw+BPCU, biochar+BPCU; C0, without straw or biochar addition, including CK, Urea and BPCU; straws, including straw, straw+Urea, straw+Biochar; biochars, including biochar, biochar+Urea, biochar+BPCU. Means followed by a same lowercase letter in the same column are not significantly different by Duncan's test ($p < 0.05$).

Table 4. Biomass accumulation and nitrogen use efficiency of cotton plants under different treatments.

Treatment	2014			2015		
	Biomass (g pot^{-1})	N accumulation (g plant^{-1})	NUE （%）	Biomass (g pot^{-1})	N accumulation (g plant^{-1})	NUE （%）
Types of carbon sources						
C0	250.63 b	3.98 b	44.60 b	259.02 b	4.03 b	44.90 b
straws	236.99 c	3.68 c	39.20 c	253.25 b	4.06 b	47.75 b
biochars	277.24 a	4.13 a	51.21 a	296.72 a	4.39 a	58.78 a
Types of nitrogen fertilizers						
N0	209.36 c	2.91 c	-	212.61 c	3.17 c	-
Ureas	272.39 b	4.30 b	40.37 b	291.09 b	4.52 b	46.16 b
BPCUs	283.12 a	4.58 a	49.64 a	305.29 a	4.79 a	54.79 a
Carbon sources +Nitrogen fertilizers interaction						
CK	211.64 f	3.08 e	-	192.82 e	3.12 e	-
Urea	258.53 d	4.21 d	37.44 d	279.63 cd	4.34 c	40.24 c
BPCU	281.73 bc	4.64 b	51.75 b	304.59 b	4.63 b	49.56 b
Straw	179.87 g	2.53 f	-	181.08 e	3.02 e	-
straw+Urea	268.57 bcd	4.29 cd	40.24 cd	290.5 bc	4.53 b	46.49 b
straw+BPCU	262.53 cd	4.23 d	38.16 cd	288.16 bc	4.61 b	49.01 b
biochar	236.57 e	3.12 e	-	263.92 d	3.36 d	-
biochar+Urea	290.07 ab	4.39 c	43.42 c	303.13 b	4.69 b	51.75 b
biochar+BPCU	305.09 a	4.86 a	58.99 a	323.12 a	5.12 a	65.79 a
Source of variance						
C	<0.0001	<0.0001	0.0009	<.0001	<0.0001	<0.0001
N	<0.0001	<0.0001	0.0004	<0.0001	<0.0001	0.0003
C × N Interaction	0.0276	0.0005	0.0031	0.0006	0.0459	0.0288

N0, without N fertilization, including CK, straw and biochar; Ureas, including Urea, straw+Urea and biochar+Urea; BPCU (bio-based polymer-coated urea), BPCUs, including BPCU, straw+BPCU, biochar+BPCU; C0, without straw or biochar addition, including CK, Urea and BPCU; straws, including straw, straw+Urea, straw+Biochar; biochars, including biochar, biochar+Urea, biochar+BPCU. Means followed by a same lowercase letter in the same column are not significantly different by Duncan's test ($p < 0.05$).

degree to which plant growth responding to different levels of biochar applications depends on the physicochemical properties of biochar, climatic conditions, soil conditions and types of crops [25,26]. The results of this study indicated that the application of straw and its biochar increased soil organic carbon contents (Table 2). Although equal amounts of carbon were applied between the biochar and straw applications, the biochar treatments resulted in a much greater increase in soil organic carbon, likely due to faster mineralization of straw than biochar [27].

Biochar addition also significantly increased soil pH when compared with the straw treatments (Table 2), and this may be partly due to the accumulation of alkaline substances in biochar during pyrolysis [28]. However, due to the near-neutral soil used in the study (pH = 7.50), the acidity-reduction effect of biochar [29] was not realized. While previous research suggests that the effect of biochar addition on soil available K or P content depends on soil type and the nature of biochar [30–32], our study indicated that soil-available K and P contents were not significantly affected by the straw and biochar treatments though soil-available K contents of biochar treatments were higher than C0 treatments (Table 2). High K content in biochar (1.03 g pot^{-1}) and straw (0.98 g pot^{-1}) contributed to more potent potassium in the soil (Table 1).

Biochar addition increased soil NO_3^-N contents relative to straw treatments, especially in the seeding stage. This supports existing studies in the literature about the positive control of biochar over the rate of nitrogen cycling in the soil system, especially nitrification rate and ammonia adsorption [33]. Meanwhile, straw application increased the C/N ratio, which slowed down the straw decomposition rates and caused a net immobilization of N [34].

The large specific surface area of biochar (255.50 m^2 g^{-1}) is indicative of biochar's superior adsorption performance to retain nutrients in soils while forming large stable soil aggregates after being applied to soil [35,36]. Rich functional groups as indicated by characteristic peaks in the biochar spectrum also contribute to the overall soil quality when mixed with soil. For example, hydrophilic functional groups coupled with biochar's pore structure would greatly increase soil water-holding capacity [37]. In summary, biochar's large surface area, rich functional groups, and plentiful pores are the fundamentals for improving soil quality.

4.2 *Effects of BPCU*

Cotton requires a continuous supply of nutrients, especially N, but these nutrients are absorbed in different quantities at different rates during various developmental stages [11]. In our study, the contents of soil inorganic N with N0 treatments were lowest in all growth stages. They were depleted rapidly with cotton growth. At the same time, the yields were also the lowest, indicating that nitrogen fertilizer is essential for plant growth and this cannot be supplied by biochar alone.

Synchronizing fertilizer inputs with the needs of cotton is highly important in crop production. N uptake by cotton peaks from the squaring to initial boll-opening stages [38] while little N is needed by the small plants in the seeding stage [13]. Therefore, the supply of soil NO_3^-N from urea conversion did not closely match the requirements of the cotton plants, especially in the late growth periods [39]. For the BPCU, the release rates were slow before the cotton-squaring stage, accelerated from the bloom to the boll-opening stages, and ended with rate reduction at maturity (Figure 1(b)). Note that the higher soil inorganic N contents of the Urea treatments than in the BPCU treatments at the seeding stage was indicative of rapid N release from urea while higher soil inorganic N after the bloom stage in BPCU treatments than for Urea ensured a relatively steady N supply when N was needed by cotton (Figure 3). As a matter of fact, N release from urea was instant and the NO_3^-N content increased rapidly within 2 weeks after urea fertilization [40]. Nitrate is negatively charged and not adsorbed by the soil. Consequently, Urea treatments increased the potential for leaching loss of N and nonpoint source pollution of water [33].

4.3 *Combined effects of biochar and BPCU*

The combined effect of biochar and BPCU on cotton growth lies in BPCU's continuous and controlled nitrogen supply corresponding to cotton's growth needs as well as biochar's functionalities in maintaining a healthy soil quality to ensure cotton production and N utilization efficiency (Figure 5). Our data further suggest that the combination of biochar and BPCU applications created a synergic interaction between BPCU and biochar. For example, the lint yield under the biochar combined with BPCU treatments was the highest, increasing by 14.3–108.2% over the other treatments (Table 4). The organic C content of the biochar+BPCU treatment was also the highest, reaching up to 10.82 g kg^{-1}, likely caused by increased return of residues, including roots, back to the soil, with enhanced plant growth and yield attained by this treatment (Table 3). The total N of combined application of biochar and BPCU was significantly higher than for the combined application of biochar and Urea. Most importantly, the combined biochar and BPCU provided successive releases of N from BPCU, which corresponded well to cotton N requirements, while biochar helped to retain the release N, thereby resulting in the highest NUE (59–65.8%) among all the treatment. Zheng et al. (2017) also reported that biochar compound fertilizer treatment had a 40% increase in agronomic use efficiency of applied N compared with inorganic fertilizer in maize [16].

In additional to the separate benefits of BPCU in supplying N and biochar in improving soil quality, the synergy between biochar and BPCU could also be understood in a context of two mechanisms (Figure 5). First, the high specific surface area and

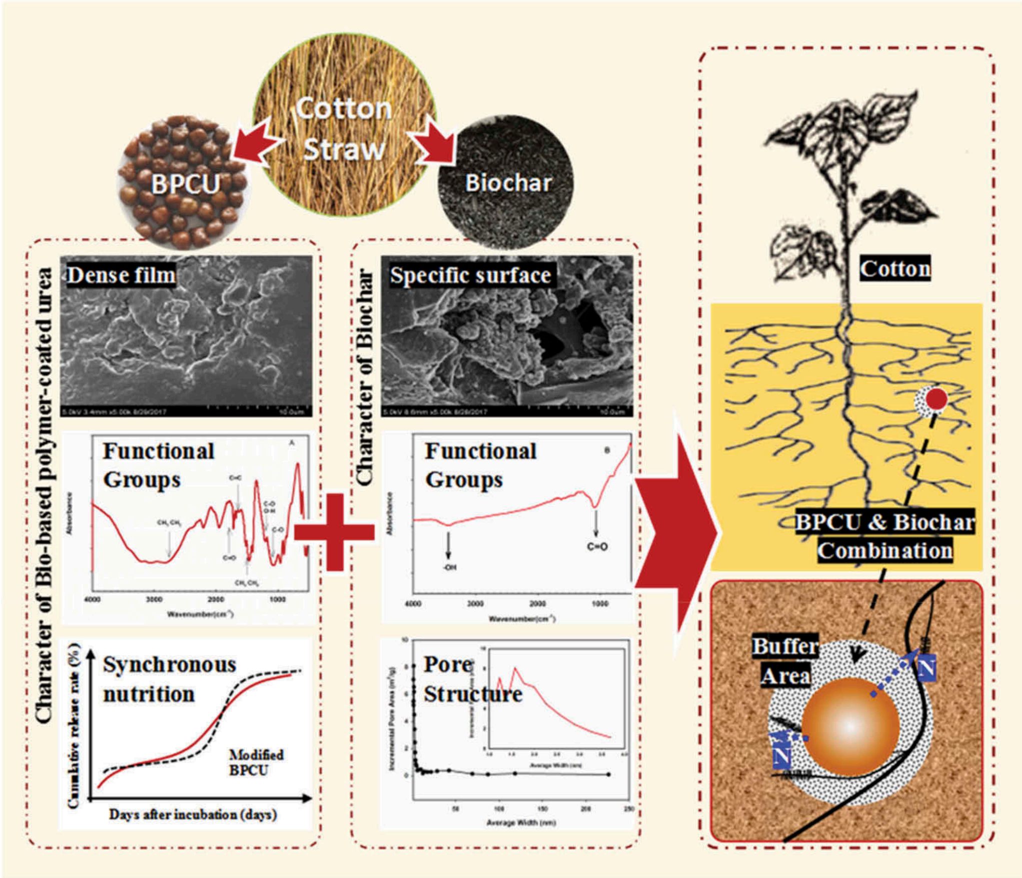

Figure 5. Mechanisms of biochar combined with BPCU for improving NUE and cotton yield. The biochar possesses high specific surface, rich functional groups and diverse pore structure. BPCU features with a dense film, rich functional groups, and synchronous nutrition release with cotton.

rich functional groups in biochar help to adsorb inorganic N in the soil. The rapid release of urea fertilizer may have exceeded the upper limit of biochar's adsorption capacity. However, controlled release fertilizers like BPCU release N slowly, allowing biochar to better adsorb nitrogen in soils. Second, the release of controlled release fertilizer in soil is mainly affected by temperature and water content. The application of biochar improves soil moisture conditions, which reduces the temperature difference between day and night. This may further improve the release performance of the controlled release fertilizer to suit for cotton growth [41]. The overall improvement of soil quality, NUE, cotton growth and yield by combined biochar and BPCU has practical implications in alternative and sustainable use of straw as biological resource, innovations in fertilizer technology, and controlling nutrient pollution.

5 Conclusions

Soil total C contents, lint cotton yields and N-use efficiency were significantly improved by bio-based polymer-coated urea (BPCU) fertilization and straw-derived biochar addition and their interactions. Biochar application increased the content of organic carbon and the pH value. The continuous release of N from BPCU increased soil NO_3^-N contents in the later cotton growth stage. Combining biochar with BPCU resulted in the highest cotton productivity, which was 14.3–108.2% higher than the other treatments. Meanwhile, the combination of biochar and BPCU treatment achieved the highest NUE of 59.0–65.8%, which was 27.1–63.5% increase over other treatments.

The combined effect of biochar and BPCU on cotton growth lies with BPCU's continuous and controlled nitrogen supply corresponding to cotton's growth need along with biochar's functionalities in maintaining a healthy soil condition to ensure cotton production and N utilization efficiency. The remarkable effects of biochar and fertilizer application demonstrated a complementary synergy at work in this study. However, soil conditions and fertilization may vary between pot and field experiments. Further research is needed to determine whether the mechanisms underlying the interactive effects of biochar and BPCU would operate similarly in the field condition.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was supported by the National Key Research and Development Program of China (2017YFD0200706 and 2017YFD0201901), the Natural Science Foundation of China (Grant no. 41571236 and 21377074) and Project of Shandong province higher education science and technology program (J18KA173).

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