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A valorization analysis towards agricultural application of biochar prepared using maize straw grown using organic or chemical fertilizers

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To assess the potential of biochar-based fertilizers, this study applied 200 kg N hm^{-2}, 180 kg P_2O_5 hm^{-2}, and 180 kg K_2O hm^{-2} for maize straw cultivation using either organic or chemical fertilizers. The resulting biochar from both treatments was analyzed. Findings indicated an increase in total carbon (C) content, pH, and mean residence time (MRT) with rising pyrolysis temperatures (300–700 °C). Biochar derived from chemically fertilized maize demonstrated higher total C content and MRT (61.3–74.4 wt% and 232.5–1473.6 year, respectively) compared to that from organically fertilized maize (54.7–59.1 wt% and 126.7–714.5 year, respectively). Potassium (43.6–113.8 g kg^{-1}) and phosphorus (9.5–12.3 g kg^{-1}) contents were notably higher in biochar from organic fertilizer. All biochar samples were generally higher in the organic fertilizer biochar than in the chemical fertilizer biochar (14.5–49.6 g kg^{-1} and 5.5–10.5 g kg^{-1}, respectively) and met industry standard of biochar-based organic fertilizer (NY/T 3618–2020). Biochar from both fertilization methods, pyrolyzed at 500 °C, can serve as nutrient carriers and facilitate C sequestration in soil.

Keywords Biochar, Chemical fertilization, Organic fertilization, Maize straw, Pyrolysis temperature

Maize (*Zea mays* L.), a key crop for both food and animal breeding, commands significant global demand with an annual yield of approximately 1148 million tons[1]. China, as the largest maize producer, recorded a production of 260.7 million tons in 2021[2]. Concurrently, maize straw production in China amounted to 226.0 million tons in the same year[3], primarily disposed of through environmentally harmful aerobic burning[4]. Biochar, a carbon-rich, porous material produced via the pyrolysis of organic materials in an oxygen-limited environment[5], offers a sustainable alternative for maize straw waste management, enhancing biomass utilization while protecting the environment[6].

The carbon (C) contents in biochar significantly vary depending on the biomass feedstock source[7,8]. Biochar derived from crop straw exhibits higher C contents compared to those from livestock-based biochar and sewage sludge. For instance, the C contents were 68.3%[9], 29.5%[9], and 33.5%[10] for straw, sewage sludge, and poultry manure, respectively, at a pyrolysis temperature of 550 °C. Conversely, the nutrient levels in crop straw biochar are lower than those in livestock and sludge-based biochars. For example, the ash contents were reported as 13.0%[5], 57.4%[7], and 60.6%[11] for straw, sewage sludge, and poultry manure biochars, respectively, at a pyrolysis temperature of 500 °C. Moreover, the nutrient effect of straw biochar alone is considerably less than that of fertilizer. The nutrients essential for crop growth and development are primarily derived from fertilizer. To address this nutrient deficiency, biochar could be combined with chemical fertilizer to produce biochar-based inorganic fertilizer, or with organic fertilizer to create biochar-based organic fertilizer. Consequently, two industry standards, biochar-based fertilizer (NY/T 3041–2016)[12] and biochar-based organic fertilizer (NY/T 3618–2020)[13], have been established by the Ministry of Agriculture and Rural Affairs (MARA) in China, considering appropriate timing and conditions. Biochar-based fertilizer offers the benefits of both biochar

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and fertilizer, while mitigating their respective limitations. It is suggested as a strategy to enhance fertilizer use efficiency, improve soil properties, and simultaneously sequester C in soil, compared to conventional fertilizers[14].

Previous research indicates that maize straw biochar contains recalcitrant organic C, suggesting its potential role in global C sequestration[15]. Additionally, maize straw biochar has been identified as an effective soil amendment for greenhouse gas emission mitigation when incorporated into soil[16]. Studies have also examined the application of biochars in soils as absorbents in environmental remediation[17]. Research has focused on the simultaneous effects of organic and chemical fertilizers on maize production and nitrogen (N) use efficiency, with N fertilizer rates ranging from 225 kg hm^{-2} to 405 kg hm^{-2} in maize cultivation in China[18]. The sole use of chemical fertilizer addresses the increase in maize production, but excessive application raises concerns about soil and environmental degradation. The application of organic fertilizer, recognized for sustaining soil organic C stock, yields delicious, safe, and healthy agricultural products, yet does not increase crop yields as effectively as chemical fertilizers. Few studies have explored the effects of fertilization methods on maize straw and the resultant impact on maize straw biochar. This study aims to investigate the effects of chemical or organic fertilizer on the characteristics of biochar produced from two maize straws and to evaluate the potential of these biochars for C sequestration and agricultural uses. The objectives are to (1) determine the characteristics of different biochar samples; (2) analyze the effects of pyrolysis temperature and fertilization methods on biochar properties; and (3) evaluate the potential contribution of nutrient supply and carbon sequestration as biochar-based fertilizers in soil when applied at normal application rates.

Materials and methods

Study site

The experiments utilized maize straw grown at Zhuanghang Experimental Station (Fig.S1), China (30°53′N, 121°23′E), characterized by a mean annual temperature of approximately 16 °C and average annual rainfall of 1200 mm. The experimental soil was a haplaquept and sandy clay loam, as classified by the US Department of Agricultural Soil Taxonomy. The detailed characteristics of pre-experimental soil before greenhouse built was as follows: pH 7.0 ± 0.2; EC 434.2 ± 58.1 μS cm^{-1}, soil total carbon 23.8 ± 1.1 g kg^{-1}, total nitrogen 3.0 ± 0.1 g kg^{-1}, available phosphorus 27.3 ± 5.2 mg kg^{-1}, available potassium 266.7 ± 30.0 mg kg^{-1}.

Experimental design

The treatments included chemical fertilizer (CF) and organic fertilizer (OF)[19]. Compound fertilizer from Tianyuan Agrochemical International Co. Ltd., Hong Kong, China, was evenly distributed across the pre-experimental soil surface. The proportion of N, P_2O_5 and K_2O was 15:15:15. Organic fertilizer (Xinge Organic Fertilizer Factory, Shanghai, China) was composted with swine manure and straw. The contents of organic C and N was 215.3 ± 1.1 g kg^{-1} and 20.0 ± 0.5 g kg^{-1}, respectively. Each plot, measuring 80 m^2 (10 m x 8 m), was replicated thrice. Each plot was fertilized with the respective fertilizer. A drip irrigation system irrigated all plots, the quality (Table S1) met the requirement of GB5084-2021[20]. Both treatments received equal amounts of N, P, and K: 200 kg N hm^{-2}, 180 kg P_2O_5 hm^{-2}, and 180 kg K_2O hm^{-2} for the CF treatment. Maize was sown on April 22nd and harvested on August 28th, 2022, at a density of 6.0×10^4 plants hm^{-2}. The experimental site experienced one maize season annually. Consistent management of weeds, diseases, and insect pests was maintained throughout the experiment. The environmental-friendly plant protection technologies (yellow plates, sexual attractants, biopesticide, manual weeding) and were adopted to biological prevention and control. The straw at harvest was healthy and free of pests and diseases.

Harvested maize straw was categorized as OF–MS (organic fertilizer–maize straw) and CF–MS (chemical fertilizer–maize straw). Surface post-harvest soil samples (0–20 cm layer) were collected using a stainless-steel auger and labeled as OF–soil and CF–soil according to the respective fertilizer treatment.

Maize straw Biochar Preparation

Prior to pyrolysis, maize straw was air-dried to eliminate residual moisture. Biochar production occurred in an electric furnace (HTL1100–100, Haoyue Co., Shanghai, China). Approximately 30 g of maize straw, cut into 3–5 cm sections, was placed in a crucible and inserted into the furnace connected to a steel tube for N_2 gas flow. The furnace's air was replaced with N_2 before heating at a rate of 10 °C min^{-1}. Pyrolysis temperatures were set at 300 °C, 500 °C, and 700 °C, respectively, each maintained for 2.0 h[5]. After that, the furnace was turned off to allow the samples to cool to room temperature. The solid residue, defined as the biochar sample, was labeled according to the fertilization type. Figure S2 explained the process from maize straw to prepared biochar. Each straw was prepared (300 °C, 500 °C, and 700 °C) at three times, and a total of 18 biochar samples were obtained. These were categorized into two groups: (1) the OF group (OF–300, OF–500, and OF–700) and (2) the CF group (CF–300, CF–500, and CF–700). All analyses were conducted in duplicate.

Analytical methods

Yield of maize Biochar samples

All mature maize plants in each plot were manually harvested. After air-drying, the maize plants from each plot were threshed.

The yield of biochar was calculated using the following equation after re-weighing the charred material:

$$Yield\,(\%) = \frac{W_{biochar}}{W_{maize\ straw}} \times\ 100\%$$

Where $W_{maize\ straw}$ and $W_{biochar}$ are the weights (g) of the original maize straw and its biochar, respectively.

The air-dried samples, including straw, biochar, and soil, underwent crushing, sieving through a 2 mm mesh, and subsequent grinding to 75 µm. The 2 mm and 75 µm samples were utilized in the subsequent analyses.

pH and EC
The 2 mm samples were employed for elemental analysis. Biochar pH was determined using a 1:20 (w: v) biochar-to-deionized water ratio[5,7]. Straw pH was measured with a 1:25 (w: v) straw-to-deionized water ratio[5], while soil pH was assessed using a 1:5 (w: v) soil-to-deionized water ratio[21]. The suspension was agitated for 4 h at 200 rpm in a horizontal shaker at room temperature. The pH of the supernatant was analyzed using a pH electrode (ST2100, Ohaus, Parsippany, NJ, USA). Soil electrical conductivity (EC meter DDSJ-318, Jingke, China) was determined using a 1:5 (w: v) soil-to-deionized water suspension, following the protocol[22].

Elemental composition and Ash content
The 75 µm samples of straw and biochar were employed for elemental analysis. Total C, total N, total hydrogen (H), and total sulfur (S) were analyzed using an elemental analyzer (Vario EL cube, Elementar, Langenselbold, Germany). The ash content was determined through dry combustion in a muffle furnace at 650 °C in an oxygen (O) atmosphere for 4.0 h. The O content was estimated as follows:

$$O\,(\%) = 100\% - C\,(\%) - N\,(\%) - H\,(\%) - S\,(\%) - ash\,(\%)$$

Where C (%), N (%), H (%), S (%), and ash (%) are the contents in the original maize straw or its respective biochar. The organic carbon (C_{org}) content was calculated[5]. Total C and total N were determined using an elemental analyzer (Vario EL cube, Elementar, Langenselbold, Germany). The H/C, O/C and (O + N)/C atomic ratios were calculated to evaluate the aromaticity and polarity of the biochars. The MRT is the residence time (yr) and calculated from the following equations[23].

$$MRT = 4501\, e^{-3.2\left(\mathrm{H}/C_{org}\right)}$$

here, H/C_{org} is based on the molar ratio, H was the contents in the biochar (%), C_{org} is the organic C content of the biochar (%).

Total concentrations of the nutrient elements and heavy metals
The 75 µm samples, comprising straw, biochar, and soil, were digested using concentrated HCl–HNO_3 and H_2O_2[5]. The macro and micro elements: P, K, Ca, Mg, Na, Fe, Mn, Cu, Zn, and B, as well as the heavy metals: Cd, Hg, Pb, and Cr, were analyzed by inductively coupled plasma optical emission spectroscopy (iCAP 7600, Thermo Fisher, Waltham, MA, USA).

Scanning electron microscopy (SEM) and scanning electron microscopy-Energy dispersive spectrometer (SEM–EDS) analysis
SEM (Gemini 300, Zeiss, Oberkochen, Germany) was employed to observe the structure and morphology. An SEM–EDS analysis was conducted to ascertain the surface structure and surface element composition of both straw and biochar samples[24]. The surface elemental composition (C, N, O, K, P, and Ca) was determined using Electron Dispersion Spectroscopy (Regulus 8100, Hitachi, Tokyo, Japan). The surface particles formed a dot field on the biochar samples.

Cellulose, hemicellulose, and lignin contents of maize straw
Cellulose, hemicellulose, and lignin in the original maize straw were quantified using the Van Soest method[25].

Data analysis
Multi-factor repeated measures analysis of variance (ANOVA) was employed to investigate the main effect of fertilization methods on the properties of straw, biochar, and post-harvest soil. Multi-factor repeated measures ANOVA and multi-factor ANOVA, along with the least-significant difference (LSD) test to assess pairwise differences, were conducted using SPSS for Windows statistical software (V13, SPSS, Inc., Chicago, IL, USA). Each data point in the figures represents an average value, with vertical bars indicating the standard error of the means. All significant levels were set at $p < 0.05$.

Results
Soil properties and maize straw components
The post-harvest soil properties are presented in Table 1. After continuous fertilizer application, the soil pH (6.9) of the OF treatment remained unvaried, while the pH (5.7) of the CF treatment decreased significantly. Higher total soil C content (29.5 g kg^{-1}) was in the OF treatment, while lower content (18.1 g kg^{-1}) was in the CF treatment. OF treatment decreased the soil EC, while CF treatment increased the soil EC. Compared the 2 treatments, higher concentrations of Fe, Al, Mn and B presented in the CF treatment; higher concentrations of Cu and Zn showed in the OF treatment. Table 2 shows the cellulose, hemicellulose, and lignin contents of harvested maize straw. Higher cellulose content (227.5 g kg^{-1}) in the OF treatment, while lower cellulose content (201.8 g kg^{-1}) was in the CF treatment.

Soil	pH	TC (g kg^{-1})	TN (g kg^{-1})	EC (μS cm^{-1})		
OF-soil	6.9 ± 0.1**	29.5 ± 3.7*	3.4 ± 0.0	340.5 ± 4.4*		
CF-soil	5.7 ± 0.0**	18.1 ± 0.7*	2.9 ± 0.0	860.2 ± 9.6*		
	Total Fe (mg kg^{-1})	Total Al (mg kg^{-1})	Total Zn (mg kg^{-1})	Total Mn (mg kg^{-1})	Total Cu (mg kg^{-1})	Total B (mg kg^{-1})
OF-soil	29,160 ± 42**	49,635 ± 290**	410.1 ± 4.2**	1110 ± 8.0**	149.7 ± 1.1**	18.9 ± 1.1*
CF-soil	32,235 ± 21**	54,910 ± 50**	124.3 ± 5.0**	687.6 ± 27.0**	47.9 ± 1.4**	25.5 ± 1.9*

Table 1. The post-harvest soil properties of different treatments. *and** indicate statistical significance at the $p < 0.05$ level and $p < 0.01$ level.

Maize straw	Cellulose (g kg^{-1})	Hemicellulose (g kg^{-1})	Lignin (g kg^{-1})
OF-MS	201.8 ± 1.8*	159.7 ± 7.6	10.4 ± 0.3
CF-MS	227.5 ± 4.5*	148.0 ± 4.3	8.6 ± 0.3

Table 2. Cellulose, hemicellulose, and lignin contents in the maize straw of different treatments. * indicates statistical significance at the $p < 0.05$ level.

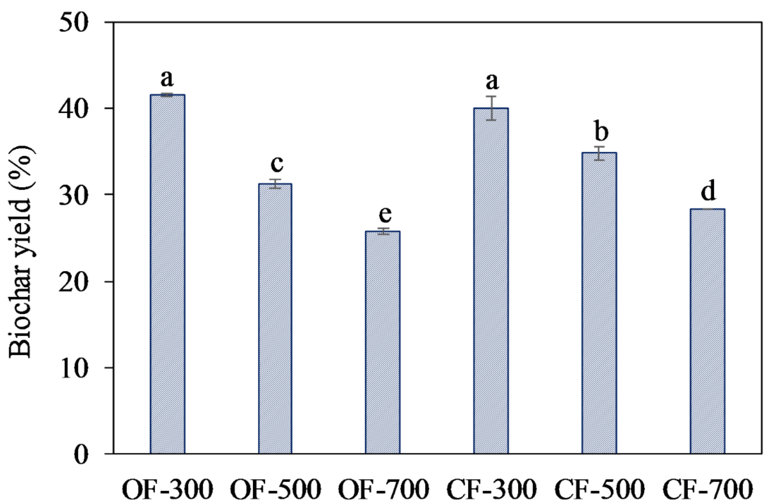

Fig. 1. Biochar yield of different treatments. Different lowercase letters in the same column indicate significant differences among biochar samples ($p < 0.05$).

Biochar yield

The biochar yields are presented in Fig. 1. The results demonstrate that the yields decreased from 41.6% to 25.8% as the pyrolysis temperature increased. The CF-treatment notably outperformed the OF-treatment at 500 °C ($p < 0.05$) and 700 °C ($p < 0.05$) in terms of biochar yield (Fig. 2).

Ultimate composition, nutrient elements and heavy metals in the solid phase

Table 3 displays the elemental contents of maize straw and biochar produced between 300 °C and 700 °C. The C contents increased to varying degrees as the pyrolysis temperature increased. The C content in biochar ranged from 61.3 wt% to 74.4 wt% for the CF-group and 54.8–59.1 wt% for the OF-group, with a significant difference ($p < 0.05$) between the two fertilization methods. N contents increased as the pyrolysis temperature increased. A significant difference ($p < 0.05$) in N content in biochar was also observed between the two fertilization methods. The S contents in maize straw and their corresponding biochar ranged from 0.07 wt% to 0.17 wt%, with no significant difference between the two treatments ($p > 0.05$). The higher ash content was produced at 500 °C for both treatments, and their difference between 500 °C and 700 °C was not significant ($p > 0.05$).

Total concentration of nutrient elements in the biochar samples includes P, K, Na, Ca, Mg, and Si, as illustrated in Fig. 3. The order of abundance was K (14.6–113.8 g kg^{-1}) > P (5.6–12.3 g kg^{-1}) > Na (4.7–12.9 g kg^{-1}) > Mg (3.6–4.9 g kg^{-1}) > Ca (1.5–4.7 g kg^{-1}) > Si (0.3–1.1 g kg^{-1}). The P and K were the primary nutrient elements in the biochar. Elemental contents were higher in the biochar samples at 300 °C and 500 °C whether OF-group or CF-group. Elemental composition distributions differed between OF and CF-treatment. The total K and P contents were generally higher in the OF-group than in the CF-group. Total concentration of nutrient elements in the post-harvest soil and straw are also shown in Fig. 2. The order of abundance was K (20.1–20.2 g

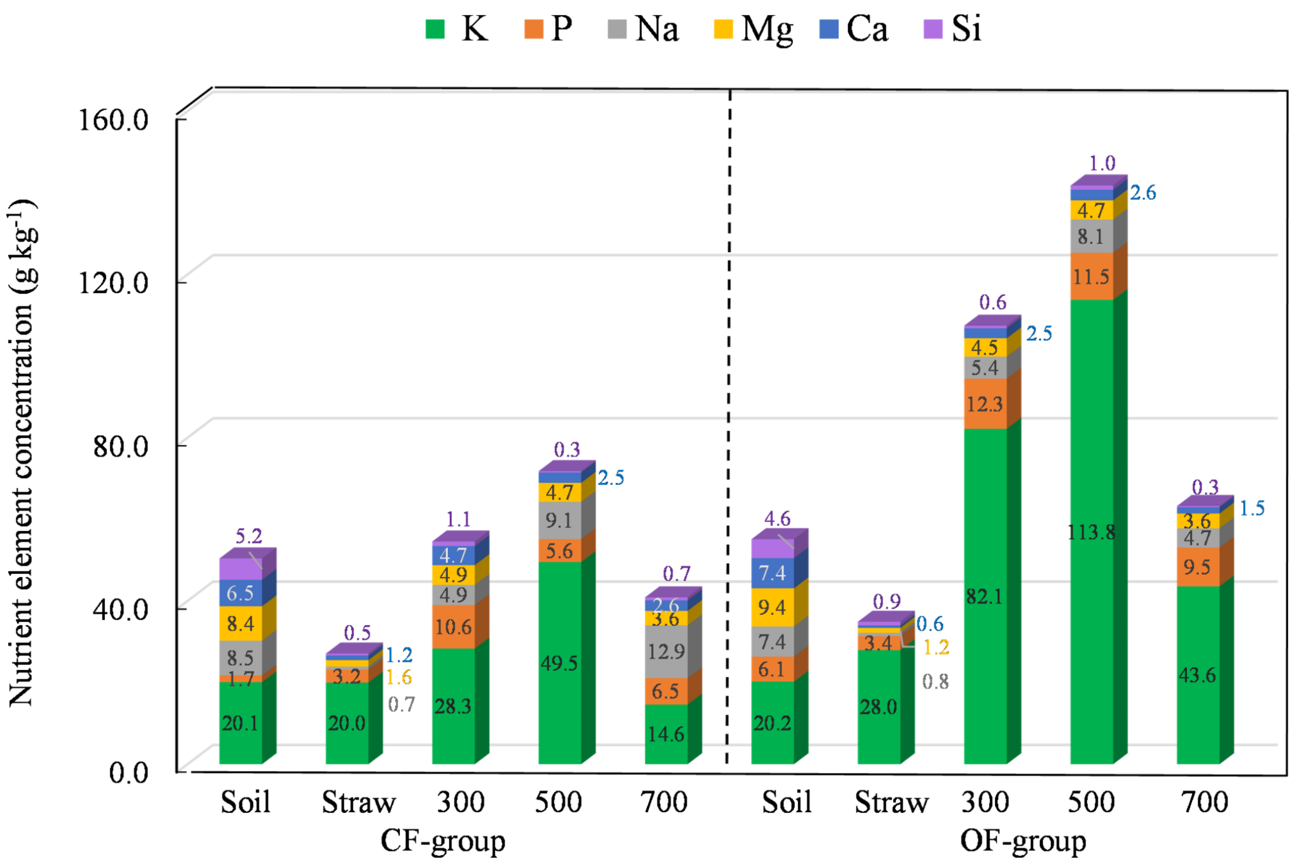

Fig. 2. Concentrations of K, P, Na, Mg, Ca and Si in the post-harvest soil, maize straw, and prepared biochar samples of different treatments.

Treatments		Ultimate composition (%)					Ash (%)
		C (%)	N (%)	H (%)	S (%)	O (%)	
Organic fertilizer (OF)	OF-MS	42.77 ± 0.35	1.79 ± 0.05	6.25 ± 0.03	0.12 ± 0.0	41.38 ± 0.72	7.70 ± 0.29
	OF-300	54.77 ± 1.88e	3.31 ± 0.07a	4.50 ± 0.24a	0.15 ± 0.0ab	22.54 ± 1.65a	14.73 ± 3.85b
	OF-500	57.19 ± 1.05de	2.22 ± 0.04c	2.41 ± 0.08b	0.17 ± 0.0a	6.84 ± 1.87d	31.17 ± 0.96a
	OF-700	59.07 ± 0.17 cd	1.41 ± 0.05e	2.53 ± 0.08b	0.07 ± 0.0d	8.22 ± 3.03 cd	28.70 ± 2.78a
Chemical fertilizer (CF)	CF-MS	43.23 ± 0.09	1.43 ± 0.02	6.29 ± 0.03	0.11 ± 0.0	42.72 ± 0.67	6.21 ± 0.81
	CF-300	61.33 ± 1.36c	2.48 ± 0.06b	4.18 ± 0.02a	0.16 ± 0.0ab	17.10 ± 2.52b	14.75 ± 1.07b
	CF-500	70.98 ± 1.48b	1.98 ± 0.03d	2.59 ± 0.20b	0.11 ± 0.0c	11.88 ± 0.87c	12.46 ± 0.85b
	CF-700	74.44 ± 0.06a	2.17 ± 0.03c	1.91 ± 0.02c	0.14 ± 0.0b	9.09 ± 0.52 cd	12.25 ± 0.57b

Table 3. The ultimate composition of the maize straw and its biochar samples of different treatments. Different lowercase letters in the same column indicate significant differences among biochar samples ($p < 0.05$).

kg^{-1}) > Mg (8.4–9.4 g kg^{-1}) > Na (7.4–8.5 g kg^{-1}) > Ca (6.5–7.4 g kg^{-1}) > Si (4.6–5.2 g kg^{-1}) > P (1.7–6.1 g kg^{-1}) in the both soil samples. The K was the dominant nutrient element in the studied soil samples, and least significant between OF-soil and in CF-soil. The P and Ca contents were 270.2% and 14.1% greater in OF-soil than in CF-soil, respectively. The Na and Si contents were 13.1% and 11.7% lower in OF-soil than in CF-soil, respectively. Concentrations of other trace elements, including Fe, Mn, Cu, Zn, Al, and B, of biochar samples are detailed in Table 4. The order of abundance was Fe > Al > Zn > Mn > Cu > B. Fe concentrations were higher (average values) in the CF-group treatment than in the OF-group treatment, and Zn was the opposite.

SEM and SEM-EDS analysis

The SEM images reveal the dense and compact structure of corn straw (Fig. 3). They also show an increase in porosity on the biochar surface with an increase in pyrolysis temperature. More pores are present in the images of the CF-group than that of the OF-group. SEM-EDS was employed to visualize element distribution in the biochar samples[24]. Comparative SEM-EDS images reveal element distribution on the pores and mineral phases

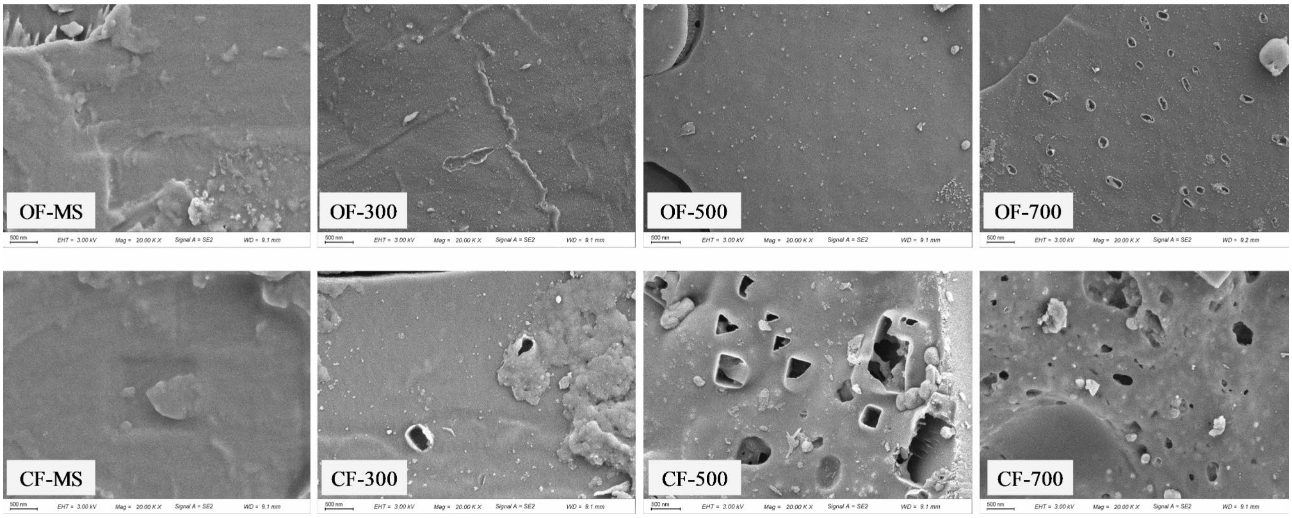

Fig. 3. SEM images of both maize straw and the prepared biochar samples of different treatments.

Treatment		Total Fe (mg kg^{-1})	Total Mn (mg kg^{-1})	Total Cu (mg kg^{-1})	Total Zn (mg kg^{-1})	Total Al (mg kg^{-1})	Total B (mg kg^{-1})
Organic Fertilizer (OF)	OF-300	171.7 ± 4.8c	42.0 ± 4.3c	31.6 ± 3.3b	142.7 ± 1.6b	96.8 ± 3.7c	16.4 ± 0.1a
	OF-500	167.3 ± 5.4c	59.4 ± 4.4b	18.8 ± 3.5c	168.7 ± 0.6a	142.5 ± 5.1b	13.8 ± 0.1b
	OF-700	180.1 ± 2.3b	67.2 ± 2.3b	13.8 ± 2.7d	100.1 ± 0.7c	198.8 ± 1.9a	14.4 ± 0.1b
Chemical Fertilizer (CF)	CF-300	260.8 ± 12.4a	87.9 ± 1.4a	46.6 ± 2.4a	149.9 ± 3.6b	144.7 ± 11.6b	10.0 ± 0.1c
	CF-500	186.4 ± 3.7b	22.2 ± 2.6d	9.7 ± 0.5e	67.3 ± 0.8d	150.6 ± 7.7b	13.6 ± 0.1b
	CF-700	272.3 ± 5.2a	22.3 ± 2.1d	26.5 ± 3.3b	27.9 ± 0.5e	151.6 ± 5.7b	11.7 ± 0.1c

Table 4. The concentrations of other trace elements in the biochar samples of different treatments. Different lowercase letters in the same column indicate significant differences among biochar samples ($p < 0.05$).

of the straw and biochar exterior surface. Figure 4 presents elemental mapping images of the straw and biochar samples. The letters a-d represent results of the OF-group, while e-h represent results of the CF-group. The upper right corner of each small square symbolizes an element (C, O, N, P, K, and Ca). The dots within a small square are color-coded to differentiate between various elements. Colorful dots indicate elements with diffused distribution across the image. The size of the dots reflects the total element content. Gradual darkening of the red spots (a–d or e–h) indicates that C is the primary component element, with C content increasing as pyrolysis temperature rises from 300 °C to 700 °C. Blue dots represent the distribution of O, which gradually decreases on the biochar surface as temperature increases. These changes align with the contents presented in Table 3. K, P, and Ca colors indicate predominantly concentrated distribution. Their colors darken from 300 °C to 500 °C and then fade or remain at 700 °C. Element N shows no obvious regional color change due to its low levels (1.41–3.31 wt%) in the studied biochars.

MRT and molar ratios

Table 5 displays the MRT results for the biochar. At pyrolysis temperatures of 300 °C, 500 °C, and 700 °C, corresponding MRTs were OF300 (126.7 year) < CF300 (232.5 year), OF500 (722.6 year) < CF500 (927.9 year), and OF700 (745.0 year) < CF700 (1473.6 year). These values were significantly higher in the CF-group than in the OF-group. Biochar produced at temperatures above 500 °C can potentially remain in the soil for over 1000 year after amending the soil in the CF-group.

The C_{org} values were listed in Table S2. H/C_{org}, O/C_{org}, and $(O+N)/C_{org}$ molar ratios decreased significantly with increasing pyrolysis temperature, indicating increased aromaticity and polarity of the biochar. CF treatments exhibited longer MRT and lower molar ratios. H/C_{org} showed a significant difference ($p < 0.05$) between the two fertilization methods.

Chemical analysis of biochars based on maize grown with chemical fertilizer or organic fertilizer

Table 6 lists the pH values of the samples, which ranged from 8.0 to 9.7 between 300 °C and 700 °C. The lowest pH was recorded at lower pyrolysis temperatures, with a significant pH difference ($p < 0.05$) between the two fertilization methods at 700 °C. The contents of separate N, P_2O_5 and K_2O was listed in Table S3. Table 6 further presents the total nutrient ($N + P_2O_5 + K_2O$) contents of the biochar samples, which ranged from 3.7 to 12.2%. The concentrations of total As (7.5–13.7 mg kg^{-1}), Cd (BD–2.3 mg kg^{-1}), Pb (BD–13.1 mg kg^{-1}), and Cr (8.8–

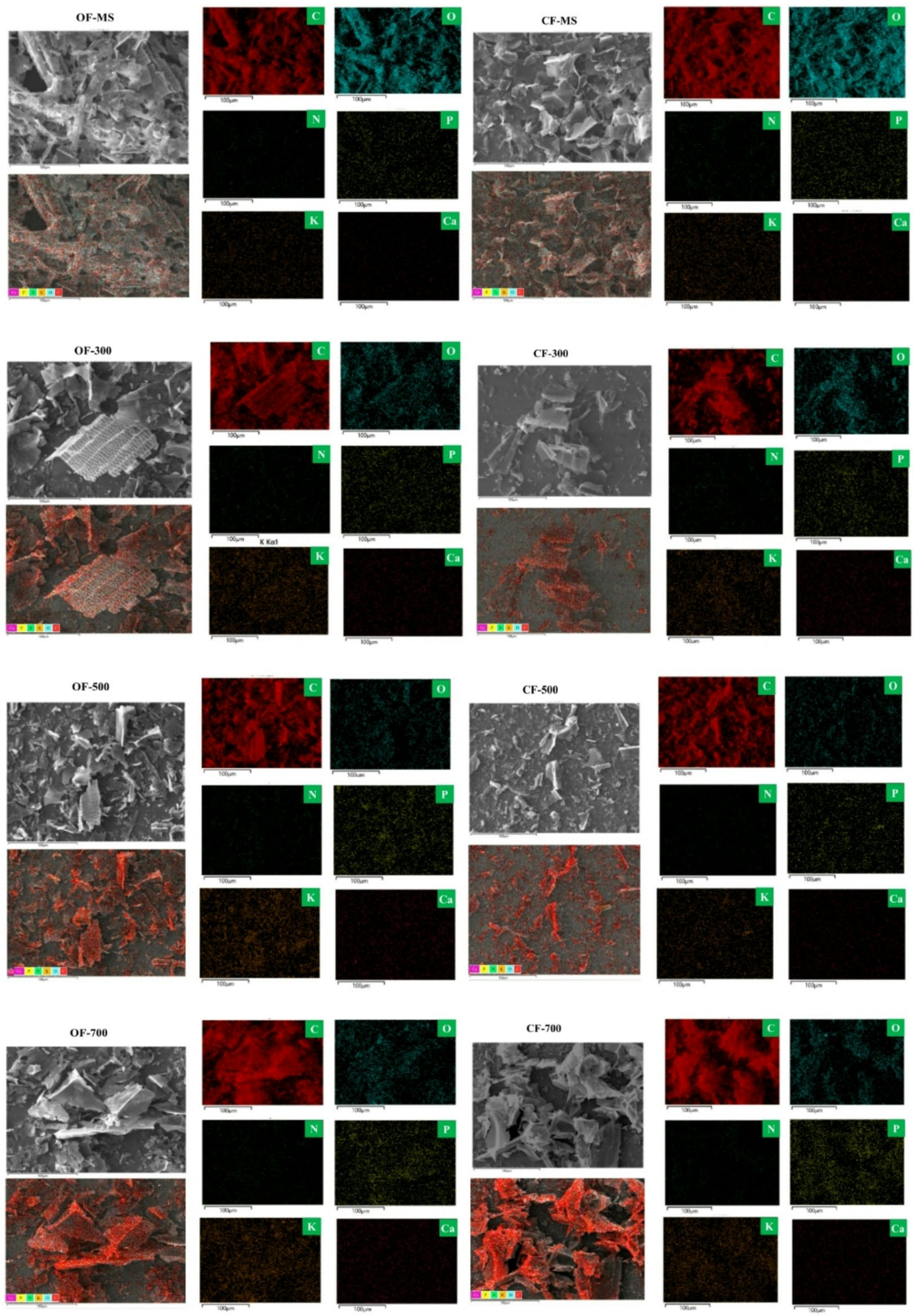

Fig. 4. Elemental mapping images for both straw and biochar composites based on the SEM-EDS analysis of different treatments.

36.4 mg kg^{-1}) were within standard controls. Hg concentration was not detected. Based on the biochar-based fertilizer standard[12], the $N + P_2O_5 + K_2O$ content in the biochar samples did not meet the requirements. However, according to the biochar-based organic fertilizer standard[13], all biochar samples (except biochar sample at CF-700) met the requirements.

Treatment		MRT (yr)	Molar H/C_{org}	Molar O/C_{org}	Molar $(O+N)/C_{org}$
Organic Fertilizer (OF)	OF-300	126.7 ± 8.8c	1.12 ± 0.0a	0.35 ± 0.0a	0.41 ± 0.0a
	OF-500	722.6 ± 69.1b	0.57 ± 0.0c	0.10 ± 0.0c	0.14 ± 0.0c
	OF-500	745.0 ± 61.6b	0.58 ± 0.0c	0.12 ± 0.0c	0.14 ± 0.0c
Chemical Fertilizer (CF)	CF-300	232.5 ± 11.6b	0.93 ± 0.0b	0.24 ± 0.0b	0.28 ± 0.0b
	CF-500	927.9 ± 85.4ab	0.49 ± 0.0d	0.14 ± 0.0c	0.17 ± 0.0c
	CF-700	1473.6 ± 11.9a	0.35 ± 0.0e	0.10 ± 0.0c	0.13 ± 0.0c

Table 5. Molar ratios and MRTs in the biochar samples of different treatments. Different lowercase letters in the same column indicate significant differences among biochar samples ($p < 0.05$).

Treatment		pH	$N+P_2O_5+K_2O$ (%)	Total As (mg kg^{-1})	Total Cd (mg kg^{-1})	Total Pb (mg kg^{-1})	Total Cr (mg kg^{-1})	Total Hg (mg kg^{-1})
Organic fertilizer (OF)	OF-300	8.0 ± 0.2c	10.7 ± 0.0b	12.5 ± 1.2a	BD	1.2 ± 1.6b	10.9 ± 1.4de	BD
	OF-500	9.3 ± 0.1b	12.2 ± 0.1a	13.7 ± 1.1a	BD	BD	18.0 ± 1.2c	BD
	OF-500	9.4 ± 0.2b	5.4 ± 0.0d	7.9 ± 1.0b	BD	BD	8.8 ± 0.1e	BD
Chemical fertilizer (CF)	CF-300	8.2 ± 0.1c	5.2 ± 0.1e	12.4 ± 0.9a	0.6 ± 0.1b	13.1 ± 2.5a	14.7 ± 1.5 cd	BD
	CF-500	9.5 ± 0.2ab	6.3 ± 0.0c	13.1 ± 1.3a	2.3 ± 0.7a	BD	23.6 ± 0.1b	BD
	CF-700	9.7 ± 0.2a	3.7 ± 0.0f	7.5 ± 1.1b	BD	BD	36.4 ± 4.6a	BD
Biochar-based fertilizer (NY/T 3041 – 2016)		6.0–8.5	≥ 20	≤ 50	≤ 10	≤ 150	≤ 500	≤ 5
Biochar-based organic fertilizer (NY/T 3618 – 2020)		6.0–10.0	≥ 5.0	≤ 15	≤ 3	≤ 50	≤ 150	≤ 2

Table 6. Heavy metal concentrations, pH, and $N + P_2O_5 + K_2O$ contents in the biochar samples of different treatments. BD means below the detection. Different lowercase letters in the same column indicate significant differences among biochar samples ($p < 0.05$).

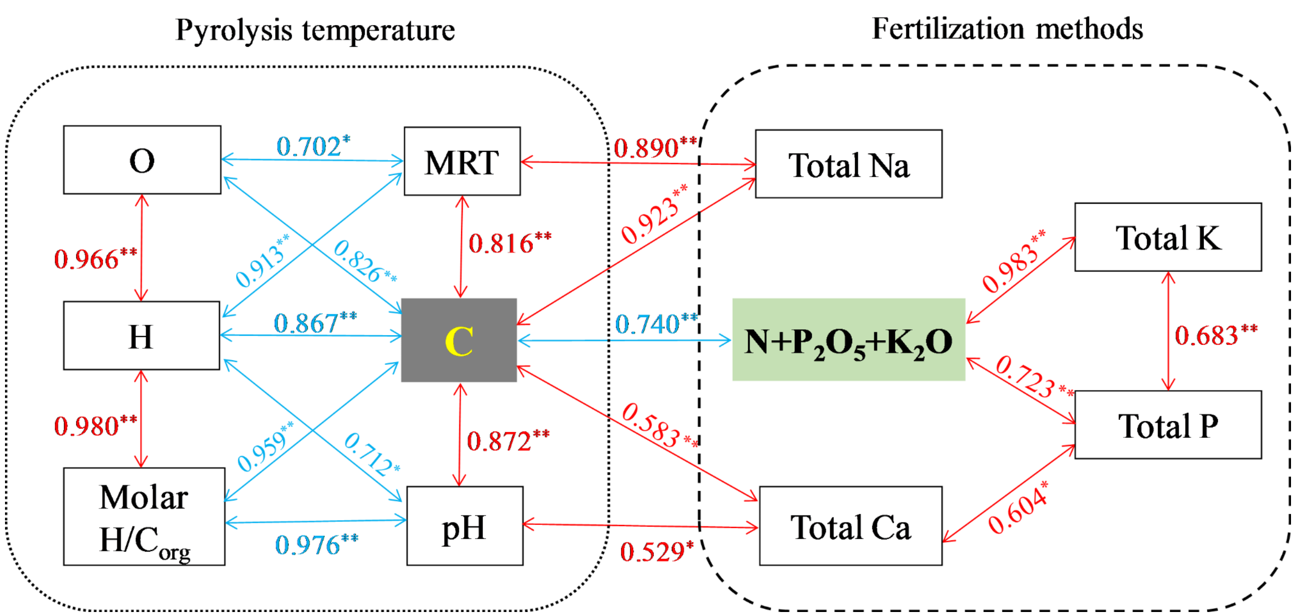

Fig. 5. Correlation coefficients for the studied biochar properties.

Correlation coefficients of the studied Biochar properties

Various properties of biochar have been investigated in this study, and correlations among different indicators were analyzed to identify the main factors affecting the C content of biochar. The correlation coefficients of the studied biochar properties are presented in Fig. 5. It is evident that pH is positively correlated with the C content of the studied biochars (correlation coefficient: 0.872^{**}), while the $N + P_2O_5 + K_2O$ content is negatively correlated with the C content of the studied biochar (correlation coefficient: 0.740^{**}). Figure 6 describes a schematic diagram of organic or chemical fertilizers affecting on the biochar prepared using maize straw.

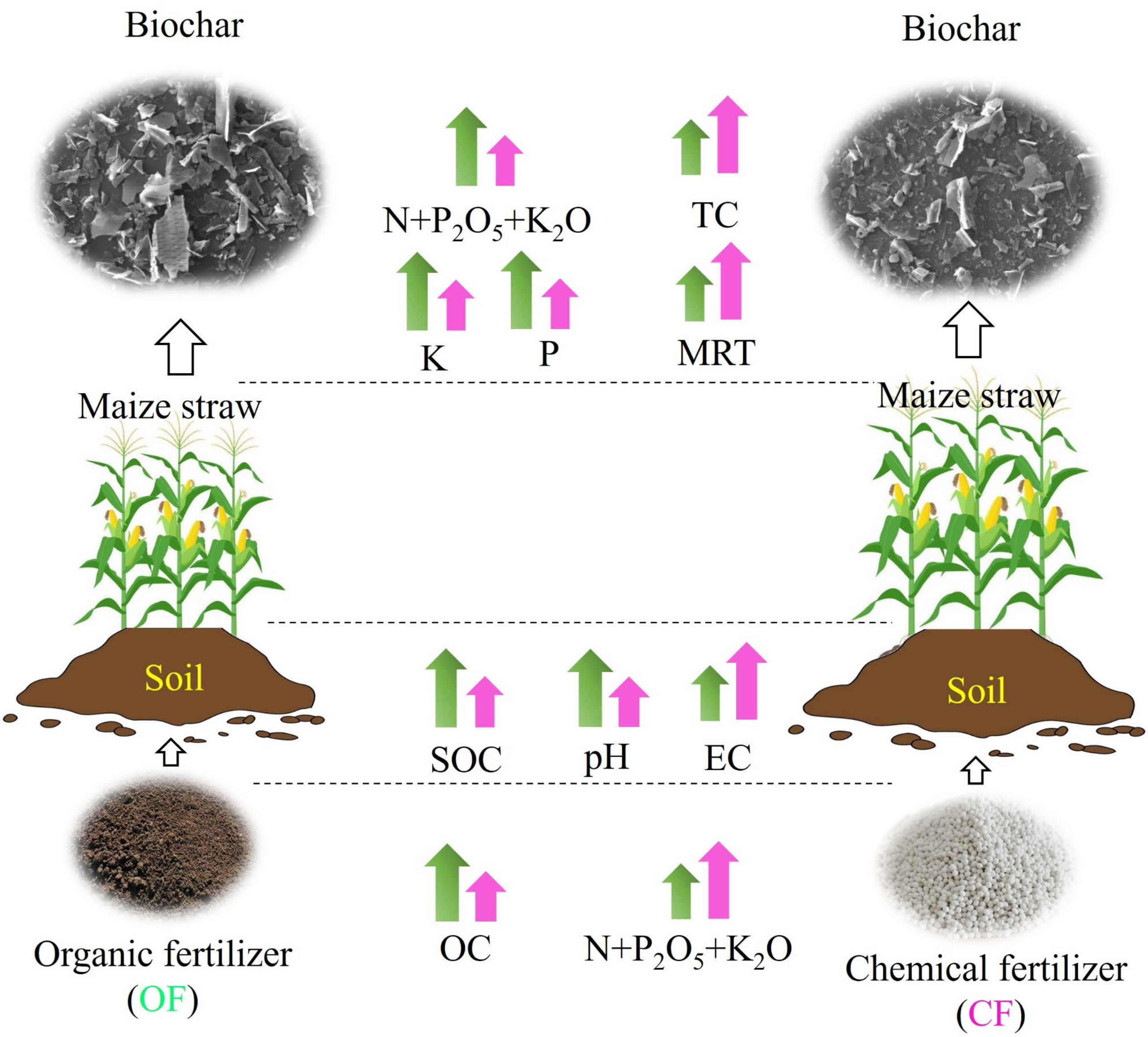

Fig. 6. A schematic diagram of organic or chemical fertilizers affecting on the biochar prepared using maize straw.

Discussion

Pyrolysis temperature and fertilizer methods affected C contents of the maize straw and Biochar

The C content was 42.8 wt% and 43.2 wt% in the maize straw investigated from the organic fertilizer and chemical fertilizer treatment plots, respectively. The C content remained consistent between both treatments. Divergence in C content occurred after converting the straw into biochar, with the variation increasing with higher pyrolysis temperatures, following the trend observed for wheat straw[26]. The primary factors influencing biochar C content typically include biomass feedstock, water moisture, pyrolysis temperature, and residence time[7,27]. The C content increased as pyrolysis temperature increasing. During pyrolysis, dehydration, cleavage, and polymerase reactions caused easily degradable C compounds to be restructured, while other elements could be lost to volatilization, the conversion of C into a more recalcitrant form during the pyrolysis process of biomass. The N content decreased as pyrolysis temperature increasing. The available forms of N (such as NH_4^+-N and NO_3^--N) disappeared, and the N gradually transformed into pyridine-like structure occurring in heterocyclic compounds with the increasing temperature[5,7,27].

In this study, the primary influencing factor was biomass feedstock, which correlated with fertilization methods. Biochar produced from straw grown with chemical fertilizer contained more C than that grown with organic fertilizer (Table 3). This difference can be attributed to (1) the variations in lignocellulose content in the straws. As observed, hemicellulose decomposed completely during pyrolysis, cellulose underwent molecular rearrangement forming crystallized areas in biochar, while lignin, with its complex cross-linked structure, melted during pyrolysis, forming amorphous carbon areas in biochar. A higher cellulose content in maize grown with chemical fertilizer (227.2 mg g^{-1}), a 12.7% increase compared to maize grown with organic fertilizer (201.9 mg g^{-1}) in this study. (2) The presence of metal minerals in biomass plays a crucial catalytic role in biomass pyrolysis. These minerals are generally found as oxides, silicates, carbonates, chlorates, and phosphates, with few existing in organic form. Plant-derived biomass typically contains high levels of K, Ca, P, and Si[28]. For instance, a higher K element content (2.8%) was detected in the investigated straw grown with organic fertilizer, a 28.5% increase compared to straw from the chemical fertilizer treatment. Consequently, the investigated biochar from the organic fertilizer treatment in this study contained much higher K element content (4.4–11.4%). These mineral components can influence the pyrolysis process, affecting carbon structure and product properties, ultimately reducing the C content.

Pyrolysis temperature and fertilizer methods affected nutrients donating of prepared Biochar samples

Pyrolysis temperature and feedstock are crucial factors for designing specialized biochars to provide nutrients. An increase in pyrolysis temperature has been shown to raise the ash content and pH in the biochar[7,29]. The ash concentration of biochar rose as the pyrolysis temperature rises because the organic parts of the biomass volatilize and break down at higher temperatures, leaving behind inorganic minerals such as ash. It could be used as a reference index for nutritional evaluation. The findings[7,29,30] indicated that the ash content of straw biochars promoted radically from 300 to 500 °C and showed less change when the pyrolysis temperature exceeded 500 °C. The current result also exhibited in Table 3, the ash of two straw biochars tended to stabilize after 500 °C. This further confirmed the increasing trends of P, K, Mg, and Ca with rising temperatures. After pyrolysis temperatures over 500 °C, the ash content might decrease as the Cu and Zn volatilized (Table 4). Due to the K, Mg and Ca enriched in the biochar with the increasing temperature, the pH of biochar samples also showed a gradual increase trend. The ash content was positively and exponentially associated with pH ($R^2 = 0.77–0.89$)[30].

Pyrolysis temperature and N fertilizer levels affected biochar nutrient supply characteristics. The optimum biochar was produced with a 500 °C pyrolysis temperature and an N fertilizer rate of 150 kg N hm^{-2} for wheat straw[5]. The 150 kg N hm^{-2} fertilization level induced the best nutrient donor, and 500 °C influenced the C stability of biochar after incorporation into the soil. Different fertilization methods resulted in varying soil fertilities, thus altering nutrient levels in the subsequent biochars. Phosphorus and K are vital for plant physiological processes and are required in large quantities for maize production. In this study, greater total K and total P levels were observed in the soil fertilized with organic fertilizer (Fig. 2). This could be attributed to the higher C content (29.5 g kg^{-1}) in the soil fertilized with organic fertilizer, resulting in a higher concentration of total K and total P elements. This study showed that higher $N + P_2O_5 + K_2O$ content was in the final prepared biochar when organic fertilizer was applied. A study found that correlation coefficient R^2 ranged from 0.48 to 0.82 between available P and total P content; 0.66 between available K and total K content; from 0.02 to 0.41 between available N and total N content ($n = 50800$, 5400 peer-reviewed journal articles)[31]. The relationship between available N/P/K content and total N/P/K content was not linear, but the total nutrient contents of the prepared biochar could predict the amount of available P and available K stored and the supply capacity for the soil.

Mineral elements like P, K, Ca, and Mg in biochar can be released into the soil and absorbed by crops and microorganisms as nutrient sources. However, the content of these mineral elements in biochar is lower compared to fertilizer. A biochar alone provides limited nutrients, but biochar-based (organic) fertilizers, formulated with (organic) fertilizer, offer precise plant nutrition and improved soil properties[32]. The $N + P_2O_5 + K_2O$ content of the biochar samples in this study did not meet industry standards for biochar-based fertilizer[12]. However, it did meet the industry standards for biochar-based organic fertilizer[13]. Therefore, compared to pure chemical fertilizers, biochar-based fertilizers typically have lower nutrient content and may need to be combined with other fertilizers to provide adequate nutrients. Compared with straw, traces elements were condensed and retained in the prepared biochar samples. Taking Cu as an example, with the increase of ash content in biochar, Cu could create oxides, hydroxides or carbonate phased (e.g., CuO, $Cu(OH)_2$, or $CuCO_3$) in the ash, so that its total concentration increased. At pyrolysis temperatures of 500 °C or more, it could be volatilized. Therefore, the variation of trace elements is not regular with the increase of pyrolysis temperature. A biochar containing Fe, Cu, Zn, Mn, and B could potentially be used to supply micro-nutrients to soil and plants[31].

Pyrolysis temperature and fertilizer methods affected C stability of prepared Biochar samples

The C enhancement correlated with increased aromaticity, improving biochar's thermal stability. Molar ratios for H/C_{org}, O/C_{org}, and $(O+N)/C_{org}$ significantly decreased with increasing temperature, consistent with previous studies[5,7]. At low temperatures, minimal loss of aliphatic fractions and surface functional groups, such as H and O. At high temperature, the loss of hydroxyl groups as a result of dehydration, cellulose, and hemicellulose's thermal breakdown led to lower values of H/C_{org}, O/C_{org}, and $(O+N)/C_{org}$. Biochar under chemical fertilizer treatment had higher C content, resulting in lower H/C_{org}, O/C_{org}, and $(O+N)/C_{org}$ ratios compared to biochar under organic fertilizer treatment at each pyrolysis temperature. Maize straw biochar had greater C stability when straw was fertilized with chemical fertilizer.

Molar H/C_{org} and O/C_{org} ratios were also linearly correlated with MRT, respectively, as shown in Table 5. When molar $H/C_{org} \leq 0.5$ and $O/C_{org} \leq 0.1$, biochar can remain in the soil for over 1000 year. When molar H/C_{org} is ≥ 1.0 and O/C_{org} is ≥ 0.3, biochar remains in the soil for less than 100 year. Values in between indicate biochar remains in the soil for 100 to 1000 year. The correlation between O/C and years biochar remained in the soil was calculated. When the O/C ratio is < 0.2, biochar can remain in the soil for over 1000 year; when $0.2 < O/C$ ratio < 0.6, biochar can remain in the soil for 100 to 1000 year, but when O/C ratio is > 0.6, biochar can remain in the soil for less than 100 yr[33]. This study's results slightly differ from that study[33], because it used C_{org}, and H/

C_{org} and O/C_{org} were less than H/C and O/C[5]. Biochar's stability in soil fundamentally impacts the C balance and its role as a climate change mitigation tool.

Potential effects of maize straw Biochar application on soil properties

Numerous studies have investigated the impact of biochar on soil fertility and have reported positive effects on crop yield. These effects are primarily attributed to biochar's ability to absorb plant nutrients. Changes was examined in soil nutrient content and microbial activity in calcareous soil two years after applying maize straw biochar at rates of 0–22.5 t hm^{-2} [34]. The results revealed significant increases in soil available P and K contents as the maize straw biochar application rate increased. Soil microbial biomass and soil carbon-nitrogen-cycling enzyme activities also saw increases. When biochar is applied in conjunction with mineral N fertilizers, it has the potential to reduce N_2O emissions[16] and NO_3^- leaching[21]. A prior study demonstrated that maize straw biochar applied at 2.5–22.5 t hm^{-2} resulted in soil organic C content being 26.1–164.9% higher than in the control group (without biochar)[34].

Raising the pyrolysis temperature from 300 °C to 700 °C resulted in a decrease in biochar yield. The destruction of organic matter was accelerated into volatile chemicals that are emitted as gases at higher temperatures[30]. Therefore, a reduced yield of biochar is prepared since less solid carbonaceous material remained. The cost of biochar can be prohibitive for farmers, potentially limiting its adoption for soil improvement. Therefore, using biochar-based fertilizers is a more optimal solution. Figure 5 illustrates a negative correlation between total C content and $N + P_2O_5 + K_2O$ content, indicating that maize straw biochar has a strong C sequestration ability while fertilizer is not as effective at providing nutrients. Thus, when applying biochar-based fertilizer, it is essential to consider the respective advantages of biochar and fertilizer. Biochar-based fertilizers can serve as a partial substitute for chemical fertilizers, providing nutrients, enhancing nutrient cycling, and supplying recalcitrant C to improve agricultural soil[35]. Based on significant correlations between pH and SOC of biochar samples in Fig. 5, this phenomenon could probably be associated with the characteristics of biochar with porous structure and liming effect. Although N fertilizer application decreased the soil pH, the biochar addition postponed the soil acidification process in the entire experimental period[36]. When applying biochar-based fertilizer, it is essential to consider the potential effect of biochar-based fertilizer potentially to slow the soil acidification rate caused in the intensive vegetable field.

Conclusion

This study investigated the C stability of maize straw biochar and explored the underlying mechanisms. Pyrolysis temperature was found to be a crucial factor influencing the physicochemical properties of biochar. Maize straw biochar pyrolyzed at 500 °C exhibited higher $N + P_2O_5 + K_2O$ content than those pyrolyzed at 300 °C and 700 °C. Fertilization methods used for growing maize straw also impacted biochar characteristics, although the effects were not as pronounced as those of pyrolysis temperature. Maize straw biochar contained more C and displayed greater C stability when the straw had been fertilized with chemical fertilizer. However, when the straw had been fertilized with organic fertilizer, the maize straw biochar had higher P and K contents and could serve as a nutrient carrier. All biochar samples met the industry standards for biochar-based organic fertilizer. Biochar-based organic fertilizer from maize straw should be applied at appropriate rates to maintain soil and environmental sustainability.

Data availability

All the data is available in the manuscript.

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Author contributions
Z.J., G.L., Z.X.,W.C. and S.H. performed the experiment and prepared figures. C.H. and H.J. analyzed, interpreted the data and drafted the manuscript. Z.S was responsible for the project conception and study design. All authors read and approved the submitted version.

Declarations

Competing interests
The authors declare no competing interests.

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