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Effects of Combined Application of Chemical Fertilizer and Straw-Derived Organic Amendments on Potassium Supply Capacity of Black Soil

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Abstract

This study investigated the mechanism underlying how the integration of chemical fertilizer and maize straw-derived organic amendments affects different potassium (K) pools, K saturation, K fixation characteristics, and non-exchangeable potassium (NEK) release kinetics in black soil. A field experiment involving five treatments was conducted: no fertilizer (CK), chemical fertilizer alone (NPK), chemical fertilizer plus maize straw (NPK+ST), chemical fertilizer plus straw compost (NPK+CP), and chemical fertilizer plus straw biochar (NPK+BR). The findings demonstrated remarkably increased contents of different K pools and K saturation in the black soil following the combined application of straw-derived organic amendments, with NPK+CP exhibiting the most significant effect. Exogenous K fixation simulation tests indicated that the amount of K fixation in the black soil increased with the incorporation of exogenous K, while the fixation rate showed the opposite trend. The quadratic regression model well fitted the relationship between the amount of K fixation and the addition of exogenous K; the treatments were ranked according to the soil K fixation capacity as follows: CK > NPK > NPK+BR > NPK+ST > NPK+CP. The simplified Elovich model well fitted the NEK release process in the black soil under different treatments. Significant differences in total cumulative NEK release and apparent release rate coefficients were observed among the treatments, which showed an identical trend: NPK+CP > NPK+BR > NPK+ST > NPK > CK. The application of straw-derived organic amendments could effectively reduce the K fixation capacity of black soil and promote NEK release. In this study, chemical fertilizer combined with straw compost was the optimal measure for improving black soil's potassium availability.

Keywords: black soil; straw-derived organic amendments; potassium supply capacity

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1. Introduction

As one of the world's four principal black soil zones, Northeast China's black soil area serves as a central hub for grain production, constituting a critical foundation for guaranteeing the nation's food security [1]. However, with the enrichment of high-yield crop varieties and the intensive application of nitrogen and phosphorus fertilizers, soil potassium (K) in

this region has long remained in a state of imbalance (deficit) [2]. Concurrently, affected by the dual constraints of inorganic K fertilizer's limited abundance in China as well as its consistently high prices in the global market, farmers generally have low willingness to apply it. This depletion of soil K reserves has threatened the sustainable grain production in this region. Therefore, adopting efficient fertilization strategies is crucial to minimize chemical K inputs and maximize K utilization [3,4].

K represents an essential macronutrient for the growth and development of crops [5–8]. Furthermore, K holds considerable significance in soil health by stabilizing diverse mineral components [9]. The neutral NH_4OAc extraction method is a classic approach for evaluating soil K supply capacity. However, this method has limitations as it only extracts the water-soluble and exchangeable K pools, which are readily available for crop uptake, while neglecting the non-exchangeable K (NEK) pool [10]. NEK functions as a potential mineral K reserve; its progressive release is intrinsically linked to sustaining the medium- and long-term K supply for crop growth [11]. Therefore, determining the content and release characteristics of the NEK is essential for accurately evaluating the soil K supply to plants. K saturation of the exchange complex, defined as the share of K among exchangeable cations, is also an important parameter for assessing soil K supply capacity [12]. Among the numerous mechanisms regulating K availability in soil, K fixation stands out as a particularly critical process governing this nutrient's accessibility. Soil K fixation is the process of K^+ diffusing into the interlayer spaces of clay minerals and forming inner-sphere surface complexes with mineral oxygen atoms [13]. Obtaining reliable data on soil K fixation holds significant practical value in agronomy: not only can it provide data support for clarifying the soil–plant system's response to K fertilizer utilization, but it can also enable evaluations of the K demand of crops, which holds much guiding value for formulating targeted soil fertility management strategies.

Organic amendments have been regarded as one of the best options for enhancing soil K availability and supply capacity [14]. The notable feature of organic amendments lies in maintaining or increasing soil K pools and K saturation through direct K input and indirect contribution by increasing soil properties and biological properties [15–17]. The combined application of chemical fertilizer and organic amendments promoted the release of soil NEK and enhanced the K supply capacity [18,19]. Simultaneously, this fertilization strategy reduced the soil K fixation capacity; as a result, exogenous K fertilizer could more easily satisfy the soil K fixation demand under this strategy, thereby exerting a yield-increasing effect [20,21]. Maize straw is the most readily available local organic amendment in Northeast China's black soil area [22]. Previous studies have widely demonstrated that maize straw-derived organic amendments are highly beneficial for the preservation of the soil carbon pool, as well as the dynamic transformation and availability of nitrogen and phosphorus [23,24]. However, research on their regulatory effects on soil K availability and transformation dynamics in black soil is still insufficient, especially under the typical continuous maize cropping system in this region, and relevant studies urgently need to be supplemented. Therefore, an in-depth investigation into the response of black soil K supply capacity to various maize straw-derived organic amendments is of great significance for enhancing soil K availability, promoting straw resource utilization, and ultimately achieving sustainable agricultural production.

Our objective was to delve into the influences of the prolonged (10 years) combined utilization of chemical fertilizer as well as multiple maize straw-derived organic amendments (maize straw, straw compost, and straw biochar) on different soil K pools, K saturation, K fixation characteristics, and NEK release kinetics under the typical continuous maize cropping system in black soil. Ultimately, these findings can help identify the optimal straw-derived organic amendment for field application, thereby providing a scientific basis

for sustainable K management in black soil agroecosystems. The following hypotheses were proposed: (1) The long-term combined application of maize straw-derived organic amendments increases the contents of multiple K pools and K saturation in black soil, reduces the soil K fixation capacity, and simultaneously increases the total cumulative release of NEK and its release rate. (2) Different maize straw-derived organic amendments have divergent effects on improvements in soil K fertility.

2. Materials and Methods

2.1. Experimental Site Overview

The experiment site is located in Gongzhuling City, Jilin Province, Northeast China (124°48′33.8″ E, 43°30′23″ N), at an altitude of 218 m (Figure 1a). The region features a typical temperate continental climate, with a mean annual temperature of 5.6 °C, annual rainfall of 560 mm, and an annual average effective accumulated temperature (≥10 °C) of 2800–3000 °C·d during the crop growing season [25]. Figure 1b illustrates the meteorological conditions at the study site, detailing the rainfall and the maximum, minimum, and mean air temperatures during the maize growth period (May to October) from 2012 to 2021 (https://data.cma.cn/, accessed date 15 May 2026).

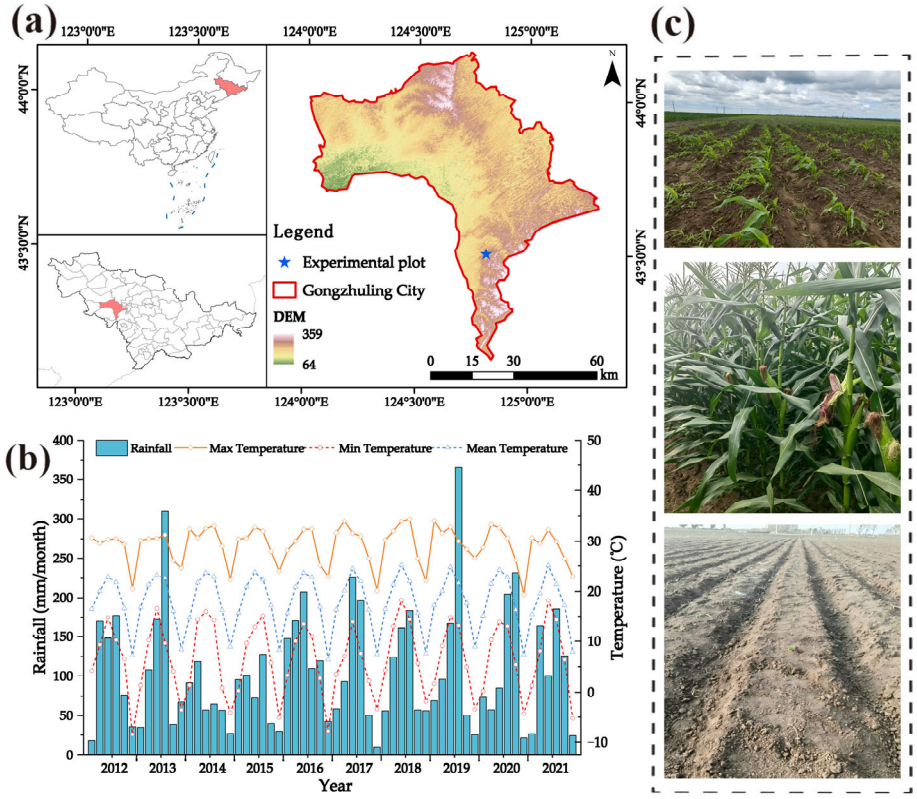


Figure 1. (**a**) Geographic location of the experimental field; (**b**) Rainfall and temperature data during maize growing season at the experimental site (2012–2021); (**c**) Field photograph of the experimental plot.

Following USDA taxonomy criteria, the soil is identified as mesic, mixed, fine-silty typic Hapludoll, whereas under Chinese Soil Taxonomy, it is designated as typical black soil. Table 1 presents the properties of the topsoil (0–20 cm depth) measured at the beginning of the study [25].

Table 1. Selected basic soil properties of the topsoil (0–20 cm depth) at the beginning of the experiment in 2012.

pH	Soil Organic Carbon (g/kg)	Total Nitrogen (g/kg)	Total Phosphorus (g/kg)	Total Potassium (g/kg)	Bulk Density (g/cm^3)
6.20	15.10	1.56	0.54	18.00	1.42

2.2. Experimental Design

A field experiment was initiated in 2012. A total of 5 fertilization treatments were designed: (1) CK, no fertilizer; (2) NPK, chemical fertilizer alone; (3) NPK+ST, NPK plus maize straw; (4) NPK+CP, NPK plus straw compost; and (5) NPK+BR, NPK plus straw biochar. All treatments had three replicates. All the experimental plots were arranged with a randomized block design, each covering 104 m^2 (10.4 m × 10 m). In each treatment, the chemical fertilizer was applied at the recommended rate: the annual average application rates were 200 kg/hm^2 N (supplied as urea), 90 kg/hm^2 P_2O_5 (supplied as diammonium phosphate), and 75 kg/hm^2 K_2O (supplied as potassium chloride). All the phosphorus and potassium fertilizers, along with 40% of the nitrogen fertilizer, served as the base fertilizer, whereas the remaining 60% functioned as the topdressing fertilizer during the maize jointing. The three maize straw-derived organic amendments were adopted at an identical carbon input rate, and the average carbon input was 3200 kg/hm^2 annually. The maize straw utilized in the present investigation was harvested from the exact field and subsequently processed into smaller segments. Maize straw compost was prepared by blending maize straw with pig manure at a fresh mass ratio of 4:1, within managed temperature (50–60 °C) and hydration (40%, v/w) parameters. Maize straw biochar was produced by thermally decomposing maize straw at 450 °C under oxygen-deficient conditions. Table 2 presents the basic attributes of the maize straw-derived organic amendments [25]. To attain the specified amount of applied carbon, the carbon input of each material was calculated. After the autumn harvest, these organic materials were employed by broadcasting on the soil surface, followed by rotary tillage to mix them into the soil layer to 0–15 cm. During the following spring, a no-till fertilization seeder was used for fertilization and sowing. The flat planting method and continuous maize cropping system were adopted, and the planting density was 60,000 plants/hm^2, dependent on ambient rainfall for irrigation and consistent field operations adhering to established agronomic norms.

Table 2. Basic properties of the maize straw-derived organic amendments.

	Maize Straw	Straw Compost	Straw Biochar
pH	6.70	8.43	8.91
Total organic carbon (g/kg)	443	255	595
Total nitrogen (g/kg)	7.00	13.0	10.0
Total phosphorus (g/kg)	0.40	3.10	1.10
Total potassium (g/kg)	5.50	13.6	8.50
Carbon-to-potassium ratio	80.5	18.8	70.0

2.3. Soil Sampling and Analysis

Following a decade of experimental operation, topsoil samples were derived from the profile with a 0–20 cm depth after maize harvest in October 2021. Quintuplicate soil cores were systematically taken from each experimental plot and homogenized to generate a representative composite sample. After removing visible plant residue and gravel from the soil samples, these samples were naturally air-dried while passing them through a 2 mm sieve for subsequent use.

2.3.1. Soil Phsicochemical Analysis

The methods used to determine the soil K pools and cation exchange parameters are presented in Table 3.

Table 3. Measurement methods for soil physicochemical properties.

Soil Property	Soil Indicator	Unit	Method	Reference
Soil potassium pools	Water-soluble potassium (WSK)	mg/kg	Ultrapure water extraction; flame photometry	[26]
	Exchangeable potassium (EK)	mg/kg	1 mol/L neutral NH_4OAc extraction; flame photometry	
	Non-exchangeable potassium (NEK)	mg/kg	Boiling 1 mol/L HNO_3 extraction; flame photometry	
	Total potassium (TK)	g/kg	0.2 mol/L HCl after NaOH dissolution extraction; flame photometry	
Cation exchange parameters	Cation exchange capacity (CEC)	cmol/kg	1 mol/L neutral NH_4OAc displacement; AAS	[27]
	Potassium saturation	%	EK/CEC × 100	[28]

2.3.2. Soil Potassium Fixation Characteristics

Soil K fixation characteristics were determined by the equilibrium method with minor modifications [29].

Next, a 5 g aliquot of the soil sample was precisely weighed and transferred into a 50 mL centrifuge tube. Then, a 5 mL portion of KCl solution with a K^+ concentration of 0, 0.1, 0.4, 0.8, 1.0, 1.6, 2.4, 3.2, or 4.0 g/L was added, equivalent to an amount of added external K of 0, 100, 400, 800, 1000, 1600, 2400, 3200, or 4000 mg/kg soil, respectively. The mixture was fully homogenized and air-dried naturally at 25 ± 2 °C. After the soil sample was air-dried, 50 mL of 1 mol/L neutral NH_4OAc solution was incorporated. After shaking for 30 min, the resulting mixture was then filtered, and a flame photometer was used to analyze the K concentration. The amount and rate of K fixation were determined using the following equation [30]:

$$\text{K fixation amount (mg/kg)} = \text{Amount of added external K} - (\text{NH}_4\text{OAc-extractable K with external K addition} - \text{NH}_4\text{OAc-extractable K without external K addition})$$

$$\text{K fixation rate (\%)} = (\text{K fixation amount} \times 100)/\text{Amount of added external K}$$

2.3.3. Soil Non-Exchangeable Potassium Release Kinetics

The release of soil NEK was determined using a modified continuous exchange method, with the specific steps as follows:

(1) Preparation of Ca^{2+}-saturated soil: 10.00 g of the sample was transferred into a centrifuge tube. Then, 50 mL of 0.25 mol/L $CaCl_2$ solution was introduced; the resulting mixture was completely shaken while being centrifuged, and this operation was repeated 3 times. Next, 50 mL of absolute ethanol was further incorporated; the mixture was thoroughly shaken and then subjected to centrifugation, and this operation was repeated 2 times. Finally, 50 mL of distilled water was introduced, after which the resulting mixture was fully shaken and centrifuged until no Cl^- was detected. The soil sample was then dried, ground, and set aside for subsequent use [31].

(2) Soil NEK release test: 2.00 g of the above Ca^{2+}-saturated soil was transferred into a centrifuge tube. Then, 20 mL of 0.01 mol/L $CaCl_2$ solution was added, after which the mixture was subjected to intermittent oscillation at 25 ± 2 °C, followed by centrifugation. The supernatant was poured out and set aside. The above process was repeated with extraction times of 1, 6, 12, 24, 48, 96, 168, 272, 416, 560, 728, 896, 1064, and 1232 h. The K^+ concentration in the supernatant was identified utilizing a flame photometer [32].

Six kinetic models were used to describe the cumulative K release curves (Table 4). The applicability of each kinetic equation was compared by using the coefficient of determination (R^2) and standard error (SE) obtained from least-squares analysis. The larger the R^2 and the smaller the SE, the better the fitting effect. The SE was calculated as follows:

$$SE = \sqrt{\frac{\sum(K_t - K_t')^2}{(n-2)}}$$

where K_t and K_t' are, respectively, the measured and predicted cumulative K releases at time t, while n represents the number of observations (n = 14).

Table 4. Kinetic models used to describe soil non-exchangeable potassium release.

Model	Equation	Reference
Zero-order	$(K_{max} - K_t) = a - bt$	[33]
First-order reaction	$\ln(K_{max} - K_t) = a - bt$	
Power function	$K_t = at^b$	
Parabolic diffusion	$K_t = a + bt^{0.5}$	
Simplified Elovich	$K_t = a + b\ln t$	
Exponential	$\ln K_t = \ln a - bt$	

K_{max} denotes the total cumulative potassium release (mg/kg) throughout the entire experimental period; K_t denotes the cumulative potassium release (mg/kg) at time t (hours); and b is a constant, which can be regarded as the apparent release rate coefficient.

2.4. Statistical Analysis

All data presented are averaged across three replicates for each treatment. Statistical analysis was carried out with SPSS 27.0. Data for soil K pools, cation exchange parameters, average K fixation amount and rate, and total cumulative K released were analyzed using the Shapiro–Wilk and Levene's test for normality and variance homogeneity. One-way ANOVA with LSD post hoc test was used when assumptions were met; the Kruskal–Wallis test with Dunn's post hoc test was applied otherwise (Table A1). The significance threshold was set at $p < 0.05$. Data visualization and model fitting were performed using Origin 2021.

3. Results

3.1. Soil Potassium Pools

As clearly illustrated in Figure 2, following a decade of sustained differential fertilizer management practices, the soil WSK fell within the range of 19.50 to 39.67 mg/kg, the EK spanned from 157.50 to 193.67 mg/kg, the NEK ranged from 724.33 to 832.00 mg/kg, and the TK was 16.77 to 21.28 g/kg. Relative to CK treatment, the NPK failed to significantly increase the soil WSK, EK, or NEK. However, the additional application of straw-derived organic amendments significantly increased the contents of WSK, EK, NEK, and TK. Compared with the CK treatment, the NPK+ST, NPK+CP, and NPK+BR treatments significantly increased the soil WSK content by 84.62%, 103.42%, and 56.41% ($p < 0.05$); enhanced the content of soil EK by 7.72%, 22.96%, and 22.22%, respectively; significantly increased the NEK by 5.80%, 14.86%, and 13.16% ($p < 0.05$); and remarkably increased TK by 17.48%, 26.91%, and 18.29%, respectively ($p < 0.05$). Among the organic amendment treatments, the NPK+CP treatment exhibited the highest content of all the K pools in the soil.

3.2. Cation Exchange Parameters

As shown in Figure 3a, after 10 years of long-term different fertilization treatments, the soil CEC ranged from 25.37 to 28.31 cmol/kg. The NPK treatment had the lowest soil CEC, while the treatments with additional straw-derived organic amendments better maintained

soil CEC at higher levels, among which the NPK+BR treatment had the highest soil CEC. The soil K saturation ranged from 1.57% to 1.87% (Figure 3b). Relative to CK treatment, NPK failed to significantly increase the soil K saturation; however, the additional application of straw-derived organic amendments better maintained it at higher levels. Compared to the CK treatment, the NPK+ST, NPK+CP, and NPK+BR treatments, respectively, increased the soil K saturation by 2.55%, 19.11%, and 10.83%. Among them, NPK+CP achieved the best soil K saturation.

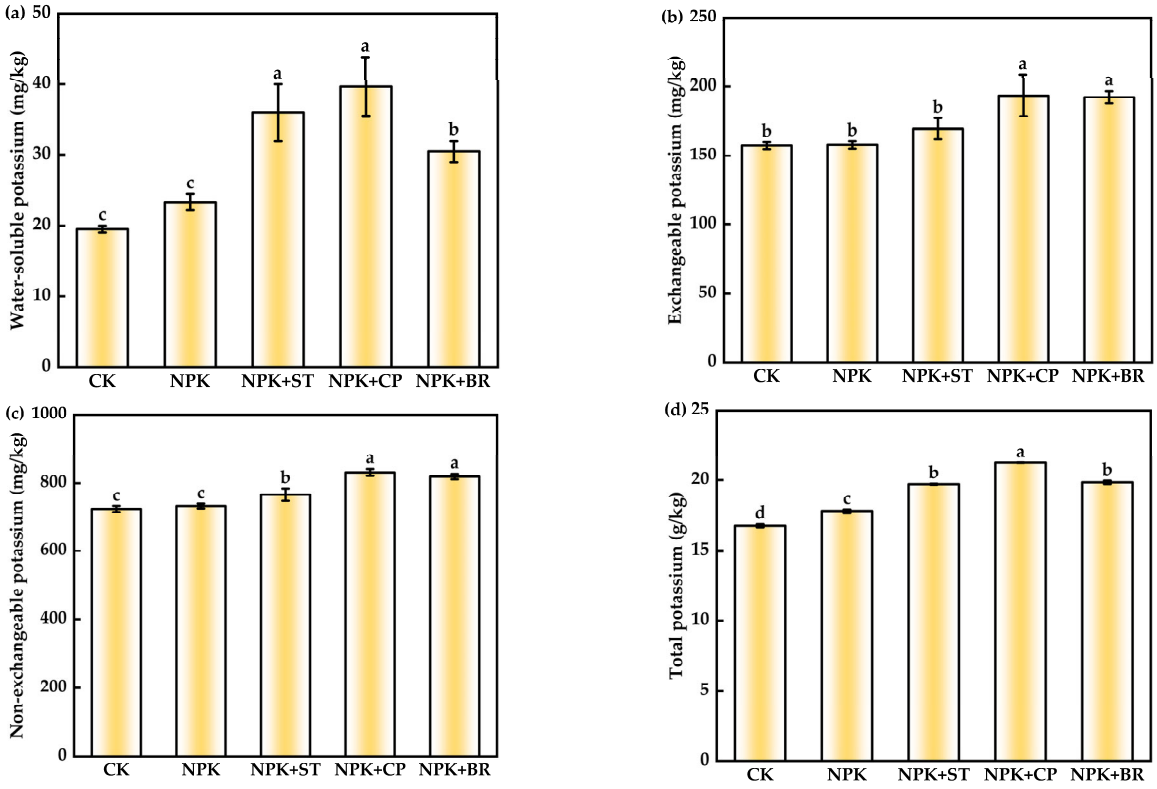


Figure 2. Effects of chemical fertilizer combined with different straw-derived organic amendments on soil potassium pools. (**a**) Water-soluble potassium (mg/kg); (**b**) Exchangeable potassium (mg/kg); (**c**) Non-exchangeable potassium (mg/kg); (**d**) Total potassium (g/kg). Values are means ± SE (n = 3). Different lowercase letters indicate significant differences among treatments at $p < 0.05$. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

3.3. Soil Potassium Fixation Characteristics

This study then examined the association between the addition of exogenous K and the K fixation amount in soils under different treatments (Figure 4a). In all treatments, the K fixation amount rose as exogenous K was increasingly added within the range of 0.1 to 4.0 g/kg. At most levels of exogenous K addition, the treatments could be roughly ranked according to the amount of potassium fixation as follows: CK > NPK > NPK+BR > NPK+ST > NPK+CP. The same trend was observed for the average amount of K fixation across all levels of exogenous K addition (Figure 4b). The average amount of potassium fixation under CK was the highest, at 600.25 mg/kg. The NPK treatment significantly decreased the average soil K fixation amount ($p < 0.05$). Meanwhile, the utilization of straw-derived organic amendments further remarkably decreased the average soil K fixation amount. Relative to the NPK, NPK+ST, NPK+CP, and NPK+BR significantly reduced the average amount of soil K fixation by 27.62%, 40.89%, and 18.85%, respectively ($p < 0.05$).

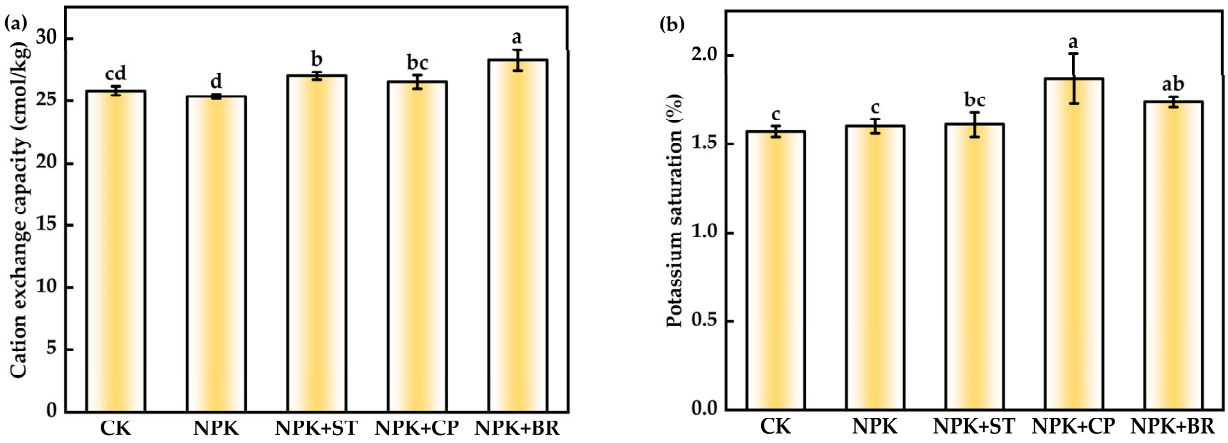


Figure 3. Effects of chemical fertilizer combined with different maize straw-derived organic amendments on soil cation exchange parameters. (**a**) Cation exchange capacity (cmol/kg); (**b**) Potassium saturation (%). Values are means ± SE (n = 3). Different lowercase letters indicate significant differences among treatments at $p < 0.05$. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

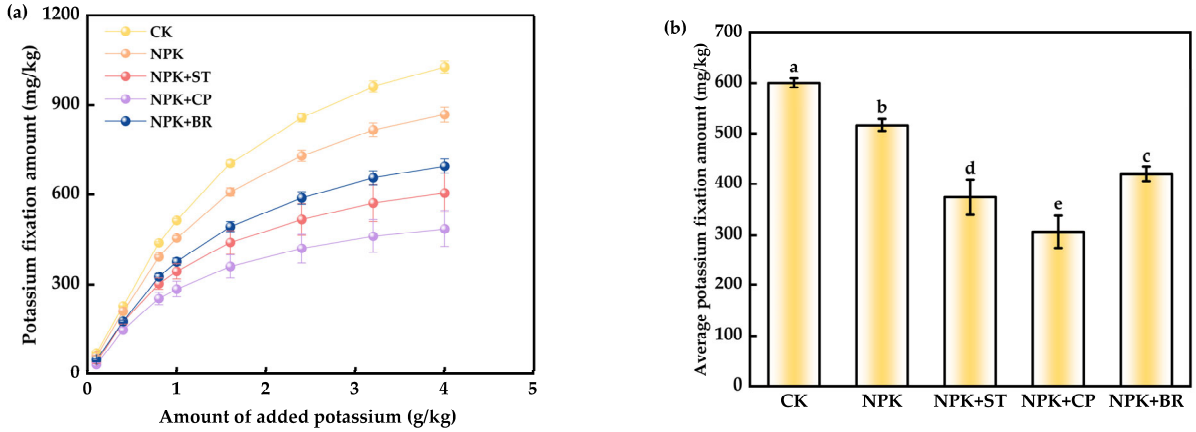


Figure 4. Effects of chemical fertilizer combined with different maize straw-derived organic amendments on soil potassium fixation amount and average potassium fixation amount. (**a**) Potassium fixation amount (mg/kg) vs. amount of added potassium (g/kg); (**b**) Average potassium fixation amount (mg/kg). Values are means ± SE (n = 3). Different lowercase letters indicate significant differences among treatments at $p < 0.05$. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

As shown in Figure 5a, the K fixation rates under different treatments showed a consistent trend: the rate of K fixation declined with increasing exogenous K addition. At most levels of exogenous K addition, the treatments could be roughly ranked according to the K fixation rate as follows: CK > NPK > NPK+BR > NPK+ST > NPK+CP. The same trend was observed for the average K fixation rate across all levels of exogenous K addition (Figure 5b). The average K fixation rate under CK was the highest, at 46.66%. The NPK treatment significantly decreased the average K fixation rate ($p < 0.05$). Meanwhile, the addition of straw-derived organic amendments further significantly decreased the average soil K fixation rate. Relative to the NPK, NPK+ST, NPK+CP, and NPK+BR significantly reduced the average soil K fixation rate by 26.15%, 39.75%, and 18.15%, respectively ($p < 0.05$).

As shown in Table 5, the quadratic regression model was used to fit the relationship between the added exogenous K amount and K fixation amount. With R^2 ranging from 0.9693 to 0.9932, the model exhibited excellent goodness-of-fit. The model allowed for

the calculation of the maximum amount of K fixation (Q_{max}) in soils under the different treatments. The treatments could be roughly ranked according to Q_{max} as follows: CK > NPK > NPK+BR > NPK+ST > NPK+CP. This trend is the same as that for the K fixation amount and rate. The Q_{max} under the CK treatment was the highest, reaching 1009.04 mg/kg. The NPK treatment reduced the soil Q_{max}; compared with the CK treatment, the NPK treatment Q_{max} was reduced by 19.05%. Relative to NPK treatment, the integration of chemical fertilizer with straw-derived organic amendments reduced the soil Q_{max} by 16.26% to 40.95%, with the NPK+CP treatment leading to the largest decrease.

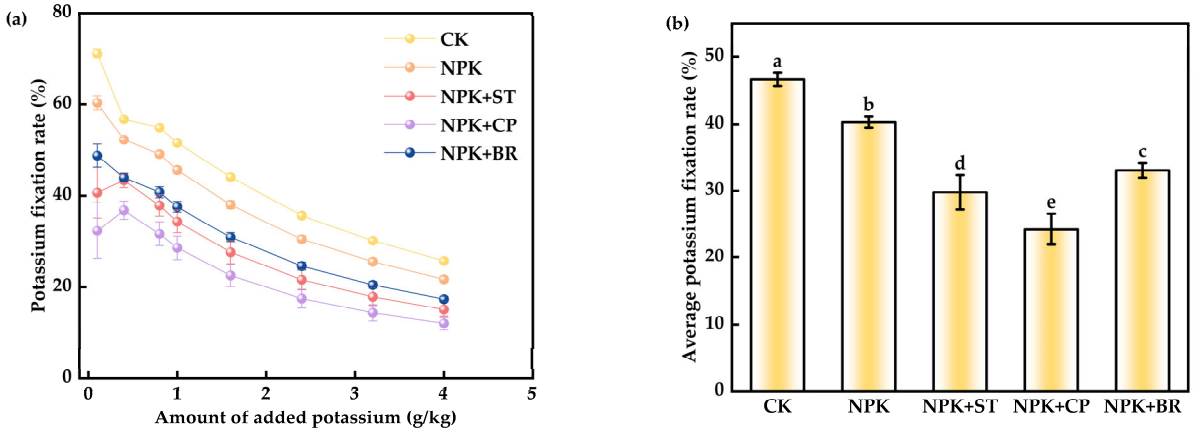


Figure 5. Effects of chemical fertilizer combined with different maize straw-derived organic amendments on soil potassium fixation rate and average potassium fixation rate. (**a**) Potassium fixation rate (%) vs. amount of added potassium (g/kg); (**b**) Average potassium fixation rate (%). Values are means ± SE (n = 3). Different lowercase letters indicate significant differences among treatments at $p < 0.05$. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

Table 5. Quadratic regression models of soil potassium fixation and the calculated maximum amounts of potassium fixation under different fertilization treatments.

Treatment	Equation	R^2	Q_{max} (mg/kg)
CK	$y = -68.71x^2 + 515.22x + 43.18$	0.9932	1009.04
NPK	$y = -60.85x^2 + 433.07x + 46.25$	0.9891	816.79
NPK+ST	$y = -45.83x^2 + 317.65x + 46.74$	0.9759	597.15
NPK+CP	$y = -38.16x^2 + 259.37x + 41.54$	0.9693	482.28
NPK+BR	$y = -50.20x^2 + 358.95x + 42.28$	0.9855	684.00

R^2, coefficient of determination; Q_{max}, maximum amount of potassium fixation (mg/kg); y, potassium fixation amount (mg/kg); x, amount of added potassium (g/kg). CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

3.4. Soil Non-Exchangeable Potassium Release Kinetics

As shown in Figure 6a, under all the experimental conditions, soil NEK release exhibited a biphasic pattern: an initial rapid-release stage spanning 1–168 h, followed by a subsequent slow and steady release phase extending from 168 to 1232 h. The total cumulative NEK release from soils under the different treatments ranged from 231.90 to 320.60 mg/kg, with significant differences among them (Figure 6b). The total cumulative NEK released showed small differences among the CK, NPK, and NPK+ST treatments. Relative to CK treatment, NPK+CP and NPK+BR significantly increased the total cumulative NEK released by 38.25% and 31.82%, respectively ($p < 0.05$). This suggests that the supplementary application of straw compost as well as straw biochar is more conducive to the release of NEK in the soil.

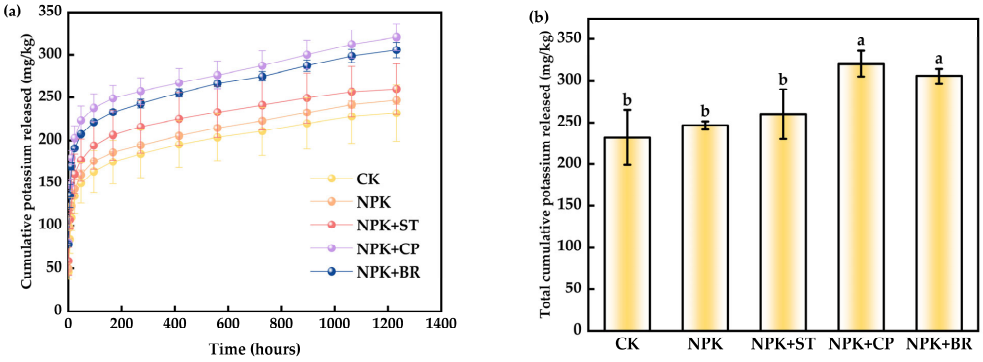


Figure 6. Cumulative release kinetics (**a**) and total cumulative release (**b**) of soil non-exchangeable potassium under different fertilization treatments. Values are means ± SE (n = 3). Different lowercase letters indicate significant differences among treatments at $p < 0.05$. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

Different kinetic models were hereby utilized to characterize the soil NEK's release process (Table 6). The average coefficients of determination (R^2) for the fitting of the six kinetic models were ordered as follows: the simplified Elovich model (0.9883) > power function model (0.9603) > first-order kinetics model (0.8385) > parabolic diffusion model (0.8325) > zero-order kinetics model (0.6670) > exponential model (0.5911). The simplified Elovich model had the smallest standard error (SE); thus, it served as the optimal model for characterizing the NEK release process in black soil under different treatments.

Table 6. Goodness-of-fit indices for six kinetic models describing soil non-exchangeable potassium release under different fertilization treatments.

Treatment	Zero-Order		First-Order		Power Function		Parabolic Diffusion		Simplified Elovich		Exponential	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE
CK	0.6807	33.13	0.8649	21.56	0.9674	10.59	0.8486	22.82	0.9932	4.83	0.5962	35.78
NPK	0.6824	34.04	0.8482	23.42	0.9633	11.43	0.8442	23.80	0.9897	5.99	0.6023	36.61
NPK+ST	0.6404	37.83	0.8555	23.49	0.9572	13.05	0.8161	27.07	0.9918	5.74	0.5582	40.29
NPK+CP	0.6489	41.13	0.7959	31.35	0.9514	15.49	0.8154	30.25	0.9816	9.51	0.5885	43.40
NPK+BR	0.6825	38.33	0.8282	28.19	0.9619	13.26	0.8383	27.33	0.9851	8.33	0.6103	40.80
Mean	0.6670	36.89	0.8385	25.60	0.9603	12.77	0.8325	26.25	0.9883	6.88	0.5911	39.37

R^2, coefficient of determination; SE, standard error. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

The soil NEK release processes under different treatments were fitted using the simplified Elovich model (Table 7). The constant b represents the apparent release rate coefficient, with a range of 25.52–30.46. The treatments were ranked according to the constant b values as follows: NPK+CP > NPK+BR > NPK+ST > NPK > CK.

Table 7. Parameter of the simplified Elovich model for soil non-exchangeable potassium release under different fertilization treatments.

Treatment	Simplified Elovich $K_t = a + b\ln t$	b
CK	$K_t = 45.68 + 25.52 \times \ln t$	25.52
NPK	$K_t = 53.35 + 26.27 \times \ln t$	26.27
NPK+ST	$K_t = 64.08 + 27.41 \times \ln t$	27.41
NPK+CP	$K_t = 94.15 + 30.46 \times \ln t$	30.46
NPK+BR	$K_t = 85.95 + 29.53 \times \ln t$	29.53

K_t, cumulative potassium (mg/kg) release at time t (hours); a, the kinetic model constant; b, the apparent release rate coefficient. CK, no fertilizer; NPK, chemical fertilizer alone; NPK+ST, NPK plus maize straw; NPK+CP, NPK plus straw compost; NPK+BR, NPK plus straw biochar.

4. Discussion

Herein, no significant differences in the contents of soil WSK, EK, or NEK were identified between the NPK and CK regimes. The lack of significant differences in soil available K pools between CK and NPK was attributed to lower crop yield and K removal under CK [34]. However, the combined application of chemical fertilizer and straw-derived amendments significantly increased all soil K pools compared to CK. The promoting effect of organic amendments on soil K pools may be attributed to two mechanisms: (i) direct K input and modulation of K pools equilibria [35,36], and (ii) improved soil physicochemical properties that favor microbial communities (e.g., K-solubilizing bacteria) involved in K cycling [15–17].

Straw-derived organic amendments supplied substantial organic colloids, which elevated soil CEC in the combined treatments. Generally, K saturation is important because a higher K saturation of the exchange complex minimizes exogenous K adsorption in the solid phase and may promote K release into the soil solution. This parameter should not be ignored when comprehensively assessing soil K dynamics during long-term cropping [12]. The present study found that the lowest K saturation in the CK treatment resulted from long-term insufficient K input, which led to K depletion at soil exchange sites. The integration of chemical fertilizer with straw-derived organic amendments better maintained soil K saturation at a high level, and this finding well aligns with that previously reported [37].

This study found that the soil K fixation amount in black soil rose as more exogenous K was introduced, whereas the K fixation rate showed a decreasing trend. This aligns well with the result reported by Li et al. [38]. However, some studies have found that increasing exogenous K addition did not remarkably affect the soil K fixation rate [39]. Zhang et al. [30] reported significantly greater K fixation capacity in black soil than in purple, gray desert, and fluvo-aquic soils. This was mainly because soil K fixation capacity is closely related to the type and physicochemical properties of clay minerals. The clay minerals of black soil are dominated by expansive 2:1-type minerals, including montmorillonite and vermiculite [40], and such minerals' K fixation capacity is significantly stronger than that of 1:1-type ones like kaolinite. This serves as the core internal reason that black soil has a higher K fixation capacity than other soil types. Extensive research has confirmed that applying K fertilizer or organic materials in the long term can effectively reduce the soil K fixation capacity [21]. Similar results were obtained in the present study: the different fertilization treatments were ranked according to the Q_{max} of the black soil as follows: CK > NPK > NPK+BR > NPK+ST > NPK+CP. The highest Q_{max} in the CK treatment reflects progressive K depletion under a decade of unfertilized maize monoculture, which generated abundant vacant high-energy adsorption sites on soil minerals and consequently enhanced K fixation [21].

Soil NEK release followed a biphasic pattern: an initial rapid phase (1–168 h) followed by a slow, steady phase (168–1232 h). This release pattern is highly consistent with that in previous related studies [41,42]. The high initial release rate was driven by rapid K^+–Ca^{2+} exchange on clay mineral surfaces. After K^+ at these exchange sites was depleted, further exchange between K^+ and Ca^{2+} slowed down significantly. This was because the ionic radius of hydrated Ca^{2+} is larger than that of hydrated K^+, making it difficult for it to enter the interlayer spaces of clay minerals in order to complete ion exchange [43]. Six kinetic models were used to fit NEK release kinetics under different treatments. Findings revealed that the simplified Elovich model provided optimal fitting performance, indicating a diffusion-controlled process [44]. Das et al. [37] and Jalali et al. [45] also used the simplified Elovich model to describe K release from Inceptisols, Vertisols, and calcareous soils, supporting its broad applicability for soil K release kinetics. The present study found that total NEK release and apparent release rate coefficients in black soil varied

significantly across treatments, ranking as: NPK+CP > NPK+BR > NPK+ST > NPK > CK. Numerous studies have confirmed [18,19] that soils amended with organic materials exhibit higher potassium release-related parameters at all stages of K extraction. Long-term combined application of chemical fertilizer and organic amendments sustained high soil NEK content. Additionally, integrating chemical fertilizer with organic materials could effectively optimize soil physicochemical characteristics, foster a beneficial growth and metabolic environment for soil microbial communities [46], and further promote soil NEK release by regulating soil microecological processes and mineral weathering [47].

This study applied equal carbon inputs across treatments to exclude carbon quantity effects, thereby distinguishing the specific impacts of amendment type and properties on soil K pools and dynamics. Among organic amendment treatments, the NPK+CP treatment was significantly superior in increasing the contents of various K pools and K saturation, as well as in promoting NEK release in black soil. The reasons were mainly twofold: First, the straw compost had undergone partial decomposition, with a low carbon-to-potassium ratio and abundant available K nutrients (Table 2), which could directly supplement K to the soil and thus significantly increase various K pool contents and K saturation in the black soil. Second, the straw compost contained high concentrations of organic acids, which could effectively activate soil mineral K through solubilization and chelation, further enhancing the effective K supply capacity of the soil [48,49]. In addition, the NPK+CP treatment had the lowest soil K fixation capacity, and exogenous K fertilizer could more easily meet the soil K fixation demand under this treatment, thereby exerting a yield-increasing effect [20,21]. Therefore, chemical fertilizer combined with straw compost was the optimal strategy for improving soil K availability under the present experimental conditions.

5. Conclusions

This study demonstrated that co-applying chemical fertilizer with straw-derived amendments significantly enhanced soil K pools and fertility compared with the CK and NPK treatments. This integrated approach reduced soil K fixation capacity, thereby enabling exogenous K fertilizer to more readily satisfy soil K fixation demand and strengthening the yield response to K fertilization. Additionally, it enhanced the release capacity of soil NEK, facilitating the medium- and long-term K supply required for crop growth. Under the present experimental conditions, the combined application of chemical fertilizer with straw compost represents the optimal strategy for improving K supply capacity in black soil. We recommend that agricultural managers make rational use of crop residues following harvest. In conclusion, these findings provide evidence-based guidance for sustainable soil K management and the efficient utilization of maize straw resources in Northeast China's black soil region.

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Abbreviations

The following abbreviations are used in this manuscript:

CK	Control (no fertilizer)
NPK	Chmical fertilizer alone
ST	Maize straw
CP	Straw compost
BR	Straw biochar
K	Potassium
WSK	Water-soluble potassium
EK	Exchangeable potassium
NEK	Non-exchangeable potassium
TK	Total potassium
CEC	Cation exchange capacity
K_t	Cumulative non-exchangeable potassium release at time t
K_{max}	Total cumulative non-exchangeable potassium release
a	Kinetic model constant
b	The apparent release rate coefficient
Q_{max}	Maximum amount of potassium fixation
y	Potassium fixation amount in quadratic regression model
x	Amount of added exogenous potassium in quadratic regression model
R^2	Coefficient of determination
SE	Standard error

Appendix A

Table A1. The results of assumption testing and the non-parametric test of selected soil traits.

Soil Trait	Shapiro–Wilk Test		Levene Test		Non-Parametric Test	
	W	*p*-Value	F	*p*-Value	H	*p*-Value
Water-soluble potassium	0.9331	0.3038	1.1188	0.4006	12.9044	0.0118
Exchangeable potassium	0.8766	0.0422	0.9970	0.4529	12.0465	0.0170
Non-exchangeable potassium	0.8712	0.0352	0.2927	0.8762	12.9667	0.0114
Total potassium	0.8879	0.0623	0.5316	0.7157	13.5000	0.0091
Cation exchangeable capacity	0.9386	0.3654	0.9894	0.4564	12.4000	0.0146
Potassium saturation	0.8698	0.0335	1.0814	0.4160	10.9333	0.0273
Average potassium fixation amount	0.9362	0.3371	0.5734	0.6884	12.9333	0.0116
Average potassium fixation rate	0.9427	0.4180	0.6675	0.6290	13.2333	0.0102
Total cumulative potassium released	0.9552	0.6103	0.6376	0.6475	10.8861	0.0279

The Shapiro–Wilk W statistic evaluates the conformity of data to a normal distribution, while Levene's F statistic assesses homogeneity of variances across groups. In both tests, $p \leq 0.05$ leads to the rejection of the null hypothesis, whereas $p > 0.05$ indicates a failure to reject it. For the non-parametric Kruskal–Wallis test, the H statistic, derived from ranked data, quantifies the divergence among group distributions, and the associated *p*-value determines whether this divergence is statistically significant. The between-group degrees of freedom for all omnibus tests were 4.

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