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Synergy of Biochar and Organic Fertilizer Reduces Phosphorus Leaching

Danni Ma [1,2], Yaofeng Wang [1,2,*], Tong Zheng [3,4,5], Qixing Zhou [3,4,5] and Jiandong Sheng [1,2]

[1] College of Resources and Environment, Xinjiang Agricultural University, Urumqi 830052, China; 320223533@stu.xjau.edu.cn (D.M.); sjd@xjau.edu.cn (J.S.)
[2] Xinjiang Key Laboratory of Soil and Plant Ecological Process, Urumqi 830052, China
[3] College of Environmental Science and Engineering, Nankai University, Tianjin 300350, China; 13940214881@163.com (T.Z.); zhouqx@nankai.edu.cn (Q.Z.)
[4] MOE Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin 300350, China
[5] Tianjin Key Laboratory of Environmental Remediation and Pollution Control, Carbon Neutrality Interdisciplinary Science Centre, Tianjin 300350, China
* Correspondence: yfwang@xjau.edu.cn

Abstract

To address rising global food demand, improving phosphorus (P) use efficiency in agriculture is crucial. Organic fertilizers and biochar are recognized for their potential to improve soil phosphorus availability and reduce environmental losses. However, the synergistic effects of their combined application on phosphorus retention and transformation have received insufficient attention. This study investigated the synergy between cow dung-derived biochar (produced at 400 °C and 700 °C) and organic fertilizer using P fractionation, leaching, and extraction tests. Results indicated that the H_2O-P content in organic fertilizer as high as 42.17 $mg \cdot g^{-1}$, resulting in a cumulative leaching loss of up to 11.62 $mg \cdot g^{-1}$. In contrast, biochar exhibited lower leaching due to more stable C–P compounds, as confirmed by X-ray photoelectron spectroscopy (XPS). When biochar and organic fertilizer were co-applied, complexation with Ca^{2+} on their surfaces reduced phosphorus leaching from the mixture by 83.69%. The formation of $Ca_2P_2O_7$ crystals, detected through X-ray diffraction (XRD), indicates a strong synergistic effect between biochar and organic fertilizer. Additionally, the porous structure of biochar adsorbed phosphorus from organic fertilizer, further inhibiting leaching losses. This synergy enhances P retention, offering an effective strategy to improve P use efficiency and support sustainable soil management.

Keywords: biochar; organic fertilizer; phosphorus leaching; calcium ion; combined application

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1. Introduction

Phosphorus, as an essential nutrient, plays an irreplaceable role in plant growth, development, and metabolic processes. However, its low solubility and limited mobility in soil constrain its bioavailability [1]. Studies indicate that even in farmland soils where Olsen-P concentrations substantially exceed the optimal range for conventional crop production (46.0–58.0 $mg \cdot kg^{-1}$), phosphorus use efficiency continues to decline gradually [2,3].

Organic fertilizers enhance the conversion of insoluble phosphorus into plant-available forms, promoting dissolution and uptake [4,5]. However, organic fertilizers are not without limitations. Excessive application of organic fertilizers can cause both phosphorus migration and accumulation [6,7]. Phosphorus balance has developed in a polarized manner, elevating the risks of phosphorus contamination in both surface waters and soils [8].

Farmlands in southeastern China a paradox: high exogenous phosphorus inputs (annual accumulation of 70–400 kg·hm^{-2}) coexist with persistently low plant-available phosphorus [9]. This is largely attributable to the weak phosphorus retention capacity of the subsurface soil, facilitating phosphorus leaching rather than crop uptake [10]. In response, biochar has emerged as a promising material for synergistically regulating the phosphorus cycle. Its porous structure and surface metal ion adsorption sites can effectively mitigate the migration and loss of active phosphorus, making it particularly suitable for remediating soils with low phosphorus retention capacity [11,12]. Moreover, phosphorus-rich biochar derived from specific feedstocks (e.g., livestock manure) not contains substantial available phosphorus but can also release fixed phosphorus through competitive complexation via surface oxygen-containing functional groups (–COOH, –OH) with cations such as Ca^{2+} [13]. Nonetheless, biochar alone cannot serve as a sustainable nutrient source for plants [14], and its metal ions may reduce phosphorus availability through adsorption [15].

In recent years, growing emphasis on soil quality and environmental protection has spurred interest in biochar–organic fertilizer systems as an innovative soil amendment strategy. However, research outcomes have been inconsistent. These complexities can be attributed to several key factors such as biochar application rate, pyrolysis temperature, and environmental pH. An improper biochar-to-fertilizer ratio may lead to phosphorus fixation or excessive release. For instance, high biochar proportions can suppress phosphorus availability, though this can be partially alleviated by appropriate organic fertilizer supplementation [16]. Furthermore, pyrolysis temperature critically affects biochar properties; high-temperature biochar can reduce phosphorus fixation in acidic soils but may enhance adsorption in alkaline conditions, thereby differentially influencing phosphorus mobility and availability [16]. Collectively, these variable outcomes underscore the need to clarify the mechanisms underlying biochar–organic fertilizer interactions.

To elucidate how biochar and organic fertilizer jointly influence phosphorus effectiveness, this study produced two biochar types pyrolyzed at 400 °C and 700 °C cow manure and combined them with commercial chicken manure-based organic fertilizer at mass ratios of 7:3 and 3:7. We aimed to (1) characterize changes in phosphorus composition under combined applications, (2) clarify their effects on phosphorus dissolution, (3) evaluate the interact with phosphorus in a coordinated manner via a calcium-mediated complexation mechanism, and (4) conduct phosphate adsorption experiments to uncover the mechanisms affecting phosphorus availability. This study provides an optimized strategy and scientific guidance for the sustainable fertilization of soils facing phosphorus deficiency and leaching.

2. Materials and Methods

2.1. Source of Materials

The biochar raw material used in this experiment was selected from cow dung. The cow manure utilized was randomly collected from a dairy farm located in Xinjiang Uygur Autonomous Region, China. The organic fertilizer was procured as a commercial product from the Huocheng County Jiazheng Agricultural Materials Distribution Department, with chicken manure serving as its primary raw material. The total nutrients ($N + P_2O + K_2O$) $\geq$ 4%, organic matter $\geq$ 30%.

2.2. Preparation of Sample

The organic fertilizer and cow manure were first air-dried indoors for three days. The dried materials were then processed by grinding and sieving through a 100-mesh sieve, followed by storage in sealed bags for subsequent use. For biochar synthesis, the cow manure powder was placed in a crucible and subjected to anaerobic pyrolysis in a muffle furnace. The process was conducted at temperatures of 400 °C and 700 °C, respectively, for a duration of six hours, after which the resulting biochar was allowed to cool to room temperature [17,18].

The prepared biochar was mixed with organic fertilizer in different weight ratios (3:7 and 7:3) to prepare eight samples (Table 1).

Table 1. Dosing rates and treatment names of test samples.

Treatment	Organic Fertilizer	400 °C Biochar	700 °C Biochar
CK	0	0	0
OF	100% (50 mg)	0	0
4BC	0	100% (50 mg)	0
7BC	0	0	100% (50 mg)
$4BC_7OF_3$	30% (15 mg)	70% (35 mg)	0
$4BC_3OF_7$	70% (35 mg)	30% (15 mg)	0
$7BC_7OF_3$	30% (15 mg)	0	70% (35 mg)
$7BC_3OF_7$	70% (35 mg)	0	30% (15 mg)

2.3. Determination of Phosphorus Fractionations

This research was conducted in the Key Laboratory of Soil and Plant Ecological Processes at the College of Resources and Environment, Xinjiang Agricultural University, under controlled environmental conditions with the temperature maintained at 24 ± 2 °C and relative humidity at 50% ± 10%.

The phosphorus forms in the samples were analyzed using the modified Hedley fractionation method [19]: 50 mg of each sample was placed in a 50 mL centrifuge tube, and 50 mL of each of the following extracting solutions was added successively deionized water, 0.5 mol·L^{-1} $NaHCO_3$, 0.1 mol·L^{-1} NaOH, and 1 mol·L^{-1} HCl. After each addition of the extracting solution, the tubes were shaken for 16 h. Then, they were centrifuged at 3000 rpm for 10 min. The supernatant was filtered through a 0.45 µm filter paper, and the phosphorus content in the supernatant was determined by the molybdenum blue colorimetric method.

2.4. Kinetic Leaching of Phosphorus

The kinetic leaching of P was monitored under three Ca^{2+} concentrations (1, 10, 50 mmol·L^{-1}). 50 mg biochar and organic fertilizer was added into the plastic centrifuge tube containing 50 mL extraction solution, and blank controls without biochar and organic fertilizer were set. The plastic centrifuge tubes were placed in an oscillator and shaken at 150 rpm and 25 °C for 2 h. Samples were taken at 0.5, 1, 3, 7, 11, 15, 20, 30, 45, and 60 days, respectively. After centrifugation at 3000 rpm for 10 min, the supernatants were filtered through 0.45 µm filter paper [20]. The determination method is the same as above. Each set of experiments was replicated three times.

2.5. Sequential Extraction of Phosphorus

Based on the previous kinetic leaching test, a medium concentration $CaCl_2$ solution (10 mmol·L^{-1}) was selected as the leaching agent for the continuous extraction test. 50 mg biochar and organic fertilizer was loaded in plastic centrifuge tubes containing 50 mL of 10 mmol·L^{-1} $CaCl_2$ solution, and a blank control (without biochar and organic fertilizer) was also prepared. The tubes were inverted three times daily. Samples were taken at 1, 2, 4, 10, 20, 30, 45, and 60 days, respectively. The samples were centrifuged at 3000 rpm for 10 min, and 40 mL of the supernatant was extracted, then 40 mL of the same solution was added. The supernatant was filtered through a 0.45 µm qualitative filter paper [20]. The determination method is the same as above. Each group of experiments was repeated three times.

Following the sequential extraction, samples of the biochar/organic fertilizer mixture that had been filtered for 60 days were collected. These samples were then dried at 70 °C for 2 h in preparation for subsequent analysis. To examine changes in surface morphology and elemental composition, the samples were observed before and after extraction using a scanning electron microscope coupled with an X-ray energy dispersive spectrometer (SEM-EDX, ZEISS Sigma 300, Germany). To determine the specific phosphate compounds present, the materials were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA). Furthermore, the crystalline phases formed by Ca^{2+} and P binding were identified using X-ray diffraction (XRD, Rigaku Ultima IV, Japan).

2.6. P Sorption Experiment

Measure 50 mg of biochar and organic fertilizer samples into 50 mL plastic centrifuge tubes, add 50 mL of KH_2PO_4 solution (10, 20, 30, 40, 50 $mg \cdot g^{-1}$), and adjust the pH of the solution to 7.0 with 0.1 mol HCl and NaOH. At room temperature, shake in a constant temperature shaker for 2 h (150 rpm, 25 °C), and filter the supernatant through a 0.45 μm qualitative filter paper. The determination method is the same as above. Each group was repeated three times, and the average value of the determination results was taken.

2.7. Statistics Analysis

All the data was processed using Excel 2021. And analyzed using SPSS 26.0 for independent one-way ANOVA, and multiple comparisons were made using the Duncan method to assess the significance of the differences between the indicators ($p < 0.05$). Origin 2021 and Figdraw 2.0 was used to map the final data.

3. Results

3.1. Sample Analysis

Table 2 summarizes the fundamental properties of the biochar and organic fertilizer. The available phosphorus content in the organic fertilizer (OF) was 51.77 $mg \cdot g^{-1}$, which is fourteen times that of 700 °C biochar (7BC). The 400 °C biochar (4BC) and 7BC available phosphorus contents measuring 21.77 and 3.62 $mg \cdot g^{-1}$ respectively. As the pyrolysis temperature increased, the porous structure of the biochar became more compact, characterized by fluffy or fragmented fracture openings [21], this structural evolution resulted in higher ash content and lower yield (Figure 1a–c).

Table 2. Properties of the biochar and organic fertilizers.

Samples	Available Phosphorus ($mg \cdot g^{-1}$)	pH	EC (1:5) ($\mu S \cdot cm^{-1}$)	Ash (%)	Productivity (%)
Organic fertilizer (OF)	52.03 ± 0.48	9.47 ± 0.03	10.99 ± 0.67	/	/
400 °C Biochar (4BC)	21.77 ± 0.29	9.59 ± 0.01	6.22 ± 0.07	74.45 ± 0.38	66.25 ± 2.93
700 °C Biochar (7BC)	3.62 ± 0.15	11.07 ± 0.06	6.87 ± 0.18	82.04 ± 0.58	51.75 ± 1.97

3.2. Effect of Combined Application of Biochar and Organic Fertilizer on Phosphorus Fractionations

The phosphorus composition of biochar and organic fertilizer differed significantly (Figure 2). Among the materials, OF primarily consisted of H_2O-P, with a content as high as 42.17 $mg \cdot g^{-1}$—more than 60 times that of 7BC (0.63 $mg \cdot g^{-1}$). In the combined application groups, the $4BC_3OF_7$ treatment showed the highest H_2O-P content, reaching 34.7 $mg \cdot g^{-1}$, which was 67.81% higher than that of 4BC (11.17 $mg \cdot g^{-1}$) alone. All treatments released a certain amount of $NaHCO_3$-P, with the highest value extracted from 4BC at 18.52 $mg \cdot g^{-1}$. The HCl-P fraction was greatest in 7BC, measuring 32.56 $mg \cdot g^{-1}$, which was 8.77 $mg \cdot g^{-1}$ higher than that in the $7BC_3OF_7$ group. Furthermore, a significant interaction was observed between biochar pyrolysis temperature and the application ratio in shaping phosphorus component distributions.

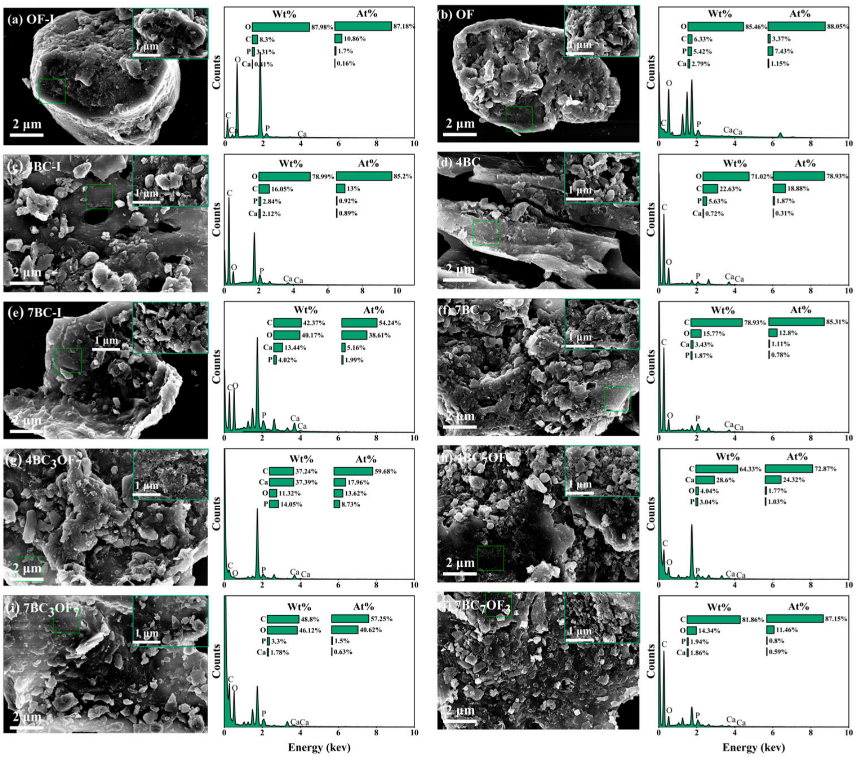
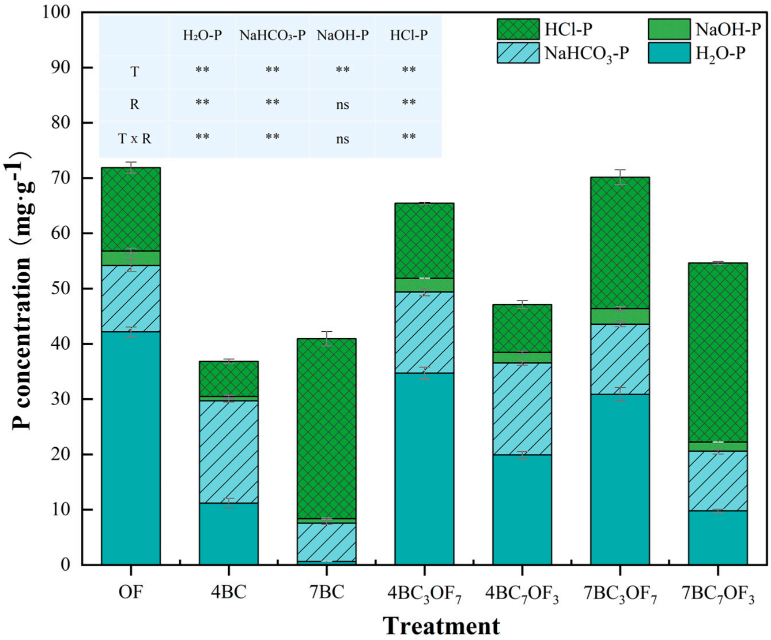


Figure 1. SEM-EDS patterns of the pristine samples and those obtained after the sequential extraction experiment. Note: panels (**a**,**c**,**e**) correspond to OF before water washing, 4BC, and 7BC, respectively; panels (**b**,**d**,**f**–**j**) represent OF after water washing, 4BC, 7BC, $4BC_3OF_7$, $4BC_7OF_3$, $7BC_3OF_7$, and $7BC_7OF_3$, respectively.



	H_2O-P	$NaHCO_3$-P	NaOH-P	HCl-P
T	**	**	**	**
R	**	**	ns	**
T x R	**	**	ns	**

Figure 2. Phosphorus fractionation for biochar and organic fertilizers and temperature and ratio of phosphorus fractions in biochar and organic fertilizers. The interaction table does not include the measured value OF, and T is the temperature of biochar; R is the proportion of application; T × R is the interaction between carbonization temperature and application ratio. ** The correlation was very significant ($p < 0.01$); ns correlation was not significant.

3.3. Effect of Ca^{2+} on Available Phosphorus Leaching from Biochar and Organic Fertilizer

Ca^{2+} concentration was the key factor controlling available phosphorus (AP) release (Figure 3). When $CaCl_2$ concentration increased to 50 mmol·L^{-1}, the phosphorus leaching rates were significantly slower. While organic fertilizer (OF) released the most phosphorus in deionized water (DI water), it was also the most susceptible to suppression by Ca^{2+}. Its available phosphorus content decreased significantly by 77.22%. In contrast, the $4BC_7OF_3$ treatment emerged as the optimal strategy. It not only maintained high AP levels in DI water but also exhibited remarkable resilience, showing the smallest reduction in AP content under high Ca^{2+} stress, thereby offering the most stable and efficient phosphorus management.

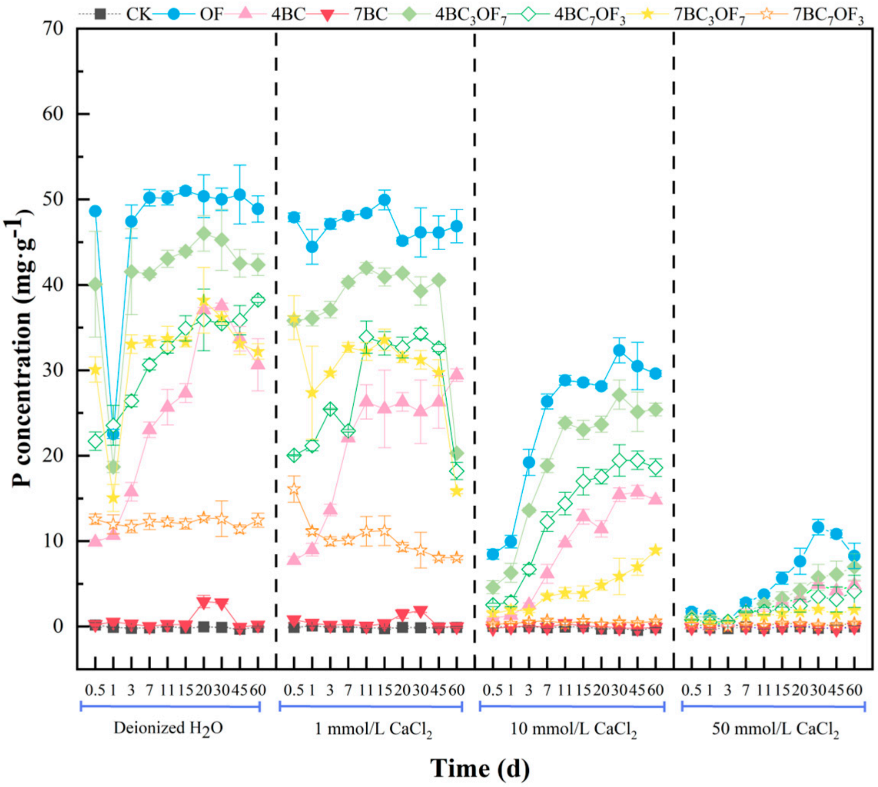


Figure 3. The influence of Ca^{2+} on the leaching amount of available phosphorus in biochar and organic fertilizer within 60 days.

3.4. The Effects of Combined Application of Biochar and Organic Fertilizer on Cumulative Phosphorus Content

Over time, the cumulative phosphorus release gradually increased in all treatments and eventually reached equilibrium after 20 days (Figure 4). The initial phosphorus leaching rates followed the order: OF > $4BC_3OF_7$ > $4BC_7OF_3$ > $7BC_3OF_7$ > 4BC > $7BC_7OF_3$ > 7BC > CK. OF exhibited the highest cumulative phosphorus release, reaching 1.21 mg by day 60, while 7BC showed nearly zero release. Among the combined application treatments, $4BC_3OF_7$ had the highest cumulative phosphorus content, exceeding that of $7BC_7OF_3$ by 0.85 mg. Over the 60-day period, the overall pH values showed a gradual decreasing trend, with OF having the lowest average pH. Furthermore, differences among treatments became less pronounced over time.

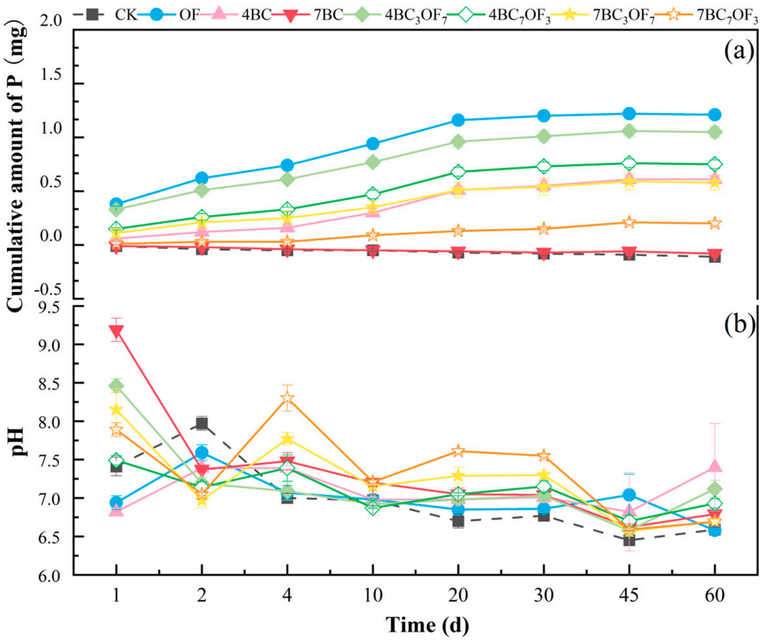


Figure 4. Effects of combined application of biochar and organic fertilizer on accumulation phosphorus content (**a**) and pH (**b**).

4. Discussion

The results demonstrated that the combined application of biochar and organic fertilizer modified the original composition and distribution of phosphorus forms. Specifically, as the biochar dosage increased, a significant decrease in H_2O-P content was observed in the organic fertilizer (Figure 2), indicating that a considerable portion of phosphorus in the organic fertilizer is soluble and likely associated with Al and Fe compounds, as supported by XRD analysis (Figure 5). Such soluble phosphorus is highly mobile [22] and may lead to phosphorus leaching during rainfall or irrigation [23]. With the incorporation of biochar, the H_2O-P content in the organic fertilizer was markedly reduced, leading to a more homogeneous distribution of phosphorus forms. Biochar itself contains substantial amounts of phosphorus, albeit primarily in stable forms that are not readily available. The combined application promoted the dissolution of otherwise insoluble phosphorus compounds via organic acids derived from the organic fertilizer, thereby enhancing the release of stable phosphorus fractions (e.g., HCl-P, NaOH-P) within the biochar [24]. This suggests that, from the perspective of phosphorus speciation, the combined application not only reduces the risk of phosphorus loss but also improves the potential for phosphorus utilization efficiency [23]. During high-temperature pyrolysis, orthophosphates tend to crystallize and precipitate with insoluble Fe and Ca, transforming phosphorus into more recalcitrant forms [25].

The initial release of phosphorus in the kinetics reflects the desorption from the surfaces of biochar and organic fertilizer, while the subsequent release over time indicates the diffusion and dissolution of phosphorus from both materials [26]. The results clearly demonstrate that the presence of Ca^{2+} significantly inhibits phosphorus leaching from biochar and organic fertilizer. This inhibitory effect becomes more pronounced with increasing Ca^{2+} concentration, consistent with previous findings [27]. The mechanism underlying this phenomenon is that phosphorus in biochar primarily exists as HPO_4^{2-} [28], which readily forms insoluble calcium phosphate precipitates with Ca^{2+} [29], thereby reducing the mobility of water-soluble phosphorus from organic fertilizer. Consequently, in solutions with low Ca^{2+} concentrations, fewer restrictions apply, and phosphorus leaching exhibits time-dependent behavior [26]. In this study, the available phosphorus content in the combined application treatment was intermediate between those of the single applications, indicating a reduction in phosphorus leaching from organic fertilizer. This is likely attributed to the addition of biochar, which enhances the exchange capacity of calcium and magnesium [30,31] and promotes the formation of calcium phosphate crystals with phosphate ions (Figure 5). During the dissolution process, the phosphorus content in the co-application group showed an initial decrease followed by an increase. This pattern may be explained by the high porosity of biochar, which has a strong affinity for phosphorus. Phosphate ions are initially adsorbed onto the biochar surface, reducing phosphorus release. Additionally, environmental pH influences the adsorption capacity of biochar. In the later stage of the kinetics experiment for the combined treatment, the overall pH exhibited a gradual decreasing trend (Figure 6). Previous research [32] has shown that within a pH range of 2.0 to 7.0, hydrogen ions promote the dissolution of calcium phosphate minerals in biochar, thereby enhancing phosphate adsorption via electrostatic attraction [30]. These findings suggest that phosphorus retention in organic fertilizers is closely associated with Ca^{2+} complexation and the adsorption capacity of biochar.

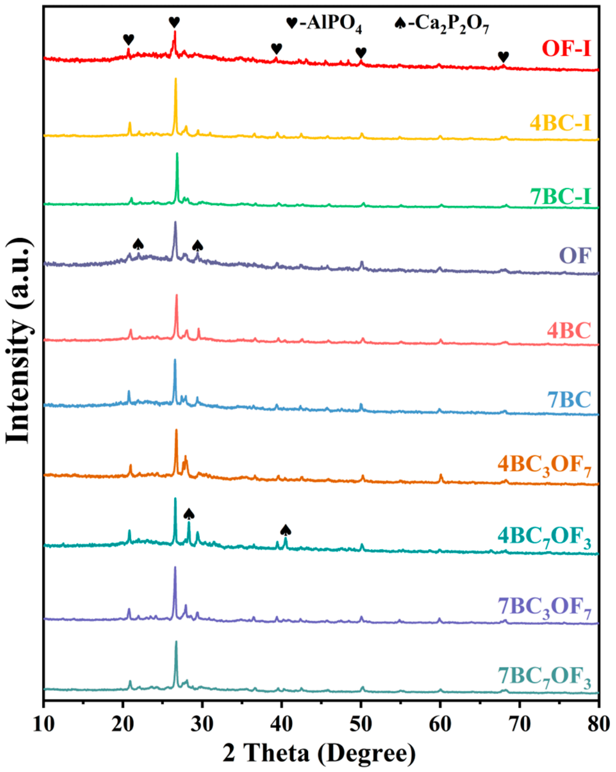


Figure 5. X-ray diffraction patterns of pristine samples, and the samples after the sequential extraction experiment. OF-I, 4BC-I and 7BC-I represent the pristine samples of OF, 4BC and 7BC, respectively.

As previously reported [33] Ca^{2+} restricts phosphorus mobility—a finding corroborated by the present study. However, this inhibitory effect was less pronounced in the case of high-temperature biochar (7BC). XPS analysis revealed that phosphorus in biochar primarily exists in the more stable form of carbon-phosphorus (C-P) bonds, particularly in high-temperature biochar (Figure 7). In contrast, medium- and low-temperature biochars (4BC) contain more C-O-P compounds, making its phosphorus leaching less sensitive to Ca^{2+} [24]. Although high-temperature biochar itself inhibits the dissolution rate of phosphorus, the co-application with organic fertilizer enhances phosphorus release from biochar. The dissolution and fixation of phosphorus are strongly influenced by Al and Fe present in the environment [25]. Organic fertilizer contains a certain amount of Al (Figure 5). The soluble Al inhibits the formation of calcium precipitates, mobilizing the otherwise less available phosphorus in biochar [30]. Additionally, substances from decomposing organic fertilizer can compete with phosphate for adsorption sites (e.g., organic matter, humic acids, and other low-molecular-weight organic acids) [34]. This competition displaces weakly bound phosphate and reduces phosphorus adsorption [35] (Figure 8).

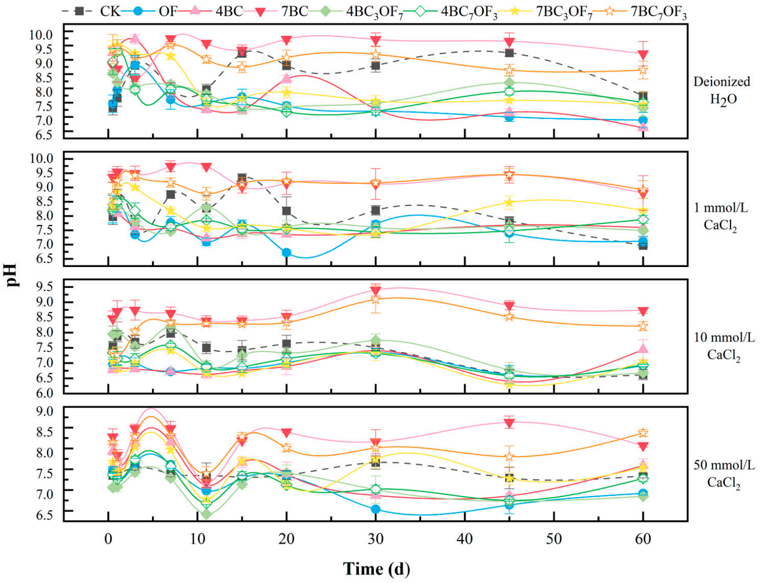


Figure 6. Effect of Ca^{2+} on the pH of biochar and organic fertilizer.

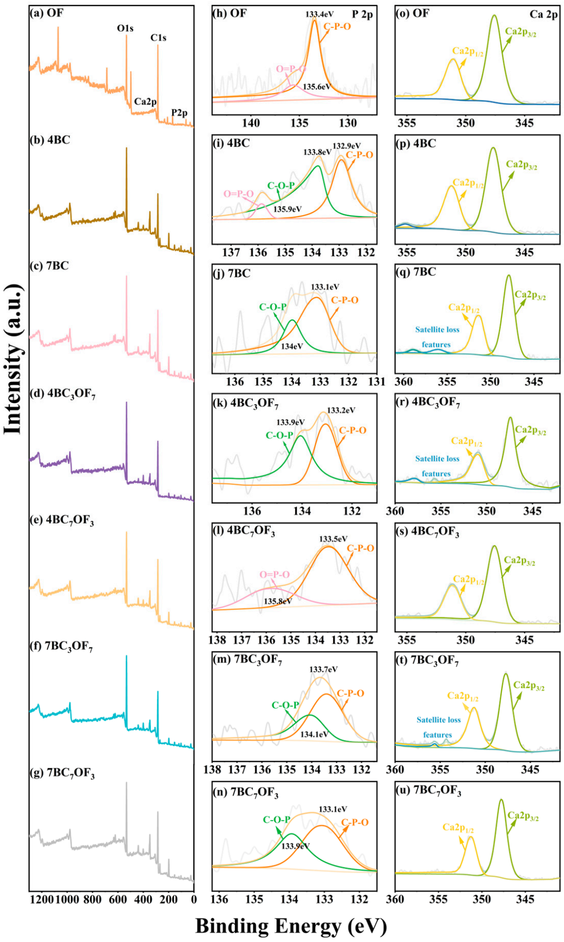


Figure 7. XPS spectra of the general spectrum (**a**–**g**), P 2p (**h**–**n**) and Ca 2p (**o**–**u**) region for the samples after the sequential extraction experiment.

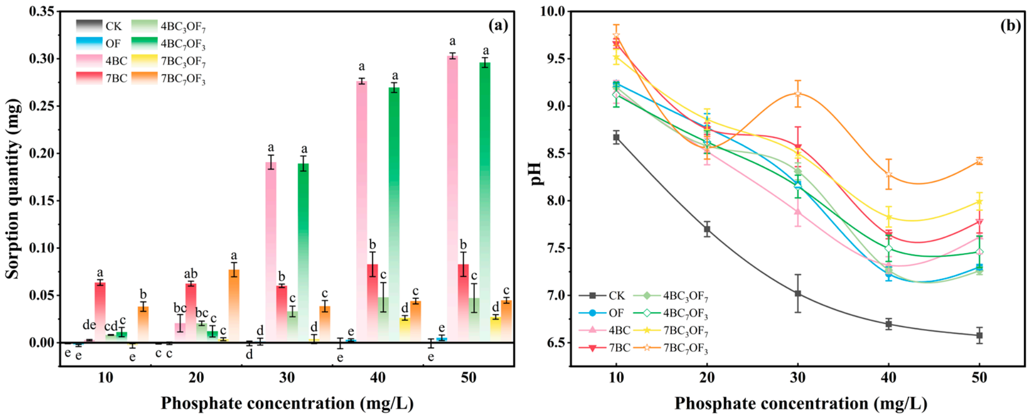


Figure 8. The impact of the combined application of biochar and organic fertilizer on phosphate adsorption capacity (**a**) and solution pH (**b**). The different letters on the column within the same treatment indicate significance at $p < 0.05$.

High-temperature biochar has a relatively low capacity for adsorbing phosphorus (Figure 8). This observation is consistent with the results reported by Zhao et al. [32]. As pyrolysis temperature increases, biochar tends to lose its original structure and undergoes fragmentation. This results in fewer adsorption sites for phosphorus [32]. Consequently, the overall adsorption capacity decreases. In particular, biochar derived from cow manure inherently contains a certain amount of phosphorus, which is continuously released during the adsorption process [36]. This leads to a slower phosphorus leaching rate in high-temperature biochar compared to that in organic fertilizer and low-temperature biochar.

Based on the kinetic leaching behavior of phosphorus from biochar and organic fertilizer, a sequential extraction experiment was further conducted to analyze phosphorus release. In the presence of exogenous Ca^{2+}, phosphorus from both biochar and organic fertilizer exhibited rapid leaching in the initial stage, followed by a gradually declining release rate in the later phase (Figure 3). Notably, whether in the kinetic leaching test or the continuous extraction experiment, the amount of leached phosphorus was highest from organic fertilizer alone and decreased significantly when biochar was applied in combination. As previously reported [37] the cumulative phosphorus release from organic fertilizer may be influenced by competition for anion adsorption sites between phosphorus and organic carbon. In this study, the comparison of the surface morphology of biochar and organic fertilizer before and after continuous extraction (Figure 1) revealed a noticeable increase in adherent particles after washing, with the appearance of plate-like structures that were more aggregated compared to the pre-washing state [30], combined with XPS analysis, in which the Ca^{2+} peak was consistently observed around 347.5 eV (Figure 7); these results indicate that in the combined application, phosphate derived from organic fertilizer was adsorbed onto the biochar surface [31] and precipitated with Ca^{2+} from the extractant. This process increased the content of active substances in the organic fertilizer and altered the chemical activity and adsorption capacity of metal oxides [38–40]. The combined application significantly enhanced phosphate adsorption capacity, leading to greater phosphorus accumulation compared to single applications. These findings clearly demonstrate the distinct advantages of biochar and organic fertilizer co-application in improving phosphorus nutrient utilization. During this process, available phosphorus does not leach unrestricted, thereby effectively mitigating the risk of phosphorus loss or environmental enrichment. Simultaneously, this approach alleviates the issue of low phosphorus availability by reducing the proportion of phosphorus in fixed forms that are poorly accessible for crop uptake. As research on the mechanisms of biochar and organic fertilizer interaction continues to deepen, their combined application exhibits great potential for enhancing soil phosphorus availability. This strategy is promising for promoting sustainable agricultural production through improved phosphorus use efficiency.

5. Conclusions

This study demonstrated that the co-application of biochar and organic fertilizer significantly improves phosphorus retention and optimizes phosphorus form distribution in agricultural systems. The combined use effectively reduced water-soluble phosphorus content and cumulative leaching losses by up to 83.69%, primarily through Ca^{2+}-mediated precipitation and adsorption within biochar's porous structure. These findings confirm that the integrated amendment enhances phosphorus availability while minimizing environmental risks, offering a practical strategy for improving phosphorus use efficiency in soils prone to leaching. However, this study was conducted under controlled laboratory conditions; further field validation is necessary to assess long-term effects under varying soil types, climate conditions, and crop systems. Future research should also explore economic feasibility and optimal application protocols for different agricultural contexts.

Author Contributions: Conceptualization, D.M. and Y.W.; methodology, D.M. and Y.W.; formal analysis, D.M. and Y.W.; data curation, D.M.; writing—original draft preparation, D.M.; writing—review and editing, Y.W., T.Z., Q.Z. and J.S.; supervision, Y.W.; funding acquisition, Y.W. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article; further inquiries can be directed to the corresponding author.

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