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Adsorption and Desorption of Phosphorus in Biochar-Amended Black Soil as Affected by Freeze-Thaw Cycles in Northeast China

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Abstract: Substantial soil phosphorus (P) losses often occur in the northern temperate regions owing to soil freeze-thaw cycles (FTCs). Presumably, biochar amendment is an efficient method of conserving P and sustaining agricultural production in the black soil region of northeast China. However, how biochar interacts with FTCs to affect soil P adsorption and desorption is unclear. A simulated laboratory FTC experiment was conducted on untreated and biochar-amended soil with varying moisture content to assess their effects on P adsorption and desorption. Soil P adsorption and desorption values were fitted with Langmuir and Freundlich isotherms to determine the interaction of the frequency of FTCs with moisture content and biochar amendment. Higher soil moisture content increased soil P adsorption, whereas biochar amendment mitigated decreased P retention by decreasing soil P adsorption capacity. Biochar amendment significantly increased the desorption ratio (D_{avg}) under all the FTCs. The desorption ratio of soil and biochar-amended soil in saturated moisture content treatment was significantly higher than that of 12 FTCs. The FTCs decreased the P availability of biochar-amended soil by enhancing P desorbability. Our results suggest that biochar amendment in arable black soil should not be conducted during FTCs, particularly during snowmelt.

Keywords: batch equilibrium method; biochar amendment; black soil; freeze-thaw cycle; phosphorus availability

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1. Introduction

Phosphorus (P) is an important nutrient, which determines agricultural productivity, because it plays key roles in plant metabolism, structure, and energy transformation [1,2]. Plants can acquire P as phosphate anions ($H_2PO_4^-$ and HPO_4^{2-}) from the soil solution [3,4]. Previously, the P transformation rate between soil solution and soil solids was reported to be highly dependent on phosphate adsorption and desorption characteristics [5]. Therefore, P adsorption and desorption restricts the capacity of supplying soil P, which affects P uptake and utilization by plants [6]. A better understanding of P adsorption and desorption in agricultural systems is critical for improving P sustainability and increasing crop productivity.

The black soil region in northeast China has been one of the most important crop production areas in the country owing to the productive physical and chemical capacity of black soil [7]. However, unsustainable land-use practices (e.g., intensive soybean production) have resulted in a substantial decline in soil fertility during recent decades [8]. Phosphorus fertilizers have been intensively applied to cope with this situation; however, eutrophication [9] and low utilization of P fertilizers [10] followed.

A relatively understudied method of increasing the efficiency of P fertilization in black soil involves soil amendment using biochar. Biochar is an important bio-resource that is produced by pyrolysis under limited air supply [11,12]. Because of the high physical and chemical capacity of biochar, it has been used as a potential soil-amending agent for improving soil P availability by reducing soil P leaching [13] and increasing crop productivity [14]. Biochar not only alters P availability directly through its anion exchange capacity or effects on the activity of cations that interact with P [15], but also exerts indirect effects on P retention and release through changes in the soil microbial environment [16]. Some investigations involving biochar-amended soil have shown that biochar amendment can reduce the leaching of PO_4-P [13,17,18]. Therefore, characterizing P adsorption and desorption in black soil under biochar amendment is necessary for the development of effective P fertilizer-use strategies.

Phosphorus cycling and leaching in the black soil of northeast China are affected by freeze-thaw cycles (FTCs) through the associated biochemical and physicochemical processes [19]. Previous studies on biochar amendment have mainly focused on crop productivity during the growing period [20,21]. However, few studies have assessed the effects of biochar amendment on P adsorption and desorption after FTCs. Soil freezing and thawing is a natural process that occurs regularly in cool temperature and high-latitude regions [22,23]. Previous studies suggested that repeated FTCs can increase total dissolved P and water-extractable P in soil owing to damage caused to plant cells, microbial biomass, and/or physical disruption of soil aggregates [22,24–27]. Freeze-thaw cycles can change the extent of P leaching, and significantly affect the adsorption and desorption characteristics of soil P. Some laboratory studies have examined the effect of FTCs on soil P adsorption and desorption. Wang et al. [28] observed that FTCs increased P adsorption and decreased P desorption in wetland soils. However, Qian et al. [29] and Fan et al. [30] showed that decreasing P adsorption would promote the release of adsorbed P, thereby increasing the risk of soil P losses in the brown and black soils of China.

In the present study, a simulated laboratory freeze-thaw experiment was conducted to assess the effect of biochar application on P adsorption and desorption in black soil. This study aimed to (i) identify the effects of FTCs and (ii) examine the interactions among FTC treatments and soil moisture conditions on P adsorption and desorption after biochar amendment. We expected that our results would improve our understanding of the effects of biochar on P sustainability in agricultural production systems. This would be important for the validation of the effect of biochar application on agriculture.

2. Materials and Methods

2.1. Site Description

The study site is located within Keshan Farm in the black soil region of northeast China (48°12′–48°23′ N, 125°08′–125°37′ E) [31]. The study area was chosen because the soil type and tillage practices were representative of intensive soybean production in the region. Soil in the study area was classified as a Mollisol with 22% sand, 33% silt, and 45% clay content. The annual mean temperature of the study area is 0.9 °C, with a lowest monthly mean temperature of −21.4 °C in January and a highest monthly mean temperature of 22.0 °C in July. The mean annual precipitation is 501.7 mm, 68.3% of which is concentrated from June to August [32]. The soil freezing period typically occurs from early November to mid-June, and the average annual frost-free period is 115 days. The mean annual maximum frozen soil depth is 2.5 m [33].

2.2. Experimental Design

2.2.1. Soil Sampling and Analysis

Arable surface soils samples (0–10 cm soil depth) were collected from five randomly assigned points in the study site. Soil samples were homogenized, air-dried at 25 °C, and passed through a 2 mm sieve. Soil pH was determined using the electrometric method using a suspension in deionized water (soil: water ratio of 1:2.5, *w*/*v*). Soil organic carbon (SOC) was measured using dry combustion using a total organic carbon analyzer (Elementar, Vario EL cube, Germany). Soil total nitrogen (TN) was measured using the Kjeldahl distillation method [34]. Soil total P (TP) was measured by digestion with a mixture of acids consisting of H_2SO_4 and $HClO_4$ [35], followed by the molybdenum blue method [36]. The available P (AP) present in soil was extracted with 0.03 M NH_4F and 0.025 M HCl [37] and measured using the molybdenum blue method. Soil available nitrogen (AN) was measured using the alkaline hydrolysis diffusion method. Each analysis was conducted with four replications.

2.2.2. Biochar Production and Amendment

The applied biochar was composed of soybean straw that had been pyrolyzed at 500 °C under anaerobic conditions. The temperature was raised at a rate of approximately 13 $°C \cdot min^{-1}$ and maintained at 500 °C for 2 h. The furnace was then turned off, and the sample was allowed to cool to 25 °C. The biochar was ground and passed through a 0.15 mm sieve before application. It was added uniformly to 400 g soil as a rate of 4% [38], and an incubation experiment using 500 cm^3 plastic incubation containers was conducted for 60 days at 25 °C with a moisture content equal to 70% of field capacity of the soil in the study area. As a control, soil samples without biochar amendment were incubated under the same conditions.

2.2.3. Freeze and Thaw Experiment

A laboratory-simulated freeze-thaw experiment was conducted after biochar amendment incubation. Deionized water was added to each assigned soil sample in order to maintain soil moisture content at 30.5% (MC1), 22.4% (MC2), and 44.8% (MC3), respectively. Thereafter, these soil samples were pre-incubated at 5 °C for 3 days. At the conclusion of pre-incubation, the soil samples were subjected to freezing at −10 °C for 12 h and thawing at 5 °C for 12 h. The frequencies of FTCs were 1 (1 FTC), 3 (3 FTCs), 6 (6 FTCs), and 12 (12 FTCs) as compared with the frequency of the unfrozen control (0 FTCs), which was kept at 5 °C throughout the entire experimental period.

2.2.4. Isothermal Adsorption and Desorption

The P adsorption of each soil sample was examined by placing 1.5 g dried soil in 30 mL of 0.01 $mol \cdot L^{-1}$ KCl (pH = 7) solution that contained 0, 20, 40, 60, 80, 100, 120, 180, and 240 $mg \cdot L^{-1}$ P. Two drops of chloroform were added to the soil samples to prevent microbial activity. All the samples were shaken at 25 °C for 24 h, centrifuged (5000 $r \cdot min^{-1}$) for 10 min, and filtered. The P concentration of the equilibrium solution was then determined by the molybdenum blue method.

Desorption of soil P was measured after the supernatants obtained in the adsorption experiment were removed, and the residual soil samples were washed twice with 30 mL saturated NaCl to remove free P. After the samples were centrifuged and filtered, 30 mL of 0.01 $mol \cdot L^{-1}$ KCl (pH = 7) and two drops of chloroform were mixed with each sample, followed by centrifugation. The supernatants were examined to determine the desorbed P content. Each analysis was conducted with four replications.

2.3. Data Analysis

2.3.1. Phosphorus Adsorption and Desorption

Adsorption isotherms models, such as the Langmuir and Freundlich isotherms, describe solute adsorption by solids in aqueous solution at constant temperature and pressure. The P adsorption data for the soils used in the present study were fitted to the following Langmuir adsorption Equation (1) and Freundlich adsorption Equation (2).

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (1)$$

in which C_e is the equilibrium P concentration in solution ($mg \cdot L^{-1}$), Q_e is the mass of P adsorbed per unit mass of soil ($mg \cdot kg^{-1}$), K_L is the Langmuir constant related to bonding energy ($L \cdot mg^{-1}$), and Q_m is the sorption maximum ($mg \cdot kg^{-1}$) calculated by the Langmuir equation. The maximum P buffer capacity (MBC) of the soil was calculated from the product of Langmuir constants Q_m and K_L [39].

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

in which K_F is an approximate indicator of adsorption capacity ($L \cdot mg^{-1}$), and $1/n$ is a function of the strength of adsorption in the adsorption process. Freundlich function $1/n$ is also representative of the P adsorption intensity. An average value of desorption ratio (D_{avg}) was defined as an average ratio of the desorbed phosphate to the total phosphate adsorbed by the adsorbents.

2.3.2. Statistical Analysis

One-way analysis of variance (ANOVA) with Least Significant Difference (LSD) was used to assess significant differences in the chemical properties of soil, biochar, and biochar-amended soil, and significant differences in P adsorption parameters and D_{avg} among biochar amendment treatments, soil moisture content, and FTC treatments. Linear regression analysis was applied to the Langmuir and Freundlich isotherms of P adsorption on soil and biochar-amended soil with different moisture contents. A multivariate ANOVA was used to determine the interaction among biochar amendment, soil moisture content, and FTC treatment on P adsorption and desorption. All statistical analyses were conducted using SPSS 22.0 (IBM Institute, Armonk, NC, USA) with a significance threshold of $p < 0.05$.

3. Results and Discussion

3.1. Soil and Biochar Properties

Biochar application improved the general chemical properties of soil. The values of pH, SOC, AP, and TN in biochar-amended soil were significantly higher than those in the untreated soil (Table 1). Similarly, Sun and Lu [38] reported that the application of biochar to the soil significantly increased the available N and P content of soils. However, according to Arthur et al. [21] and Trazzi et al. [12], the values of pH and SOC increased after biochar amendment. The increases in pH, TP, and TN of soil after biochar amendment are most likely due to the effects of biochar [40,41], whereas the increases in AP and AN were due to the interaction between biochar and soil [15].

Table 1. Chemical properties of soil, biochar, and biochar-amended soil in the black soil region of northeast China.

Sample (*n* = 4)	pH (1:2.5 H_2O)	SOC ($g \cdot kg^{-1}$)	TP ($g \cdot kg^{-1}$)	AP ($mg \cdot kg^{-1}$)	TN ($g \cdot kg^{-1}$)	AN ($mg \cdot kg^{-1}$)
Soil (*n* = 4)	5.77 ± 0.09c	51.03 ± 1.08c	0.86 ± 0.02b	43.05 ± 1.29c	3.01 ± 0.01c	120.25 ± 11.12b
Biochar (*n* = 4)	7.82 ± 0.07a	169.11 ± 3.92a	1.47 ± 0.13a	78.96 ± 5.95a	6.44 ± 0.30a	156.43 ± 13.89a
Biochar-amended soil (*n* = 4)	6.89 ± 0.11b	65.81 ± 1.85b	0.95 ± 0.04ab	62.79 ± 5.23b	4.17 ± 0.31b	132.79 ± 15.52ab

Note: SOC: soil organic carbon, TP: total P, AP: available P, TN: total N, AN: available N. Different lowercase letters in the same column indicate significance among soil, biochar, and biochar-amended soil at $p < 0.05$.

3.2. Phosphorus Adsorption

Adsorption procedures have been suggested for use in predicting the partition of P between solution and solid phases in the environment [28,42]. The relationship of P equilibrium concentration with the amount of adsorbed P was expressed as linear correlations (Figure 1). The P adsorption data of each sample could be described by the Langmuir ($r^2 > 0.65$) and Freundlich ($r^2 > 0.70$) isotherms. Among the moisture content and biochar amendment, MC1(SB) had the lowest Q_e (176.73 $mg \cdot kg^{-1}$), followed by MC3(SB) (277.99 mg·kg^{-1}), which was comparable to that of MC2(SB) (286.69 mg·kg^{-1}) at an equilibrium P concentration of 6 mg·L^{-1}. Meanwhile, the Q_e of MC1(S) (221.78 mg·kg^{-1}) was lower than that of MC2(S) (355.50 mg·kg^{-1}) and MC3(S) (355.56 mg·kg^{-1}) at equilibrium concentrations of 13, 8, and 4 mg·L^{-1}, respectively. At >110 mg·L^{-1} equilibrium concentration, MC1(SB) (654.55 mg·kg^{-1}) had the lowest Q_e, followed by MC1(S) (738.55 mg·kg^{-1}), which was comparable to that of MC3(SB) (799.43 mg·kg^{-1}), MC2(SB) (827.12 mg·kg^{-1}), MC2(S) (942.65 mg·kg^{-1}), and MC3(S) (1009.78 mg·kg^{-1}). Xu et al. [43] evaluated the effects of biochar amendment on P sorption and desorption in three soils with different acidities. The results showed lower P loading on the biochar-amended black soil, which might be due to differences in biochar production conditions and feedstock types [44].

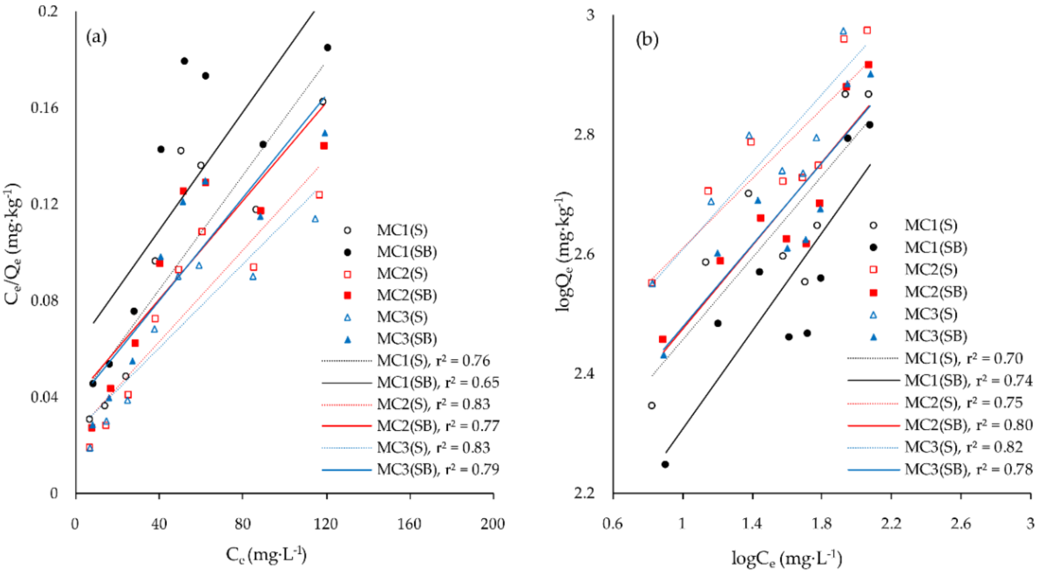

Figure 1. Langmuir (**a**) and Freundlich (**b**) isotherms of P adsorption on soil and biochar-amended soils with different soil moisture contents. MC1, MC2, and MC3 represent natural moisture content (30.5%), half of saturated moisture content (22.4%), and saturated moisture content (44.8%), respectively. (S) and (SB) represent soil and biochar-amended soil, respectively.

Soil P adsorption parameters with different moisture contents, calculated by Langmuir and Freundlich isotherms, are shown in Table 2. The response of P adsorption to soil tends to be highly dependent on biochar amendment and moisture content. The Q_m and K_F of MC2 and MC3 in soils are significantly higher than natural moisture content (MC1), suggesting that altering soil moisture content may help to increase soil P adsorption capacity. According to Peltovuori and Soinne [45], the increase in P adsorption in air-dried soil can be attributed to a destruction of organic matter enveloping the short-range ordered oxide surfaces. In addition, Shukla et al. [46] reported that P adsorption capacity could increase under saturated moisture conditions associated with the change in soil redox condition. Under saturated moisture conditions, a type of amorphous iron oxide complex forms [46]. As compared with ferric hydroxide, the larger surface areas and increased number of P adsorption sites of the amorphous iron oxide complex should increase the P adsorption capacity [47].

After biochar amendment, the variation in Q_m and K_F decreased to 817.82–979.21 mg·kg^{-1} and 79.35–135.73 L·mg^{-1}, respectively, and the Q_m and K_F for MC2 and MC3 in biochar-amended soils were lower than those in soils not subjected to biochar amendment treatment. These results indicated that biochar amendment could reduce soil P adsorption capacity. The decreases in P adsorption with biochar amendment could be affected by increasing pH [48]. Soil surface becomes more negatively charged, thereby increasing anion repulsion and decreasing P adsorption. Higher pH conditions depress the formation of HPO_4^{2-}, which is preferentially adsorbed by soil colloids [43].

Table 2. Parameters of P adsorption on soil and biochar-amended soil with different moisture contents.

Sample (n = 4)	Moisture Content	Langmuir				Freundlich		
		Q_m ($mg \cdot kg^{-1}$)	K_L ($L \cdot mg^{-1}$)	MBC ($L \cdot kg^{-1}$)	R^2	K_F ($L \cdot mg^{-1}$)	1/n	R^2
Soil (n = 4)	MC1	847.74 ± 67.53cA	0.032 ± 0.006aA	27.23 ± 3.32bA	0.75	131.02 ± 18.19bA	0.34 ± 0.03aB	0.70
	MC2	1051.29 ± 20.98bA	0.038 ± 0.002aA	39.96 ± 1.37aA	0.83	208.66 ± 11.36aA	0.29 ± 0.01bB	0.75
	MC3	1152.32 ± 65.98aA	0.034 ± 0.003aA	39.13 ± 2.25abA	0.83	190.95 ± 9.53aA	0.33 ± 0.02aA	0.82
Biochar-amended soil (n = 4)	MC1	817.82 ± 19.10bA	0.020 ± 0.001aB	16.47 ± 0.41bB	0.65	79.35 ± 8.59bB	0.41 ± 0.03aA	0.74
	MC2	979.21 ± 30.94aB	0.026 ± 0.002bB	25.12 ± 1.92aB	0.77	133.31 ± 6.98aB	0.35 ± 0.01bA	0.80
	MC3	943.44 ± 63.36aB	0.028 ± 0.003bB	26.69 ± 1.21aB	0.79	135.73 ± 9.01aB	0.35 ± 0.02bA	0.78

Note: Q_m: Langmuir sorption maximum, K_L: bonding energy constant, MBC: maximum buffer capacity, K_F: Freundlich sorption capacity factor, and 1/n: Freundlich function. Different lowercase letters in the same column indicate significance among different moisture contents at $p < 0.05$; different uppercase letters in the same moisture treatment indicate significant differences between soil and biochar-amended soil at $p < 0.05$.

The effect of moisture content treatments on P adsorption intensity was more obvious in biochar-amended soil than in the untreated soil. After biochar amendment, the bonding energy constant (K_L) of MC2 and MC3 was significantly higher than that of MC1. The value of 1/n in MC2 and MC3 was significantly lower than that in MC1. Our findings suggest that adsorbed P is not easily desorbed in the moisture content treatment.

Similar to Q_m and K_F, the MBC of MC2 and MC3 were higher than that of MC1 in biochar-amended soil. However, the MBC of biochar-amended soils was significantly lower than that of untreated soils, revealing that a lower P concentration is required when biochar is added to the soil.

Soil P adsorption parameters can be affected by moisture content and biochar amendment. However, P adsorption parameters were not significantly different among the five FTCs of the same soil group (Table 3). A similar study had focused on the effects of freeze-thaw environments on ion exchange resin stability. Mamo et al. [49] showed that FTC had no effects on P adsorption characteristics. Another study showed that air-drying had a greater effect on soils than freezing had [45].

Table 3. Changes in P adsorption parameters in response to moisture content (MC), biochar amendment, and freeze–thaw cycle (FTC) treatment.

Source	df	Langmuir						Freundlich			
		Q_m ($mg \cdot kg^{-1}$)		K_L ($L \cdot mg^{-1}$)		MBC ($L \cdot kg^{-1}$)		K_F ($L \cdot mg^{-1}$)		1/n	
		F	Sig.	F	Sig.	F	Sig.	F	Sig.	F	Sig.
MC	2	42.62	0	33.09	0	167.12	0	130.91	0	33.75	0
TrT	1	99.97	0	84.65	0	448.50	0	285.28	0	42.93	0
FTCs	4	1.43	0.23	1.38	0.25	0.90	0.47	1.01	0.41	2.17	0.08
MC × TrT	2	4.99	0.01	0.30	0.74	12.23	0	9.49	0	0.03	0.97
MC × FTCs	8	5.50	0	3.14	0.004	3.31	0.002	3.16	0.003	3.61	0.001
TrT × FTCs	4	0.57	0.69	0.85	0.50	1.10	0.36	1.78	0.14	1.65	0.17
MC × TrT × FTCs	8	4	0	2.03	0.05	2.25	0.03	1.26	0.28	1.15	0.34

Note: df: degrees of freedom, Q_m: Langmuir sorption maximum, K_L: bonding energy constant, MBC: maximum buffer capacity, K_F: Freundlich sorption capacity factor, 1/n: Freundlich function, MC represents natural moisture content, a half of saturated moisture content, and saturated moisture content; TrT represents soil and biochar-amended soil; FTCs include 1, 3, 6, and 12 FTCs and an unfrozen control.

3.3. Phosphorus Desorption

Desorption of P in soil is a reversible process, which is directly related to adsorbed P re-use and P bioavailability in soil [50]. The desorbability of P in soil can be used to indicate the degree of P desorption from the adsorptive materials [51]. Phosphorus desorbability is mainly affected by soil moisture content, biochar amendment, and the frequency of FTCs. However, FTCs interacted with moisture treatment and biochar amendment treatments (Figure 2). The D_{avg} values of biochar-amended soil were always higher than those of untreated soil, which indicated that biochar amendment could enhance soil P desorption ability. The D_{avg} values of MC2 and MC3 were relatively lower than that of MC1 in all the FTC treatments. The D_{avg} values of untreated and biochar-amended soil increased owing to the increasing frequency of FTCs under each moisture content treatment. After 12 FTCs, the D_{avg} values of saturated moisture content in untreated and biochar-amended soil had significantly increased from 9.63% to 10.75% and 15.93% to 17.44%, respectively. Our findings suggest that both untreated soil and biochar-amended soil with higher moisture content are more sensitive to FTCs.

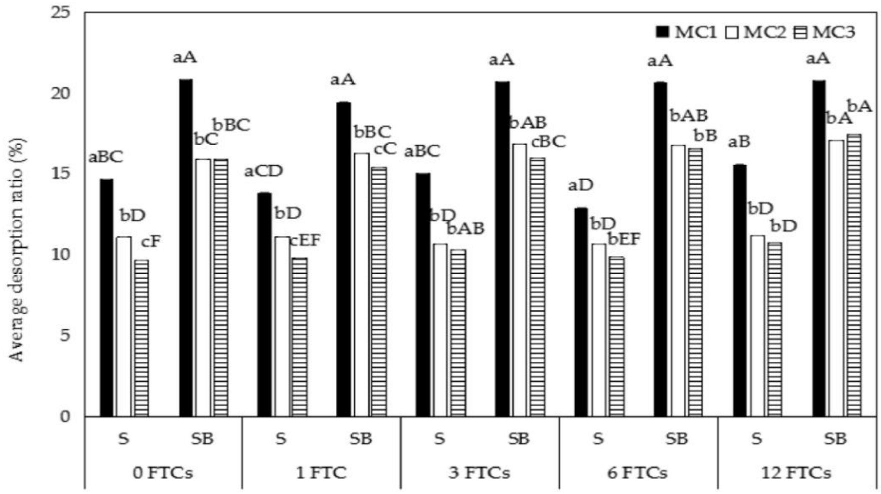

Figure 2. Average desorption ratio among moisture content, biochar amendment, and freeze–thaw cycles (FTCs). S and SB represent soil and biochar-amended soil, respectively. Different lowercase letters in the same FTCs indicate significant differences among different moisture contents within the same sample at $p < 0.05$. Different uppercase letters in the same moisture content indicate significant differences among different FTCs at $p < 0.05$.

In the present study, the desorbability of P increased after biochar amendment. This result may be due to the significantly lower bonding energy of adsorption (Table 2). Moreover, FTC treatment enhanced P desorbability, because the stability of soil aggregates decreased with repeated FTCs, and such a disturbance could increase the release of soil inorganic and organic substrates [52,53]. It has been suggested that FTCs damage and lyse microbial cells, leading to the release of potential dissolved nutrients [54]. The destruction of soil aggregates and decomposition of organic matter leads to increased competition between phosphates and fulvic acids for adsorption sites, thereby increasing P desorbability [55].

4. Conclusions

The biochar amendment decreased the P adsorption capacity and intensity of black soil. Freeze-thaw cycles aggravated the release of P in biochar-amended soil by increasing P desorbability. However, the effects of FTCs on P release are more pronounced at saturated moisture levels in black soil. Therefore, biochar amendment in arable black soil should not be conducted during FTCs, particularly during snowmelt. The P fraction of biochar-amended black soil under FTCs should be further investigated to verify the underlying mechanisms.

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