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Research article

Investigation of the effects of biochar amendment on soil under freeze–thaw cycles and the underlying mechanism

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ABSTRACT

Biochar (BC) is widely utilized as a soil amendment; however, for widely distributed seasonally frozen soils, the effect of BC on soil and the optimal utilization of BC during the freeze–thaw process are still unclear. In this study, the effects of freeze–thaw aged biochar (FT-BC) and BC on soil properties and wheat cultivation were systematically investigated, and the underlying interaction mechanism between BC and soil was explored. The results show that FT-BC dramatically reduces the adverse effects of freeze–thaw cycles on soil, enhances wheat growth, and increases dry matter yield by 17.5 %, which is mainly attributed to the ability of FT-BC to maintain soil structure, reduce water loss rates to below 0.20 g/h, and decrease nitrogen leaching by more than 20 % during freeze–thaw cycles. Additionally, fresh BC had a greater effect on the fixation of cadmium than FT-BC in the soil, reducing its accumulation in wheat by 22.5 %. Multiple characterizations revealed that the freeze–thaw process increased the porosity and specific surface area of FT-BC, providing more sites for water and nitrogen adsorption, whereas the dissolved organic matter released from fresh BC had a better ability to trap cadmium. These findings provide insights into the interactions between BC and soil components during the freeze–thaw process and suggest the optimized utilization of fresh BC and FT-BC for different soil repair purposes.

1. Introduction

Seasonally frozen soils are widespread in high-latitude regions globally and are characteristic of soils in North China, Northeast China, and Northwest China, covering approximately 53.5 % of China's arable land [1,2]. These regions are crucial grain-producing areas in China. Winter wheat, which is typically sown before winter, is well suited for cultivation in such soils. Seasonal freeze–thaw cycles can significantly alter soil structure and hydrodynamics, leading to reduced agricultural productivity [3]. These cycles are considered abiotic stressors that cause changes in soil stability, water retention, and organic matter content, markedly affecting microbial growth and organic matter decomposition [4–8].

Biochar (BC), a carbonaceous solid derived from the pyrolysis of biomass in an oxygen-depleted environment, has emerged as a versatile soil amendment since its initial recognition. The utility of BC in soil enhancement is marked by its ability to modulate soil pH,

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immobilize heavy metals, and augment soil fertility while also contributing to carbon sequestration and altering soil microbial biomass, resulting in the colloquial designation of “black gold” [9]. Functionally, BC acts as a structural scaffold in soil, significantly enhancing the total porosity and interconnectivity of pores within frozen soils, which strengthens soil aggregate stability and improves soil hydraulic conductivity [1].

Exposure of BC to freeze−thaw cycles induces substantial changes in its physicochemical properties and functional performance, including alterations in the prevalence of surface functional groups, ash content, pH, and biological toxicity [10]. For instance, Wang et al. demonstrated that the pH of BC transitions toward neutrality following 30 freeze−thaw cycles, accompanied by an increase in the specific surface area and the quantity of oxygen-containing functional groups (-OH, –COOH, –C═O). However, this aging process is also associated with a reduction in pore volume and diameter. Notably, aged BC exhibits a considerable increase in its maximum adsorption capacity for copper and zinc [11].

The contents of water, nutrients, and heavy metals in soil significantly influence plant growth [12]. Soil water retention capacity, a fundamental physical property, is vital for sustaining soil ecosystems, ensuring food production, and directly impacting plant growth and soil fertility. According to previous studies, incorporating 1 %–3 % straw or grass-derived BC (produced at 500–600 °C) into the soil can enhance its water holding capacity [13]. In seasonally frozen soils, the application of BC at various soil stages has differential effects on soil structure [3]. Furthermore, the decreased retention of essential plant nutrients has resulted in environmental issues such as water pollution and eutrophication, exacerbated by increasing application rates [14]. BC addition reduces the leaching of macronutrients such as nitrogen (N) and carbon (C) from the soil [15]. The nitrogen adsorption capacity of BC is also enhanced following freeze−thaw cycles, which is attributed to alterations in the surface structure and chemical properties of BC due to aging [16].

Heavy metal pollution poses health risks through plant uptake and bioaccumulation. Lu et al. reported that the extractable concentrations of heavy metals such as cadmium (Cd) and lead (Pb) in bamboo BC-treated soils were significantly lower than those in untreated soils [17]. Qiu et al. utilized a mixture of kaolin and Spartina alterniflora-derived BC to immobilize cadmium by forming complexes containing silicon, aluminum, and cadmium [18]. After freeze−thaw cycling and dry−wet aging, the average Tessier exchangeable cadmium fraction in the soil and BC decreased, indicating the long-term stability of cadmium in BC-repaired soil [19].

Biochar has demonstrated remarkable improvements across various soil properties. Nonetheless, the majority of studies have tended to concentrate on changes in individual soil attributes. Systematic studies on the interaction between soil and BC, especially freeze−thaw soil, are scarce. Moreover, the application conditions and timing of BC should be further explored for soils with different remediation needs, such as improved water and nutrient retention and heavy metal immobilization. These knowledge gaps hamper the development of BC in cold region agriculture, where seasonal freeze−thaw cycles play a critical role in soil health and productivity.

Therefore, the objective of this study was to assess and compare the impacts of freeze−thaw-treated biochar (FT-BC) and fresh BC—representing biochar application before winter and after winter, respectively—on soil remediation. To this end, 1) wheat growth was tested in soil samples subjected to different treatments, 2) key criteria related to the remediation effect (including soil water retention, nitrogen retention, and cadmium fixation) were systematically explored, and 3) multiple characterizations were employed to elucidate the mechanisms by which BC aids in soil remediation under frozen conditions. These findings aim to provide insights into optimizing biochar application strategies under different soil conditions and enhancing soil resilience in seasonally frozen agricultural regions.

2. Materials and methods

2.1. Biochar production and characterization

The straw biomass utilized in this study was sourced from Lianyungang city, Jiangsu Province. The protocol for producing BC via oxygen-limited pyrolysis of biomass has been described previously [10]. The clean straw biomass was first dried overnight in an oven at 80 °C. Then, the straw biomass was crushed and passed through a 100-mesh sieve to collect straw particles with a diameter smaller than 0.15 mm. The obtained biomass particles were put into a crucible wrapped with tin foil and placed in a tubular furnace. A 0.6 L min^{-1} flow of nitrogen was applied continuously for 20 min to remove air from the system. The temperature of the tubular furnace was increased to 500 °C at a rate of 10 °C $\mathrm{min}^{-1,}$ and the temperature was maintained for 30 min under a nitrogen atmosphere. After cooling to room temperature, BC was obtained. The characterization of biochar before and after the aging process was primarily conducted using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The detailed characterization methods are described in Text S1.

2.2. Freeze−thaw cycle of soil

To simulate the effects of seasonal freeze−thaw cycles on BC amendment in frozen soil, BC was aged for 30 days after being uniformly blended with soil at a 1 % application rate. The freeze−thaw cycle followed a specific regimen: the soil mixed with BC was frozen at −20 °C to 70 % of its maximum water-holding capacity for 16 h, followed by a thawing period at room temperature for 8 h (Fig. S1). This process was repeated to mimic the natural conditions of seasonally frozen soil and to amend the soil with BC under these conditions. The FT-BC was obtained through this freeze−thaw cycle treatment. The contents of water-stable aggregates (<2 mm, 0.25–2 mm, 0.25–0.05 mm, and <0.05 mm) were determined by the wet-sieve method [20]. The dry bulk density was measured using the method described in Text S2 [21]. Changes in soil organic matter were characterized mainly by a fluorescence excitation-emission matrix (EEM), with the detailed method provided in Text S1.

2.3. Column N leaching experiment

To assess the retention of nitrogen in soil amended with FT-BC, a glass column apparatus measuring 3 cm in diameter and 30 cm in height was used. Urea was chosen as the representative nutrient for this evaluation. To minimize the impact of confounding factors and create a controlled experimental setup, quartz sand with a mesh size of 26–40 was used instead of natural soil to provide a homogeneous leaching environment. The column was packed with a uniform blend of 75 g of quartz sand and 1 % of either BC or FT-BC.

A quantity of 43 mg of urea, corresponding to a total nitrogen content of 20 mg, was uniformly distributed 2 cm above the quartz sand layer. To ensure orderly water flow, glass beads with a diameter of 3 mm were placed at the top and bottom of the quartz sand column (refer to Fig. 1 for details). Water was introduced into the column at a rate of 3 drops/minute, simulating an average rainfall intensity of 0.5 cm in 30 min. Effluent samples were collected at volumes of 5, 10, 15, 20, 30, and 50 mL, and the total nitrogen content in these samples was quantified using UV spectrophotometry in accordance with the national standard (GB11894-89) for alkaline potassium persulfate digestion. Additionally, a leaching experiment without urea was conducted to determine the nitrogen content derived from the dissolved organic matter in the BC and FT-BC, which was then subtracted from the measured values to obtain accurate nitrogen retention data.

2.4. Pot experiment

One hundred grams of soil was weighed and placed in each pot. Six treatment groups were established: soil only (soil), soil subjected to freeze−thaw cycles (FT-soil), soil modified by freeze−thaw-treated biochar (FT-BC-soil), soil spiked with cadmium (Cd), soil spiked with cadmium and subjected to freeze−thaw cycles (Cd-FT), and soil modified by freeze−thaw-treated biochar and spiked with cadmium (Cd-FT-BC). Biochar (at a rate of 1 %) and cadmium (at a concentration of 400 mg/kg) were added to the respective experimental groups as per the experimental design. Subsequently, freeze−thaw cycles were applied (−20 °C freezing for 16 h, followed by thawing at room temperature for 8 h). Throughout the experiment, the soil was maintained at 70 % of its maximum field water holding capacity, and data were collected periodically by weighing and recording the soil weight.

After 4 weeks of freeze−thaw cycling, wheat plants with comparable growth characteristics were transplanted into pots for further cultivation. The plants were maintained under controlled conditions (26 °C with 16 h of light; 20 °C in darkness for 8 h) and were harvested and dried following a 2-week incubation period. The content of Cd in wheat was measured using the inductively coupled plasma-atomic emission spectrometry (ICP−AES) method. For details, see Text S1. We also measured the morphological changes in cadmium in the soil, as described in Text S3, according to previous work [22].

3. Results and discussion

3.1. Effect of BC addition on wheat cultivation in frozen soil

The seasonally frozen soils prevalent in China significantly impact crop cultivation. To assess the influence of BC addition on crop growth in frozen soil, wheat was chosen as a model crop. The dry weight of wheat is a critical parameter reflecting the overall growth

Fig. 1. Diagram of the column N leaching experimental device.

status of plants. As shown in Fig. 2 and S2, after two weeks under constant temperature conditions, the dry weight of wheat in untreated soil reached 0.148 ± 0.006 g. In contrast, the dry weight of wheat in freeze−thaw soil was significantly lower at 0.114 ± 0.004 g. This reduction is attributed to soil structure disruption and nutrient depletion during freeze−thaw cycles. Moisture migration during thawing leads to a gradual decline in soil nutrient content.

Interestingly, adding BC to frozen-thawed soil resulted in an 18 % increase in the dry weight of the wheat plants. This suggests that BC acts as a supplementary carbon source, enhancing plant growth under challenging conditions. BC likely serves as a fertilizer, replenishing soil carbon and promoting growth in freeze−thaw soil. Consequently, BC application mitigates soil structure damage and maintains stability during freeze−thaw cycles while providing an external carbon source to counteract disturbances in the soil carbon and nitrogen balance [23]. Additionally, BC may facilitate nutrient retention through absorption mechanisms.

3.2. Effect of BC amendment on the properties of soil after freeze−thaw cycles

3.2.1. Soil water retention

A previous study showed that biochar amendment can alleviate the detrimental effects of freeze−thaw cycles on wheat growth in soil. To further elucidate the underlying mechanism, the present study investigated and analyzed various soil properties, including soil water retention, nutrient retention, and metal accumulation.

Fig. 3a illustrates the changes in the soil water retention rate during the freeze−thaw cycle. Initially, during the incubation period, the water loss rates of the three experimental groups were comparable. The water retention rates of the soils incubated at room temperature remained relatively constant, all below 0.10 g/h. In contrast, the water loss rate of the freeze−thaw cycle soil showed a positive correlation with the number of cycles. After four freeze−thaw cycles, the water loss of the soil significantly increased, doubling after six cycles, indicating that the freeze−thaw cycle significantly reduced the soil's water retention rate. After 30 days of cycling, the water loss rate of the freeze−thaw-treated soil reached as high as 0.28 g/h, approximately three times that of the soil incubated at room temperature (0.096 g/h). These results suggest that the freeze−thaw cycle severely diminished the soil's water retention performance, likely due to damage to the soil structure caused by the cycles. For instance, freeze−thaw cycles can alter the pore size distribution and enhance connectivity between small, medium, and large pores, thereby reducing soil aggregate stability and inducing changes in both soil water and thermal conductivity [1].

Compared to that of the freeze−thaw soil, the water retention capacity of the soil amended with biochar was superior to that of the unamended soil. Specifically, the water loss rate of the biochar-amended soil increased by only two times (0.20 g/h) after 30 days of freeze−thaw cycling. These results indicate that biochar can attenuate the decline in the water retention property of freeze−thaw soil. Consequently, it can be inferred that biochar effectively mitigates the damage inflicted by freeze−thaw cycles on the soil and preserves the soil's water retention capacity.

Biochar influences soil water-holding capacity through two primary mechanisms. First, biochar undergoes a reduction in ash content upon aging, exposing more pores. These internal pores enable biochar to retain water, thereby directly enhancing the soil water content [24]. Second, the hydrophilic nature of the added biochar particles allows them to act as adhesives, linking soil microaggregates to larger ones. This action plugs the macropores created by freeze-thawing, helping to maintain soil structure integrity and impeding water flow, thus improving the soil's water-holding capacity [1,25]. Additionally, hydrophilic functional groups on the surface of FT-BC may further contribute to increasing the maximum soil water-holding capacity. Consequently, the incorporation of FT-BC can effectively increase the moisture content of seasonally frozen soils and reduce water consumption.

3.2.2. Soil nutrient retention

Nitrogen is a critical nutrient for plant growth, and its management is a significant aspect of agricultural production. Nitrogen-based fertilizers are widely used to meet crop demands [26], yet a substantial portion (50%–80 %) of these fertilizers are not taken

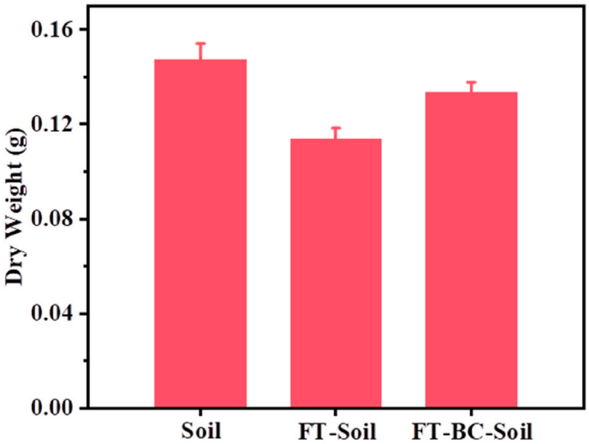

Fig. 2. Dry weight of wheat cultivated in freeze−thaw soil and FT-BC-amended soil.

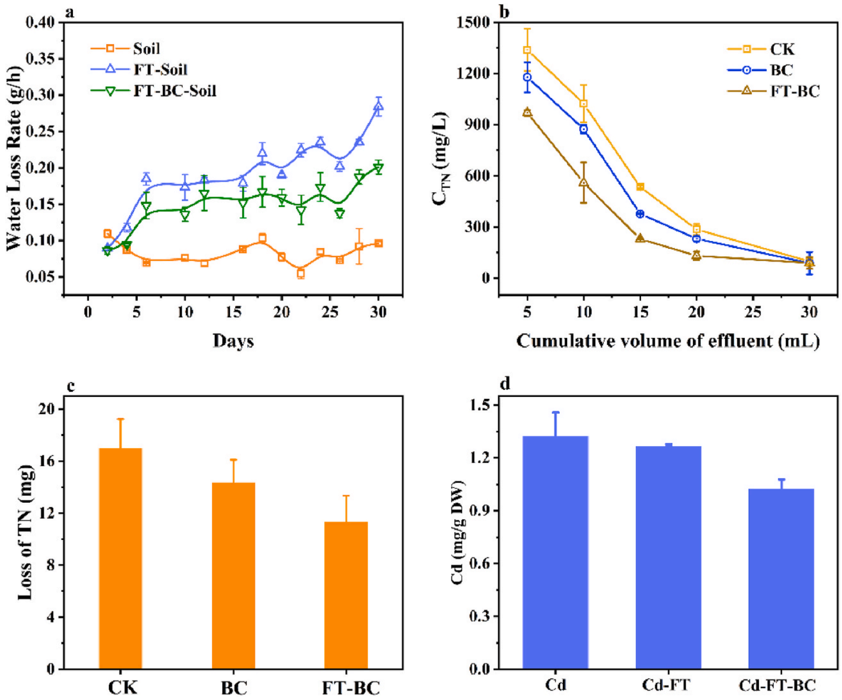

Fig. 3. Changes in the soil water retention of soil with or without BC addition after freeze−thaw aging (a). N concentration variations (b) and total loss of effluents (c) during the leaching experiment with FT-BC. FT-BC enhanced the Cd concentration in wheat plants grown in Cd-containing soil (d).

up by plants [27,28]. This unutilized nitrogen is often lost to the environment through the water cycle, leading to issues such as groundwater pollution and eutrophication [29].

The leaching experiment conducted to assess the nitrogen retention capacity of FT-BC is presented in Fig. 3b–c. The overall total nitrogen removal efficiency of the various treatments decreased in the following order: FT-BC treatment > BC treatment > no treatment. The incorporation of BC effectively retained nitrogen in quartz sand under conditions of rain erosion, with the retention effect being more pronounced for FT-BC. There was minimal variation in nitrogen content among the effluent samples from the three groups after 30 mL of leaching, but there was a notable difference in nitrogen release rates between the BC and FT-BC treatments up to that point. The total nitrogen (TN) concentration in the effluent from the FT-BC-treated soil was consistently lower than that from the BC-treated soil, while the TN concentration in the control group, without any treatment, remained the highest.

At the onset of the leaching experiment, when the nitrogen content of the first 5 mL of effluent was as high as 1.3 g/L, 33 % of the nitrogen was retained in the soil, compared to 29 % under the BC treatment and 24 % under the FT-BC treatment. FT-BC released nitrogen at significantly lower concentrations throughout the first 50 mL of leachate. When evaluating the total nitrogen loss during the entire leaching process, it was found that the total nitrogen loss for the CK group reached 17 mg (accounting for 85 % of the total), which was 1.2 times and 1.5 times greater than that of the BC and FT-BC groups, respectively. The BC/FT-BC treatment effectively retained more nitrogen in fertilized soil, enabling plants to utilize a greater proportion of the applied nitrogen [29,30]. This finding aligns with the results reported by Sun et al. [31].

3.2.3. Heavy metal accumulation

Heavy metal contamination in agricultural soils is characterized by its nondegradability, high toxicity, and tendency to bioaccumulate, posing a substantial risk to food safety and human health [32,33]. The successful remediation of contaminated soil by BC relies on the stability of heavy metal immobilization over an extended period, as short-term fixation is insufficient. However, the stability of heavy metal fixation can be influenced by the characteristics of BC and the aging process [34]. Consequently, it is imperative to evaluate the heavy metal immobilization capacity of FT-BC.

The cadmium content in wheat plants grown in polluted soil for two weeks is depicted in Fig. 3d. After two weeks of cultivation under constant temperature conditions, the wheat plants were harvested, chopped, and analyzed for their Cd content via inductively coupled plasma (ICP) analysis. The addition of 400 mg/kg Cd to the soil led to the accumulation of 1.3 mg/g dry weight (DW) of Cd in the wheat. Although the Cd content in the wheat plants grown in freeze-thawed soil was not significantly reduced, the addition of FT-BC resulted in a substantial decrease in the Cd content, indicating that FT-BC effectively immobilizes cadmium in the soil. We also measured the morphological changes caused by cadmium in the soil, and the results are shown in Table S1. The results of the soil analysis showed that the exchangeable fraction was significantly reduced after the addition of biochar, and the cadmium was converted into a carbonate-bound fraction and an Fe/Mn oxide-bound fraction. At the same time, the organic matter-bound fraction also increased slightly. According to previous studies, the exchangeable fraction, which includes soluble metal ions, has a great toxic effect on the growth of plants [35]. This indicates that the addition of biochar has a positive effect on the fixation of cadmium.

BC immobilizes heavy metals through both direct and indirect interactions. On the one hand, BC interacts with heavy metals through mechanisms such as complexation, precipitation, and cation exchange, leading to adsorption and fixation [36,37]. On the other hand, BC can induce changes in soil pH, soil potential, and microbial composition, indirectly reducing the biological availability of heavy metals in the soil [34,38]. Electrostatic interactions play a primary role in Cd(II) adsorption [39]. For FT-BC, the surface modification caused by freeze−thaw aging significantly impacts its fixation performance. The increase in the contents of –CO, –OH, and –COOH functional groups in FT-BC provides more sites for Cd adsorption [40], which are highly reactive to soil clay minerals and metals, resulting in the formation of stable complexes.

3.3. Characterizations and analysis

3.3.1. SEM image of FT-BC-amended soil

Scanning electron microscopy revealed a more pronounced alteration in the soil structure following the addition of FT-BC. As depicted in Fig. 4a–f, the soil in the control group exhibited aggregates with a uniform particle size distribution. However, after undergoing a freeze−thaw cycle, the soil particle size decreases, the structure becomes fragmented, and cracks form within the soil particles, leading to the breakdown of large aggregates into smaller particles [41].

During the freezing process, the water between the soil particles freezes and forms an ice lens, causing a change in the volume of the water. As reported by Winkler [42], a change in water volume of 1 atm of pressure results in a volume change of approximately 0.6 %. Consequently, the volume expansion of ice is greater than the pore volume of soil. Upon thawing, the ice melts into liquid water and migrates under the influence of gravity. However, the soil structure does not fully revert to its original state [43], leading to the expansion of micropores. With repeated freeze−thaw cycles, the internal pressure between soil particles causes the microvoids to expand and increase in size, eventually connecting to form crack lines. As the number of cycles increases, these cracks further expand and develop into larger cracks, ultimately causing larger soil particles to fragment into smaller ones [44].

The freeze−thaw cycle also contributes to aggregation while causing coarse particles to break up. Consequently, the soil structure transitions from a flocculent structure to a granular accumulation structure [41], indicating that the soil particle structure undergoes significant changes after the freeze−thaw cycle. This structural alteration is a key factor contributing to the decrease in soil water retention.

Upon the addition of FT-BC, a uniform tubular bundle structure and a distinct skeletal framework were observed after 30 days of freeze−thaw cycling [45]. Although the FT-BC surface was partially fractured and coated with minerals from the soil, resulting in a roughened texture, it also contributed to the formation of a large, blocky structure centered around the FT-BC. This structural stability of the FT-BC substantially increased the size and stability of the soil particles, providing a robust foundation for the retention of water within the soil.

3.3.2. Changes in the soil aggregate distribution

In addition to direct observation through images, it is also possible to test for changes in soil particles by measuring soil aggregates. Soil aggregates are the smallest structural unit in soil, and the physical and chemical properties of soil are closely related to their distribution. Fig. 4g–h shows that after two weeks of freeze−thaw aging, the <5 mm aggregates increased by 12 %, while the 0.05–0.25 mm and 0.25–2 mm aggregates decreased by 11 % and 1 %, respectively, indicating that the freeze−thaw treatment reduced the particle size of the soil aggregates. This was consistent with the results of previous studies [46,47]. The few >2 mm aggregates that

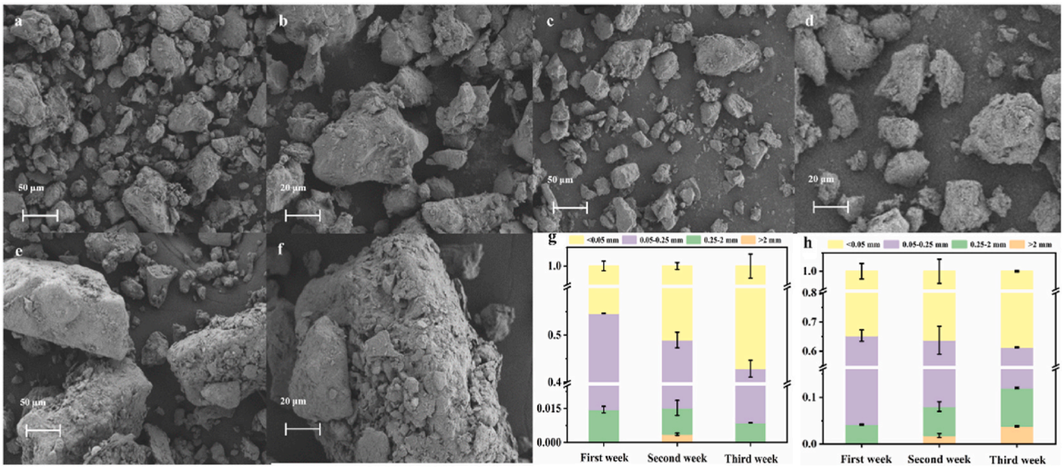

Fig. 4. SEM images of the soil (a–b), freeze−thaw-treated soil (c–d) and FT-BC-modified soil (e–f). Changes in the soil aggregate distribution after three weeks of freeze−thaw cycling in soil (g) and BC-soil (h).

appeared during the freeze−thaw process may have been formed by fragmentation and recombination of large aggregates. After the addition of BC and undergoing aging, the contents of >2 mm and 0.25–2 mm aggregates in the soil increased significantly compared to those at the beginning, and the proportion of <0.05 mm aggregates also increased by 4 %, but the content of 0.05–0.25 mm aggregates decreased. These results are in good agreement with the SEM images. Additionally, according to the dry bulk density calculation results (Table S2), compared with that of the original soil, the dry bulk density of the BC-added soil increased slightly after aging. In general, the addition of biochar tends to result in a reduction in dry density if it does not undergo a freeze−thaw cycle [48]. We hypothesize that these seemingly contradictory results may be related to the protective effect of biochar on soil aggregates during freeze−thaw cycling. According to the aggregate results, the content of small particles (<0.05 mm) in common soil after the freeze−thaw cycle is significantly greater than that after the freeze−thaw cycle when BC is added together, and these particles are most likely to be lost with the loss of water, resulting in a decrease in soil dry density and fertility.

As an aromatic organic matter, BC has strong stability and absorbability [49], and its porous structure enables it to further interact with other forms of organic matter and minerals in the soil to promote the formation of soil aggregates [50]. Gao et al. also noted that with increasing macroaggregate content (>0.25 mm), the soil water holding capacity increased [51]. Therefore, BC can reduce water loss in the freeze−thaw process by maintaining the stability of soil aggregates and structures and improving the water retention rate of soil to retain more small particulate matter, improve the dry density of soil and further improve the fertility of soil.

3.3.3. XPS analysis of FT-BC before and after leaching

The XPS spectra of FT-BC before and after nutrient leaching are presented in Fig. 5. Prior to nitrogen adsorption, the C 1 s core level spectrum of FT-BC can be resolved into three distinct atomic orbitals corresponding to the C–C/C–H/C═C, C–O, and C═O functional groups, with peak binding energies at 283.99, 284.98, and 286.68 eV, respectively. Following the leaching experiment, these peaks shift to 284.08, 285.14, and 287.48 eV, respectively, due to the adsorption of ammonium by these functional groups [45]. The O 1 s spectrum indicates the presence of H_2O and –OH orbitals, with binding energies of 531.59 and 532.75 eV, respectively. The –OH

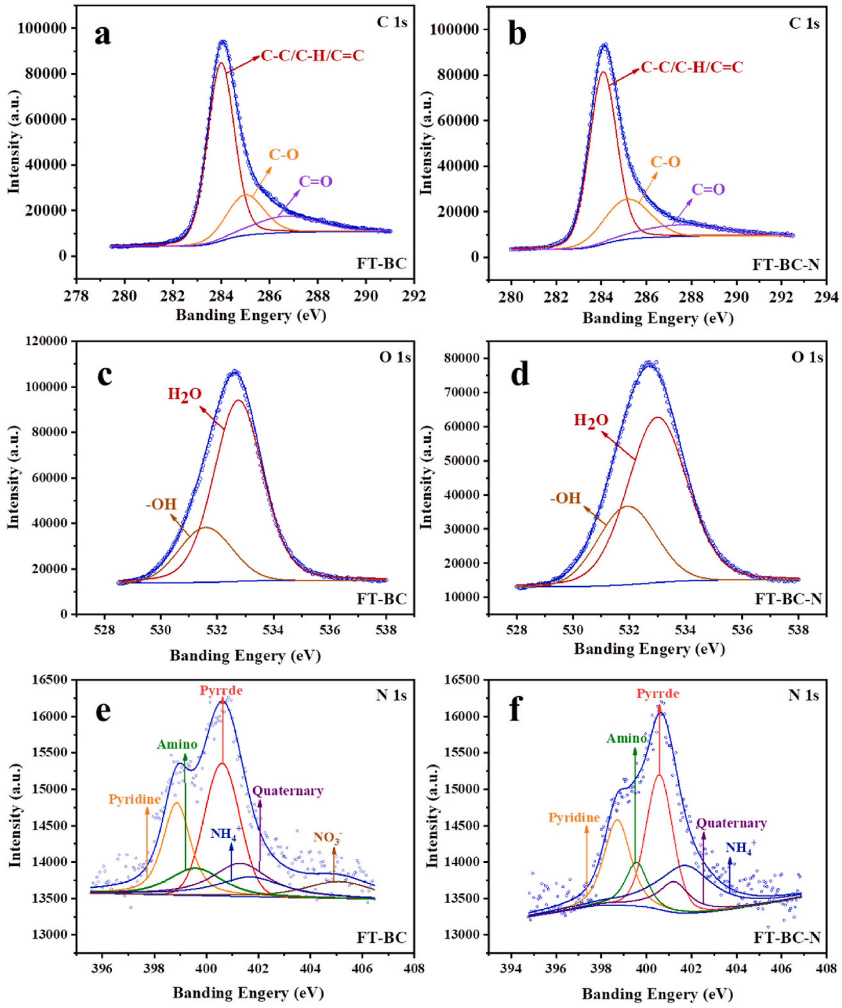

Fig. 5. High-resolution XPS spectra of C 1 s (a–b), O 1 s (c–d) and N 1 s (e–f) of FT-BC before and after the leaching experiment.

content decreases after ammonium adsorption, primarily attributed to the effect of ammonium adsorption [52].

The nitrogen in FT-BC exists in four main forms: pyridine N (398.86 eV), amino N (399.59 eV), pyrrole N (400.6 eV), and quaternary N (401.3 eV). Additionally, FT-BC may contain small amounts of NH_4^+-N and NO_3^--N [53,54]. After the leaching experiment, the NO_3^--N content decreased, and the levels of pyridine N, amino N, pyrrole N, and quaternary N decreased to varying degrees. This reduction is likely due to the scouring effect of water droplets during simulated rainfall, which removes dissolved organic matter and ash from FT-BC, resulting in a decrease in nitrogen content. The NH_4^+-N content on the surface of FT-BC increased, indicating that FT-BC can effectively adsorb ammonium ions after urea dissolves in water to minimize nitrogen loss.

Compared with fresh BC, FT-BC after freeze−thaw cycling has a greater specific surface area, which suggests the presence of a greater number of active adsorption sites on FT-BC, enhancing its ammonium adsorption capacity [45]. Moreover, during the aging process, oxygen-containing acid functional groups are formed on the surface of FT-BC, endowing it with a high cation exchange capacity. This facilitates the substitution of other cations with lower affinity [55–57]. Consequently, FT-BC demonstrated excellent nitrogen retention performance.

3.3.4. *BET surface analysis of BC and FT-BC*

BET analysis was conducted to compare the relative surface area and pore volume of BC and FT-BC. The results are presented in Fig. 6 and Table S3. The BET surface area of BC increased from 81.78 m^2/g to 101.01 m^2/g, representing a 23.5 % increase compared to that of the original BC. Similarly, the total pore volume increased from 0.05937 cm^3/g to 0.06840 cm^3/g, with micropore volumes increasing from 0.02909 cm^3/g to 0.03272 cm^3/g for FT-BC. This translates to a 15.2 % increase in total pore volume and a 12.5 % increase in micropore volume for FT-BC compared to BC.

Interestingly, the average pore size of FT-BC decreased from 8.5849 nm to 5.4664 nm. These findings indicate that after freeze−thaw aging, a significant number of pores were exposed, and a substantial number of micropores were formed in FT-BC [58]. This resulted in an increase in the relative surface area but also a decrease in the average pore size [59]. This phenomenon can be attributed to the enhanced nitrogen retention capability of FT-BC, which has a lower toxicity and a larger specific surface area, allowing for better utilization of FT-BC in inhibiting excessive nitrogen in soil.

The use of FT-BC for the control of nitrogen in soil can effectively promote corn growth, reduce farming expenses, and optimize biodegradation performance, which is crucial for the advancement of sustainable and environmentally friendly agricultural practices [60].

3.3.5. *3D-EEM maps of the FT-BC DOM*

The three-dimensional fluorescence diagram of the dissolved organic matter (DOM) of BC after undergoing different aging cycles, as depicted in Fig. 7, indicates that the content and composition of substances within the DOM of BC decrease with increasing aging time. This reduction in DOM content and diversity could be a significant factor contributing to the lower Cd content (0.7 mg/g) in wheat in the BC-modified soil at room temperature, which was approximately half that of the blank control group. This suggests that fresh BC may possess a greater capacity to immobilize heavy metals. It is plausible that unaged BC contains a higher concentration of DOM, which may interact with Cd to form Cd-DOM complexes [61]. However, the presence of excessive DOM in fresh BC may also be associated with potential biotoxicity [62].

After conducting the aforementioned analysis and characterization of biochar and soil properties, we can comprehensively discuss and analyze strategies for utilizing biochar in freeze−thaw soils. In terms of total nitrogen loss rate analysis, it is evident that FT-BC exhibits a better nutrient retention effect than fresh BC, with a loss rate of only 80 % of that of BC. Conversely, when examining the removal effect of metal ions, the opposite trend was observed, as the concentration of Cd in BC-cultured plants was merely 73 % of that found in FT-BC. This necessitates different usage strategies for varying soil conditions: for unpolluted soil subjected to the freeze−thaw process, direct dosing of fresh BC before winter or FT-BC is recommended, which can maximize water and fertilizer retention during winter crop growth; for heavy metal-polluted soils, it is better to add biochar after undergoing the freeze−thaw cycle as much as possible to minimize the impact of heavy metals on plants.

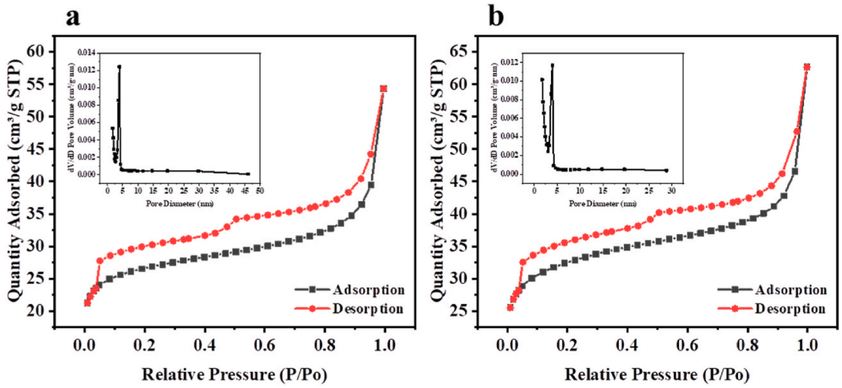

Fig. 6. BET analysis results of BC (a) and FT-BC (b).

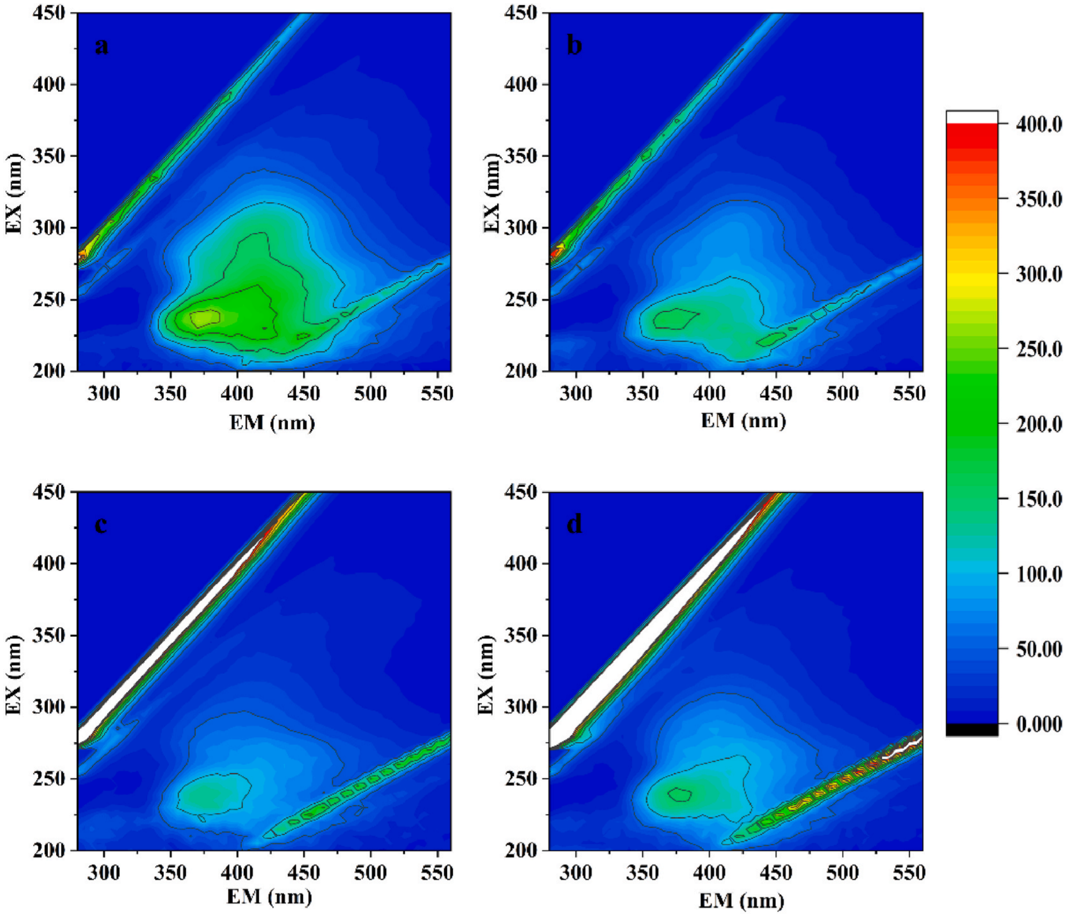

Fig. 7. 3D-EEM maps of the FT-BC DOM during different freeze−thaw aging cycles. (a-d correspond to different freezing and thawing aging times in weeks 1–4).

4. Conclusion

FT-BC demonstrated exceptional and satisfactory performance in these three aspects. First, the robust structure of FT-BC can withstand the damage to the soil structure caused by large temperature fluctuations. Additionally, it provides an external carbon source to the soil. Second, the exposure of more pores and adsorption sites in FT-BC following the freeze−thaw cycle increases the available space and potential for N adsorption and Cd immobilization. Third, while unaged BC exhibits a greater capacity to fix Cd, the reduced toxicity and enhanced environmental friendliness of FT-BC make it an alternative material for soil remediation. This finding underscores the potential of FT-BC for soil remediation even under harsh temperature variations. Therefore, in most application scenarios, BC or FT-BC should be applied before winter to improve soil fertility. To remediate heavy metal pollution, the use of fresh BC after winter might be effective.

However, it is important to note that this study primarily focused on the soil environment characterized by seasonally frozen soils. This specificity limits the generalizability of our findings to other soil environments. For instance, different soil conditions, such as drought-prone soils, swampy areas, and arid regions, were not considered in this study. These diverse environments could have unique interactions with biochar that differ from those observed in seasonally frozen soils. Additionally, this study was limited by the use of several key soil performance indicators. While these indicators are critical, they do not encompass the full range of soil health metrics. Future research should expand the range of performance indicators to include factors such as soil microbial activity, carbon sequestration potential, and impacts on other essential nutrients such as phosphorus and potassium. Furthermore, the long-term effects of biochar application were not within the scope of this study. Biochar may also play an important role in the late winter when wheat starts to sprout. Future studies should assess the durability and sustained effectiveness of biochar. These studies should also consider the economic feasibility and practical aspects of large-scale biochar application in different agricultural settings.

Availability of data and materials

The datasets used or analyzed during the current study are available from the corresponding author upon reasonable request.

CRediT authorship contribution statement

Yi He: Conceptualization, Investigation, Methodology. **Xia Chen:** Data curation, Investigation, Writing – original draft. **Yu Peng:** Methodology, Project administration. **Zhen-Bao Luo:** Data curation, Methodology. **Shun-Feng Jiang:** Data curation, Writing – original draft, Writing – review & editing. **Hong Jiang:** Conceptualization, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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