Mobility of exogenous lead in acidic soil treated with wheat straw biochar after aging process of freeze-thaw cycles
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ABSTRACT
Although biochar has been investigated extensively to stabilize soil heavy metals, there were limited investigation on the stabilization of soil heavy metals by using biochar under the natural ageing processes of alternate-cooling/heating. In this study, wheat-straw-biochar-treated soil samples contaminated with Pb(II) ions/PbO were subjected to 12 h-freeze/12 h-thaw cycles simulating the natural alternate-cooling/heating process. After the freeze-thaw process, the mobile fractions of lead reduced by 30.0% (500 mg kg⁻¹ Pb(II) spiked soil) and 19.5% (PbO spiked soil) due to biochar’s addition evaluating via 0.01 M HCl batch extraction. Compared with the control, the mobile Pb in treated groups decreased in column leaching. Exchangeable lead decreased by 6.4%–80.9% due to biochar addition. Freeze-thaw ageing had no significant effects on lower lead leaching and lower exchangeable lead resulted from biochar’s addition. Therefore, wheat-straw-biochar treatment is helpful for stabilization of both dissolved Pb and particulate Pb in soil under the alternate-cooling/heating ageing process.

1. Introduction
Lead contamination, which is closely related to human activities, such as mining and smelting, affects the normal physiological process of organisms [1] and seriously endangers human health [2]. Entering into human body through various pathway, lead is difficult to eliminate from body with a long half life time [3]. As it is persist and can’t decompose like organic compounds in soil, control of mobile lead in soil is vital to reduce lead exposure through food chain for human [4]. Among various immobilization techniques, biochar remediation shows prosperous potential in soil heavy metals stabilization [5] and soil restoration [6,7] in recent years. Biochar has been reported binding lead with different mechanisms, e.g. adsorption and chemical precipitate, effectively stabilizing heavy metals including lead, cadmium, and other metal elements [8–10].

As large proportion of the area of China is in temperate zone, seasonal freeze-thaw process in winter days occurs from year to year in certain area [11]. The seasonal freeze and thaw process results in changes in the structure and stability of soil aggregates and water holding capacity of soil matrix [11]. Release and migration of soil components (e.g. organic matter and minerals) were reported in response to freeze-thaw cycles [12]. At the same time, heavy metals binding in soil particles may release during thawing with increased moving of soil moisture in soil pore, and their speciation binding in soil particles may also change due to the changed soil conditions. Soil contaminated by heavy metals may be caused by wastewater from industrial discharge contained dissolved metal ions and by atmospheric deposition of primary and secondary particulate minerals from mining and metallurgical industries. Dissolved and particulate metals have different environmental behaviors such as adsorption/desorption, leaching/precipitation, and oxidation/reduction in soil. Immobilization of water-soluble lead spiked in soil after aging has been investigated extensively in recent years; however, few investigations have been done on the spiked particulate lead after freeze-thaw aging process. Increased lead and cadmium washing efficiency was found from soil after seven freeze-thaw cycles [13], and increased desorption of Pb²⁺ from soils was also found after six cycles of 24 h freeze/ 24 h thaw, suggesting lower binding of heavy metals to soil surface after freeze-thaw processes [14]. So further studies should be done on immobilization of spiked particulate heavy metals after freeze-thaw processes.

Crop stalk biochar has been considered prosperous potential in soil restoration [15–17], with cheap and large source of feedstock and high proportion of organic carbon, rich pore structure and large specific surface area, and is encouraged in land application in China. It has been widely reported that adding of crop stalk biochar increases soil organic carbon content, modifies soil aggregates, and stabilizes heavy metals [18–20]. However, biochar in soil will also experience climatic and meteorological changing, the natural
aging processes, e.g. variation of temperature and moisture. Simulated aging processes have been carried out to investigate their effects on metals stabilization by biochar and increasing and decreasing metal stabilization ability of biochar were both found after experiencing different temperature, moisture, and other conditions [21,22]. And limited literature reported the effects of natural process such as freeze-thaw cycles on the stabilization of dissolved lead or particulate lead in soil after biochar addition [9,23]. Further investigation is needed to provide more information about the effects of biochar with the aging processes of freeze-thaw cycles on lead stabilization of spiked either dissolved lead or particulate lead in agricultural soil.

Biochar has been investigated extensively as soil remediation agents to stabilize heavy metals recently as discussed above. However, there were limited investigation on the impact of the natural aging processes of alternate cold and heat among spring, summer, autumn, and winter on the stabilization of soil heavy metals after the addition of biochar. So freeze-thaw cycles are used to simulate the alternate cooling and heating ageing process on the stabilization of soil heavy metals after the addition of biochar in the current study. Moreover, dissolved Pb(II) ions (lead acetate) or particulate PbO were used to simulate contaminated soils, differing from the relevant experiments. After the freeze-thaw aging process, batch extractions, column leaching, and sequential extraction were carried out to mobility and fractionation of soil Pb. The object of this study is to assess the alternate cooling and heating ageing process on the stabilization of soil heavy metals with and without the addition of biochar. It is beneficial for evaluating biochar’s application in the stabilization of soil heavy metals in field-contaminated sites.

2. Materials and methods

2.1. Preparation of soil samples

Farmland surface soil (0–20 cm) was collected from Lianyungang, Jiangsu Province, which had days of lowest temperature below zero from about 39 days to 70 days from November to February next year in the latest five years. Debris and gravels were removed from the soil and the soil was then air dried, ground and sieved with a 20-mesh nylon sieve. Selected physicochemical properties of the soil were analyzed according to methods described in a hand book by Ministry of Ecology and Environment of PR China (2019) [24] and the results were listed in Table 1. The soil was of sandy loamy texture and acidic, having a relatively low Pb content. Neither crystal Pb chemicals nor surface Pb were detected through analysis by an X-ray diffraction analyzer (XRD, X0 TRA, ARL, Switzerland) and a scanning electron microscopy/energy dispersive X-ray analysis instrument (SEM/EDX, model S-3400 N II, Hitachi Co., Tokyo, Japan) (in supplementary materials, Figures S1 and S2). SiO2 was the predominant mineral, and albite and montmorillonite were also detected (Figure S1).

Wheat straw biochar made at 300°C was purchased from Nanjing Intellect, Integration & Connection Co., Ltd. (P.R. China). The biochar was produced under limited-oxygen conditions using a slow-pyrolysis process in a biochar oven. The programmed temperature controlling first elevated temperature at a rate of 8.5°C min⁻¹ to 300°C, then maintained at this temperature for about 4 h. Biochar pH (by a pH meter, ST3100, Changzhou Ohaus Instrument Co., Ltd, P.R. China) and EC (by a conductivity meter, DDS-11A, Shanghai Yidian Scientific Instrument Co., Ltd, P.R. China) were determined with soil/deionized water ratio of 1/20 (w/v). Ash of biochars was obtained after ashing at 550°C in a muffle furnace (SX2-4-10NP, Shanghai Yiheng Scientific Instrument Co., Ltd, P.R. China) under oxygen condition, and the ash was first dissolved with concentrated nitric acid then diluted to 10 mL for mineral elements determination. Contents of C, H, and N were determined using an elemental analyzer (Elementar Vario MICRO, German). Content of O was obtained through mass balance calculation. Morphological analysis of the biochar sample was performed using the scanning electron microscopy instrument (SEM). Infrared spectra of the biochar were recorded using a Fourier transform infrared spectrometer (FT-IR).

| Table 1. Selected physicochemical properties of the soil and the wheat straw biochar (mean ± standard deviation). |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Soil sample       | Course sand (%) | Fine sand (%)   | Silt (%)        | Clay (%)        | EC(µs·cm⁻¹)     | Ash(%)          | C(%)            | H(%)            | N(%)            | O(%)            |
| 36.2±0.1          | 39.6±0.01       | 17.6±0.3        | 6.61±0.02       | 0.95±0.02       | 160±12          | 16.9±0.1        | 54.7±0.3        | 4.31±0.08       | 0.32±0.02       | 23.9±0.7        |
| pH                | 7.82±0.07       | 8.00±0.00       | 6.80±0.21       | 2.76±0.04       | 129±5           | 1.48±0.01       | 10.6±0.3        | 0.95±0.02       | 0.33±0.01       | 6.80±0.21       |
| Pb(mg·g⁻¹)        | Al (mg·g⁻¹)     | Fe (mg·g⁻¹)     | Ca (mg·g⁻¹)     | Mg(mg·g⁻¹)      | Pb(mg·g⁻¹)      | 16.9±0.1        | 54.7±0.3        | 4.31±0.08       | 0.32±0.02       | 23.9±0.7        |
| 0.017±0.000       | 7.98±0.22       | 12.9±0.8        | 0.823±0.065     | 0.998±0.031     | 0.509±0.021     | 1.48±0.01       | 10.6±0.3        | 0.95±0.02       | 0.33±0.01       | 6.80±0.21       |

Biochar sample
(NEXUS870, NICOLET Co., USA). The crystallographic structures of the biochar was identified using the X-ray diffraction instrument. The results were showed in Table 1, Figures 1 and 2. The biochar sample had a relatively much higher pH and EC values than the soil. It was also rich of C, H, and O, and mineral elements. These may be potential impact in elevating soil pH (favoring the stabilization of Pb) and soil nutrition. The biochar was rich of pores and had course surface according to the SEM image. The adsorption in the range of 600 ~ 800 cm\(^{-1}\) in FT-IR spectrum may be attributed to aromatic and heteroaromatic C-H vibrations; the peak appeared near 1100 cm\(^{-1}\) was attributed to aromatic C-O; and the peak appeared near 3378 cm\(^{-1}\) was attributed to –OH [25–27]. XRD analysis showed minerals of quartz (SiO\(_2\)) and calcite (CaCO\(_3\)). These suggested the wheat straw biochar's potential in adsorption of Pb.

According to the surveys of farmland soil contaminated by Pb in China, 150 and 500 mg kg\(^{-1}\) of soil Pb was set via the addition of lead acetate (Pb\((C_2H_3O_2)_2\) solution and 500 mg kg\(^{-1}\) of soil Pb was simulated via the addition of PbO suspension. Therefore, agriculture soils contaminated by either dissolved Pb(II) ions or particulate PbO were simulated with soil/moisture ratio of 1/1.25 (w/v) (denoted as Pb150, Pb500, and PbO). The three kinds of soil slurry were manually stirred 30 min d\(^{-1}\) (10 min every time and three times one day) for 40d. Then they were air dried, ground and sieved with a 20-mesh sieve to gain contaminated soil samples. Biochar amount of 1%-10% was used in soil Pb and other heavy metals stabilization investigation in different reports, and amount of ≥5% showed more significant effect [28–32]. Therefore, 5% biochar was mixed with the soil samples and moisture was maintained at about 70% of the field capacity. The soils added with biochar were put in sealed plastic bags for aging. The contaminated soils without biochar were also treated synchronously as control groups. The soil samples experienced aging process of 39 freeze-thaw cycles (12 h-freeze at −10°C and 12 h-thaw at 5°C for each cycle) and subsamples were collected every three cycles. Soil pH, redox potential (Eh), and soil electric conductivity (EC) was determined every three cycles by the pH meter and conductivity meter with soil/deionized water ratio of 1/2.5 (pH and Eh) and 1/5 (EC).

2.2. Batch extraction and column leaching of lead

Batch extraction. 2.00 g subsample was extracted with 30 ml deionized water (E1), 0.01 M CaCl\(_2\) solution (E2), or 0.01 M HCl (E3) in a plastic centrifuge tube. After shaken for 8 h and then standing still for 12 h at room temperature (25 ± 2°C) in a lateral shaker (TS-80C, Shanghai Tiancheng Experimental Instrument Manufacturing Co., Ltd. P.R. China), the plastic centrifuge tubes were centrifugated at 3000 rpm for 10 min. The supernatant was separated and filtered with 0.22 μm membrane for metal determination.

Column leaching. Soil samples contaminated with 500 mg kg\(^{-1}\) Pb (Pb\((C_2H_3O_2)_2\) or PbO) with/without 39 freeze-thaw cycles were used for column flushing to assess leaching of lead and nutrients. 6.00 g soil sample was packed in a polyethylene column (1.5 cm inner diameter and 3.5 cm height), with 1.5 g quartz sand (pre-washed with 0.01 M HNO\(_3\) and deionized water) at the bottom/on the top of it. Polypropylene bolting cloth was used between the soil and the sand. According to the pre-experiment, the column was first injected with 6 ml deionized water from the top of the column which was enough for saturation and stabilization, and then the column was injected with deionized water or 0.01 M HCl solution at a flow rate of 0.2 mL min\(^{-1}\) from the top of the column and the leachate was collected from the bottom of the column. In whole experiment, the column was stable.

![Figure 1. FT-IR spectrum (a) and XRD spectrum (b) of the wheat straw biochar.](image-url)
and the leachate was limpid. Every 30 min, an accumulated leaching sample which was enough for metal elements’ analysis was collected and filtered with 0.22 μm membrane. And according to our pre-experiment, the concentration of Pb in the effluent after 720 min stably maintained at a very low concentration. Therefore, leaching time of 720 min was employed.

2.3. Fractionation of lead

Sequential extraction was carried out for soil samples with/without 39 freeze-thaw cycles to investigate lead distribution according to Tessier’s method with minor adjustment in the extraction of the residue fraction via *aqua regia* [35]. Briefly, 1.00 g soil sample was extracted with 8 ml MgCl₂ solution (1 mol L⁻¹) in a 50 ml plastic tube for 1 h, then the tube was centrifuged and the supernatant was separated for determination of lead concentration, denoted as the first fraction (F1). The residual solid from the previous step was extracted with 8 ml sodium acetate solution (1 mol L⁻¹, pH 5.0, adjusted with acetic acid) for 5 h for determining the second fraction (F2). To extract the third fraction (F3), the residual solid from the previous step was digested with 20 ml NH₃OH-HCl solution (0.04 mol L⁻¹, in 25% (v/v) acetic acid solution) at 96 ± 3°C for 6 h. To extract the fourth fraction (F4), the residual solid from step three was digested with 3 ml HNO₃ solution (0.02 mol L⁻¹) + 5 ml H₂O₂ solution (30%, pH 2) at 85 ± 2°C for 2 h, 3 ml H₂O₂ (30%, pH 2) at 85 ± 2°C for 3 h and then 5 ml ammonium acetate solution (3.2 mol L⁻¹, in 20% (v/v) HNO₃) for 30 min (the final volume was made up to 20 ml by deionized water). The residual solid from step four was digested with 8 ml *aqua regia* (HCl:HNO₃ = 3:1(v/v)) at 80°C for 3 h, and then it was made up to 20 ml with deionized water for determining the residue fraction (F5). In each step, the tube was centrifuged at 3000 rpm for 10 min, and then the supernatant was separated and filtered with a 0.22 μm membrane for heavy metal determination. The residual solid from the previous step was washed with deionized water three times before next extraction. The recovery ratios of all fractions (F1 + F2 + F3 + F4 + F5) to total lead content in soil samples extracted by *aqua regia* was in the range of 95%-105%.

2.4. Determination of lead and other metals

Lead and other metals in solution were analyzed by using an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 5300 DV, USA).

2.5. Data analysis

The descriptive statistics of experimental data were carried out using origin 8.0. Figures were drawn by using origin 8.0. One-way analysis of variance (ANOVA) was performed to analyze the significant difference (p < 0.05) among different treatments.

3. Results and discussion

3.1. Lead released in batch extraction and column flushing

Lead extracted from Pb(II) ions- and PbO-spiked soils after aging of different freeze-thaw cycles was shown in Figure 3. In both extraction using deionized water and 0.01 M CaCl₂, extractable Pb was below 1%. It was consistent with the previous report that lead had relatively low extractable amount in alluvial soil spiked with Pb(NO₃)₂ assessed by 0.01 M CaCl₂ [36]. Biochar treatment decreased the 0.01 M HCl extractable amount of Pb in soils spiked with 150 mg kg⁻¹ Pb(II) ions from 3d to 12d and from 27d to 39d (Figure 3(a)). 0.01 M HCl extractable lead in biochar treated soil was lower from 27d to 39d (average 21.4 mg·kg⁻¹) than that from 3d to 24d (average 30.5 mg·kg⁻¹), showing lower extractability of Pb at the end of the 39 days freeze-thaw aging. Soils spiked with 500 mg·kg⁻¹ Pb(II) ions had much larger extractable lead amount than soils spiked with 150 mg·kg⁻¹ Pb(II) ions. In 500 mg·kg⁻¹ Pb(II) ions spiked soil without biochar, the average contents of water extractable lead from 27 to 39 cycles (1.37 mg·kg⁻¹) were slightly higher than that from 3 to 24 cycles (0.47 mg·kg⁻¹), showing possible increase of lead mobility due to freeze-thaw process of certain time length (Figure 3(b)). In batch experiment of Li et al (2016), the adsorption amounts of Pb⁺⁺ onto soil sample reduced after six 24 h freeze/24 h thaw cycles, and this reduction was affected by freeze temperature and may be resulted from lower pH and lower organic matter after freeze-thaw processes [14]. However, research also found increased adsorption of lead by soils which pH values were higher than
7.0 after freeze-thaw treatment [37]. Therefore, the effect of freeze-thaw process on lead mobility differed with specific soils and freeze-thaw conditions. Compared to the control, biochar treatment had much lower extracted lead (p < 0.01) in deionized water extraction and 0.01 M CaCl$_2$ extraction from 27d to 39d for soils spiked with 500 mg·kg$^{-1}$ Pb(II) ions. Biochar treatment also decreased the extractable amount of lead by 13.5% – 49.1% in 0.01 M HCl extraction. These suggested good stabilization of lead in the soils spiked with biochar whether there were freeze-thaw processes. Similarly, PbO contaminated soils treated with biochar had much smaller lead extraction amount than the controls in all the three extractions (Figure 3(c)). For example, the water extractable Pb decreased by 88.4% and the 0.01 M HCl extractable Pb decreased by 19.5% in average. Compared with soils spiked with Pb(II) ions, PbO contaminated soils showed steady extractable lead amount during the whole freeze-thaw process. These result suggested the potential of wheat straw biochar in lowering extractable Pb in different Pb contaminated soils with certain soil moisture even though there may be freeze-thaw process.

The leaching of lead from soil samples contaminated with 500 mg·kg$^{-1}$ Pb (Pb(II) ions and PbO) with/without freeze-thaw cycles in column leaching was showed in Figure 4. In deionized water leaching, very low concentration of Pb in the leachate was observed and it decreased in the first 450 min and then it maintained at a nearly steady level (Figure 4(a,b)). According to the calculation of accumulated amount of lead dissolved at 720 min, biochar addition resulted in lower lead leaching in water leaching for both Pb(II) ions and PbO contaminated soils with 39 freeze-thaw cycles (p < 0.01) (Figure 5(a,b)). In 0.01 M HCl leaching, biochar treatments had much lower (p < 0.01) and later peak lead concentrations in the effluents from Pb(II) ions contaminated soils (Figure 5(c)). But biochar addition didn’t affect the accumulated amount of lead dissolved from soils without freeze-thaw cycles (p > 0.05) and enhanced dissolved lead for soils with freeze-thaw cycles (p < 0.05) according to the values at 720 min (Figure 5(c)). Compared to the control, biochar addition lowered the peak lead concentration in the effluents in 0.01 M HCl leaching from PbO contaminated soils without freeze-thaw cycles (p < 0.01) (Figure 4(d)), while biochar treatment
resulted in higher ($p < 0.01$) and later peak lead concentration with 39 freeze-thaw cycles. However, biochar treatments lowered accumulated amount of Pb dissolved from soils with 39 freeze-thaw cycles ($p < 0.05$) (Figure 5(d)). Therefore, biochar addition could lower lead leaching for different types of exogenous lead at neutral leaching condition, and freeze-thaw cycles would not impair this effect. Biochar addition could lower lead leaching in PbO contaminated soil and postpone lead leaching peak in Pb(II) ions contaminated soil at acidic leaching condition.

The reduction of lead release may partly due to the increased pH because of the introduction of the wheat straw biochar which had a pH value of 7.82 (Table 1). Every kind of contaminated soil treated with biochar had higher pH value than that without biochar during the whole freeze-thaw process (Figure S1). In the research of Yan et al. (2021), application of 2.5% rice straw biochar in an acidic soil (pH 4.30) resulted in an increase of pH with 0.81 in one year [38]. Liu et al. (2022) cultured an acidic soil with 1% wheat, corn, rice, and rape straw biochar for 60d, and the soil pH was enhanced from 4.84 to 4.92, 5.21, 5.11, and 5.28 [39]. In the current research, the biochar treated soil samples had nearly steadily higher pH values than their controls with/without aging process of freeze-thaw cycles ($p < 0.01$) (Figure S2). The average pH increased from 5.96 to 6.57 (Pb150), 6.15 to 6.64 (Pb500), and 5.56 to 5.97 (PbO). Higher pH favors lead stabilization and reduces release and transport of lead in soil system. In the report of Zhang et al. (2022), available Pb content in yellow soil declined from 17.3% to 33.9% with the means of soil pH increased by 5.36% to 24.3% at different tobacco stem biochar application ratios [40]. Moreover, there may be some other factors could promote the stabilization of lead. In the whole freeze-thaw process, released Pb$^{2+}$ might be re-deposited onto the biochar, exchanging with surface Ca$^{2+}$ of it. Pb$^{2+}$ has much larger affinity to the solid surface than other divalent cations [41,42]. In the current research, leaching of Ca$^{2+}$ was observed to increase in the biochar treatments in deionized water leaching (Figure S4). As there was considerable phosphorus in the biochar (Table 1), lead might be also cooperated into the biochar as

![Figure 4](image-url). Lead concentrations in the leachate in column leaching experiments using deionized water ((a) Pb and (b) PbO) and 0.01 M HCl ((c) Pb and (d) PbO) (CK and BC: soils without and with biochar without freeze-thaw cycles; CKF and BCF: soils without and with biochar after 39 freeze-thaw cycles) (error bars mean standard deviation).
As cited in [43], the addition of biochar had a dilution effect on Pb in soil, indicating possible effective pathways for lowering extractable Pb content.

### 3.2. Lead speciation

Fractionation of lead in soils with and without freeze-thaw cycles was shown in Figure 6. Biochar addition resulted in a decrease in the content of F1 fraction (about 63% in average) in all the contaminated soils with and without 39 freeze-thaw cycles (Figure 6(a)). F1 fraction is attributed to exchangeable species and may be transformed to other species due to addition of biochar. It has been reported that the content of F1 lead in contaminated soil treated with rice straw biochar (3%) decreased obviously compared with the control in a 90d incubation due to transformation to F2 lead [44]. It was supposed that F1 lead transformed to other fractions in the current research, but the content of other fractions was not observed to increase significantly. This may be due to the relatively low contents of F1 lead compared to other fractions. The exchangeable lead may be chemically deposited as different species, e.g., carbonate, hydroxide or phosphate since soil pH increased after the addition of the wheat straw biochar. Furthermore, carbonate and phosphorus are common chemical components in soil and biochar addition introduced more carbonates and phosphorus into the soil (Figure S1 and Table 1). Possible deposition as different species resulted in transformation of exchangeable lead to different fractions other than one specific fraction. Therefore, no significant increase in the content of all the other fractions was observed when limited exchangeable lead transformed into them. 39 freeze-thaw cycles slightly enhanced the ratio of F1 + F2 fraction in three kinds of contaminated soils without biochar, and it was different in biochar treatment (Figure 6(b)). It has been reported that freeze-thaw cycles enhanced F1 fraction of copper and zinc but decreased F2 fraction of them in pig manure [45]. So the effects of freeze-thaw cycles on metal distribution varied with specific matrix and metals. Biochar application reduced the ratio of F1 and
increased the ratio of F3 in 150 mg·kg⁻¹ Pb(II) and 500 mg·kg⁻¹ Pb(II) contaminated soil with/without freeze-thaw cycles. As for soils contaminated with PbO, biochar application reduced the ratio of F1 and increased the ratio of F3 + F4 + F5. Therefore, biochar addition did decrease mobility of different types of exogenous lead even though the soils experienced 39 freeze-thaw cycles, mainly through decreasing the amount of F1 fraction. However, the variations in fractions distribution were not really the same among different kinds of exogenous lead contamination.

3.3. Other effects of biochar addition

Soils treated with biochar had darker color (Figure S5). The color was lighter after 39 cycles of freeze-thaw process, but still darker than the control, which means biochar experienced exactly different aging process due to freeze-thaw cycles. Mineral nutrients (Ca, Mg, K, and Fe) leached from biochar treated soils in deionized water leaching were also analyzed (Figure S4). Improvement of the release of the nutrients via leaching using deionized water suggested benefits in soil restoration except for heavy metal stabilization. Larger EC values of biochar treatments also meant improved soluble electrolytes including Ca²⁺, K⁺ and other elements and improved pH meant better acidic buffering (Figure S3(a,b)). Eₚ of the soils fluctuated during the freeze-thaw process, and there was no obvious relationship between the variation of Eₚ and lead stabilization (Figure S3(c)).

4. Conclusions

Lead mobility in Pb(II) ions/PbO contaminated soil treated with wheat straw biochar and nutrients availability after 39 freeze-thaw cycles were investigated to assess the effects of wheat straw biochar addition on soil restoration. In batch extraction, biochar addition reduced the extractable content of lead for all the freeze-thaw cycles. In column leaching, biochar also reduced the leaching of lead in soils with/without 39 freeze-thaw cycles. Exchangeable fraction of lead assessed by Tessier’s sequential extraction decreased in biochar treated soils. Therefore, the addition of wheat straw biochar reduced lead mobility. However, stabilization of lead by biochar differed between two types of exogenous lead. Moreover, obvious increase in leaching of nutrients such as potassium and calcium using neutral leaching agents (deionized water) and improved pH due to the addition of wheat biochar suggested benefits in soil restoration except for lead stabilization. The addition of wheat straw biochar has prosperous potential for lead stabilization and soil restoration.

Disclosure statement

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