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1 **Salisbury biochar did not affect the mobility or speciation of lead in kaolin in a**
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3 **short-term laboratory study**
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Abstract: Salisbury biochar (produced from British broadleaf hardwood) with two different particle sizes (≤ 2 mm and ≤ 0.15 mm) was applied on a kaolin with three different lead (Pb^{2+}) contamination levels (50 mg/kg, 300 mg/kg and 1000 mg/kg) at the dosage of 1% in w/w. The short-term impact of biochar on the mobility and speciation of Pb^{2+} in the kaolin was investigated using attenuation periods of 1, 7 and 28 days. The leachability and extractability of Pb^{2+} in carbonic acid leaching and EDTA extraction tests as well as the speciation of Pb^{2+} in soils were not significantly affected by biochar treatment during all periods. The insignificant effects of biochar on Pb^{2+} immobilisation were most likely attributed to the high adsorption capacity of kaolin towards Pb^{2+} and biochar failed to competitively adsorb Pb^{2+} against kaolin. Kaolin immobilised Pb^{2+} primarily through cation exchange, which represents the readily bioavailable fractions of Pb^{2+} in soils and may still pose environmental risks. This paper suggests the inefficiency of biochar treatment on heavy-metal contaminated clay-rich soils. Therefore a laboratory treatability study with respect to the soil type may be crucial when large-scale biochar applications in heavy-metal associated soil remediation are evaluated.

Keywords: Biochar, lead, kaolin, immobilise, speciation

1 Introduction

The application of biochar in soil remediation has recently attracted global interests due to its multiple environmental benefits: (1) biochar can be produced using agricultural and industrial wastes (e.g. crop residues, manure, sludge etc.) as the feedstocks [1]; (2) the co-products (syn-gas and bio-oil) during biochar production can be used as green energy and therefore offset energy use associated with producing biochar [2]; (3) biochar can immobilise contaminants in soils and therefore reduce their leachabilities and bioavailabilities [3]; (4) biochar can help retain the nutrients and improve the water holding capacity and resilience of soils, therefore aiding the greening or revegetation of the contaminated land [4]; (5) the recalcitrant form of carbon in biochar can remain in soil for hundreds to thousands of years [2].

In order to investigate the potential of biochar application in soil remediation, Salisbury biochar, derived from British broadleaf hardwood, was characterised and applied to a contaminated site in the UK in 2011 [5,6]. The biochar treatment successfully immobilised heavy metals and reduced their leachabilities in the sand-dominated site soils three years after the treatment [6]. Due to the high availability of hardwood in the UK and the encouraging performance in the field trial, Salisbury biochar has the potential to be applied in soil remediation at a large scale. As the site soil is sand based (97% of sand particles), it is necessary to investigate the impact of this biochar on the immobilisation of metals in a soil predominantly comprising clay.

Unlike sand particles (diameter range of 0.05 - 2 mm) which are relatively chemically inert, the layer structures of phyllosilicate result in active chemical properties for clay minerals such as relatively high cation exchange capacity (CEC) and surface area [7–9]. Therefore, the clay minerals have the ability to retain heavy metals on their

1 surfaces through cation exchange and reduce its leaching to the environment under
2 field conditions [8]. However on the other hand, the retained heavy metals on clay
3 particles have the risks to be uptaken by the plants grown on clay soil, bringing
4 further hazards to human beings [8,9]. Therefore, the impact of biochar on
5 immobilisation of heavy metals in clay-rich soils is worth being investigated. However,
6 the majority of studies to date have investigated the performance of biochar in sand-
7 dominated soils, as indicated in Table S1 [3,10–14]. Studies that applied biochar on
8 clay-rich soils are very limited, leading to a poor understanding of the performance of
9 biochar on clay soils contaminated with heavy metals and the remediation
10 mechanisms involved.
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25 In this study, short-term laboratory incubation tests were carried out to investigate
26 the impact of Salisbury biochar on the immobilisation of heavy metals in kaolin, a
27 typical clay soil. Lead (Pb^{2+}) was selected as a representative heavy metal as it is
28 one of the most common contaminants in water and soil and represents serious
29 concerns to human health and environment pollution [15], and demonstrated the
30 highest sorption to Salisbury biochar in a previous study [5]. This study aims to
31 investigate: (1) the impact of biochar on the mobility of Pb^{2+} in kaolin; (2) the impact
32 of biochar on the speciation of Pb^{2+} in kaolin; (3) the short-term time dependence of
33 the two impacts.
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47 2 Materials and methods

48 2.1 Biochar

49 Salisbury biochar was purchased from Southern Woodland products (Salisbury, UK).
50 It is produced from British broadleaf hardwood at 600 °C under oxygen limited
51 ambient conditions (but no additional protective gas was added) in a retort for 13.5
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1 hours. The physical properties and adsorption characteristics of this biochar towards
2 Pb^{2+} have been investigated in a previous study [5] and are briefly summarised in
3
4 Table 1. In general, Salisbury biochar exhibited a relatively high adsorption capacity
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6 of Pb^{2+} , which was significantly affected by the biochar particle size (30.04 mg/g for
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8 samples sieved to ≤ 2 mm versus 47.66 mg/g for those sieved to ≤ 0.15 mm).
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11 12 2.2 Kaolin

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14 The kaolin, PolwhiteE, was supplied by Richard Baker Harrison LTD (Midlands, UK).
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16 Soil pH was determined in a soil:water ratio of 1:2.5 (g/mL) based on BS 1377. Its
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18 CEC was measured by a compulsive exchange method based on [16]. Kaolin (1 g)
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20 was mixed with 20 mL of 0.5 M $BaCl_2$ and shaken at 200 rpm for 2 h before filtration
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22 through a 0.45 μm filter. The concentrations of sodium, magnesium, aluminium,
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24 potassium, calcium, manganese and iron in the filtrate were tested by inductively
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26 coupled plasma/optical emission spectrometry (ICP-OES) (Perkin-Elmer, 7000DV)
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28 after acidification. CEC was calculated by the sum of the concentrations of the
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30 measured cations. The other physicochemical properties of the kaolin were obtained
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32 from the datasheet provided by the supplier and are summarised in Table 2 together
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34 with pH and CEC.
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43 2.3 Experimental design and sample preparation

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45 The experimental design is shown in Table S2. After considering the adsorption
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47 capacity and dosage (1% in w/w) of biochar, three soil contamination levels were
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49 designed: 50 mg/kg to represent lightly contaminated land (less than the adsorption
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51 capacities of biochar); 300 mg/kg to represent medium contaminated land
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53 (comparable to the adsorption capacities of biochar); and 1000 mg/kg to represent
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55 severely contaminated land (exceeds the adsorption capacities of biochar). A
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1 previous study demonstrated that particle size has a significant impact on the
2 sorption of Pb^{2+} by this biochar [5], therefore two particle sizes of ≤ 2 mm and ≤ 0.15
3 mm were selected for this study in order to represent coarse and fine particle sizes.
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5 Throughout this paper, the terms “2 mm” and “0.15 mm” will be used to represent the
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7 biochar samples sieved to ≤ 2 mm and ≤ 0.15 mm respectively.
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12 The soil and biochar (or without biochar for the control samples) were dry mixed in a
13 mixer (Kenwood, UK) and then the contaminants ($Pb(NO_3)_2$ dissolved in solution)
14 were added and thoroughly mixed with the soil-biochar mixture. The samples were
15 then incubated in order to maintain them at a moisture content of 40% (w/w)
16 (between liquid and plastic limit to avoid either too dry or too wet) and a density of
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2.4 Chemical analysis

At the designated time, soil samples were collected and oven dried at 60 °C for 48 h. Separate 1 g dry soil samples were taken for carbonic acid leaching, Ethylenediaminetetraacetic acid (EDTA) extraction and sequential extraction tests. The remainder of the dry samples were used to test soil pH, applying the same method as presented in section 2.2.

Carbonic acid leaching (based on BS EN 12457-2) was used to indicate the release potential of hazardous and toxic elements from solid waste under slightly acidic rain

1 water [17]. The dry soil (1 g) was mixed with 10 mL carbonic acid (pH = 5.6) and
2 shaken at 200 rpm for 24 h. The mixture was then filtered through a 0.45 µm filter
3 and the Pb²⁺ concentration in the leachate was tested by ICP-OES.
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7 EDTA extraction was carried out to determine the potential bioavailability of Pb²⁺ in
8 kaolin as suggested in [18]. The dry soil (1 g) was mixed with 5 mL of 0.01 M
9 Na₂EDTA and shaken at 200 rpm for 24 h. The mixture was then centrifuged at 3000
10 rpm for 5 minutes and filtered using a 0.45 µm filter, and the concentrations of Pb²⁺
11 in the leachate was measured by ICP-OES.
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20 Sequential extraction based on [14,16,17] was used to determine the different
21 geochemical phases (speciation) of Pb²⁺ present in the soils. The details of the
22 procedure can be found in a previous study [6]. The metals were partitioned into five
23 fractions through the following steps: Step 1 - exchangeable fraction (non-specific
24 adsorption); Step 2 - fraction bound to CO₃²⁻/PO₄²⁻ (specific adsorption); Step 3 -
25 fraction bound to Fe/Mn oxides; Step 4 - fraction bound to organic matter; Step 5 -
26 residual fraction. In order to investigate the speciation of Pb²⁺ on biochar, a certain
27 amount (0.1 g) of biochar sample (0.15 mm) after reaching adsorption equilibrium in
28 20 mL of 5 mM Pb²⁺ solution was collected and examined by sequential extraction.
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43 In order to investigate the adsorption capacity of Pb²⁺ on kaolin, the adsorption
44 equilibrium study was conducted. A certain amount of kaolin (0.1 g) was added to 20
45 mL solutions (pH = 5) containing different Pb²⁺ concentrations (0.1, 0.2, 0.3, 0.5, 1, 2,
46 3 or 5 mM) and 0.01 M NaNO₃. The mixture was shaken at 200 rpm at 20 °C for 24 h
47 to reach equilibrium. Then the mixture was filtered with a 0.45 µm filter and the Pb²⁺
48 concentration in the collected filtrate was measured by ICP-OES.
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1 All laboratory analysis in this study was conducted in a temperature controlled lab at
2 20 ± 1 °C and $50 \pm 2\%$ humidity based on the department lab standard.
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5 2.5 Statistical analysis 6

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8 All experiments were carried out in triplicates. The means and standard deviations
9 were calculated and presented for each experiment. The normality of the data were
10 tested and the Shapiro-Wilk results were used to indicate the normality of the data at
11 the significance level (P) of 0.05. The homogeneity of the variances were checked at
12 the significance level of 0.05. As in most cases, the data are normally distributed and
13 a homogeneity of the variances between groups was found, the difference between
14 two groups was evaluated by a one-way analysis of variance (ANOVA) at the
15 significance level of 0.05. The data that were not normally distributed or without a
16 homogeneity of the variances were indicated in the paper. The statistical analysis
17 was conducted using SPSS 16.0.
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33 3 Results and discussion 34

35 3.1 Soil pH 36

37 The soil pH values of all samples across all incubation periods were within 4.54 -
38 4.92 (Fig. 1), similar to the original pH value of the kaolin (4.78). Although the treated
39 samples exhibited a significant increase in pH compared with the control samples at
40 contamination levels of 300 and 1000 mg/kg (Fig. 1), the increases were only 0.08 -
41 0.19, suggesting that the influence of biochar treatment on soil pH was small. No
42 significant trends in the differences associated with particle sizes and incubation time
43 on soil pH were found (Fig. 1).
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57 The relatively low dosage (1%) and low biochar pH values (6.78 - 6.96) may have
58 resulted in the insignificant impact on soil pH. Puga et al. (2015) [21] employed
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biochar produced from sugar cane straw (pH = 10.2) to a contaminated soil (pH = 6.1; sand: 34%, silt: 24%, clay: 43%) and observed no significant changes in soil pH after 120 days of incubation with biochar dosages from 1.5% to 5%. Houben et al. (2013) [22] observed that the soil pH increased with biochar dosage when adding a miscanthus straw biochar (pH = 10.24) to a contaminated soil (pH = 6.57; 64% sand, 24% silt and 12% clay) at dosages of 1 - 10% after 56 days of incubation, however increases were no more than 0.5 pH units. The pH value of Salisbury biochar was even smaller than the biochars in the studies of Puga et al. (2015) [21] and Houben et al. (2013) [22], therefore considering the low dosage, the insignificant influence of biochar on soil pH in this study was reasonable.

The increase of soil pH can enhance the adsorption capacity of biochar due to deprotonation processes [23], however it requires a greater addition of biochar which will increase the cost in purchasing and transportation. A balance between performance and cost must therefore be seek during engineering application when considering the impact of biochar on soil pH.

3.2 Carbonic acid leaching and EDTA extraction tests results

The extracted concentrations of Pb^{2+} from carbonic acid leaching were low (≤ 1.04 mg/L) compared with those from EDTA extraction (7.72 - 176.87 mg/L) (Fig. 2). The Pb^{2+} concentrations in both carbonic acid leachate and EDTA extraction were strongly affected by the contamination levels, whereas no time-related dependencies associated with biochar treatments were observed over the 28 days (Fig. 2).

The Pb^{2+} leachability (extractability) for each extraction test can be obtained by dividing the amount extracted by the total amount in the soil. As shown in Fig. 3, the Pb^{2+} leachabilities in carbonic acid leaching tests were all $\leq 1.04\%$ (Fig. 3a), whereas

1 those in EDTA extraction tests range from 76.74% to 97.28% (Fig. 3b). The
2 influences of biochar treatment on Pb^{2+} leachability were not significant. Similarly, no
3 significant trends associated with contamination levels and incubation time were
4 found.
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10 The low Pb^{2+} leachabilities in carbonic acid leaching tests indicate a strong
11 adsorption or immobilisation of Pb^{2+} by the soil itself, which is highly resistant to
12 acidic rain water. The low soil pH values may have also contributed to this low
13 leachability. As shown in Fig. 1, all the sample pH values were within 4.54 - 4.92,
14 which were lower than that of the carbonic acid (5.6), making the carbonic acid
15 unlikely to reverse the deprotonation process and release adsorbed Pb^{2+} . The
16 carbonic acid leaching results suggest that the kaolin itself has successfully
17 immobilised the Pb^{2+} and the effect of biochar was negligible.
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30 The 0.01 M Na_2EDTA solution extracted a high amount of Pb^{2+} from all samples,
31 suggesting that a high proportion of Pb^{2+} is potentially bioavailable and therefore
32 presents an ecological risk. EDTA extracts Pb^{2+} through chelation between its
33 ligands and Pb^{2+} ions. The high amount of Pb^{2+} extracted indicates that high
34 proportion of Pb^{2+} was bound to the soil through binding which is weaker than
35 chelation. The high EDTA extractability (Fig. 3b) in this study is in line with the
36 findings of Kim et al. (2003) [24]. They observed Pb^{2+} leachability values higher than
37 80% at EDTA: Pb^{2+} mole ratios of 10 - 100 for one field soil (6238 mg/kg of Pb^{2+}) and
38 one artificial soil (oxidized glacial till contaminated with 2413 mg/kg of Pb^{2+}). Kim et
39 al. (2003) [24] also noted that the Pb^{2+} leachability was closely related to the
40 EDTA: Pb^{2+} mole ratios in 0.1 - 10; while it did not significantly increased with
41 EDTA: Pb^{2+} ratios in 10 - 100 for the artificially contaminated soil. The EDTA: Pb^{2+}
42 mole ratios for the samples at contamination level of 1000, 300 and 50 mg/kg were
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10, 35 and 207 in this study and did not increase the EDTA extractability, which coincides with the findings of Kim et al. (2003) [24] at high EDTA:Pb²⁺ mole ratios (10 - 100). This is most likely due to the excessive addition of EDTA: all Pb²⁺ bound weaker than chelation to the soils had been extracted while the residual Pb²⁺ which was stronger bound than chelation cannot be extracted even when EDTA was excessive.

The EDTA extraction results indicate that although the release potential of Pb²⁺ under simulated acidic rain was low, the potential bioavailability of Pb²⁺ was high and the effect of biochar treatment on this was insignificant.

3.3 Sequential extraction results

3.3.1 Recovery

The total recovery from sequential extraction tests can be obtained by dividing the total extracted Pb²⁺ in sequential extraction by the totally designated amount of Pb²⁺ in the soil and is shown and compared with that from EDTA extraction in Table S3. The total recovery from sequential extraction tests was within 61.50 - 89.30% and decreased with the increase of contamination level. No significant trend between biochar addition and the recovery was found. The recovery from sequential extraction was lower than that from EDTA extraction (76.92 - 97.28%) for most samples. Few studies have been carried out using sequential extraction tests to investigate the speciation of heavy metals in kaolin [25]. It is difficult to find the recovery of Pb²⁺ in kaolin in sequential extraction from literatures and make a relevant comparison with that in this study. The most similar one probably comes from Reddy et al., (2001) [26]. They used acid digestion method to determine the total concentrations of Chromium (Cr³⁺ and Cr⁶⁺), Nickel (Ni²⁺) and Cadmium (Cd²⁺)

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in an artificially contaminated kaolin. The recovery of the heavy metals were within ~ 78 - 113%. The recovery of Cd^{2+} and Ni^{2+} from one of the two samples were ~ 78% and ~ 88% respectively, which were comparable to the recovery of Pb^{2+} in this study.

3.3.2 Speciation of Pb^{2+} in soils

The speciation of Pb^{2+} in soils is shown in Table S4 and Fig. 4. Pb^{2+} was mainly bound to the exchangeable fraction (36.12 - 42.93%), $\text{CO}_3^{2-}/\text{PO}_4^{2-}$ (19.82-25.70%) and Fe/Mn oxides (21.63 - 26.71%) in soils at the contamination level of 50 mg/kg. At contamination levels of 300 mg/kg and 1000 mg/kg, the exchangeable fraction (64.05 - 76.26%) dominated the existence of Pb^{2+} in soils whereas the fractions bound to $\text{CO}_3^{2-}/\text{PO}_4^{2-}$ and Fe/Mn oxides decreased (to 15.00-19.53% and 5.97 - 12.59% respectively) compared with those at 50 mg/kg. The fraction bound to organics and the residual fraction were low (5.11 - 6.70% and 6.93 - 9.85% respectively) at a contamination level of 50 mg/kg while these fractions were negligible at contamination levels of 300 mg/kg and 1000 mg/kg ($\leq 2.44\%$). The biochar treatment did not have a significant influence on Pb^{2+} speciation in soil over the 28 day periods. It is difficult to find studies using biochar to remediate contaminated kaolin and make a relevant comparison. One similar study comes from Houben and Sonnet. (2015) who applied 5% miscanthus straw biochar to a contaminated soil (texture not shown) and used the same sequential extraction method to analyse Pb^{2+} speciation in the soil [27]. Only the cation exchangeable fraction was slightly reduced while the other four factions showed no significant changes 56 days after biochar treatment, although the soil pH was slightly increased from 5.66 to approximately 6.7 [27].

1 The solubility and bioavailability of heavy metals decrease with each step
2 sequential extraction and represent an increased binding strength with each step
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4 sequence [28,29]. Fractions from steps 2 to 5 account for more than 60% of the total
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6 Pb^{2+} at initial concentrations of 50 mg/kg. At higher contamination levels (300 and
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8 1000 mg/kg), the relatively tightly bound fractions (steps 2 - 5) approach saturation
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10 and therefore the weakly bound fraction (step 1: cation exchange) increases and
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12 dominates the overall fraction (64.05 - 76.26%), in part due to the high cation
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14 exchange capacity of kaolin itself. The high proportions in fraction 1 represented a
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16 high readily available lead to the environment [25].
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22 3.4 Biochar impact on the mobility and speciation of Pb^{2+} 23

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25 The kaolin itself immobilises Pb^{2+} well and the experiments in this study provide no
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27 evidence that biochar affects its speciation. Similarly, biochar did not have a
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29 significant impact on Pb^{2+} leachability in carbonic acid leaching and EDTA extraction
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31 tests. This could be caused by several reasons: (1) the addition of biochar was not
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33 sufficient to have significant influence; (2) the incubation period was too short and
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35 immobilisation by biochar had not fully developed; or (3) competitive adsorption: the
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37 adsorption capacity of kaolin itself was comparable to or higher than that of biochar.
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43 The 1 g samples of kaolin contaminated at 50 mg/kg, 300 mg/kg and 1000 mg/kg will
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45 contain 0.05 mg, 0.3 mg and 1 mg of Pb^{2+} respectively. The maximum adsorption
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47 capacity of Salisbury biochar (1% in the soil) towards Pb^{2+} , calculated based on
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49 Shen et al. (2015) [5], was 0.30 mg and 0.48 mg for 2 mm and 0.15 mm samples
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51 respectively. Therefore, although 300 mg/kg and 1000 mg/kg contamination levels
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53 were comparable to or in excess of the adsorption capacities of biochar, a 1%
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55 addition of biochar is theoretically capable of fully treating 1 g of soil contaminated at
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1 50 mg/kg Pb²⁺. However the impact of biochar on the mobility and speciation of Pb²⁺
2 at a contamination level of 50 mg/kg was insignificant, indicating reason 1 is unlikely
3 to be the most significant factor.
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7 Rees et al. (2014) applied biochar (originated from 80% coniferous and 20%
8 hardwood) to two soils (Soil A: 33% sand, 47% silt, 20% clay; soil B: 24% sand, 60%
9 silt, 16% clay) contaminated with 1120 mg/kg and 1080 mg/kg of Pb²⁺ respectively,
10 and observed that the extractabilities of Pb²⁺ in Ca(NO₃)₂ were reduced by ~ 70%
11 and ~ 10% respectively one week after biochar treatment [30]. Further, Uchimiya et
12 al. (2012) applied several biochars to a slightly acidic soil (pH 6.27) containing 14847
13 mg/kg of Pb²⁺ and observed that the soluble Pb²⁺ was significantly reduced one
14 week after biochar treatment [31]. These findings suggest that insufficient contact
15 time (reason 2) may not be a significant factor in the low impact of biochar. However,
16 the soil used in this study is different from the soils Rees et al. (2014) and Uchimiya
17 et al. (2012) used, therefore the long-term influence of biochar on immobilisation of
18 heavy metals in kaolin is still suggested to investigate to form a comparison with the
19 short-term findings in this study.
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40 In order to test reason 3, the equilibrium isotherm for Pb²⁺ adsorption onto kaolin
41 was determined and the results are shown in Fig. S1. Kaolin exhibited high
42 adsorption of Pb²⁺ at the initial adsorbate concentration of 0.1 - 5 mM (0.1 g kaolin
43 in 20 mL solution). Linear Langmuir and Freundlich models were adopted to fit the
44 data (Table S5). The poor regression for the Linear Langmuir model (R² = 0.64) and
45 good regression for the Linear Freundlich model (R² = 0.96) suggest
46 heterogeneously chemical adsorption dominates kaolin adsorption of Pb²⁺ rather
47 than monolayer adsorption (Table S5). This is in line with the finding from the
48 sequential extraction tests, which indicate that Pb²⁺ was bound to biochar through 5
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1 different fractions. The high sorption of lead by the kaolin, together with the low
2 carbonic acid leachability, suggests kaolin itself was able to immobilise Pb^{2+} in the
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4 soils in this study.
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8 In a previous study, oak wood biochar was found to transfer the readily bioavailable
9 fraction (exchangeable: step 1 in this study) of Pb^{2+} to more stable residual fraction
10 (step 5) in a sandy loam soil [32]. Likewise, wine lees biochar was found to
11 significantly increase the residual fraction (step 5) while decrease the reducible (step
12 2) and oxidizable (step 4) Pb^{2+} in a paddy soil [33]. In these two studies, biochar may
13 either have adsorbed competitively against the soil and transferred the weakly bound
14 Pb^{2+} to stable fractions by itself; or enhanced the bonds of Pb^{2+} into soil lattice
15 through increased soil pH and other mechanisms [28,29].
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18 The speciation of Pb^{2+} in salisbury biochar was investigated and shown in Table 3.
19 The Pb^{2+} was adsorbed to biochar mainly through bond to carbonates/phosphates,
20 which is an acidic soluble fraction [25]. Although it represents a slightly tighter bond
21 than cation exchange, this bond is highly pH dependent [25] and it is difficult to win
22 the competitive adsorption of Pb^{2+} against kaolin at such low soil pH values (4.54-
23 4.92). The X-ray absorption fine structure (XAFS) analysis in [32] observed that 62.7%
24 Pb^{2+} was adsorbed on kaolinite 175 days after amending the contaminated soil with 5%
25 oak wood biochar, indicating the affinity of kaolinite for Pb^{2+} . The biochar itself failed
26 to adsorb Pb^{2+} in a more stable form in this study and its influence on the soil pH
27 was insignificant or small. Therefore, no significant impact of biochar on the
28 speciation of Pb^{2+} in kaolin was observed.
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31 Hence, the insignificant influence of biochar on the mobility and speciation of Pb^{2+} in
32 kaolin was most likely due to the fact that kaolin itself has an adsorption capacity
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1 comparable to that of the biochar and biochar failed to competitively adsorb Pb^{2+}
2 against kaolin or alter its speciation by enhancing soil pH values.
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5 It is of note that kaolin is mainly made of kaolinite which is a variable charge mineral
6 with a relatively low CEC (which is confirmed in Table 1) due to its 1:1 phyllosilicate
7 layer structure [9,34]. Soils dominated by clay minerals with 2:1 phyllosilicate layer
8 structure (illite, smectite, vermiculite, palygorskite etc.) and permanently charged
9 commonly have much higher CECs [9,34]. Since Salisbury biochar failed to
10 competitively adsorb Pb^{2+} against kaolin, it could be expected that this biochar may
11 not be able to affect the mobility or speciation of Pb^{2+} in soils dominated by 2:1 clay
12 minerals.
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25 4 Conclusions

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28 In this study, it was found that biochar did not have a significant effect on the
29 mobility or speciation of Pb^{2+} in a kaolin, suggesting that the performance of biochar
30 in immobilising heavy metals in soils is related to the soil types and that biochar may
31 not perform well on contaminated soils with high clay content. The reasons may be
32 due to the high adsorption capacity (mainly CEC) of Pb^{2+} on kaolin itself and the
33 failure of biochar to competitively adsorb Pb^{2+} against kaolin. As other clay minerals
34 such as illite, smectite, vermiculite, palygorskite etc. usually have higher CECs than
35 kaolinite which forms the basis of kaolin, biochar may also fail to affect the mobility or
36 speciation of heavy metals in soils rich in these clay minerals. This paper suggests
37 the inefficiency of biochar treatment on heavy-metal contaminated clay-rich soils.
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39 According to the suggestions in this study, field applications of biochar in heavy-
40 metal associated soil remediation need to take the soil type into account, and a
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1 laboratory treatability study with respect to the soil type is crucial when large-scale
2 biochar applications are evaluated.
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5 It is of note that this was a short-term study carried out under laboratory conditions.
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7 Treatments on clay soils under field conditions and in the long term are needed in
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9 order to make a comparison with the findings in this study.
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13 Although this study found that the release potential of Pb^{2+} in kaolin under simulated
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15 acidic rain water was low, it existed primarily as the exchangeable fraction and the
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17 EDTA extractability was high. This suggests that the readily and potentially
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19 bioavailability of Pb^{2+} in kaolin was high. As biochar was found to reduce the
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21 bioavailable fractions and enhance the non-bioavailable fractions of metals in soils
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23 [25,28], it may still have the potential to be applied to reduce the bioavailability of
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25 metals in clay soils. Therefore, biochar derived from other feedstocks using different
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27 production methods (slow and fast pyrolysis) are suggested to apply on clay soils
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29 and investigate their performances in immobilising heavy metals.
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36 References

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38
39 [1] F. Ronsse, S. van Hecke, D. Dickinson, W. Prins, Production and
40
41 characterization of slow pyrolysis biochar: influence of feedstock type and
42
43 pyrolysis conditions, *GCB Bioenergy*. 5 (2013) 104–115.
44
45 doi:10.1111/gcbb.12018.
46
47
48 [2] J. Lehmann, Bio-energy in the black, *Front. Ecol. Environ*. 5 (2007) 381–387.
49
50 doi:10.1890/060133.
51
52
53 [3] X. Cao, L. Ma, Y. Liang, B. Gao, W. Harris, Simultaneous immobilization of
54
55 lead and atrazine in contaminated soils using dairy-manure biochar., *Environ.*
56
57 *Sci. Technol*. 45 (2011) 4884–9. doi:10.1021/es103752u.
58
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58
59
60
61
62
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65
- [4] L. Beesley, E. Moreno-Jiménez, J.L. Gomez-Eyles, E. Harris, B. Robinson, T. Sizmur, A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils., *Environ. Pollut.* 159 (2011) 3269–3282. doi:10.1016/j.envpol.2011.07.023.
- [5] Z. Shen, F. Jin, F. Wang, O. McMillan, A. Al-Tabbaa, Sorption of lead by Salisbury biochar produced from British broadleaf hardwood, *Bioresour. Technol.* 193 (2015) 553–556. doi:10.1016/j.biortech.2015.06.111.
- [6] Z. Shen, A.M. Som, F. Wang, F. Jin, O. McMillan, A. Al-Tabbaa, Long-term impact of biochar on the immobilisation of nickel (II) and zinc (II) and the revegetation of a contaminated site, *Sci. Total Environ.* 542 (2016) 771–776. doi:10.1016/j.scitotenv.2015.10.057.
- [7] J.K. Mitchell, K. Soga, *Fundamentals of soil behavior*, Wiley New York, 1976.
- [8] B.J. Alloway, *Heavy metals in soils*, Springer Science & Business Media, 1995.
- [9] F. Bergaya, G. Lagaly, *Handbook of clay science*, Newnes, 2013.
- [10] T. Nangay, B. Singh, Influence of biochar application to soil on the availability of As , Cd , Cu , Pb , and Zn to maize (*Zea mays* L .), *Australian Journal of Soil Research.* 48 (2010) 638–647.
- [11] L. Beesley, M. Marmiroli, The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar., *Environ. Pollut.* 159 (2011) 474–480. doi:10.1016/j.envpol.2010.10.016.
- [12] W. Hartley, N.M. Dickinson, P. Riby, N.W. Lepp, Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus.*, *Environ. Pollut.* 157 (2009) 2654–2662. doi:10.1016/j.envpol.2009.05.011.
- [13] M. Kargar, O.G. Clark, W.H. Hendershot, P. Jutras, S.O. Prasher,

1 Immobilization of Trace Metals in Contaminated Urban Soil Amended with
2 Compost and Biochar, *Water, Air, Soil Pollut.* 226 (2015). doi:10.1007/s11270-
3 015-2450-2.
4
5

- 6
7 [14] D.H. Moon, J.-W. Park, Y.-Y. Chang, Y.S. Ok, S.S. Lee, M. Ahmad, et al.,
8 Immobilization of lead in contaminated firing range soil using biochar., *Environ.*
9 *Sci. Pollut. Res. Int.* 20 (2013) 8464–8471. doi:10.1007/s11356-013-1964-7.
10
11 [15] Y. Yang, Z. Wei, X. Zhang, X. Chen, D. Yue, Q. Yin, et al., Biochar from
12 *Alternanthera philoxeroides* could remove Pb(II) efficiently, *Bioresour. Technol.*
13 171 (2014) 227–232. doi:10.1016/j.biortech.2014.08.015.
14
15 [16] G. Gillman, E. Sumpter, Modification to the compulsive exchange method for
16 measuring exchange characteristics of soils, *Aust. J. Soil Res.* 24 (1986) 61–
17 66. doi:10.1071/SR9860061.
18
19 [17] F. Wang, H. Wang, A. Al-Tabbaa, Leachability and heavy metal speciation of
20 17-year old stabilised/solidified contaminated site soils., *J. Hazard. Mater.* 278
21 (2014) 144–151. doi:10.1016/j.jhazmat.2014.05.102.
22
23 [18] N. Bolan, A. Kunhikrishnan, R. Thangarajan, J. Kumpiene, J. Park, T. Makino,
24 et al., Remediation of heavy metal(loid)s contaminated soils - To mobilize or to
25 immobilize?, *J. Hazard. Mater.* 266 (2014) 141–166.
26 doi:10.1016/j.jhazmat.2013.12.018.
27
28 [19] X. Li, B.J. Coles, M.H. Ramsey, I. Thornton, *CHEMICAL GEOLOGY*
29 Sequential extraction of soils for multielement analysis by ICP-AES, 124 (1995)
30 109–123.
31
32 [20] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for
33 the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.
34 doi:10.1021/ac50043a017.
35
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56
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65
- [21] A. P. Puga, C. A. Abreu, L.C. A. Melo, L. Beesley, Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium, *J. Environ. Manage.* 159 (2015) 86–93.
doi:10.1016/j.jenvman.2015.05.036.
- [22] D. Houben, L. Evrard, P. Sonnet, Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar., *Chemosphere.* 92 (2013) 1450–1457.
doi:10.1016/j.chemosphere.2013.03.055.
- [23] D. Mohan, H. Kumar, A. Sarswat, M. Alexandre-Franco, C.U. Pittman, Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars, *Chem. Eng. J.* 236 (2014) 513–528.
doi:10.1016/j.cej.2013.09.057.
- [24] C. Kim, Y. Lee, S.K. Ong, Factors affecting EDTA extraction of lead from lead-contaminated soils, *Chemosphere.* 51 (2003) 845–853. doi:10.1016/S0045-6535(03)00155-3.
- [25] a V Filgueiras, I. Lavilla, C. Bendicho, Chemical sequential extraction for metal partitioning in environmental solid samples., *J. Environ. Monit.* 4 (2002) 823–857. doi:10.1039/b207574c.
- [26] K.R. Reddy, C.Y. Xu, S. Chinthamreddy, Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis., *J. Hazard. Mater.* 84 (2001) 279–296.
- [27] D. Houben, P. Sonnet, Impact of biochar and root-induced changes on metal dynamics in the rhizosphere of *Agrostis capillaris* and *Lupinus albus*, *Chemosphere.* 139 (2015) 644–651. doi:10.1016/j.chemosphere.2014.12.036.
- [28] N. Basta, R. Gradwohl, Estimation of Cd, Pb, and Zn bioavailability in smelter-

contaminated soils by a sequential extraction procedure, *J. Soil Contam.* 9
(2000) 149–164. doi:10.1080/10588330008984181.

- [29] J. Jiang, R.K. Xu, T.Y. Jiang, Z. Li, Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol, *J. Hazard. Mater.* 229-230 (2012) 145–150. doi:10.1016/j.jhazmat.2012.05.086.
- [30] F. Rees, M.O. Simonnot, J.L. Morel, Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase, *Eur. J. Soil Sci.* 65 (2014) 149–161. doi:10.1111/ejss.12107.
- [31] M. Uchimiya, D.I. Bannon, L.H. Wartelle, Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil, *J. Agric. Food Chem.* 60 (2012) 1798–1809.
- [32] M. Ahmad, S.S. Lee, J.E. Lim, S.E. Lee, J.S. Cho, D.H. Moon, et al., Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions, *Chemosphere.* 95 (2014) 433–441. doi:10.1016/j.chemosphere.2013.09.077.
- [33] Q. Zhu, J. Wu, L. Wang, G. Yang, X. Zhang, Effect of Biochar on Heavy Metal Speciation of Paddy Soil, *Water, Air, Soil Pollut.* 226 (2015) 429. doi:10.1007/s11270-015-2680-3.
- [34] G.J. Churchman, Is the geological concept of clay minerals appropriate for soil science? A literature-based and philosophical analysis, *Phys. Chem. Earth.* 35 (2010) 927–940. doi:10.1016/j.pce.2010.05.009.

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Table 1 Physicochemical properties of Salisbury biochar.

	2 mm	0.15 mm
BET surface area (m ² /g)	2.46 ± 0.03 ^a	5.30 ± 0.06
Cation exchange capacity (cmol/kg)	5.62 ± 0.15	7.20 ± 0.17
pH	6.78 ± 0.01	6.96 ± 0.01
C (%)	79.91 ± 2.33	
N (%)	0.73 ± 0.02	
Pb (%)	0.01 ± 0.0004	

Adsorption capacity of Pb (mg/g)	30.04	47.66
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("2 mm" and "0.15 mm" represent the biochar samples sieved to ≤ 2 mm and 0.15 mm respectively; a - mean \pm standard, n=3)

Table 2 Physicochemical properties of kaolin.

Properties	Value
pH	4.78 \pm 0.02 ^a
CEC (cmol/kg)	5.49 \pm 0.03
BET surface area (m ² /g)	8
Specific gravity	2.6
Water soluble salt content (%)	0.15
SiO ₂ (%)	50
Al ₂ O ₃ (%)	35

Liquid limit (%)	47
Plastic limit (%)	31
Sand (0.05-2 mm) (%)	0
Silt (0.002-0.05 mm) (%)	65
Clay (0-0.002 mm) (%)	35

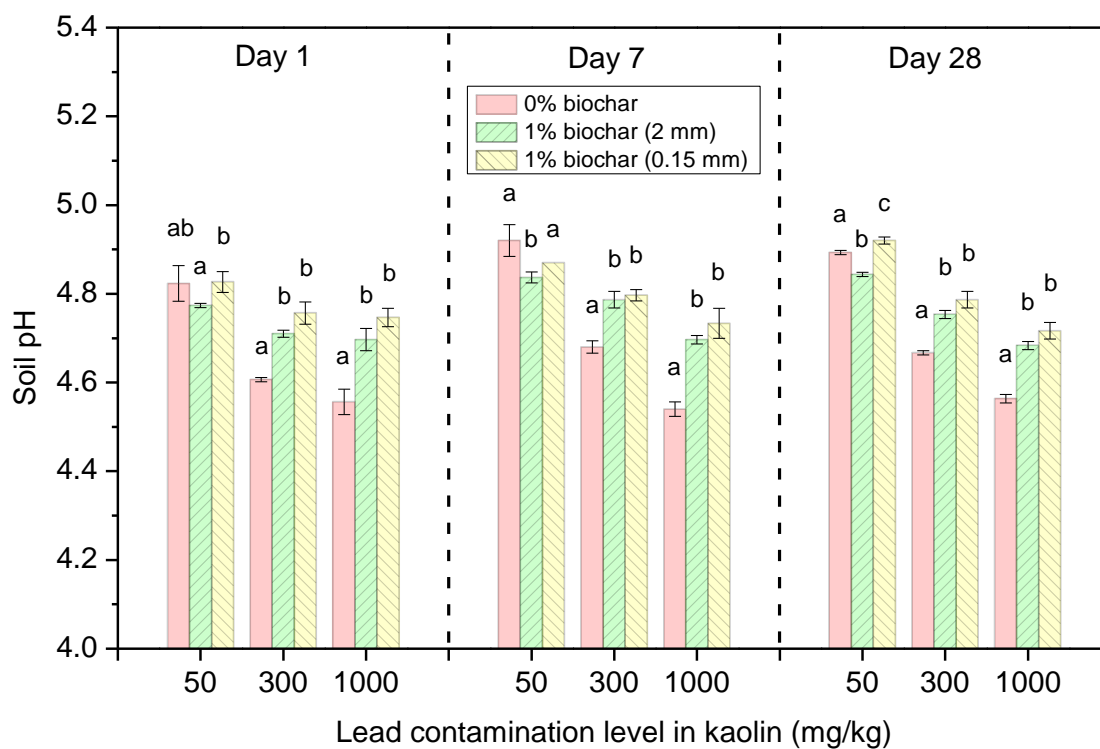
(a - mean \pm standard, n=3)

Table 3 Speciation of Pb²⁺ in biochar (0.1 g biochar sample (0.15 mm) after reaching adsorption equilibrium in 20 mL of 5 mM Pb²⁺ solution).

	Pb ²⁺ amount in biochar (mg)	%
Step 1	0.18 \pm 0.01	4.29
Step 2	3.53 \pm 0.47	85.31
Step 3	0.40 \pm 0.11	9.66
Step 4	0.02 \pm 0.007	0.41
Step 5	0.01 \pm 0.0002	0.33

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Fig. 1. Soil pH values. The different lower case letters indicate a significant difference between the treatments in each experiment with a specific contamination level at a specific time ($P < 0.05$).



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Fig. 2. Pb^{2+} concentrations in (a) carbonic acid leachate and (b) EDTA extraction.

Data not shown indicates below limit of detection (0.010 mg/L). The different lower case letters indicate a significant difference between the treatments in each experiment with a specific contamination level at a specific time ($P < 0.05$). N.N.D = not normally distributed. N.H.V = not homogeneity of variance.

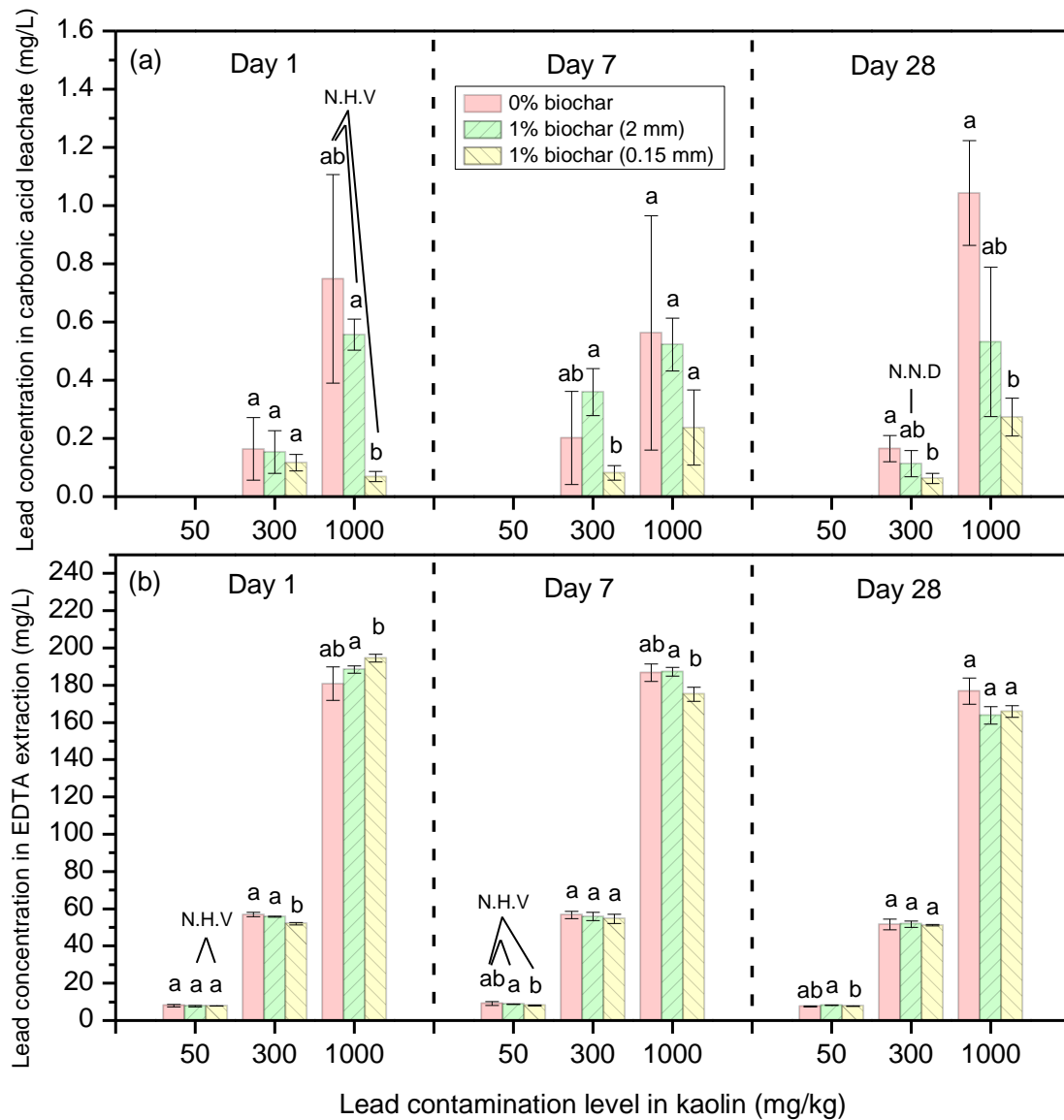


Fig. 3. Pb^{2+} leachabilities in carbonic acid leaching test (a) and EDTA extraction test (b). The different lower case letters indicate a significant difference between the treatments in each experiment with a specific contamination level at a specific time ($P < 0.05$). N.N.D = not normally distributed. N.H.V = not homogeneity of variance.

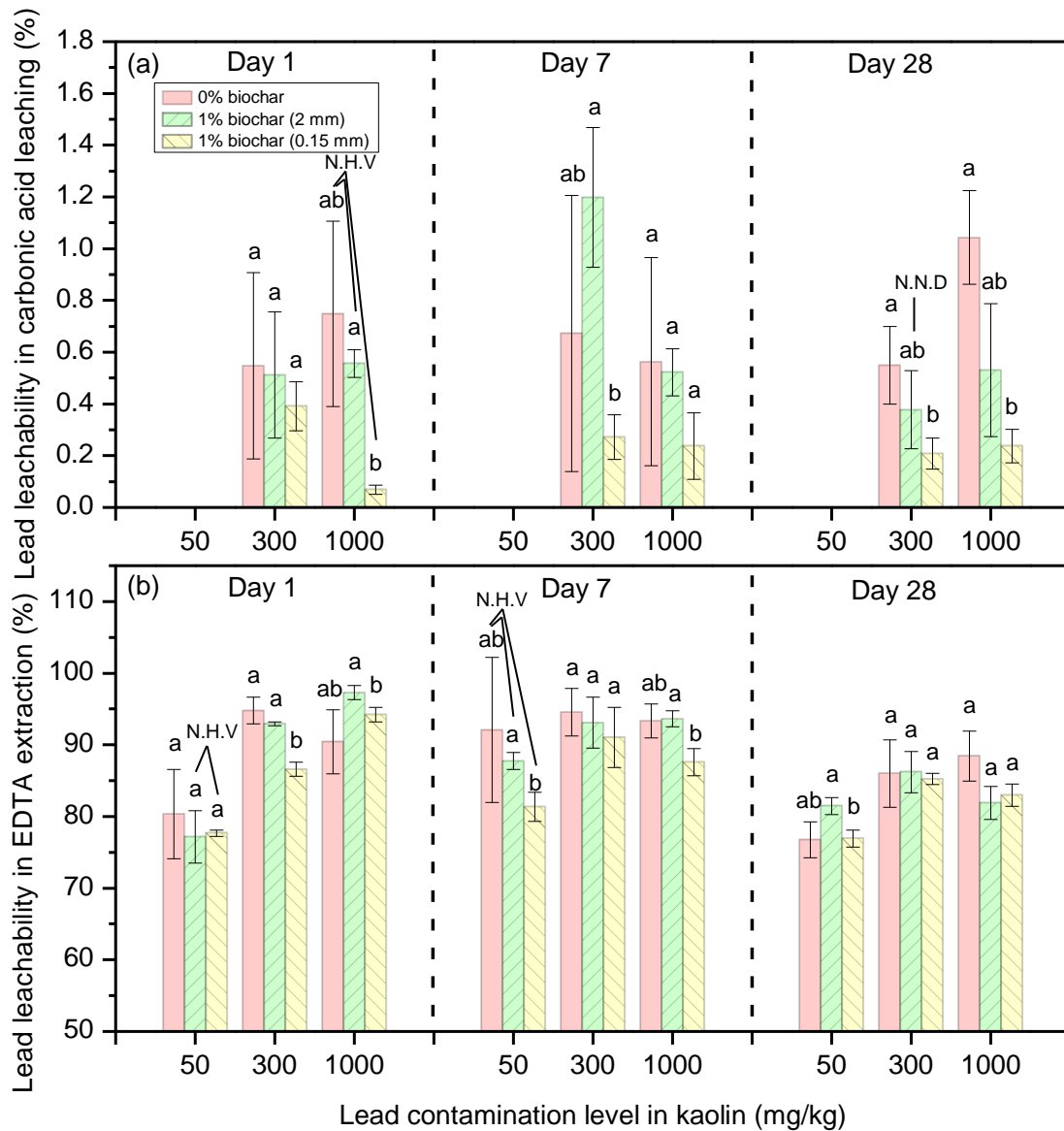


Fig. 4. Sequential extraction results. The horizontal axis indicates the contamination level (mg/kg) + the dosage of biochar treatment (0% or 1% in w/w).

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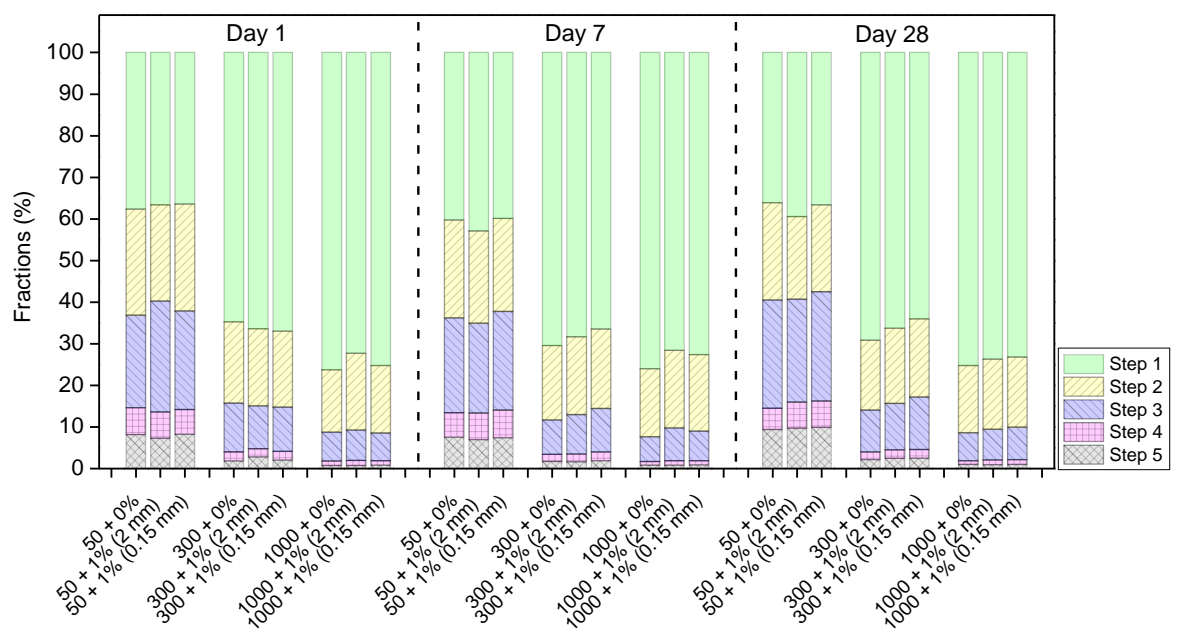


Table S1 Soil constituents in existing biochar research associated with heavy-metal contaminated land

Sand (%)	Silt (%)	Clay (%)	Reference
87.7	4.8	7.5	(Balwant and Singh 2010)
83	16	1	(Beesley and Dickinson 2011)
43	48	8	(Beesley and Marmiroli 2011)
46		17	(Bian et al. 2013)
42		18	
49		20	
52		16	
59		10	
54	39	7	
92		8	(Cao et al. 2011)
88		12	
83	6	12	(Hartley et al. 2009)
83.4	9.1	7.5	
48.3	22.3	29.3	
64	24	12	(Houben et al. 2013)
78	10	12	(Kargar et al. 2015)
	90	9.8	(Liang et al. 2014)
85	12	3	(Moon et al. 2013)
34	24	43	(Puga et al. 2015)
33	47	20	(Rees et al. 2014)
24	60	16	
42	38	20	(Riedel et al. 2015)

Table S2 Experimental design

Specimens	Biochar dosage (w/w)		Biochar particle size (mm)		Lead contamination level (mg/kg)			Incubation time (day)		
	0%	1%	< 2	< 0.15	50	300	1000	1	7	28
S1-3	x				x			x		
S4-6	x					x		x		
S7-9	x						x	x		
S10-12		x	x		x			x		
S13-15		x	x			x		x		
S16-18		x	x				x	x		
S19-21		x		x	x			x		
S22-24		x		x		x		x		
S25-27		x		x			x	x		
S28-30	x				x				x	
S31-33	x					x			x	
S34-36	x						x		x	
S37-39		x	x		x				x	
S40-42		x	x			x			x	
S43-45		x	x				x		x	
S46-48		x		x	x				x	
S49-51		x		x		x			x	
S52-54		x		x			x		x	
S55-57	x				x					x
S58-60	x					x				x

S61-63	x						x			x
S64-66		x	x		x					x
S67-69		x	x			x				x
S70-72		x	x				x			x
S73-75		x		x	x					x
S76-78		x		x		x				x
S79-81		x		x			x			x

Table S3 Recovery of sequential extraction and EDTA extraction

Soil sample (Contamination level + biochar dosage)	Day 1 (%)		Day 7 (%)		Day 28 (%)	
	Sequential extraction	EDTA extraction	Sequential extraction	EDTA extraction	Sequential extraction	EDTA extraction
50 + 0%	87.95 ± 9.19	80.33 ± 6.25	88.18 ± 6.48	92.08 ± 10.10	89.30 ± 5.18	76.74 ± 2.53
50 + 1% (2 mm)	77.13 ± 0.90	77.17 ± 3.65	72.75 ± 0.70	87.74 ± 1.18	76.96 ± 0.16	81.46 ± 1.20
50 + 1% (0.15 mm)	82.63 ± 6.02	77.67 ± 0.43	76.56 ± 3.17	81.34 ± 2.01	78.20 ± 5.66	76.92 ± 1.20
300 + 0%	69.31 ± 0.85	94.78 ± 1.85	70.14 ± 4.16	94.54 ± 3.30	74.45 ± 6.35	86.02 ± 4.70
300 + 1% (2 mm)	69.75 ± 4.07	92.92 ± 0.27	72.13 ± 4.58	93.08 ± 3.57	70.50 ± 4.52	86.22 ± 2.88
300 + 1% (0.15 mm)	74.89 ± 1.14	86.59 ± 0.96	71.92 ± 1.67	91.03 ± 4.22	72.21 ± 1.68	85.24 ± 0.76
1000 + 0%	64.29 ± 0.64	90.42 ± 4.48	66.62 ± 3.32	93.35 ± 2.38	68.32 ± 2.04	88.43 ± 3.50
1000 + 1% (2 mm)	63.72 ± 2.11	94.22 ± 1.00	61.50 ± 2.33	93.62 ± 1.12	67.41 ± 2.22	81.90 ± 2.31
1000 + 1% (0.15 mm)	71.53 ± 5.78	97.28 ± 1.02	63.66 ± 1.28	87.57 ± 1.88	66.97 ± 0.52	82.98 ± 1.57

Table S4 Sequential extraction results.

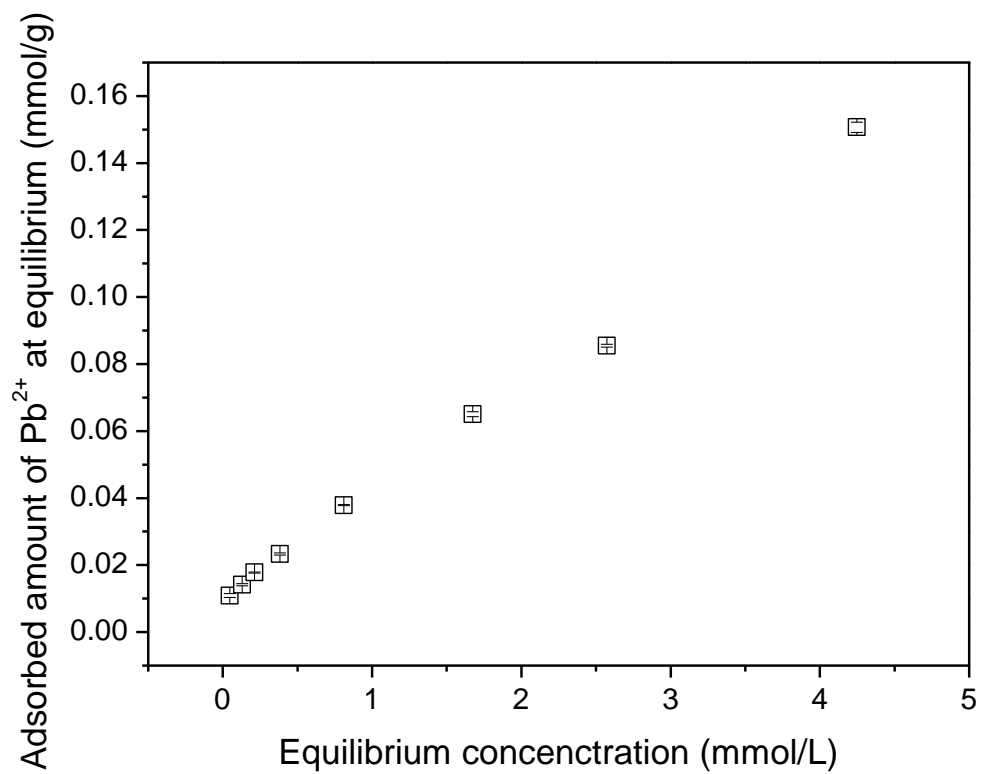
Soil sample (Contamination level + biochar dosage)	Step	Day 1		Day 7		Day 28	
		mg/kg	%	mg/kg	%	mg/kg	%
50 + 0%	1	17.56 ± 0.05	37.66	17.75 ± 1.68	40.26	16.13 ± 0.52	36.12
	2	11.20 ± 1.82	25.47	10.37 ± 0.85	23.53	10.45 ± 1.49	23.41
	3	9.80 ± 1.10	22.28	10.07 ± 0.39	22.83	11.60 ± 0.82	25.98
	4	2.84 ± 0.35	6.47	2.59 ± 0.11	5.88	2.28 ± 0.31	5.11
	5	3.57 ± 0.13	8.13	3.31 ± 0.35	7.50	4.19 ± 0.11	9.38
50 + 1% (2 mm)	1	14.12 ± 0.01	36.61	15.61 ± 0.06	42.93	15.18 ± 0.16	39.46
	2	8.92 ± 0.77	23.12	8.05 ± 0.04	22.14	7.63 ± 0.04	19.82
	3	10.30 ± 0.79	26.71	7.87 ± 0.04	21.63	9.53 ± 0.19	24.77
	4	2.44 ± 0.09	6.34	2.32 ± 0.14	6.38	2.42 ± 0.14	6.28
	5	2.79 ± 0.28	7.23	2.52 ± 0.15	6.93	3.72 ± 0.11	9.67
50 + 1% (0.15 mm)	1	15.05 ± 0.05	36.44	15.28 ± 0.72	39.90	14.32 ± 0.18	36.61
	2	10.62 ± 1.47	25.70	8.56 ± 0.52	22.36	8.19 ± 0.16	20.94
	3	9.80 ± 0.50	23.72	9.07 ± 0.14	23.69	10.27 ± 0.25	26.26
	4	2.46 ± 0.13	5.95	2.57 ± 0.16	6.70	2.48 ± 0.07	6.34
	5	3.39 ± 0.18	8.20	2.81 ± 0.15	7.35	3.85 ± 0.25	9.85
300 + 0%	1	134.61 ± 0.04	64.74	149.23 ± 8.99	70.45	153.76 ± 14.57	69.15
	2	40.60 ± 1.67	19.53	37.92 ± 2.58	17.90	37.44 ± 3.49	16.84
	3	24.47 ± 0.57	11.77	17.53 ± 0.17	8.28	22.33 ± 0.81	10.04
	4	4.56 ± 0.40	2.19	3.66 ± 0.21	1.73	4.06 ± 0.28	1.83
	5	3.68 ± 0.21	1.77	3.49 ± 0.02	1.65	4.76 ± 0.03	2.14
300 + 1% (2 mm)	1	138.93 ± 0.79	66.39	147.89 ± 11.13	68.35	140.19 ± 10.07	66.29
	2	38.82 ± 0.72	18.55	40.53 ± 1.94	18.73	38.27 ± 2.02	18.09
	3	21.61 ± 0.56	10.33	20.40 ± 0.17	9.43	23.53 ± 1.27	11.13

	4	4.13 ± 0.26	1.97	4.06 ± 0.41	1.88	4.35 ± 0.31	2.06
	5	5.76 ± 0.34	2.75	3.49 ± 0.28	1.61	5.15 ± 0.10	2.43
300 + 1% (0.15 mm)	1	150.56 ± 0.18	67.02	143.52 ± 3.54	66.52	138.75 ± 4.25	64.05
	2	40.93 ± 1.08	18.22	41.12 ± 0.53	19.06	40.69 ± 0.55	18.79
	3	24.00 ± 1.45	10.68	22.60 ± 0.19	10.47	27.27 ± 0.66	12.59
	4	4.72 ± 0.27	2.10	4.54 ± 0.28	2.11	4.63 ± 0.16	2.14
	5	4.45 ± 0.27	1.98	3.99 ± 0.16	1.85	5.28 ± 0.36	2.44
1000 + 0%	1	490.40 ± 0.06	76.27	506.43 ± 28.03	76.01	514.40 ± 15.45	75.29
	2	96.43 ± 6.01	15.00	109.07 ± 3.96	16.37	110.00 ± 3.33	16.10
	3	44.60 ± 2.83	6.94	39.80 ± 0.23	5.97	46.00 ± 1.72	6.73
	4	6.86 ± 0.43	1.07	5.62 ± 0.15	0.84	6.28 ± 0.61	0.92
	5	4.65 ± 0.59	0.72	5.33 ± 0.13	0.80	6.51 ± 0.19	0.95
1000 + 1% (2 mm)	1	460.62 ± 0.05	72.29	446.88 ± 13.75	71.59	496.93 ± 17.15	73.71
	2	117.89 ± 18.42	18.50	113.07 ± 7.42	18.70	113.89 ± 4.36	16.89
	3	46.53 ± 1.60	7.30	43.67 ± 0.37	7.82	49.60 ± 1.23	7.36
	4	7.53 ± 0.99	1.18	6.29 ± 0.48	1.09	7.79 ± 0.46	1.16
	5	4.60 ± 0.10	0.72	5.13 ± 0.19	0.97	5.93 ± 0.25	0.88
1000 + 1% (0.15 mm)	1	538.27 ± 3.45	75.25	455.68 ± 15.62	72.66	490.40 ± 2.67	73.22
	2	116.16 ± 7.73	16.24	119.07 ± 4.25	18.38	112.67 ± 2.17	16.82
	3	47.60 ± 2.86	6.65	49.80 ± 0.14	7.10	52.73 ± 1.09	7.87
	4	7.95 ± 0.48	1.11	6.96 ± 0.46	1.02	7.72 ± 0.07	1.15
	5	5.35 ± 0.11	0.75	5.05 ± 0.14	0.83	6.23 ± 0.39	0.93

Table S5 Isotherm model parameters

Isotherm models		Parameters	
<p data-bbox="204 472 461 510">Linear Langmuir:</p> $\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{1}{Q_0}\right)C_e$	<p data-bbox="512 472 1032 1025">Q_0 (mmol/g) and b (L/mmol) are the Langmuir constants related to the maximum adsorption capacity and rate of adsorption; q_e (mmol/g) is the adsorbed amount of adsorbate per unit mass of adsorbent at the equilibrium aqueous concentration of C_e (mM).</p>	<p data-bbox="1118 472 1166 510">Q_0</p> <p data-bbox="1078 539 1204 577">(mmol/g)</p>	<p data-bbox="1286 472 1350 510">0.19</p>
		<p data-bbox="1078 618 1204 656">b (mM⁻¹)</p>	<p data-bbox="1286 618 1350 656">0.45</p>
		<p data-bbox="1118 696 1166 734">R^2</p>	<p data-bbox="1286 696 1350 734">0.64</p>
<p data-bbox="204 1066 461 1104">Linear Freundlich:</p> $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	<p data-bbox="512 1066 1032 1249">K_F (mmol/g) and n are Freundlich constants; and q_e and C_e are the same as Linear Langmuir</p>	<p data-bbox="1118 1066 1166 1104">K_F</p> <p data-bbox="1078 1133 1204 1171">(mmol/g)</p>	<p data-bbox="1286 1066 1350 1104">0.05</p>
		<p data-bbox="1118 1211 1166 1249">1/n</p>	<p data-bbox="1286 1211 1350 1249">0.58</p>
		<p data-bbox="1118 1290 1166 1328">R^2</p>	<p data-bbox="1286 1290 1350 1328">0.96</p>

Figure S1. Equilibrium isotherm for Pb^{2+} adsorption onto kaolinite (0.1 g kaolinite in 20 mL solution (0.01 M NaNO_3), initial Pb^{2+} concentration 0.1-5 mM; reaction temperature 20 °C; initial solution pH 5; contact time 24 h).



References

- Balwant TN, Singh BPS (2010) Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (*Zea mays* L.). 638–647.
- Beesley L, Dickinson N (2011) Carbon and trace element fluxes in the pore water of an urban soil following greenwaste compost, woody and biochar amendments, inoculated with the earthworm *Lumbricus terrestris*. *Soil Biol Biochem* 43:188–196. doi: 10.1016/j.soilbio.2010.09.035
- Beesley L, Marmiroli M (2011) The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environ Pollut* 159:474–80. doi: 10.1016/j.envpol.2010.10.016
- Bian R, Chen D, Liu X, et al (2013) Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment. *Ecol Eng* 58:378–383. doi: 10.1016/j.ecoleng.2013.07.031
- Brennan A, Jiménez EM, Puschenreiter M, et al (2014) Effects of biochar amendment on root traits and contaminant availability of maize plants in a copper and arsenic impacted soil. *Plant Soil* 379:351–360. doi: 10.1007/s11104-014-2074-0
- Cao X, Ma L, Liang Y, et al (2011) Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environ Sci Technol* 45:4884–9. doi: 10.1021/es103752u
- Hartley W, Dickinson NM, Riby P, Lepp NW (2009) Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*. *Environ Pollut* 157:2654–62. doi: 10.1016/j.envpol.2009.05.011
- Houben D, Evrard L, Sonnet P (2013) Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. *Chemosphere* 92:1450–7. doi: 10.1016/j.chemosphere.2013.03.055
- Kargar M, Clark OG, Hendershot WH, et al (2015) Immobilization of Trace Metals in Contaminated Urban Soil Amended with Compost and Biochar. *Water, Air, Soil Pollut*. doi: 10.1007/s11270-015-2450-2
- Liang Y, Cao X, Zhao L, Arellano E (2014) Biochar- and phosphate-induced immobilization of heavy metals in contaminated soil and water: implication on simultaneous remediation of contaminated soil and groundwater. *Environ Sci Pollut Res Int* 21:4665–74. doi: 10.1007/s11356-013-2423-1
- Moon DH, Park J-W, Chang Y-Y, et al (2013) Immobilization of lead in contaminated firing range soil using biochar. *Environ Sci Pollut Res Int* 20:8464–71. doi: 10.1007/s11356-013-1964-7

Puga a. P, Abreu C a., Melo LC a., Beesley L (2015) Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. *J Environ Manage* 159:86–93. doi: 10.1016/j.jenvman.2015.05.036

Rees F, Simonnot MO, Morel JL (2014) Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. *Eur J Soil Sci* 65:149–161. doi: 10.1111/ejss.12107

Riedel T, Hennessy P, Iden SC, Koschinsky a. (2015) Leaching of soil-derived major and trace elements in an arable topsoil after the addition of biochar. *Eur J Soil Sci* n/a–n/a. doi: 10.1111/ejss.12256

The immobilisation of biochar on heavy metals in clay soils has been yet or limited investigated compared with sand-based soils. The short-term laboratory incubation study found that biochar failed to affect the mobility or speciation of lead in kaolin. Further chemical analysis suggests it was very likely due to that the biochar failed to competitively adsorb the lead against kaolin. The findings in this study offer a new view towards the biochar potential in soil remediation.

Abstract: Salisbury biochar (produced from British broadleaf hardwood) with two different particle sizes (≤ 2 mm and ≤ 0.15 mm) was applied on a kaolin with three different lead (Pb^{2+}) contamination levels (50 mg/kg, 300 mg/kg and 1000 mg/kg) at the dosage of 1% in w/w. The short-term impact of biochar on the mobility and speciation of Pb^{2+} in the kaolin was investigated using attenuation periods of 1, 7 and 28 days. The leachability and extractability of Pb^{2+} in carbonic acid leaching and EDTA extraction tests as well as the speciation of Pb^{2+} in soils were not significantly affected by biochar treatment during all periods. The insignificant effects of biochar on Pb^{2+} immobilisation were most likely attributed to the high adsorption capacity of kaolin towards Pb^{2+} and biochar failed to competitively adsorb Pb^{2+} against kaolin. Kaolin immobilised Pb^{2+} primarily through cation exchange, which represents the readily bioavailable fractions of Pb^{2+} in soils and may still pose environmental risks. This paper suggests the inefficiency of biochar treatment on heavy-metal contaminated clay-rich soils. Therefore a laboratory treatability study with respect to the soil type may be crucial when large-scale biochar applications in heavy-metal associated soil remediation are evaluated.