Solubility of Lead and Copper in Biochar-Amended Small Arms Range Soils: Influence of Soil Organic Carbon and pH

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Ⓢ *Supporting Information*

ABSTRACT: Biochar is often considered a strong heavy metal stabilizing agent. However, biochar in some cases had no effects on, or increased the soluble concentrations of, heavy metals in soil. The objective of this study was to determine the factors causing some biochars to stabilize and others to dissolve heavy metals in soil. Seven small arms range soils with known total organic carbon (TOC), cation exchange capacity, pH, and total Pb and Cu contents were first screened for soluble Pb and Cu concentrations. Over 2 weeks successive equilibrations using weak acid (pH 4.5 sulfuric acid) and acetate buffer (0.1 M at pH 4.9), Alaska soil containing disproportionately high (31.6%) TOC had nearly 100% residual (insoluble) Pb and Cu. This soil was then compared with sandy soils from Maryland containing significantly lower (0.5−2.0%) TOC in the presence of 10 wt % (i) plant biochar activated to increase the surface-bound carboxyl and phosphate ligands (PS450A), (ii) manure biochar enriched with soluble P (BL700), and (iii) unactivated plant biochars produced at 350 °C (CH350) and 700 °C (CH500) and by flash carbonization (corn). In weak acid, the pH was set by soil and biochar, and the biochars increasingly stabilized Pb with repeated extractions. In pH 4.9 acetate buffer, PS450A and BL700 stabilized Pb, and only PS450A stabilized Cu. Surface ligands of PS450A likely complexed and stabilized Pb and Cu even under acidic pH in the presence of competing acetate ligand. Oppositely, unactivated plant biochars (CH350, CH500, and corn) mobilized Pb and Cu in sandy soils; the putative mechanism is the formation of soluble complexes with biochar-borne dissolved organic carbon. In summary, unactivated plant biochars can inadvertently increase dissolved Pb and Cu concentrations of sandy, low TOC soils when used to stabilize other contaminants.

KEYWORDS: surface complexation, remediation, agricultural waste, thermochemical conversion, biomass

■ INTRODUCTION

Biochar is often considered a strong heavy metal stabilizing agent. However, biochar in some cases had no effects on, or increased the soluble concentrations of, heavy metals in soil. For example, during a 60 day field exposure pot trial study, a heavy application (50 vol %) of a hardwood biochar to contaminated soil increased aqueous Cu and As concentrations by >30-fold, along with an increase in soil pH and dissolved organic carbon (DOC).[1] At the same time, the biochar decreased the aqueous concentrations of Zn, Cd, and polycyclic aromatic hydrocarbons.[1] In a separate study employing clay-rich alkaline San Joaquin soil having high heavy metal retention ability, 350 °C broiler litter biochar increased the dissolved concentration of added Cu (but not Ni or Cd) relative to the soil-only control.[2] This biochar was able to stabilize Cu in San Joaquin soil when pretreated with 0.1 M NaOH to remove DOC.[2] In the presence of a natural organic matter (NOM) containing high levels of carboxyl and phenol functional groups, Cu concentration increased,[2] further suggesting the mobilization of Cu by a complex formation in the solution phase. These studies suggested that pH and soil organic carbon are the master variables in biochar's influence on the metal solubility. The DOC typically enhances contaminant transport when dissolved and retards it when sorbed on the solid matrix.[3] Depending on the pyrolysis conditions and solution chemistry,

biochar can release varying amounts and structures of DOC[4−6] including nanometer-sized colloids.[7]

Heavy metal speciation controls the effectiveness of biochar and other soil amendments. The speciation of heavy metals changes over time, and aged Pb and Cu showed a resistance to desorption in pH 4.9 acetate buffer.[8] Aged Pb and Cu in contaminated soils could be sufficiently dissolved only under strongly acidic conditions (0.4 M glycine at pH 1.5 for 1 h at 37 °C) used for in vitro bioaccessibility testing.[9] Aged Cu[10] and Pb[11] are expected to be strongly bound on soil by forming specific, multidentate ligand complexes with NOM, especially at low metal loadings; weaker, nonspecific interactions predominate at higher metal loadings.

The objective of the present study was to understand the influence of soil organic carbon and pH on the soluble Pb and Cu concentrations of contaminated soils amended with biochars. We employed seven Pb-contaminated small arms range (SAR) soils with known total organic carbon (TOC), cation exchange capacity (CEC), pH, and total Pb and Cu contents.[12] The Pb speciation in each soil had been determined by electron microprobe.[12] On the basis of the initial screening

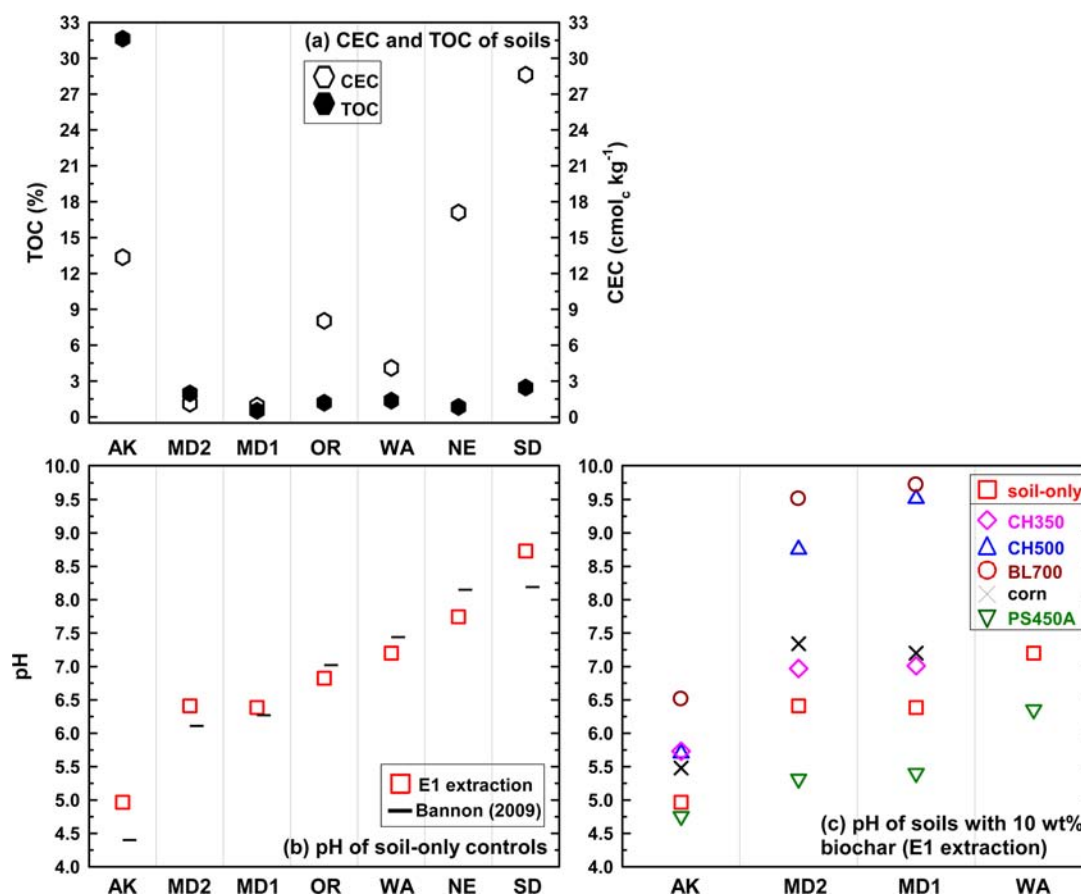**Figure 1.** Cation exchange capacity (CEC), total organic carbon (TOC) (a), and pH (horizontal lines in panel b) of small arms range soils from ref 12 and (c) pH of the first 48 h weak (pH 4.5 sulfuric) acid extraction (E1) without (squares) and with 10 wt % CH350 (diamonds), CH500 (triangles), BL700 (circles), corn (crosses), and PS450A (inverted triangles).

of seven soils, two soils having contrasting TOC and pH were selected to study the influence of (i) surface-bound carboxyl and phosphate ligands of phosphoric acid activated carbon and (ii) soluble P of manure biochar against (iii) three unactivated plant biochars produced under different pyrolysis conditions. Our future papers in this series will separately provide detailed accounts on how the CEC of contaminated soil influences the effectiveness of biochars as a heavy metal stabilizing agent.

■ MATERIALS AND METHODS

Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (Millipore, Milford, MA, USA) was used for all procedures.

Biochar Production and Characterization. Feedstock property and pyrolysis conditions were described in detail previously.[13−15] Briefly, cottonseed hull (CH) was used as received from Planters Cotton Oil Mill (Pine Bluff, AR, USA).[13] Broiler litter (BL) was obtained from a USDA-ARS facility (Starkville, MS, USA) and was milled and pelletized.[14] Feedstock was pyrolyzed at 350, 500, or 700 °C under a 1600 mL min^{-1} N$_2$ flow rate for 1−4 h using a laboratory scale box furnace (22 L void volume) with a retort (Lindberg, type 51662-HR, Watertown, WI, USA). Biochar products were allowed to cool to room temperature overnight under N$_2$ atmosphere. Biochars are here denoted by the feedstock abbreviation and pyrolysis temperature: cottonseed hull biochar produced at 350 °C (CH350) and 500 °C (CH500) and broiler litter biochar produced at 700 °C (BL700). To remove excess ash, CH500, CH350, and BL700 were washed with 0.1 M HCl (27 g char L^{-1}) by constant stirring for 1 h, rinsed three times with DDW, and dried overnight at 80 °C.

Pecan shell (PS)-derived phosphoric acid activated carbon was prepared by soaking 2 mm sized pecan shelll in 30 wt % phosphoric

acid overnight and then heating at 450 °C for 4 h under 800 mL min^{-1} air flow rate for oxidative activation.[15] The resulting activated carbon (PS450A) was washed five times in hot water (90 °C) and then oven-dried overnight at 80 °C. Corncob flash carbonization biochar (corn)[16,17] was used as received from a pilot plant facility at the University of Hawaii. All biochars (CH500, CH350, BL700, corn, and PS450A) were ground and sieved to <44 μm (325 mesh) for soil incubation experiments.

Proximate Analysis. Moisture, ash, volatile matter (VM), and fixed carbon contents of biochars were determined in triplicate by following American Society for Testing and Materials (ASTM) method D7582[18] using a LECO thermogravimetric analyzer (TGA701, LECO, St. Joseph, MI, USA). Moisture was determined as the weight loss after the sample had been heated under N$_2$ atmosphere in an open crucible to 107 °C and held at this temperature until the sample weight stabilized. The VM was determined as the weight loss after the sample had been heated under N$_2$ atmosphere in a covered crucible to 950 °C and held for 7 min. Ash was defined as the remaining mass after subsequent heating of the sample under O$_2$ atmosphere in an open crucible to 750 °C and holding at this temperature until sample weight stabilized. After the determination of moisture, ash, and VM, fixed carbon was calculated by difference.

Soil Incubation Experiment. Detailed collection, handling, and characterization of soil samples were described previously.[12] Briefly, the top 3−5 in. of small arms range soil samples from Maryland (MD1 and MD2), Alaska (AK), Nebraska (NE), Oregon (OR), Washington (WA), and South Dakota (SD) were obtained from Aberdeen Proving Ground and were air-dried and sieved (<250 μm).

Consecutive batch equilibration experiments were conducted using two extraction fluids to investigate the pH effects. Weak acid (pH 4.5

sulfuric acid solution)[19] was used to allow soil and biochar to set pH. Acetate buffer (0.1 M at pH 4.9)[20] was used to compare the metal solubility at a fixed pH. Acetate is not only a pH buffer but an organic ligand that is able to complex Pb and Cu to increase the soluble concentrations.[21] Separate reactors were prepared (each in duplicate) in polypropylene centrifuge tubes (50 mL nominal volume, Thermo Fisher Scientific, Waltham, MA, USA) for soils (20 g soil L^{-1}) with 10% (g biochar g^{-1} soil) CH350, CH500, BL700, corn, and PS450A. Soil without biochar served as the control for each experiment. The total volume of each reactor was set to 30 mL. Reactors were equilibrated by shaking end-over-end at 70 rpm.

After a 2 day equilibration, the pH of the soil suspension was measured (Orion 3-star plus benchtop pH meter, ThermoScientific, Waltham, MA, USA). The soil suspension was then centrifuged at 9180 rpm (11950g) for 20 min at 4 °C. Supernatant (20 mL determined gravimetrically) was carefully decanted into a clear glass vial and filtered (0.2 μm Millipore Millex-GS; Millipore, Billerica, MA, USA) and acidified to 4 vol % nitric acid (trace metal grade, Sigma-Aldrich) for the determination of soluble Pb and Cu concentrations using inductively coupled plasma–atomic emission spectrometer (ICP-AES; Profile Plus, Teledyne/Leeman Laboratories, Hudson, NH, USA). Blanks, blank spikes, and matrix spikes were included for quality assurance and control for the ICP-AES analysis.[22] The first equilibration step is denoted E1.

Immediately following E1, a subsequent equilibration step (E2) was initiated by adding 20 mL of weak acid to solids (soil with and without biochar) remaining after the removal of supernatant. For each batch reactor, a total of five (E1–E5) consecutive equilibration steps were employed over a 2 week period: 2 day weak acid (E1), 4 day weak acid (E2), 3 day weak acid (E3), 3 day acetate buffer (E4), and 2 day acetate buffer (E5). Each step followed the procedure described above for E1. The number and duration of equilibration were designed to account for the influence of supernatant replacement for each extraction fluid. Because lower heavy metal concentrations in weak acid (relative to acetate) can lead to confounding effects of biochar amendment,[8,9] a longer equilibration period was employed for the weak acid extraction.

■ RESULTS AND DISCUSSION

TOC, CEC, pH, and Pb Speciation of Small Arms Range Soils. Figure 1, panels a and b, presents reported CEC (open hexagons in Figure 1a), TOC (solid hexagons in Figure 1a), and pH (horizontal lines in Figure 1b) of small arms range soil samples.[12] Figure 1 also presents measured pH of soil suspensions after 48 h of equilibration in weak acid (E1) without (squares in Figure 1b,c) and with 10 wt % biochar (Figure 1c). In Figure 1b, the pH trend of E1 extraction (squares) agreed with the literature values (horizontal lines)[12] for soil-only controls. As shown in Figure 1b, the pH of unamended soils ranged from acidic (AK), to near-neutral (MD2, MD1, OR, and WA), to slightly alkaline (NE and SD). The 10 wt % biochar amendment increased the pH of sandy soils (MD1 and MD2) by as much as 4 units except for PS450A, which showed decreased pH (Figure 1c). The pH increase was greater for CH500 (pH 8.5) than for CH350 (pH 6.9), because CH500 contained higher ash and lower acidic functionality.[13] The highest pH was observed for BL700 containing 39.9 ± 0.1 wt % (on a dry weight basis) ash in the forms of alkaline silicates and sulfates.[23] The acidic activated carbon PS450A was estimated to contain 0.8 wt % P, of which 15–30% was the residual phosphoric acid (rather than the surface-bound P).[24] The 10 wt % PS450A decreased the pH of sandy soils having low buffering capacity by (i) releasing as much as 0.15 mM phosphoric acid and (ii) buffering pH by carboxyl and other acidic surface functional groups. In acidic, high TOC, peat soil (AK in Figure 1c), the pH stayed within

1.5 units of the soil-only control when amended with the same series of biochars. Similarly, the pH decrease by PS450A amendment was less significant for WA compared to MD1 and MD2 (Figure 1c).

Electron microprobe Pb speciation study[12] indicated the predominance of readily soluble PbCO$_3$ phases in sandy MD1 and MD2 soils. AK is acidic peat soil containing disproportionately high TOC (Figure 1a) and was the only soil dominated by the organic Pb species.[12] The CEC of AK was >10-fold greater than that of MD1 or MD2. The CEC and TOC of WA were only slightly higher than those of MD1 and MD2, and Pb existed as cerussite or was associated with MnOOH and FeOOH. The Pb speciation of OR was similar to that of WA, except for a large fraction of elemental Pb. Lead existed primarily as carbonates and oxides in SD,[12] where the Pb solubility is expected to be the lowest because of the highest CEC and pH. Similarly to SD, NE is a clay-rich, alkaline soil, and CEC was as high as that of AK; Pb existed mainly as PbO and cerussite.[12]

Proximate Analysis of Biochar and Soil. The VM provides an estimate for the thermally labile C component of biochar that may dissolve to become DOC of amended soil.[4−6] For different feedstocks, a higher pyrolysis temperature progressively decreases the DOC of biochar,[25] concurrently with the decreasing VM content.[13] The AK soil had disproportionately the highest TOC and VM of all soil samples examined. The TOC of AK soil (32% in Figure 1a) was close to its VM (35.7 ± 0.2 wt % in Figure 2). The VM content of AK
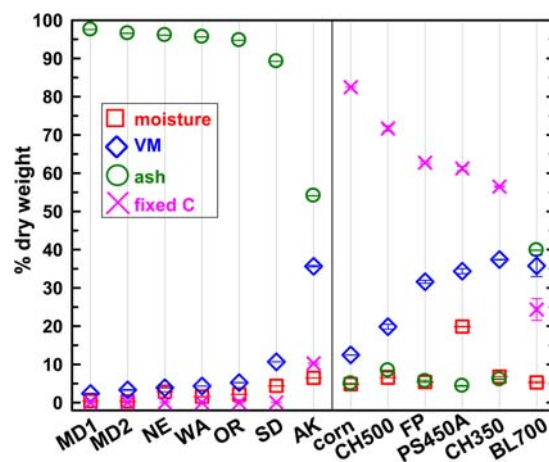

Figure 2. Moisture, volatile matter (VM), ash, and fixed carbon content of seven soil samples (MD1, MD2, NE, WA, OR, SD, AK); corncob flash carbonization charcoal (corn); slow pyrolysis cottonseed hull (CH500, CH350) and broiler litter (BL700) biochars; fast pyrolysis biochar (FP); and phosphoric acid activated carbon (PS450A). Values are given as the mean ± SD of triplicate measurements on a dry weight basis.

was as high as the low pyrolysis temperature plant biochar (CH350), ash-rich manure biochar (BL700), and phosphoric acid activated carbon (PS450A). Oxidative activation made PS450A thermally unstable and decreased fixed C content, compared to a plant biochar pyrolyzed under intert atmosphere (CH500). Oppositely, steam activation under inert atmosphere can increase the fixed C of biochar[8] to the level of flash carbonization (corn) charcoal in Figure 2. Flash carbonization is designed to maximize the fuel quality of charcoal by utilizing the upward transfer of fire through a packed bed of biomass
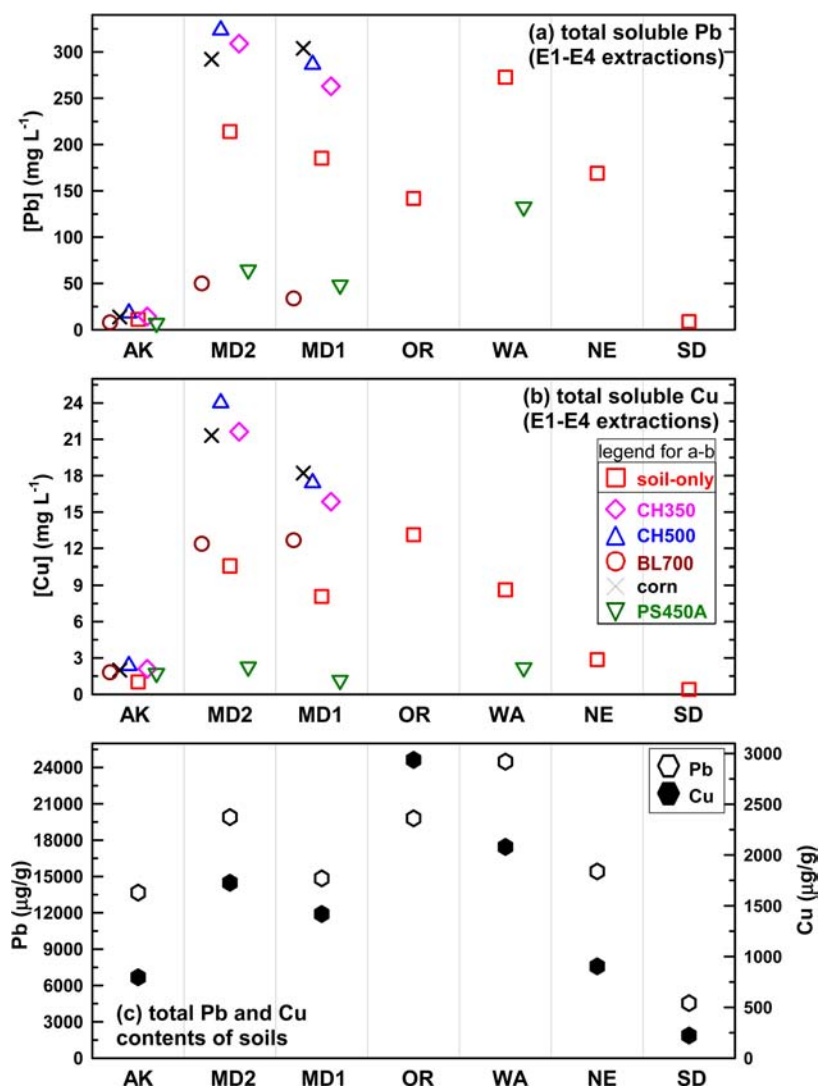
Figure 3. Sum of soluble (a) Pb and (b) Cu concentrations from successively extracting 20 g soil L^{-1} without (squares) and with 10 wt % biochar. Extraction steps were as follows: 2 days weak acid (E1), 4 days weak acid (E2), 3 days weak acid (E3), and 3 days acetate buffer (E4). (c) Total Pb (left y-axis) and Cu (right y-axis) contents of seven soil samples from ref 12.

against the downward flow of air to rapidly carbonize biomass at approximately 1 MPa pressure.[26]

The long-term influence of biochar on heavy metals depends partly on the recalcitrance of biochar in soil[27] that is expected to increase as a function of fixed C content. Figure 2 compares the fixed C content of slow pyrolysis, flash carbonization, and fast pyrolysis (FP) biochars. The FP was obtained from an industrial scale pyrolyzer (mixed sawdust pyrolyzed at 500 °C) of Dynamotive Energy Systems (Vancouver, BC, Canada). The fast pyrolysis system was optimized to yield 60−75 wt % bio-oil.[28] Proximate analysis results for FP are the literature values.[29] The fixed C content of FP was significantly lower than that of the 500 °C slow pyrolysis biochar (CH500) and was equivalent to that of PS450A (Figure 2, crosses). On the basis of the proximate analysis, PS450A will not be as stable in amended soil because of its lower fixed C compared to corn (Figure 2). However, biochars having high fixed C can be oxidized to increase the heavy metal sorption ability while maintaining the longevity in amended soil.[8] Separately from plant biochars discussed above, the lowest fixed C (24 ± 3 wt %, Figure 2) of BL700 manure biochar resulted from its disproportionately high ash content (39.9 ± 0.1 wt %). The

high VM content (36 ± 3 wt %) of BL700, despite high pyrolysis temperature (700 °C), likely resulted from a shorter residence time (1 h) compared to CH350 and CH500 (4 h).

Sum of Soluble Pb and Cu Concentrations from Consecutive Equilibrations. Figure 3, panels a and b, presents the sum of aqueous Pb and Cu concentrations determined at each of four consecutive equilibrations of biochar-amended soils using weak acid (E1−E3) and acetate buffer (E4): 2 days weak acid (E1), 4 days weak acid (E2), 3 days weak acid (E3), and 3 days acetate buffer (E4). The values were calculated by adding soluble concentrations from each equilibration and were not corrected for residual (10 mL) supernatant remaining from the previous equilibration. As we shall see, the majority of soluble Pb and Cu in Figure 3a,b resulted from the first acetate buffer extraction step (E4), and the contribution of weak acid extracts (E1−E3) was minor. In the absence of biochar (soil-only control shown as squares in Figure 3a,b), total aqueous Cu concentrations followed the trend of the total Cu content (by nitric/hydrofluoric acid digestion) in each soil[12] (Figure 3c). The only exception was AK, which had a lower soluble Cu (Figure 3b) than predicted from the trend in total Cu (Figure 3c, solid hexagons). Total
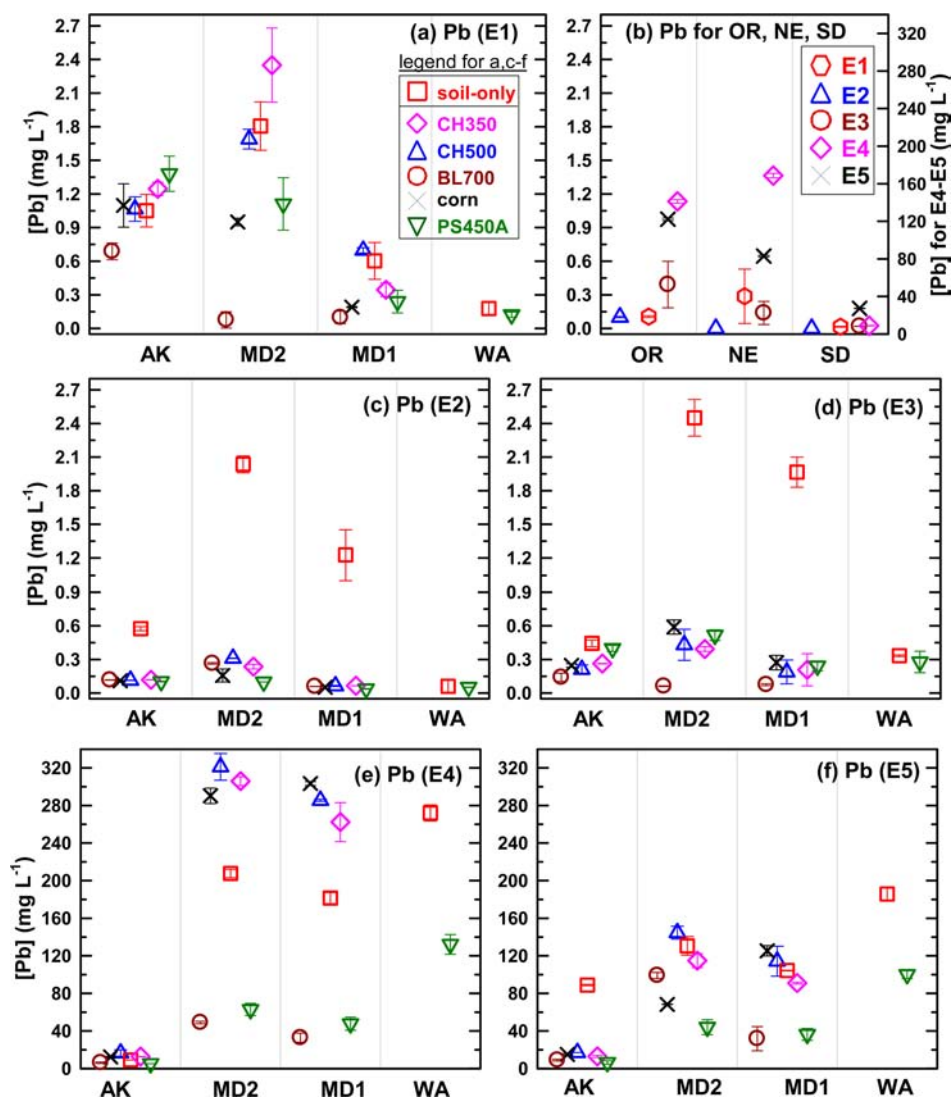
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Figure 4. Soluble Pb concentration at each consecutive equilibration step for 20 g soil L^{-1} without (squares) and with 10 wt % biochar: 2 days weak acid (E1), 4 days weak acid (E2), 3 days weak acid (E3), 3 days acetate (E4), and 2 days acetate (E5). Results in (b) are dedicated to OR, NE, and SD soil-only controls; separate y-axes are given for weak acid E1−E3 (left) and acetate E4−E5 (right) extractions. Values are given as the mean ± SD for duplicate experiments.

(E1−E4) soluble Pb concentrations in AK and OR were lower than expected from the trend in total Pb content of soil (open hexagons in Figure 3c). Of all soil-only controls in Figure 3a,b, SD had the lowest soluble Pb and Cu concentrations because of the lowest total Pb and Cu contents (Figure 3c) as well as the highest CEC and pH (Figure 1a,b). These trends for different soils remained unchanged when the second acetate extraction step (E5; 2 days in acetate buffer) was included to calculate total Pb and Cu for E1−E5 extraction steps (Figure S1 in the Supporting Information).

In Figure 3a,b, 10 wt % of the following biochars were examined: (i) plant biochar that was activated to increase the surface-bound carboxyl and phosphate ligands (PS450A),[24] (ii) manure biochar enriched with soluble P (BL700),[9] and (iii) unactivated plant biochars produced at two different temperatures (CH350 and CH500) and by flash carbonization (corn). Relative to the soil-only control (squares in Figure 3a,b), surface ligand-enriched PS450A significantly decreased the total soluble Pb and Cu concentrations in MD1 and MD2 soils (inverted triangles). Phosphorus-enriched BL700 significantly

decreased Pb concentration and slightly increased Cu concentration in MD1 and MD2 (Figure 3a,b). All unactivated plant biochars (corn, CH350, and CH500), in contrast, dissolved Pb and Cu in MD1 and MD2. Compared to sandy soils (MD1 and MD2), the influence of biochar was less visible in high TOC peat (AK) soil. Whereas PS450A and BL700 decreased the total Pb concentration in AK soil, the Cu concentration was not affected. In conclusion, biochars exerted the greatest influence on pH (Figure 1c) and soluble Pb and Cu concentrations (Figure 3a,b) of the following soil properties: sandy, low CEC, and low TOC. Regardless of soil or biochar type, both soluble (Figure 3a) and total (open hexagons in Figure 3c) Pb were an order of magnitude higher than Cu (Figure 3b and solid hexagons in Figure 3c). Subsequent sections will examine each extraction period to understand how, relative to the soil-only control, Pb and Cu were (i) stabilized by PS450A and BL700 (for Pb) and (ii) mobilized by corn, CH350, and CH500. To understand the effects of pH and TOC, we shall compare the sandy, near-neutral, low TOC soil
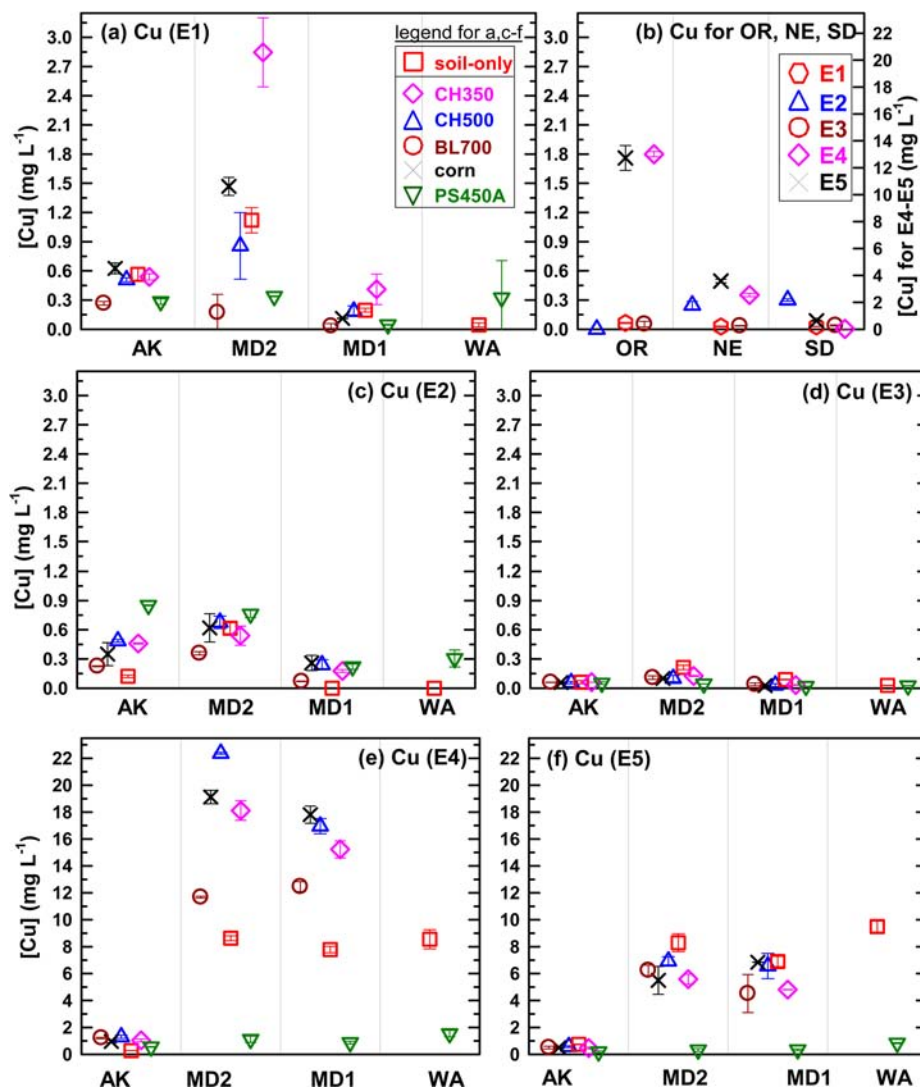
Figure 5. Soluble Cu concentrations corresponding to the extraction steps in Figure 4. Weak acid (panels a, c, d, and left *y*-axis of panel b) and acetate buffer (panels e, f, and right *y*-axis of panel b) extractions are each plotted to scale. Results in panel b are dedicated to OR, NE, and SD soil-only controls.

having minimal pH buffering capacity (MD1, MD2) with acidic, high TOC, peat soil (AK).

Soluble Pb and Cu Concentrations at Individual Equilibration Steps. Figures 4 and 5 present soluble Pb and Cu concentrations at each weak acid (E1−E3) and acetate buffer (E4−E5) equilibration step. Values in Figures 4 and 5 are given as the mean ± the standard deviation (SD) of duplicate experiments for a soil (AK, MD2, MD1, WA; 20 g soil L^{-1}) amended with 10% (g biochar g^{-1} soil) BL700 (circles), CH500 (triangles), corn (crosses), CH350 (diamonds), and PS450A (inverted triangles). Controls (without biochar) are shown as squares. Figures 4b and 5b separately present results for OR, NE, and SD soils that were investigated only without biochar. The pH during repeated extraction using weak acid (E1−E3) did not significantly change from E1 (Figure 1b,c) for different soils and biochars. Acetate was able to buffer pH near 5.0 for E4 and E5 extractions regardless of biochar amendment, except for the alkaline SD soil (Figure 1b) that increased the pH to 6. Table S1 of the Supporting Information presents the pH of each data point (E1−E5) in Figures 4 and 5. Biochars exerted the greatest influence on the MD2 soil that had the highest soluble Pb and Cu concentrations before amendment.

The greatest change in Cu concentration was observed at E1 for MD2: CH350 ≫ corn > control ≈ CH500 > PS450A ≈ BL700. The trend for Pb was CH350 ≈ control ≈ CH500 > corn ≈ PS450A > 700BL. Compared to MD2, the influence of biochar on Pb and Cu was less clear on MD1 and AK soils when plotted to scale (Figures 4 and 5). Figures S2 and S3 of the Supporting Information provide Figures 4 and 5 with expanded *y*-axes. Overall, BL700 most effectively stabilized Pb and Cu in E1 for AK, MD1, and MD2 soils. In contrast, CH350 solubilized Pb and Cu especially in MD2.

During the second weak acid extraction (E2), all biochars decreased the Pb concentration relative to the control in MD1, MD2, and AK soils. This change in biochar effects (from E1) can result from (i) depletion of soluble Pb by repeated extractions and/or (ii) enhanced ability of biochars to stabilize Pb. For different soils, soluble Pb concentrations of the control did not significantly change from E1, to E2 to E3. Therefore, the reduction in Pb concentration in the second and third weak acid extractions by biochar likely resulted from enhanced stabilization ability. Oppositely, Cu concentrations of the soil-only controls progressively decreased from E1 to E2 to E3, suggesting the depletion of weak acid-extractable Cu from E1
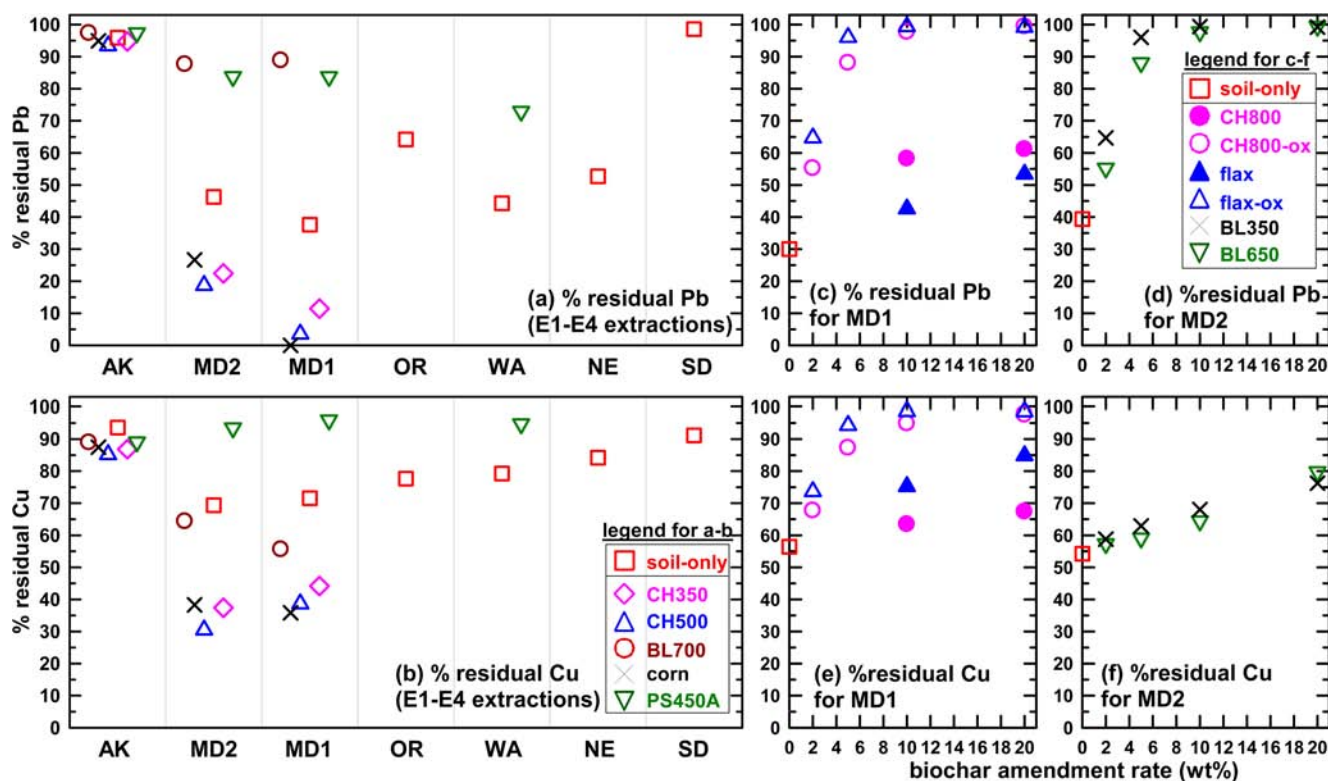
Figure 6. Percent residual (a) Pb and (b) Cu in small arms range soils without (squares) and with 10 wt % biochars calculated from E1−E4 extractions: 2 days weak acid (E1), 4 days weak acid (E2), 3 days weak acid (E3), and 3 days acetate buffer (E4). Results in panels c and d were based on ref 8 and those in panels e and f were based on ref 9; values were calculated by adding soluble Pb and Cu concentrations from consecutive weak acid and acetate extractions (1 week each).

to E3. Figure S4 of the Supporting Information presents dissolved Pb and Cu concentrations calculated using HYDRAQL[30] equilibrium speciation software with amorphous Pb and Cu (hydr)oxides as the solubility limiting phases.[31] Across the pH range of Figure S4, Cu is less soluble than Pb with respect to hydrolysis. Because the pH did not significantly change from E1 to E3 (Table S1), the progressive decrease in Cu concentration likely resulted from factors other than pH. A possible cause is the change in DOC composition leading to the depletion of labile Cu species during successive extractions.[32] By the third weak acid extraction (Figures 4d and 5d), soluble Pb and Cu concentrations were within the error range for different biochars: all biochars decreased Pb concentration relative to the control for MD1 and MD2. Likewise, all biochars decreased Cu concentrations in E3 relative to the control for MD1 and MD2 (Figure S3). In each soil, the difference in Pb and Cu concentrations among biochars diminishes with successive extractions from E1 to E2 to E3.

Soluble Pb and Cu concentrations in acetate buffer (panels e and f of Figures 4 and 5) were as much as 100-fold higher than in weak acid (panels a, c, and d of Figure 4 and 5). Acetate is a metal ion-coordinating organic ligand and causes metal desorption from soils with[33] and without[34] biochar. Stability constants (log K) for the 1:1 complex with acetate are 2.58 for Pb^{2+} and 2.21 for Cu^{2+} (25 °C, zero ionic strength).[31] Acetate buffer brought back the Pb mobilization effects (observed in E1) of CH350, CH500, and corn biochars in sandy soils. The same trends in soluble Pb concentrations were observed in the first weak acid (E1) and the first acetate (E4) extraction steps for MD1 and MD2: CH500, CH350, corn > control > PS450A,

BL700. During the consecutive extractions using acetate (E4 and E5 for MD1 and MD2), PS450A and BL700 stabilized Pb, whereas only PS450A stabilized Cu. Much like the second weak acid extraction (E2), the second acetate extraction (E5) diminished the Pb mobilization effects of corn, CH350, and CH500, making all biochars either below or within the error range of control. These trends for Pb were also observed for Cu: (i) >10-fold increase in Cu concentration from E3 to E4, along with the return of Cu solubilization by CH350, CH500, and corn; and (ii) reduced Cu mobilization by CH350, CH500, and corn from E4 to E5. In conclusion, unactivated (CH350, CH500, and corn) plant biochars mobilized Pb and Cu during the first extraction using a given fluid. Such mobilization effects gradually disappeared with repeated extractions using the same fluid (weak acid or acetate buffer).

For N- and O-donor ligands of DOC, the stability constant for transition metal ions increases from left to right of the periodic table and maximizes for Cu^{2+}, which is a d^9 metal ion and engages in Jahn−Teller distortion.[35] As a result, Cu^{2+} preferentially (over Cd^{2+} and Ni^{2+}) formed soluble complexes with DOC of 350 °C broiler litter biochar.[2] Similar Cu−DOC complexes formed in the presence of CH350, CH500, and corn biochars can pass through the 0.2 μm filter used in this study and add to soluble Cu in Figure 5. Copper sorbed on colloids (of clay, ferrihydrite, and other soil components)[32] can also contribute to Figure 5. In addition, the affinity of Cu for the solid phase (soil and biochar) can gradually increase during repeated extraction, because of decreased DOC (by supernatant replacements) to keep Cu in solution.[36,37] Such change in DOC composition can contribute to the progressively

greater stabilization of Pb and Cu by biochar, as a result of repeated extraction using a given fluid.

Among the soil-only controls in E4−E5 extractions, Pb concentration was the highest in WA (Figure 4b). Cerussite was the primary Pb phase in WA[12] and dissolved under acidic pH set by acetate (E4−E5), but not under the native neutral pH maintained by the soil in weak acid (E1−E3). Only when soluble Pb and Cu concentrations were sufficiently high (acetate extractions in Figures 4 and 5) could the stabilization effects of PS450A be observed in the WA soil. Likewise, Pb and Cu concentrations of pH 7 (Figure 1b) OR soil increased to nearly as high as MD soils in acetate buffer (right axes in Figures 4b and 5b for E4−E5). NE and SD soils, having among the highest pH and CEC (Figure 1a,b), had much lower Cu (and Pb for SD) concentrations in acetate than all other soils examined.

Of different soils in Figures 4 and 5, acidic AK soil had among the lowest Pb and Cu in acetate, despite the predominance of organic Pb species[12] that can prevent the stabilization of Pb.[38] Overall, acidic soil (AK) and acidic biochar (PS450A) were best able to retain Pb and Cu under acidic pH set by the acetate buffer. To quantitatively assess the influence of soil and biochar properties, percent residual Pb was calculated for each experiment:

$$[\text{Pb}]_{\text{total}} \ (\text{mg L}^{-1}) = [\text{Pb}]_{\text{soil}} \left(\frac{m}{V} \right)$$

$$\% \text{ residual Pb}$$
$$= \frac{[\text{Pb}]_{\text{total}} - ([\text{Pb}]_{\text{E1}} + [\text{Pb}]_{\text{E2}} + [\text{Pb}]_{\text{E3}} + [\text{Pb}]_{\text{E4}})}{[\text{Pb}]_{\text{total}}}$$
$$\times 100\%$$

$[\text{Pb}]_{\text{soil}}$ (in mg kg^{-1}) is the total Pb content of soil on a dry weight basis (Figure 3c), m is the dry weight of soil used in each experiment, V is the reactor volume, and $[\text{Pb}]_{\text{E1}}$ (in mg L^{-1}) is the soluble Pb concentration from the E1 extraction (Figure 4). An analogous equation was used to calculate the percent residual Cu. In addition, percent residual Pb and Cu were calculated on a previous MD1 and MD2 soil (20 g soil L^{-1}) study that employed consecutive 1 week weak acid and 1 week acetate buffer extractions. In that study,[8] MD1 soil was amended with 0 (soil-only control), 2, 5, 10, and 20 wt % of 800 °C cottonseed hull (CH800) and steam-activated flax (flax) biochars without and with oxidation (CH800-ox and flax-ox) to increase carboxyl surface functionality. The MD2 soil was amended with 350 °C (BL350) and 650 °C (BL650) broiler litter biochars.[9]

Comparison of MD1 and MD2 soil-only controls (squares in Figure 6) indicates higher residual Pb and Cu in the present study that employed a shorter acetate equilibration period (3 days in E4; squares in Figure 6a,b) than in prior reports (1 week; squares in Figure 6c−f).[8,9] Figure 6, panels a and b, indicates that SD and AK soils possessed an intrinsic ability to retain Pb and Cu (nearly 100% residual) before biochar amendment. For MD soils, 10 wt % PS450A was required to reach 100% residual Pb and Cu. Figure 6c−f indicates biochar amendment rate-dependent stabilization of Pb and Cu by oxidized biochars enriched with carboxyl functionality (CH800-ox and flax-ox) as well as manure biochars (CH350 and CH650). In Figure 6c−f, residual Pb and Cu increased to nearly 100% by 5 wt % amendment rate, except for manure chars on Cu (Figure 6f).

Figure 6 highlights the importance of surface ligands (especially carboxyl) to complex and stabilize heavy metals, most likely through a specific, inner-sphere coordination.[21] Surface ligand-enriched biochars (PS450A, CH800-ox, and flax-ox) were especially effective under acidic pH buffered by acetate, where Pb and Cu were most soluble.[8] Oxidatively activated PS450A, CH800-ox, and flax-ox in Figure 6 are enriched with carboxylic, phenolic, and carbonyl surface functional groups[8,24] that can coordinate and stabilize Pb and Cu.[8,15] In addition, phosphoric acid activated carbon (PS450A) contains phosphate surface functionality.[24] In our previous study,[33,39] PS450A more effectively retained Cu than BL700 in sandy Norfolk soil equilibrated with acetate buffer. In both sandy (Norfolk) and clay-rich (San Joaquin) soils, Cu remained nearly 100% residual when amended with 20 wt % PS450A; residual Cu was as low as 50% for BL700.[33] This observation is in agreement with greater residual Cu in the presence of PS450A, relative to BL700, in Figure 6b. Manure biochar and other waste-derived sources of soluble P are known to stabilize Pb in contaminated soils by forming thermodynamically stable Pb phosphate minerals.[40,41] For Cu, Figure 6 indicates that manure biochars are not as effective stabilizers as carboxyl-enriched plant biochars.

Figure 6, panels a and b, shows a decrease in residual Pb and Cu by CH350, CH500, and corn biochars in sandy soils. That is, all unactivated plant biochars, relative to the soil-only control, mobilized Pb and Cu in sandy soils. Increased solubility of target metal contaminants is undesirable when the goal is to reduce their off-site migration.[32] On the other hand, chelate-assisted phytoremediation and soil washing approaches often utilize organic ligands to increase the soluble metal concentrations for subsequent removal by plant uptake and by other means.[42] For these applications, carboxylic/sugar/amino acids in blood meal and silage effluent wastes have been proposed as an alternative to EDTA and other synthetic ligands.[43] Chelate-assisted phytoremediation and soil washing decrease the total contaminant content of the soil and are useful for sites regulated by the total (rather than soluble/bioavailable) heavy metal content of soil.[44]

In summary, this study investigated the influence of soil organic carbon and pH on biochar−heavy metal interactions during 2 week successive equilibrations in weak acid and acetate buffer. The majority of Pb and Cu dissolution occurred during the first acetate extraction step. In the absence of biochar, soluble Pb and Cu concentrations were (i) the lowest in soils having high TOC and high CEC and (ii) the highest in sandy soils having low TOC and low CEC. Unactivated (CH350, CH500, and corn) plant biochars mobilized Pb and Cu during the first extraction using a given fluid. Such mobilization effects gradually disappeared with repeated extractions using the same fluid (weak acid or acetate buffer). By the third extraction using weak acid, all biochars stabilized Pb and Cu in sandy soils, relative to the soil-only control. These observations suggested an enhanced affinity of heavy metals to solid surfaces (soil and biochar) as a result of repeated extraction using a given fluid. A putative cause is the depletion of DOC by supernatant replacements leading to reduced solution-phase complexation of Pb and Cu. Relative to Pb, the solubility of Cu was more sensitive to (i) the changes in DOC by supernatant replacement as well as (ii) the stabilization by carboxyl surface ligand of oxidized biochars.

ASSOCIATED CONTENT

S **Supporting Information**

The pH of soil suspensions at E1−E5 extractions, total soluble Pb and Cu concentrations for E1−E5 extractions, Figures 4 and 5 plotted with expanded y-axes, and equilibrium calculation of total dissolved Cu(II) and Pb(II). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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