

## Lead Retention by Broiler Litter Biochars in Small Arms Range Soil: Impact of Pyrolysis Temperature

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### **S** Supporting Information

**ABSTRACT:** Phosphorus-rich manure biochar has a potential for stabilizing Pb and other heavy metal contaminants, as well as serving as a sterile fertilizer. In this study, broiler litter biochars produced at 350 and 650 °C were employed to understand how biochar's elemental composition (P, K, Ca, Mg, Na, Cu, Pb, Sb, and Zn) affects the extent of heavy metal stabilization. Soil incubation experiments were conducted using a sandy, slightly acidic (pH 6.11) Pb-contaminated (19906 mg kg<sup>-1</sup> total Pb primarily as PbCO<sub>3</sub>) small arms range (SAR) soil fraction (<250 μm) amended with 2–20 wt % biochar. The Pb stabilization in pH 4.9 acetate buffer reached maximum at lower (2–10 wt %) biochar amendment rate, and 350 °C biochar containing more soluble P was better able to stabilize Pb than the 650 °C biochar. The 350 °C biochar consistently released greater amounts of P, K, Mg, Na, and Ca than 650 °C biochar in both unbuffered (pH 4.5 sulfuric acid) and buffered (pH 4.9 acetate) systems, despite 1.9–4.5-fold greater total content of the 650 °C biochar. Biochars, however, did not influence the total extractable Pb over three consecutive equilibration periods consisting of (1) 1 week in pH 4.5 sulfuric acid (simulated leaching by rainfall), (2) 1 week in pH 4.9 acetate buffer (standard solution for toxicity characteristic leaching procedure), and (3) 1 h in pH 1.5 glycine at 37 °C (in vitro bioaccessibility procedure). Overall, lower pyrolysis temperature was favorable for stabilizing Pb (major risk driver of SAR soils) and releasing P, K, Ca, and other plant nutrients in a sandy acidic soil.

**KEYWORDS:** heavy metal, bioavailability, manure, fertilizer, biomass, phosphorus

### ■ INTRODUCTION

Biochars produced from manure contain a large amount of (≥50 wt %) ash<sup>1</sup> and can contain as much as 6 wt % phosphorus.<sup>2</sup> As a result, manure biochars can be utilized as a sterile fertilizer<sup>3</sup> as well as a heavy metal stabilizer.<sup>4</sup> These functions are interrelated: phosphorus is not only an essential plant nutrient, but a known Pb stabilizer (by the formation of pyromorphite phases).<sup>5,6</sup> Inhalation and incidental ingestion of Pb-contaminated dust and soil lead to impaired intellectual development in children.<sup>7,8</sup> Weathering of spent bullets leads to the formation of lead carbonate phases that are highly soluble, especially under acidic conditions.<sup>9</sup> This unique Pb contamination scenario of shooting range soils results in high (>80%) Pb bioavailability compared to former landfill and other periurban soils.<sup>10</sup> Berm soil is often replaced by sand to minimize weathering of bullets that is enhanced by high moisture and organic matter contents of soil.<sup>11</sup> Organic carbon components of biochar can stabilize heavy metals by (1) electrostatic interactions between metal cations and negatively charged biochar surface above point of zero charge (PZC); (2) ionic exchange between ionizable protons at the biochar surface and metal cations; (3) sorptive interaction involving delocalized π electrons of aromatic biochar structure by coordination of d-electrons, especially for softer Lewis acids; and/or (4) specific binding of metal ions by surface ligands (e.g., carboxyl, hydroxyl, phenol) abundant in the volatile matter (VM) component of biochar.<sup>12</sup>

This is the second in series of papers investigating the factors controlling biochar-induced heavy metal stabilization in Pb-contaminated small arms range (SAR) soils. The previous paper in this series investigated the role of carboxyl surface functional groups on biochar's ability to stabilize heavy metals in SAR soil under different equilibration conditions (with and without buffer) designed to understand the pH effects.<sup>13</sup> The present study focused on the elemental composition of biochar, especially phosphorus, by employing manure biochars containing >35 wt % ash. A prior paper is available on dairy manure biochar-induced Pb stabilization in a shooting range soil;<sup>6</sup> however, the study employed a single biochar sample produced at 450 °C. Pyrolysis temperature markedly affects the biochar's ability to stabilize heavy metal<sup>14</sup> as well as organic contaminants.<sup>15</sup> Limited information is currently available on how pyrolysis temperature affects the function of manure biochars as a heavy metal stabilizer. Temperature-dependent changes in the amount and speciation of P and other elements will uniquely affect the performance of ash-rich manure biochars.<sup>16</sup> To simultaneously investigate the heavy metal stabilization and nutrient (especially P, K) release, the following selected elements were measured: Pb, Cu, P, K, Na, Ca, Mg, Zn, and Sb. In vitro Pb bioaccessibility testing (in place of a

**Received:** February 24, 2012

**Revised:** April 23, 2012

**Accepted:** May 1, 2012

**Published:** May 1, 2012

**Table 1. Moisture, Volatile Matter (VM), Fixed Carbon, and Ash Contents and Selected Elemental Composition (P, Ca, K, Mg, Na, Cu, and Zn) of Broiler Litter before (BL25) and after Pyrolysis at 350, 500, 650, and 800 °C (BL350, BL500, BL650, and BL800)<sup>a</sup>**

char	Proximate Analysis Results (wt % <sub>db</sub> )				
	moisture	VM <sub>db</sub>	fixed C <sub>db</sub>	ash <sub>db</sub>	
BL25	20 ± 1	58 ± 1	12 ± 1	29 ± 1	
BL350	3.10 ± 0.02	36.9 ± 0.1	27.6 ± 0.1	35.48 ± 0.04	
BL500	3.15 ± 0.03	19 ± 1	31 ± 1	50.1 ± 0.2	
BL650	4.75 ± 0.03	12.0 ± 0.1	33.7 ± 0.1	54.3 ± 0.2	
BL800	6.65 ± 0.01	9.8 ± 0.2	32.4 ± 0.1	57.8 ± 0.1	

char	Elemental Composition <sup>b</sup> (mg g <sup>-1</sup> <sub>wb</sub> )						
	P	Ca	K	Mg	Na	Cu	Zn
BL25	18 ± 2	28 ± 2	29 ± 2	4 ± 1	8.5 ± 0.5	0.259 ± 0.003	0.36 ± 0.02
BL350	30 ± 2	50 ± 1	45 ± 1	14 ± 1	13 ± 1	0.48 ± 0.01	0.59 ± 0.02
BL500	38 ± 1	61 ± 7	60 ± 7	17.1 ± 0.3	17 ± 0	0.57 ± 0.02	0.68 ± 0.03
BL650	39 ± 9	66 ± 9	67 ± 8	18 ± 2	18 ± 1	0.62 ± 0.02	0.7 ± 0.1
BL800	18 ± 2	75 ± 19	71 ± 14	17 ± 4	19 ± 5	0.6 ± 0.1	0.5 ± 0.1

<sup>a</sup>Values are given as the mean ± SD for triplicate (proximate analysis) or duplicate (elemental composition) measurements. Proximate analysis results are given on a dry weight basis (db); elemental composition is given on a wet basis (wb) without correction for the moisture content. <sup>b</sup>Pb and Sb values were below detection limit for all samples.

costly in vivo bioavailability approach<sup>5</sup>) was conducted after the sequential equilibration steps and was compared to previously reported in vitro and in vivo results<sup>9</sup> for the the SAR soil employed in this study.

## MATERIALS AND METHODS

Detailed biochar production and characterization<sup>14,17</sup> and SAR soil incubation<sup>13</sup> methods were reported previously and are summarized below. Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (Millipore, Milford, MA, USA) was used for all procedures.

**Biochar Production.** Preparation of broiler litter biochars was described in a previous paper.<sup>17</sup> Briefly, broiler litter samples (BL25) were milled (<25% moisture content), pelletized, and pyrolyzed at 350, 500, 650, and 800 °C for 1 h under 1600 mL min<sup>-1</sup> nitrogen flow rate using a box furnace (22 L void volume) with a retort (Lindberg, Type 51662-HR, Watertown, WI, USA). The resulting chars (BL350, BL500, BL650, BL800) were allowed to cool to room temperature overnight under nitrogen atmosphere. Biochar samples were ground and sieved to <44 μm (325 mesh) for subsequent analyses and soil incubation experiments.

**Elemental Analysis.** The elemental composition of unpyrolyzed broiler litter (BL25) as well as biochars (BL350, BL500, BL650, BL800) was determined in replicate by microwave-assisted (Ethos EZ microwave digester, Milestone, Inc., Shelton, CT, USA) digestion (concentrated HNO<sub>3</sub>/HCl + 30% H<sub>2</sub>O<sub>2</sub>) following U.S. EPA method 3052.<sup>18</sup> Digested samples were analyzed for the total Cu, Pb, Zn, P, Ca, K, Mg, and Na contents using inductively coupled plasma atomic emission spectrometer (ICP-AES; Profile Plus, Teledyne/Leeman Laboratories, Hudson, NH, USA).

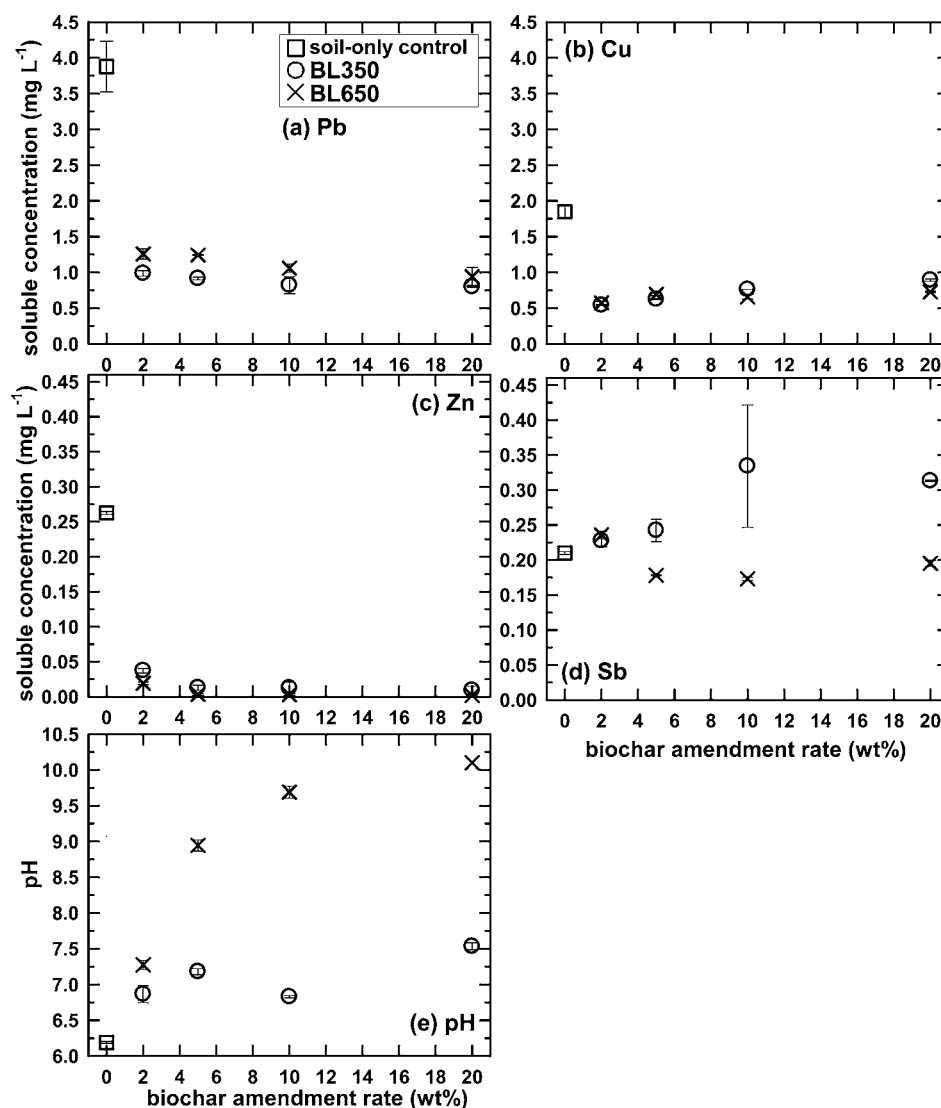
**Proximate Analysis.** Moisture, ash, volatile matter (VM), and fixed carbon contents of BL25, BL350, BL500, BL650, and BL800 were determined in triplicate by following American Society for Testing and Materials (ASTM) method D5142<sup>19</sup> using a LECO thermogravimetric analyzer (TGA701, LECO, St. Joseph, MI, USA). Moisture was determined as the weight loss after heating the sample under N<sub>2</sub> atmosphere in an open crucible to 107 °C and holding at this temperature until the sample weight stabilized. Volatile matter was determined as the weight loss after heating the sample under N<sub>2</sub> atmosphere in a covered crucible to 950 °C and a 7 min hold. Ash was defined as the remaining mass after subsequently heating the sample under O<sub>2</sub> atmosphere in an open crucible to 750 °C and holding at this temperature until the sample weight stabilized. After the determination of moisture, ash, and VM, fixed carbon was calculated by difference.

**Soil Incubation Experiment.** Detailed soil sample collection, handling, and characterization procedures were provided previously.<sup>9</sup> The top 2–3 in. of berm soil from a SAR in Maryland (MD2) was obtained from Aberdeen Proving Ground. A composite of five or six subsamples was air-dried and sieved (<250 μm). This soil particle size fraction is commonly employed in bioaccessibility studies as the fraction that adheres to the hands of children and causes Pb hand-to-mouth transfer.<sup>10</sup> There was limited vegetation at the sampling site, and MD2 was characterized as a sandy, slightly acidic (pH 6.11) soil containing low total organic carbon (TOC; 1.966%) and low cation exchange capacity (CEC; 1.1 cmol<sub>c</sub> kg<sup>-1</sup>).<sup>9</sup> Total metal concentrations were determined by nitric/hydrofluoric acid digestion<sup>20</sup> of MD2 followed by ICP-MS and were (in μg g<sup>-1</sup> for three to five subsamples) 19906 ± 371 for Pb, 1727 ± 35 for Cu, 157 ± 1.6 for Zn, and 91 ± 1.1 for Sb.<sup>9</sup> In MD2, Pb existed primarily (≈80% by electron microprobe) in highly bioavailable PbCO<sub>3</sub> phases.<sup>9</sup> Minor Pb fractions (<20%) were associated with FeOOH or were present as PbOOH, PbO, and PbSO<sub>4</sub>.<sup>9</sup> Although a range of metals such as Pb, Cu, Sb, As, and Zn are used to manufacture bullets, Pb is the major risk driver of range soils because of its high concentration and toxicity.<sup>9</sup>

Batch equilibration experiments were conducted using a standard weak acid solution prepared by adding 10 mM H<sub>2</sub>SO<sub>4</sub> to DDW until a pH of 4.5 was attained. Separate reactors were prepared in polypropylene centrifuge tubes (50 mL nominal volume, Thermo Fisher Scientific, Waltham, MA, USA) for MD2 (20 g soil L<sup>-1</sup>) with and without 2, 5, 10, and 20% (g biochar g<sup>-1</sup> soil) BL350 and BL650. The total volume of each reactor was set to 30 mL. Reactors were equilibrated for 1 week by shaking end-over-end at 70 rpm. Each equilibration experiment was performed in duplicate.

After 1 week of equilibration, the pH of the soil suspension was measured (Oakton pH/Ion 510 benchtop pH-meter, Oakton Instruments, Vernon Hills, IL, USA). The soil suspension was then centrifuged at 9180 rpm (11950g) for 20 min at 4 °C. A known volume of the supernatant (20.0 ± 0.5 mL for 18 reactors 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% (v/v) nitric acid (trace metal grade, Sigma-Aldrich) for the determination of soluble Pb, Cu, P, K, Na, Ca, Mg, Zn, and Sb concentrations using ICP-AES. The first equilibration step is hereby denoted “weak acid extraction”.

Immediately following the weak acid extraction, a subsequent 1 week equilibration step was initiated by adding 20 mL of 0.1 M acetate buffer (pH 4.9) to solids (soil with and without biochar) remaining after the removal of supernatant. The pH 4.9 acetate buffer is a standard solution employed in the Toxicity Characteristic Leaching



**Figure 1.** Soluble Pb, Cu, Zn, and Sb concentrations and pH after 1 week of equilibration of MD2 (20 g soil L<sup>-1</sup>) amended with 0 (soil-only control), 2, 5, 10, and 20% (g biochar g<sup>-1</sup> soil) of 350 °C (BL350) and 650 °C (BL650) broiler litter biochars in pH 4.5 sulfuric acid solution (weak acid extraction). Values are presented as the mean  $\pm$  SD for duplicate experiments.

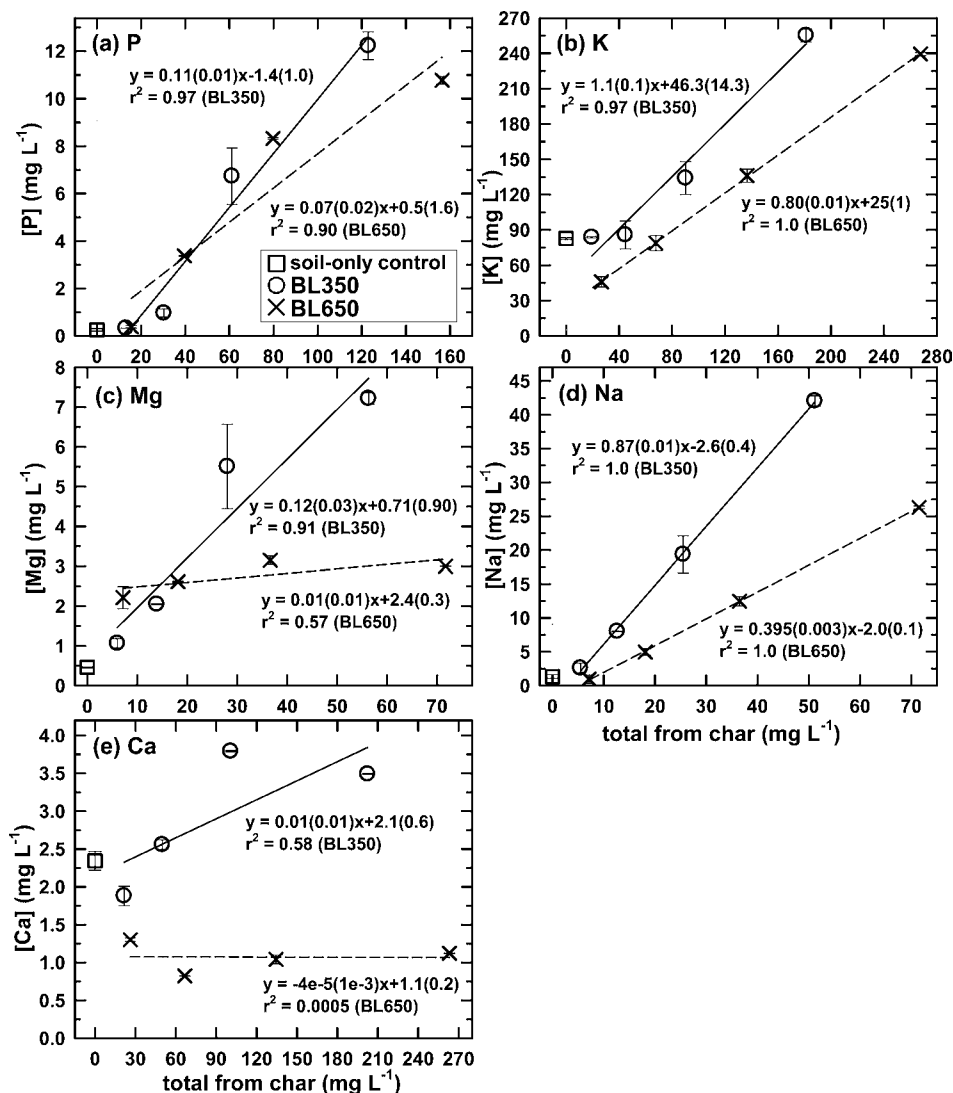
Procedure (TCLP).<sup>21</sup> Reactors were equilibrated for 1 week by shaking end-over-end at 70 rpm. After 1 week of equilibration, the pH of the soil suspension was measured. The soil suspension was subsequently centrifuged to collect the supernatant for ICP-AES analyses as described above for the weak acid extraction. The second equilibration step is hereby denoted “acetate buffer extraction”.

Immediately following acetate buffer extraction, *in vitro* Pb bioaccessibility analysis<sup>22</sup> was conducted by rinsing all remaining solids (soil with and without biochar after supernatant removal; remaining supernatant from acetate buffer extraction was  $8 \pm 1$  mL for 18 batch reactors) with 0.4 M glycine (tissue culture grade, Sigma-Aldrich) extraction fluid (preadjusted to pH 1.5 using trace metal grade HCl) into 125 mL Nalgene bottles. The ratio of dry solids (soil + char) to glycine extraction fluid was maintained for each sample at 1 g/100 mL. Each Nalgene bottle was placed in a 37 °C water bath and was rotated end-over-end (120 rpm) for 1 h and then was filtered (0.2  $\mu$ m) and analyzed for Pb. Total leached Pb from weak acid extraction, acetate buffer extraction, and *in vitro* Pb bioaccessibility analysis were added and then converted to percent of total Pb content in MD2 (dry weight). The resulting values were compared with previously reported *in vitro* Pb bioaccessibility result for MD2.<sup>9</sup>

## RESULTS AND DISCUSSION

**Elemental and Proximate Analyses.** Table 1 presents results from proximate (moisture, volatile matter, fixed C, and ash contents) and elemental (P, Ca, K, Mg, Na, Cu, and Zn contents) analyses of broiler litter before (BL25) and after pyrolysis at 350, 500, 650, and 800 °C. Values are given as the mean  $\pm$  SD for triplicate (proximate analysis) or duplicate (elemental composition) measurements. Proximate analysis results are given on a dry weight basis (wt %<sub>db</sub>), and elemental compositions are given on a wet basis (mg g<sup>-1</sup><sub>wb</sub> without correction for the moisture content). Pyrolysis at 350 °C decreased the moisture and VM contents and increased fixed C and ash contents of broiler litter (Table 1). Stepwise increase in pyrolysis temperature (in 150 °C intervals, Table 1) from 350 to 800 °C resulted in a progressive increase in moisture, fixed C (except for a decrease from 650 to 800 °C), and ash contents and a decrease in VM (Table 1). Observed temperature trends are in agreement with previously reported proximate analysis results for biochars produced from manure.<sup>1–3</sup>

For all samples in Table 1, Pb and Sb contents were below the detection limit. Wet basis contents of all elements in Table

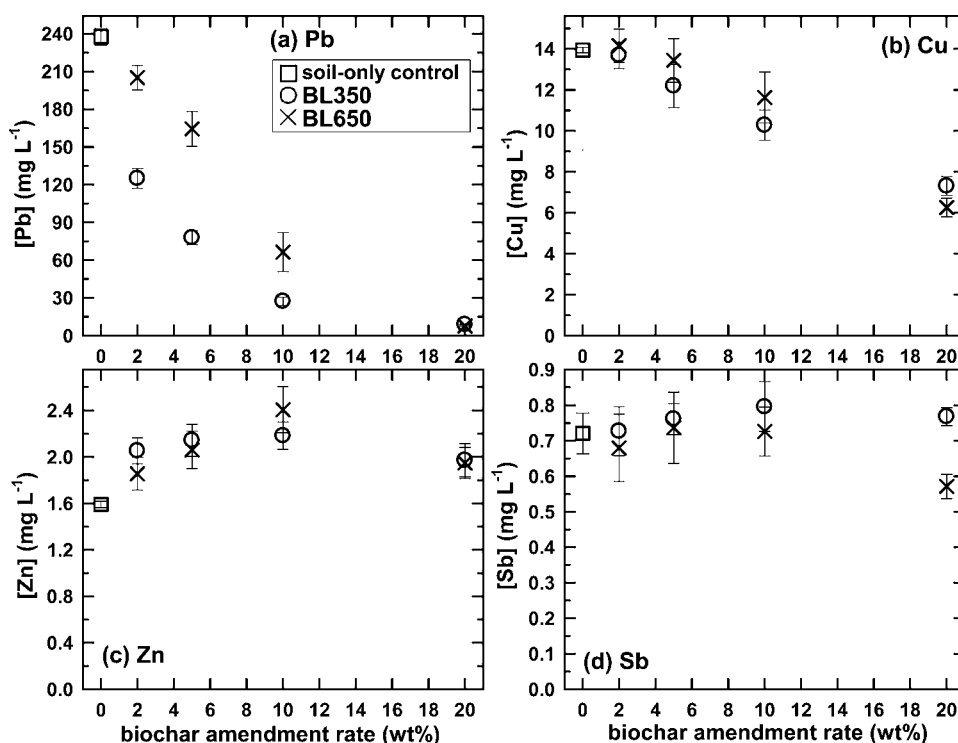


**Figure 2.** Soluble P, K, Mg, Na, and Ca concentrations as a function of total available amount in biochar. Soluble concentrations ( $y$ -axis in mean  $\pm$  SD for duplicate experiments) were determined after 1 week of equilibration of MD2 (20 g soil L<sup>-1</sup>) with 2–20 wt % BL350 and BL650 in weak acid (pH 4.5 sulfuric acid). Total amounts in biochar ( $x$ -axis) were calculated using values in Table 1 and the biochar amendment rate. Lines represent linear regression for BL350 (solid) and BL650 (dash). Values in parentheses are SD for the slope and intercept.

1 increased when broiler litter was pyrolyzed at 350 °C. Pyrolysis at 500 °C resulted in a further increase for all elements in Table 1. Additional increase in pyrolysis temperature resulted in a negligible change (within the error range) for 500–650 °C, except for a slight increase in Cu (Table 1). An increase from 650 to 800 °C resulted in a dramatic decrease in P content, whereas other elements were within the error range (Table 1). Phosphorus-containing compounds are known to vaporize near 760 °C.<sup>23</sup> To understand how the elemental composition of biochar affects the heavy metal stabilization ability, BL350 and BL650 were selected for the soil incubation studies to represent biochars containing lowest (BL350) and highest (BL650) P, Ca, K, Mg, Na, Cu, and Zn (Table 1).

Animal waste is among the highest ash-containing biomass enriched in CaO (57 wt % by high-temperature ash analysis for chicken litter), P<sub>2</sub>O<sub>5</sub> (15%), and K<sub>2</sub>O (12%).<sup>24</sup> Pyrolysis results in the enrichment of some elements in the biochar product and volatilization loss of other elements. For example, phosphorus is commonly used as a flame retardant to increase the char yields for textiles and wood,<sup>25</sup> and char product becomes

enriched with phosphorus, compared to the feedstock.<sup>3</sup> Pyrolysis of mallee tree at 350–750 °C resulted in an enrichment of alkali and alkaline earth metals (AAEM; Na, K, Mg, Ca) and P in biochar, as opposed to a substantial loss of S, N, and Cl.<sup>26</sup> For wastewater sludge containing 34% ash, greater pyrolysis temperature (300–700 °C) increased Ca, Fe, Mg, S, Cu, and Zn contents.<sup>27</sup> In contrast, Cr, Ni, Pb contents were increased up to 500 °C and then decreased by a further temperature increase (500–700 °C), and the greatest loss was observed for Cr.<sup>27</sup> Pyrolysis of coal resulted in volatilization of Na and Cl separately (most likely as carboxylate complexes), and monovalent species (Na) was volatilized more easily than divalent species (Mg, Ca).<sup>28</sup> In addition to the changes in the total amount of each element, pyrolysis of biomass significantly affects the chemical speciation and bioavailability of plant nutrients such as P and K.<sup>29,30</sup> For example, pyrolysis at 450 °C decreased the water-soluble P fraction of sewage sludge from >60 to <20%.<sup>30</sup> Calcium-bound P phases (HCl-extractable) increased to >30% in the char fraction, whereas Fe- and Al-bound fractions (NaOH extractable) did not change signifi-



**Figure 3.** Soluble Pb, Cu, Zn, and Sb concentrations after 1 week of equilibration of MD2 (20 g soil L<sup>-1</sup>) amended with 2, 5, 10, and 20% (g biochar g<sup>-1</sup> soil) BL350 and BL650 in pH 4.9 acetate buffer. Values are given as the mean  $\pm$  SD for duplicate experiments.

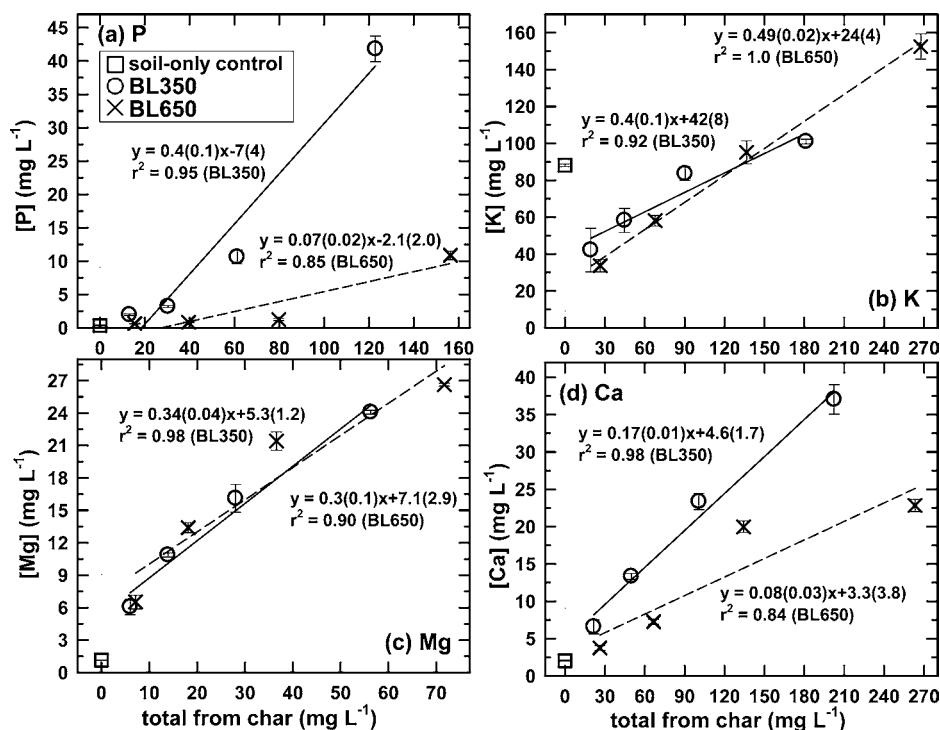
cantly.<sup>30</sup> Fast pyrolysis of cornstraw increased exchangeable and acid-extractable K, at the expense of water-soluble K fractions.<sup>29</sup>

Ash analysis of biochar also provides a way of evaluating the fuel quality. Because the melting points of silicon oxides and calcium silicates are higher than those of potassium carbonate and potassium chloride, lower Si/K and Ca/K fuels are ideal for minimizing slagging and fouling problems during combustion.<sup>31</sup> Because K and other AAEM are water-soluble, leaching and washing pretreatments of biomass are employed to minimize slagging/fouling problems.<sup>32</sup> On the other hand, transition metals (Ni, Fe, Cu) as well as AAEM (especially Ca) catalyze the combustion and gasification of biochar, and washing can significantly diminish the oxidative reactivity of biochar.<sup>33</sup>

**Equilibration 1: Weak Acid Extraction.** Soil incubation experiments employed MD2 to represent a berm (that serves as a bullet backstop) soil containing a large amount of highly bioavailable Pb carbonate phases. Figure 1 presents solution phase Pb, Cu, Zn, and Sb concentrations and pH after 1 week of equilibration of MD2 in weak acid (DDW adjusted to pH 4.5 using sulfuric acid). The x-axis represents the amendment rates: 0 wt % control (soil-only as squares) and 2–20 wt % (BL350 and BL650). All values are given as the mean  $\pm$  SD for duplicate experiments to allow analysis of variance for different treatment conditions. Figure 1 is dedicated to elements that were stabilized (Pb, Cu, Zn) or unaffected (Sb) by the biochar amendment. For elements that were stabilized by biochars (Pb, Cu, Zn), no clear influence of pyrolysis temperature or amendment rate was observed (Figure 1). The lowest (2 wt %) amendment rate allowed as much as an order of magnitude decrease in soluble concentrations (for Zn in Figure 1c). Greater Cu and Zn contents of BL650 (compared to BL350, Table 1) did not influence the soluble concentrations in MD2. In Table 1, Pb and Sb contents were below the detection limit for both BL350 and BL650.

Figure 1e provides the pH corresponding to Figure 1a–d. Pyrolysis of broiler litter at 650 °C resulted in an increase in ash content from 29.3  $\pm$  0.7 wt %<sub>db</sub> (before pyrolysis) to 54.3  $\pm$  0.2 wt %<sub>db</sub> (after pyrolysis). Heat-induced formation of potassium and sodium hydroxides and magnesium and calcium carbonates and the breakdown of acidic functional groups cause alkaline pH.<sup>23</sup> As a result, 2–20 wt % amendment of BL650 increased the pH of the soil suspension (6.2 without biochar) to as high as 10 (20 wt % amendment rate). Compared to BL650, BL350 contained much lower ash (35.48  $\pm$  0.04 wt %<sub>db</sub>) and the pH increase was less significant (7.5 at the highest amendment rate, 20 wt %; Figure 1e). Comparison of pH and Pb, Cu, and Zn stabilization in Figure 1 indicates similar effectiveness of BL650 and BL350 despite as much as a 3 pH unit difference at higher amendment rates. This result suggests controlling factors other than pH. The elemental composition of MD2 (in  $\mu\text{g g}^{-1}$  for three to five subsamples) was 19906  $\pm$  371 for Pb, 1727  $\pm$  35 for Cu, 157  $\pm$  1.6 for Zn, and 91  $\pm$  1.1 for Sb.<sup>9</sup> This order generally agrees with the soluble Pb, Cu, and Zn concentrations without biochar (squares in Figure 1). As widely discussed,<sup>10</sup> the mobility and bioavailability of Pb and other heavy metals in soils depend not only on the total amount but their chemical speciation and the release kinetics.

To understand the role of P and other elements in observed Pb, Cu, and Zn stabilization (Figure 1), Figure 2 presents soluble concentrations of additional selected elements (P, K, Na, Mg, Ca) corresponding to Figure 1. In Figure 2, solution phase concentrations of each element (y-axis as the mean  $\pm$  SD for duplicate experiments) are plotted as a function of total amount that can originate from BL350 or BL650 (x-axis). The values on the x-axis were calculated using the elemental composition for BL350 and BL650 presented in Table 1 (on a wet basis) and the biochar amendment rate (2–20 wt %). Lines in Figure 2 represent linear regression for each element and



**Figure 4.** Solution phase P, K, Mg, and Ca concentrations after 1 week of equilibration of MD2 (20 g soil L<sup>-1</sup>) amended with 2, 5, 10, and 20% (g biochar g<sup>-1</sup> soil) BL350 and BL650 in pH 4.9 acetate buffer. Soluble concentrations (y-axis in mean  $\pm$  SD for duplicate experiments) were plotted versus total available amount in biochar (x-axis). The values on x-axis are the same as in Figure 2 and were not corrected for the loss during weak acid extraction. Lines represent linear regression for BL350 (solid) and BL650 (dash).

biochar (solid line for BL350; dashed line for BL650), and squares show soluble concentrations determined in the soil-only control. The coefficient of determination for the linear regression ( $r^2$  in Figure 2) was  $>0.57$  for all elements, except for Ca in the presence of BL650 (Figure 2e).

In Figure 2, a greater slope indicates greater soluble concentration for a given total content (based on the elemental composition and amendment rate) of char. For each linear regression in Figure 2, values in parentheses represent the standard deviation for the slope and intercept. Comparison of slopes in Figure 2 indicates consistently greater release of each element by BL350 (solid line) than BL650 (dashed line) for a given biochar amendment rate (2–20 wt %). The results indicate a greater ability of lower temperature pyrolyzed biochar to release P, K, and other elements that are of nutrient value to agricultural crops. For both BL350 and BL650, the following increasing release trend was observed (based on the slopes in Figure 2): Ca < Mg  $\approx$  P < Na < K. For K (especially BL350, and BL650 to a lesser extent; Figure 2b) and Na (BL350, Figure 2d), the slope was close to 1.0, indicating that the majority of BL350-borne K and Na were soluble (note MD2 contained a significant amount of K, squares in Figure 2b). In contrast, the slope was slightly negative for Ca in the presence of BL650, indicating that a greater BL650 amendment resulted in the consumption of soluble Ca. Low  $r^2$  and slope values were also observed for Ca in the presence of BL350 and for Mg in the presence of BL650. For P, Mg, and Ca, the slope was 0.12 or lower for both BL350 and BL650, indicating much lower solubility compared to Na and K. Considering the higher Ca and Mg contents of BL650 than of BL350 (Table 1), lower soluble Mg and Ca concentrations for BL650 likely resulted from (1) the stability of Mg and Ca species (especially carbonates<sup>23</sup>) formed at higher pyrolysis temperature; (2) the

exchange between the biochar's Ca and Mg (Table 1) and the soil's Pb, Cu, and Zn (Figure 1); and (3) the Mg and Ca stabilization induced by the higher pH of BL650 (Figure 1e). The high pH condition of BL650 amended system (Figure 1e) can also stabilize hydroxyapatite (HAP; Ca<sub>10</sub>(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>·5H<sub>2</sub>O) phases.<sup>34</sup> However, Mg<sup>2+</sup> can covalently interact with PO<sub>4</sub><sup>3-</sup> and inhibit the HAP formation.<sup>34</sup> These calcium and magnesium phosphate phases can cause BL650 amendment rate-independent Ca and Mg concentrations in Figure 2c,e. Element-specific release behaviors in Figure 2 are in agreement with previous results for biochars in aqueous media without soil.<sup>26,29</sup> Triplicate overnight washing of mallee tree biochars (pyrolyzed at 350–750 °C) in DDW resulted in as much as  $>90\%$  leaching of K, Na, and Cl and much lower leaching of S, P, and Mg.<sup>26</sup> Release of P, Ca, and Mg from fast pyrolysis biochar proceeded via initial (24 h) rapid pH-dependent kinetics, followed by a pH-independent zero-order kinetics.<sup>29</sup>

**Equilibration 2: Acetate Buffer Extraction.** Figure 3 presents soluble Pb, Cu, Zn, and Sb concentrations after subsequent 1 week of equilibration in pH 4.9 acetate buffer (0.1 M). Results in Figure 3 were obtained using the TCLP extraction fluid; however, the standard TCLP procedure (an 18 h mixing period at a liquid-to-solid ratio of 20)<sup>35</sup> was not employed. The regulatory limit for Pb by TCLP extraction is 5 mg L<sup>-1</sup>. The pH of the soil suspension was  $5.1 \pm 0.1$  for the 18 batch experiments presented in Figure 3. This is as much as a 5 pH unit decrease (for BL650) from the without-buffer case in Figure 1. In acetate buffer (Figure 3), soluble concentrations of Pb and Cu in soil-only control were several orders of magnitude higher than without buffer (Figure 1). Acetate, like other organic ligands (especially at high concentration), causes Pb and Cu desorption from soil with and without biochar.<sup>36</sup> In Figure 3, the total amount of each element in soil

(Pb > Cu > Zn > Sb)<sup>9</sup> followed the trend for soluble concentrations.

In acetate buffer, Zn stabilization was no longer observed (Figure 3c). The acidic pH of acetate buffer can cause Zn desorption in biochar-amended soils. Compared to Pb<sup>2+</sup> and Cu<sup>2+</sup>, Zn<sup>2+</sup> is a harder acid that is less easily stabilized by softer phosphate ligands. To illustrate the relative affinity of Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> toward phosphate ligands, stability constants were obtained for model ligands: CH<sub>3</sub>-O-PO<sub>3</sub><sup>2-</sup>, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-PO<sub>3</sub><sup>2-</sup>, phenyl phosphate, and ribose-5-phosphate.<sup>37</sup> The following increase in stability constant was consistently observed (Table S1, Supporting Information): Zn<sup>2+</sup> < Cu<sup>2+</sup> < Pb<sup>2+</sup>. Greater affinity toward phosphate ligands can cause the stabilization trends (Zn < Cu < Pb) in Figures 1 and 3. The high affinity of Pb for phosphate-based ligands (to form Pb phosphate precipitates) is a well-described stabilization mechanism for phosphorus-rich amendments including manure biochars.<sup>6</sup>

Compared to Pb and Cu, Sb concentrations were independent of biochar amendment rate in both weak acid and acetate buffer extraction steps (Figures 1 and 3). In analogous experiments,<sup>13</sup> oxidized, carboxyl-rich biochars decreased the concentrations of cations (Pb, Cu, and Zn) to a much greater extent than unoxidized biochars. Oppositely, only oxidized biochars increased the oxoanion (Sb) concentration. Cations are able to form complexes with carboxyl functional groups on the surface of oxidized biochars.<sup>12</sup> Antimony oxoanions cannot form complexes with negatively charged carboxyl functional groups of oxidized biochars (above PZC). Repulsive electrostatic interactions<sup>12</sup> between anions and biochar/soil surfaces can result in desorption of Sb. Similarly, hardwood biochar increased soluble As (that existed predominantly in anionic forms) concentration by as much as 30-fold, concurrently with the stabilization of Cd and Zn.<sup>38</sup> A previous study reported Sb desorption by apatite amendments on a sandy SAR soil.<sup>39</sup> Desorption of Sb has been attributed to the competition between negatively charged phosphate (as well as carbonate) and antimony (Sb<sup>V</sup>(OH)<sub>6</sub><sup>-</sup>) species for available sorption sites.<sup>40</sup> In contrast, iron (hydr)oxides stabilize Sb<sup>V</sup> in soil by the formation of inner-sphere surface complexes.<sup>41</sup> Likewise, ash components of biochar (e.g., Al<sub>2</sub>O<sub>3</sub>, MgO) may prevent desorption of Sb despite high phosphate concentration.

Similarly to Figure 1, BL350 and BL650 stabilized Pb and Cu in acetate buffer (Figure 3). A clear correlation was observed between Pb and Cu stabilization and the biochar amendment rate, in a distinct fashion from Figure 1 (without buffer). A similar transition in the amendment rate dependence was observed in analogous experiments conducted using oxidized and unoxidized plant-based biochars.<sup>13</sup> Figure 3 also shows the greater ability of BL350 to stabilize Pb, relative to BL650 (especially for 2–5 wt % amendment rates), whereas Cu concentrations stayed within the error range for BL350 and BL650. Because the pH was buffered at 5.1 ± 0.1, additional factors, such as the amount of leachable elements (especially P), likely caused the temperature dependence in Figure 3a.

Figure 4 presents soluble P, K, Mg, and Ca concentrations corresponding to Figure 3 (mean ± SD for duplicate experiments). Similarly to Figure 2, soluble concentrations were plotted as a function of the total contents in BL350 and BL650 at each amendment rate. On the *x*-axis, no corrections were made for the loss during preceding equilibration in pH 4.5 sulfuric acid solution (weak acid extraction in Figure 2). The Na concentration was 48 ± 6 mM for all experiments in Figure

4, because of the 100 mM acetate buffer used in this equilibration period. In a striking contrast to weak acid extraction (Figure 2), soluble Mg and Ca concentrations linearly increased with the biochar amendment rate in acetate buffer (Figure 4). This is most likely due to the dissolution of Mg and Ca carbonate/phosphate phases under acidic conditions.<sup>42</sup> A higher soluble P concentration of BL350 (relative to BL650, Figure 4a; note much less significant temperature effects on soluble K, Mg, Ca concentrations) is a likely the cause of greater Pb stabilization (Figure 3a) by the formation of stable lead phosphate phases.<sup>5</sup>

To visualize the pH effects, solution phase P, K, Mg, and Ca concentrations in the first equilibration step without buffer (Figure 2) are provided in the same scale as the second equilibration step in acetate buffer (Figure 4) in Figures S1–S2 of the Supporting Information. A dramatic pH decrease in acetate buffer resulted in higher Ca (Supporting Information, Figure S1c-d) and Mg (Supporting Information, Figure S2c-d) concentrations for both BL350 and BL650. In contrast, soluble K concentrations were significantly lower in acetate buffer than weak acid (Supporting Information, Figure S1a-b), because the majority of the biochar's K dissolved during the initial equilibration in weak acid (Figure 2b). For P, the solution phase concentration in acetate increased for BL350 and did not change significantly for BL650 (Supporting Information, Figure S2a-b). Solution pH controls the dissolution kinetics of P-containing minerals, for example, variscite, strengite, apatite and their precursors, as well as adsorption properties of major P-fixing minerals such as aluminum and iron (hydr)oxides and clay minerals.<sup>43</sup> In addition, Ca, Mg, and other cations promote P adsorption by decreasing repulsive interactions between phosphorus ions and mineral surfaces.<sup>43</sup> Greater effects of pyrolysis temperature on soluble P concentration in acetate buffer (compared to weak acid; Supporting Information, Figure S2), likely caused the temperature-dependent Pb stabilization (Figure 3a).

In analogous experiments conducted using oxidized and unoxidized plant-based biochars,<sup>13</sup> the pH decrease from the first to second extraction step minimally affected the K, Ca, P, and Mg concentrations. These results are attributable to much lower ash content of plant-based biochars (≤10 wt %),<sup>13</sup> compared to manure biochars employed in this study (>35 wt %, Table 1). Ash in manure contains higher P<sub>2</sub>O<sub>4</sub> and lower SiO<sub>2</sub>, compared to the plant biomass.<sup>24</sup> The greater P release by BL350 (relative to BL650, Figure 4a) is in agreement with nearly an order of magnitude greater bioavailable (Colwell; pH 8.5 sodium bicarbonate<sup>44</sup>) P content of poultry litter biochar produced at 450 °C than the steam-activated 550 °C biochar.<sup>45</sup> In contrast, Mehlich I (50 mM HCl + 12.5 mM H<sub>2</sub>SO<sub>4</sub>) P did not significantly differ for poultry litter biochars produced at 400 and 500 °C.<sup>46</sup> However, for both biochars, steam activation decreased the Mehlich I P concentrations.<sup>46</sup> In a separate study, Mehlich I P was higher for poultry litter biochar formed at 700 °C than at 350 °C.<sup>3</sup> Thermal treatment, for example, forest fire, converts organic phosphorus to more bioavailable orthophosphate.<sup>23,47</sup> Thermal treatment of orthophosphate in turn results in a less soluble polyphosphate species.<sup>47</sup> These mineralization, or ashing, processes lead to an increase in available P immediately after a fire; however, this increase is often short-termed and leads to the long-term P loss and reduced forest productivity.<sup>47</sup> Although limited information is available on P speciation of manure biochars, acidulation<sup>48</sup> and other pretreatments such as blending with more soluble fertilizer

and compost<sup>49</sup> may be necessary to fully utilize less soluble P of manure biochars under alkaline conditions.

**In Vitro Bioaccessibility Analyses.** Table 2 provides in vitro bioaccessibility analysis results for MD2 with and without

**Table 2. In Vitro Bioaccessibility Testing Results for Small Arms Range Soils (MD1 and MD2) Amended with 350 °C (BL350) and 650 °C (BL650) Broiler Litter Biochars, 800 °C Cottonseed Hull Biochars (CH800), and Flax Shive Steam-Activated Biochars (flax) without and with (CH800-ox, Flax-ox) Oxidation<sup>a</sup>**

char	amendment rate (wt%)	in vitro (%)
<b>MD2<sup>b</sup></b>		
soil-only		98 ± 3
BL350	2	107.3 ± 0.3
	5	112 ± 1
	10	103 ± 10
	20	104 ± 1
BL650	2	107 ± 3
	5	114 ± 2
	10	112 ± 5
	20	94.1 ± 0.5
<b>MD1<sup>c</sup></b>		
soil-only		109 ± 3
CH800	10	94 ± 2
	20	105 ± 4
CH800-ox	2	104 ± 13
	5	101 ± 8
	10	82 ± 4
	20	79 ± 2
flax	10	106 ± 1
	20	106 ± 2
flax-ox	2	102 ± 5
	5	95 ± 6
	10	106 ± 18
	20	118 ± 11

<sup>a</sup>Results are given as the total Pb extracted in weak acid (1 week in pH 4.5 sulfuric acid), acetate buffer (1 week in pH 4.9 acetate buffer), and in vitro bioaccessibility procedure (pH 1.5 for 1 h at 37 °C). <sup>b</sup>pH 6.11, 1.966% TOC, 1.1 cmol<sub>c</sub> kg<sup>-1</sup> CEC, 19906 ± 371 μg g<sup>-1</sup> total Pb; ≈80% Pb existed as PbCO<sub>3</sub>, and <20% associated with FeOOH or with PbOOH, PbO, and PbSO<sub>4</sub>. <sup>c</sup>pH 6.27, 0.518% TOC, 0.95 cmol<sub>c</sub> kg<sup>-1</sup> CEC, 14847 ± 193 μg g<sup>-1</sup> total Pb; ≈80% Pb existed as PbCO<sub>3</sub>, and <10% associated with TiO<sub>2</sub>, FeOOH, and clay, or with PbOOH, PbO, and PbSO<sub>4</sub>.

2–20 wt % BL350 and BL650. Table 2 also provides results for a closely related sandy SAR soil sample (MD1). Compared to MD2, MD1 had slightly higher pH (6.27), lower TOC (0.518%), and lower CEC (0.95 cmol<sub>c</sub> kg<sup>-1</sup>).<sup>9</sup> The total Pb concentration of MD1 (14847 ± 193 μg g<sup>-1</sup>) was similar to that of MD2, and Pb existed primarily (≈80% by electron microprobe) in PbCO<sub>3</sub> phases with minor fractions (<10%) associated with TiO<sub>2</sub>, FeOOH, and clay and in PbOOH, PbO, and PbSO<sub>4</sub> phases.<sup>9</sup> The MD1 was amended with oxidized (CH800-ox, flax-ox) and unoxidized 800 °C cottonseed hull biochar (CH800) and flax shive steam-activated biochar (flax)<sup>13</sup>

and was exposed to the same equilibration periods as MD2 (1 week of weak acid, 1 week of acetate buffer, and in vitro bioaccessibility procedure). The bioaccessibility results for closely related soil samples (MD1 and MD2) will allow comparison between manure and plant-derived biochars. The CH800-ox and flax-ox are expected to affect results in Table 2 by complexing Pb via abundant carboxyl functional groups,<sup>13</sup> whereas BL350 and BL650 are likely to stabilize Pb by the formation of pyromorphite and other lead phosphate phases.<sup>5</sup>

The values for MD2 and MD1 soil-only controls are close to the literature values (94 ± 2 for MD1, 98 ± 2 for MD2)<sup>9</sup> obtained using dry soil samples (without preceding weak acid and acetate buffer equilibration steps employed in Figures 1–4). Regardless of the amendment rate and biochar type, biochars did not decrease the Pb bioaccessibility of MD1 and MD2 soils in the gastric phase (pH 1.5 for 1 h at 37 °C, Table 2). The nature (weathering of spent bullets) and amount (>14000 mg kg<sup>-1</sup>) of Pb contamination, as well as poor Pb retention abilities (sandy, acidic, low CEC, and low TOC) of MD1 and MD2 soils resulted in >80% PbCO<sub>3</sub> phases<sup>9</sup> that are soluble in strongly acidic simulated stomach solution employed in Table 2. Gastric phase Pb bioaccessibility results for MD1 and MD2 (soil-only) closely agreed with in vivo juvenile swine bioavailability results.<sup>9</sup> Lead bioavailability for MD1 and MD2 soils are at the highest end<sup>9</sup> compared to urban<sup>5</sup> and other types of Pb contaminated soils where Pb bioaccessibility ranged from 10 to 90%.

Previous daily manure biochar (450 °C) amendment (2.5 and 5 wt %) study showed the stabilization of Pb in shooting range (pH 7.1, CEC 13.5 cmol<sub>c</sub> kg<sup>-1</sup>) and battery recycling (pH 6.9, CEC 21.3 cmol<sub>c</sub> kg<sup>-1</sup>) soils during 210 days of incubation in CaCl<sub>2</sub> and TCLP.<sup>6</sup> Biochar also suppressed Pb uptake by earthworms (after 15 days) in the battery recycling soil containing 5000 mg kg<sup>-1</sup> Pb, but not in the shooting range soil containing 14-fold greater Pb (70000 mg kg<sup>-1</sup>).<sup>6</sup> No live earthworms were found after 15 days of exposure to the shooting range soil, and bioavailable Pb likely reached threshold for earthworm mortality (100 mg kg<sup>-1</sup> body load),<sup>50</sup> regardless of biochar amendment because of excessive Pb contamination.<sup>6</sup> Similarly, phosphorus-rich broiler litter biochars stabilized Pb in MD2 (Figures 1 and 3), but did not influence Pb bioaccessibility in the gastric phase (Table 2). In vitro Pb bioaccessibility procedure assumes that low pH mobilizes Pb in stomach, which is then absorbed in the small intestine (pH 6.5).<sup>10</sup> Gastric phase extraction (Table 2) alone does not fully address Pb bioavailability in the presence of biochar, especially at higher pH<sup>5</sup> lower in the intestine. Further bioavailability and bioaccessibility studies are necessary to fully address the effectiveness of biochar for decreasing Pb bioavailability by the formation of pyromorphite phases<sup>5</sup> and other mechanisms.

In conclusion, broiler litter biochars were able to stabilize Pb and Cu in a SAR soil at a practical (≤5 wt %) amendment rate without causing the desorption of Sb (Figures 1 and 3). Therefore, manure biochars can be particularly useful for remediation of sites where oxoanion-forming elements such as Sb and As are potential risk drivers. However, compared to plant-derived biochar engineered to have high carboxyl contents,<sup>13</sup> a higher amendment rate (>10 wt %) may be required to bring the Pb level below the regulatory limit (5 mg L<sup>-1</sup> by TCLP extraction). When additional phosphorus input is beneficial as a plant nutrient (instead of adding to existing excess phosphorus problems), soluble phosphorus concentrations (Figures 2 and 4) can provide an initial screening



parameter for utilizing manure biochars for Pb stabilization in contaminated soils.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Stability constants for phosphate-based ligands and comparison of soluble K, Ca, P, and Mg concentrations for weak acid and acetate buffer extractions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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The authors declare no competing financial interest.

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