

## Immobilization of Heavy Metal Ions (Cu<sup>II</sup>, Cd<sup>II</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup>) by Broiler Litter-Derived Biochars in Water and Soil

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Chars, a form of environmental black carbon resulting from incomplete burning of biomass, can immobilize organic contaminants by both surface adsorption and partitioning mechanisms. The predominance of each sorption mechanism depends upon the proportion of organic to carbonized fractions comprising the sorbent. Information is currently lacking in the effectiveness of char amendment for heavy metal immobilization in contaminated (e.g., urban and arms range) soils where several metal contaminants coexist. The present study employed sorbents of a common biomass origin (broiler litter manure) that underwent various degrees of carbonization (chars formed by pyrolysis at 350 and 700 °C and steam-activated analogues) for heavy metal (Cd<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup>) immobilization in water and soil. ATR-FTIR, <sup>1</sup>H NMR, and Boehm titration results suggested that higher pyrolysis temperature and activation lead to the disappearance (e.g., aliphatic –CH<sub>2</sub> and –CH<sub>3</sub>) and the formation (e.g., C–O) of certain surface functional groups, portions of which are leachable. Both in water and in soil, pH increase by the addition of basic char enhanced the immobilization of heavy metals. Heavy metal immobilization resulted in nonstoichiometric release of protons, that is, several orders of magnitude greater total metal concentration immobilized than protons released. The results suggest that with higher carbonized fractions and loading of chars, heavy metal immobilization by cation exchange becomes increasingly outweighed by other controlling factors such as the coordination by  $\pi$  electrons (C=C) of carbon and precipitation.

**KEYWORDS:** Biochar; heavy metals; soil; pH; broiler litter; activated carbon

### INTRODUCTION

Chars are a form of environmental black carbon (BC), a ubiquitous geosorbent found in soils and sediments as a result of incomplete burning of carbon-rich biomass (1). In recent years, chars have received considerable interest as a large-scale soil amendment to improve soil fertility, crop production, and nutrient retention and to serve as a recalcitrant carbon stock (2). Chars are resistant to chemical/biological degradation and are estimated to have mean residence times of thousands of years in soils (3). Chars contain functional surface groups, for example, carboxylic, phenolic, hydroxyl, carbonyl, and quinones (4), and porous structures that significantly affect essential soil properties such as cation exchange capacity (CEC), pH, and retention of water and nutrients (2). The physical and chemical properties of chars vary significantly depending on the biomass source, pyrolysis conditions, and post- and pretreatments, and fundamental knowledge of the sorption mechanism is in demand for engineering chars for specific environmental applications.

Extensive studies have been conducted to determine the sorption mechanisms of organic contaminants on chars. Chars sorb organic contaminants such as atrazine (5) via two distinct

mechanisms: (1) surface adsorption on carbonized fractions and (2) partitioning into the residual (noncarbonized) organic fraction. In the surface adsorption mechanism,  $\pi$ -systems of BC exhibit a substantial sorptive potential for aromatic sorbates via specific, noncovalent electron donor–acceptor interactions distinct from hydrophobic interactions (6). The partitioning mechanism is dominant for chars formed at low pyrolytic temperatures that contain high organic fractions (7).

In comparison to organic contaminants, limited information is available on the factors controlling the immobilization of inorganic contaminants on BC and the impact of BC on heavy metal retention in soils. Studies employing activated carbons have suggested that depending on the solution composition and the carbon type, the following mechanisms predominate: (1) electrostatic interactions between metal cations and negatively charged carbon surface (above pH<sub>pzc</sub> of carbon), (2) ionic exchange between ionizable protons at the surface of acidic carbon and metal cations, and (3) sorptive interaction involving delocalized  $\pi$  electrons of carbon (8). Interaction at delocalized  $\pi$  electrons is particularly important for metal sorption by basic carbon via proton exchange (–C $\pi$ –H<sub>3</sub>O<sup>+</sup>) (8) or coordination of d-electrons (5). Mineral impurities (ash) and basic nitrogen groups (e.g., pyridine) can serve as additional adsorption sites of the carbonaceous materials (9). Solution pH is an essential

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parameter that affects both the surface charge density of the carbon and the metal ion speciation (8).

Heavy metal pollutants such as  $\text{Cd}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  often coexist in contaminated urban (10) and arms range (11) soils, and their mobility is of global concern. The objective of this study was to systematically determine the impact of char amendment in soil and water containing several heavy metals. Chars formed by pyrolysis of broiler litter manure at 350 and 700 °C (350BL and 700BL) and steam-activated analogues (350ABL and 700ABL) were systematically characterized by ATR-FTIR,  $^1\text{H}$  NMR, Boehm titration, and BET surface area analyses. Then, a mixture of four divalent metal ions ( $\text{Cd}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$ ) was screened for immobilization on biochars in water. Subsequently, selected metal ions were tested for mobility in soil amended with 5–20% (w/w) chars. Thermodynamic considerations for the metal speciation were given to understand the impacts of pH rise by the addition of basic chars and complexation on the immobilization of inorganic contaminants.

## MATERIALS AND METHODS

**Chemicals.** All chemical reagents were of the highest purity commercially available. Lead(II) nitrate, nickel(II) nitrate, copper(II) chloride dehydrate, cadmium(II) nitrate tetrahydrate, sodium chloride, and sodium hydroxide were purchased from Sigma-Aldrich (Milwaukee, WI). Distilled, deionized water (DDW) with a resistivity of 18  $\text{M}\Omega\cdot\text{cm}$  (Millipore Corp., Milford, MA) was used for all procedures. Stock solutions (0.2 M) of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , and  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  were prepared in DDW.

**Biochar Source and Preparation.** Collection and handling of broiler litter manure samples, pyrolysis conditions, and surface area measurement are described in a previous paper (12). Briefly, broiler litter samples were obtained from the USDA-ARS Poultry Research Unit (Starkville, MS), milled to < 1 mm (< 25% moisture content), pelletized to cylinders of 4.8 mm diameter and 4.8 mm length, and pyrolyzed at either 350 or 700 °C for 1 h under 0.1  $\text{m}^3 \text{h}^{-1}$  nitrogen flow. The resulting chars (350BL and 700BL) were allowed to cool to room temperature overnight in the retort. Activated analogues of 350BL and 700BL (350ABL and 700ABL, respectively) were prepared by steam activation at 800 °C for 45 min at 3 mL  $\text{min}^{-1}$  steam flow, following the pyrolysis step. Pyrolyzed samples were washed with 0.1 M HCl (27 g of char  $\text{L}^{-1}$ ) by constant stirring for an hour, rinsed three times with DDW, dried overnight at 80 °C, and then ground and sieved to < 44  $\mu\text{m}$  (325 mesh).

Surface areas were measured in duplicate by nitrogen adsorption isotherms at 77 K using a Nova 2000 surface area analyzer (Quantachrome Corp., Boynton Beach, FL). Specific surface areas were determined from adsorption isotherms using the Brunauer, Emmett, and Teller (BET) equation. Moisture contents were determined as the weight loss after 2 h of sample degassing under vacuum at 200 °C.

**Boehm Titration.** The pH of aqueous char suspension (10 g  $\text{L}^{-1}$ ) was set to 5.0 using 0.1 M HCl. After stirring for 24 h, sample was dried at 80 °C, and 10 mL of 0.1 M base ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ , or  $\text{NaHCO}_3$ ) was added to make 10 g  $\text{L}^{-1}$  char suspension. After stirring for 24 h, char suspension was filtered (0.45  $\mu\text{m}$  Millipore Millex-GS; Millipore Corp., Billerica, MA), and 10 mL of 0.1 M HCl was added to 5 mL of filtrate. The resulting solution was titrated with 0.1 M NaOH (Titrande 835 autotitrator, Metrohm ion analysis, Herisau, Switzerland). Blanks were prepared by adding 5 mL of 0.1 M base titrant to 10 mL of 0.1 M HCl. Surface acidity (in  $\text{mequiv g}^{-1}$ ) was determined on the basis of the following assumptions: (1)  $\text{NaHCO}_3$  neutralizes only strong (primarily carboxylic) acids; (2)  $\text{Na}_2\text{CO}_3$  neutralizes moderate acid, primarily low  $\text{p}K_a$  phenols and hydrolysis products of lactones, in addition to strong acids; and (3) NaOH neutralizes all organic acids with  $\text{p}K_a < 12$ , including high  $\text{p}K_a$  phenols (13).

**ATR-FTIR and  $^1\text{H}$  NMR Analyses.** Attenuated total reflectance Fourier transform infrared spectra (Bruker Optics Tensor 27 FTIR spectrometer equipped with a diamond crystal; Bruker Optics, Billerica, MA) for chars were obtained after adjustment of the pH to 3.0 and overnight drying at 70 °C; manure was analyzed without pH adjustments. Spectra were obtained in triplicate (64 scans each) for each sample at 4  $\text{cm}^{-1}$  resolution from 650 to 4500  $\text{cm}^{-1}$ .

The organic fraction of 350BL was base-extracted (14) by (1) shaking the char suspension (9.5 g  $\text{L}^{-1}$ ) end-over-end at 85 rpm in 0.1 M NaOH for 24 h, (2) centrifugation at 10000 rpm for 10 min at 20 °C, (3) filtering (0.2  $\mu\text{m}$ ) and acidifying the supernatant to pH 5.0 using 1 M HCl, and (4) drying for 24 h at 65 °C. The resulting extracts were dissolved in  $\text{D}_2\text{O}$  and analyzed by  $^1\text{H}$  NMR (Varian Unity 400 spectrometer, 400 MHz) at ambient probe temperature. Tetramethylsilane in organic solvent and HOD (4.80 ppm) in  $\text{D}_2\text{O}$  were used as the internal references.

**Immobilization of  $\text{Cd}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  by Char in Water.** Separate suspensions (5 g  $\text{L}^{-1}$  in 0.01 M NaCl) were prepared in batch reactors for each char and manure. Suspensions were equilibrated for 24 h by shaking end-over-end at 70 rpm. After pH measurement (Orion 3-star plus benchtop pH meter, ThermoScientific, Waltham, MA),  $\text{Cd}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  were added together to each reactor, for the final concentration of 1.5 mM for each metal (i.e., each reactor contained 6 mM total added metals at  $t = 0$ ). Suspensions were shaken end-over-end at 70 rpm for 24 h and filtered (0.2  $\mu\text{m}$ ) immediately following the pH measurement. Filtrate was acidified to 4% (v/v) nitric acid (trace metal grade, Sigma-Aldrich) for the determination of metal ion concentrations using inductively coupled plasma optical emissions spectrometer (ICP-AES; Profile Plus, Teledyne/Leeman Laboratories, Hudson, NH). For each sorption experiment, performed in duplicate, ICP-AES measurements were made in triplicate for each element.

**Immobilization of  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  by Char Amendment in Soil.** All experiments involving soil were conducted using synthetic rain water (SRW) to simulate contaminant leaching by percolating rainfall (15). The SRW was prepared daily by adding 10 mM  $\text{H}_2\text{SO}_4$  to DDW until pH 4.5 was attained (16). San Joaquin NIST standard soil (2709a; NIST Standard Reference Materials, Gaithersburg, MD) in SRW (20 g of soil  $\text{L}^{-1}$ ) was equilibrated with 0, 5, 10, and 20% char (g of char/g of soil) for 24 h by shaking end-over-end at 70 rpm in amber glass vials. After pH measurement,  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  were added together to each reactor, for the final concentration of 1.5 mM for each metal (i.e., each reactor contained 4.5 mM total added metals at  $t = 0$ ). Samples were shaken end-over-end at 70 rpm for 24 h and, after pH measurement, filtered and acidified for ICP-AES analyses. Control experiments performed in the absence of metal ions indicated negligible soluble Cd, Ni, and Pb in soil and chars. Equilibrium total dissolved metal ion concentrations were calculated using HYDRAQL (17) equilibrium speciation software.

## RESULTS AND DISCUSSION

**Physical and Chemical Properties of Chars.** Table 1 provides BET surface area, micropore area and volume, and moisture content of chars. Higher pyrolysis temperature resulted in slightly higher surface area of 700BL compared to 350BL. Surface areas of chars in this study are significantly higher than those of dairy manure-derived char (5) and slightly lower than those of wheat residue-derived char (18) prepared under analogous pyrolysis temperatures. Steam activation resulted in a significant increase in surface area and micropore area and volume, and the values are comparable for 350ABL and 700ABL. Acid washing (0.1 M HCl) resulted in 16–28% (w/w) weight loss, indicating significant ash content of unwashed char samples (19). Ash removal by acid washing resulted in a significantly higher surface area for both 350BL and 700BL. Higher moisture contents of steam-activated chars relative to unactivated analogues correlate with higher surface area and micropore volume.

Table 2 reports the surface acidity of chars. Comparison of 350BL and 700BL indicates a decrease in total acidity (all organic acids with  $\text{p}K_a < 12$ , including high  $\text{p}K_a$  phenols (13)) and strong acid groups (mainly carboxylic acids) and an increase in weak (mainly high  $\text{p}K_a$  phenols) and moderate (low  $\text{p}K_a$  phenols and hydrolysis products of lactones) acid groups with pyrolysis temperature. Previous study on wheat residue-derived chars showed a sequential decrease in acidic functional groups (both total acidity and the strong acid group) with pyrolysis temperature (300–700 °C in 100 °C increments) (18). The observed trend was attributed to the removal of surface functional groups by

**Table 1.** Surface Area and Moisture Content of Char Samples<sup>a</sup>

char	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	micropore area (m <sup>2</sup> g <sup>-1</sup> )	micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	% water <sup>b</sup> (w/w)	% weight loss <sup>c</sup> (w/w)
350BL	59.5 ± 19.7	0	0	8.2 ± 0.4	16.3
700BL	94.2 ± 5.1	41.8 ± 2.0	0.018 ± 0.001	7.4 ± 1.1	22.0
350ABL	335.1 ± 6.6	276.7 ± 5.4	0.134 ± 0.001	12.7 ± 0.3	27.9
700ABL	335.3 ± 0.9	278.2 ± 3.5	0.136 ± 0.002	10.8 ± 0.2	27.9
350BL-unwashed	2.3 ± 1.9	4.3 ± 0.1	0.002		
700BL-unwashed	10.1 ± 1.2	2.6 ± 1.4	0.001 ± 0.001		

<sup>a</sup> Values are given as mean ± standard deviation for duplicate measurements. <sup>b</sup> Determined as the weight loss after 2 h of sample degassing under vacuum at 200 °C. <sup>c</sup> After washing in 0.1 M HCl.

**Table 2.** Boehm Titration Results

char	total acidity (mequiv g <sup>-1</sup> )	strong acid <sup>a</sup> (mequiv g <sup>-1</sup> )	moderate acid <sup>b</sup> (mequiv g <sup>-1</sup> )	weak acid <sup>c</sup> (mequiv g <sup>-1</sup> )
350BL	1.86	1.14	0.07	0.65
700BL	1.65	0.58	0.25	0.82
350ABL	1.97	0.66	0.28	1.03
700ABL	1.55	0.73	0.07	0.75

<sup>a</sup> Mainly carboxylic acids. <sup>b</sup> Low pK<sub>a</sub> phenols and hydrolysis products of lactones. <sup>c</sup> Mainly high pK<sub>a</sub> phenols.

carbonization of the organic source material (18). On the other hand, dairy manure-derived chars prepared at lower pyrolysis temperatures (200 and 350 °C) showed an increase in carboxyl groups with pyrolysis temperature (5). Therefore, pyrolysis temperature and activation have markedly different impacts on the amount of surface functional groups for manure-derived chars, compared to plant-derived chars.

**Figure 1** presents FTIR spectra of manure and biochars. The broad band near 3300 cm<sup>-1</sup> arises from the stretching vibration of hydroxyl groups and indicates significant hydrogen-bonding interactions (20). This band is observed for all sample studies, and the intensity increases in the following order: 350BL ≈ 350ABL < manure ≈ 700ABL < 700BL. Bands at 2940 and 2904 cm<sup>-1</sup> were assigned to -CH<sub>2</sub> and -CH<sub>3</sub> groups, respectively, of long-chain aliphatic components (20). Bands at 1373 and 1443 cm<sup>-1</sup> were assigned to -CH<sub>2</sub>- scissoring. These bands are observed only in manure and 350BL. The band at 1650 cm<sup>-1</sup> was assigned to C=O stretching vibrations of amides (20) and are observed in manure and 700BL. Amides and amines have been reported as nitrogen functional groups within broiler manure (21). A minor band at 876 cm<sup>-1</sup> was assigned to the γ-CH of furan; the band at 781 cm<sup>-1</sup> was assigned to the β-rings of pyridines (20). In 700BL, the band at 1057 cm<sup>-1</sup> was assigned to the aliphatic C-O-C functional groups of cellulose, whereas the band at 1130 cm<sup>-1</sup> was assigned to the stretching vibrations of ether C-O bonds (7). The band at 1047 cm<sup>-1</sup> arises from C-O stretching of cellulose (20). Cellulose is a major component of sawdust used as bedding material in poultry farming (21). Bedding material accounts for 20–30% of broiler litter investigated in this study (12). Considering the high phosphorus contents of broiler manure and chars (12, 20), the broad band near 1070 cm<sup>-1</sup> was assigned to phosphorus-containing functional groups, most importantly, the P-O bond of phosphate (22, 23). In 350BL, the band at 1626 cm<sup>-1</sup> was assigned to aromatic C=O and C=C stretching (7). Similarity in FTIR spectra for 350BL and manure (**Figure 1**) suggests that a large proportion of the organic functional groups in manure are retained after pyrolysis at 350 °C.

The FTIR spectrum of 350BL closely resembled the spectrum for the basic fraction of bio-oil obtained by fast pyrolysis of broiler manure at 350 °C (20), except for the absence of a broad band near 1070 cm<sup>-1</sup> (assigned to phosphorus functional groups, **Figure 1**) in bio-oil. Bio-oil is a condensed organic phase arising

from fast pyrolysis of biomass, and broiler manure-derived bio-oil is composed of several hundred organic compounds including fatty acids, phenols, sterols, alkylbenzenes, pyrazines, and pyrroles (20). Similarity in FTIR spectra suggests that the organic fraction of 350BL may contain a complex mixture of low molecular weight organic molecules similar in composition to bio-oils.

In comparison to the manure and 350BL, the intensities of C=O and CH<sub>2</sub> groups decreased in 700BL, whereas the intensities of C-O groups increased (**Figure 1**). Spectra for 350ABL and 700ABL show the disappearance of sharp peaks attributable to most functional groups, except hydroxyl and phosphorus-containing groups, as a result of steam activation. Boehm titration (**Table 2**) and FTIR (**Figure 1**) results suggest that pyrolysis and steam activation of broiler litter can result in both the removal and the formation of certain surface functional groups.

To further characterize the functional groups comprising the organic fractions of manure-derived biochars, a <sup>1</sup>H NMR spectrum was obtained for the leachable organic fraction (0.1 M NaOH extract) of 350BL. In **Figure 2**, the peaks at 1.0–3.0 ppm are assigned to aliphatic protons of CH<sub>3</sub>, CH<sub>2</sub>, and CH groups (21). The peaks at 4.0–6.0 ppm arise from alkoxy (mostly methoxy and ethoxy) groups and carbohydrates (21). The broad peak at 7.0–8.4 ppm is due to aromatic protons and indicates significant steric hindrance (21). The sharp peak at 8.7 ppm is assigned to aldehyde. Observed functional groups overlap in 350BL (FTIR spectrum in **Figure 1**) and its base extract (<sup>1</sup>H NMR spectrum in **Figure 2**). Hence, depending on the pH of the environmental media, organic functional groups within biochars are leachable when used as a soil amendment.

**Immobilization of Cd<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup> by Char in Water.** Experiments were conducted to test for the ability of each biochar to immobilize a mixture of heavy metals (Cd<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup>, 1.5 mM each at t<sub>0</sub>) in water. In addition to biochars, manure was employed to determine the roles of noncarbonized fractions of biochars. Separate batch reactors were prepared for individual chars and manure suspended in 0.01 M NaCl. Initial pH values (pH<sub>t<sub>0</sub></sub> after 24 h of equilibration in 0.01 M NaCl) of 5 g L<sup>-1</sup> biochar and manure suspensions were basic, ranging between 8.1 for manure and 10.4 for 700BL (**Figure 3a**, open triangles). After equilibration with metal ions (1.5 mM each of Cd<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup>, added together to each reactor at t<sub>0</sub>) for 24 h, a dramatic decrease in pH was observed for all sorbents investigated (pH<sub>t<sub>24</sub></sub>; **Figure 3a**, solid triangles). A plot of pH<sub>t<sub>24</sub></sub> versus pH<sub>t<sub>0</sub></sub> resulted in a positive correlation: pH<sub>t<sub>24</sub></sub> = 0.39(pH<sub>t<sub>0</sub></sub>) - 2.41 (R<sup>2</sup> = 0.83) (**Figure S1b** of the Supporting Information). The pH drop as a result of heavy metal immobilization suggests considerable CEC (maximum number of moles of dissociable proton charge (24)) of chars and the release of exchangeable protons from biochars upon sorption of divalent metal cations. However, the total amount of metals bound was 3–4 orders of magnitude greater than the amount of protons released (**Table S1**, Supporting



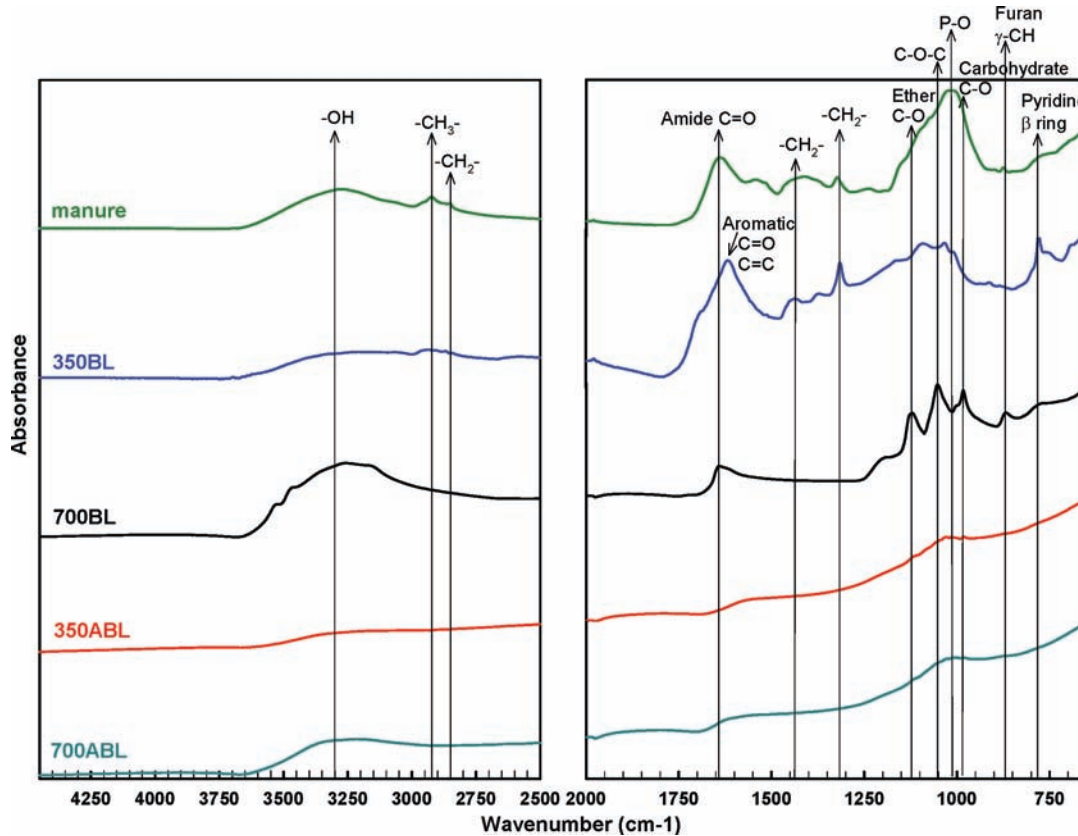


Figure 1. FTIR spectra of biochars.

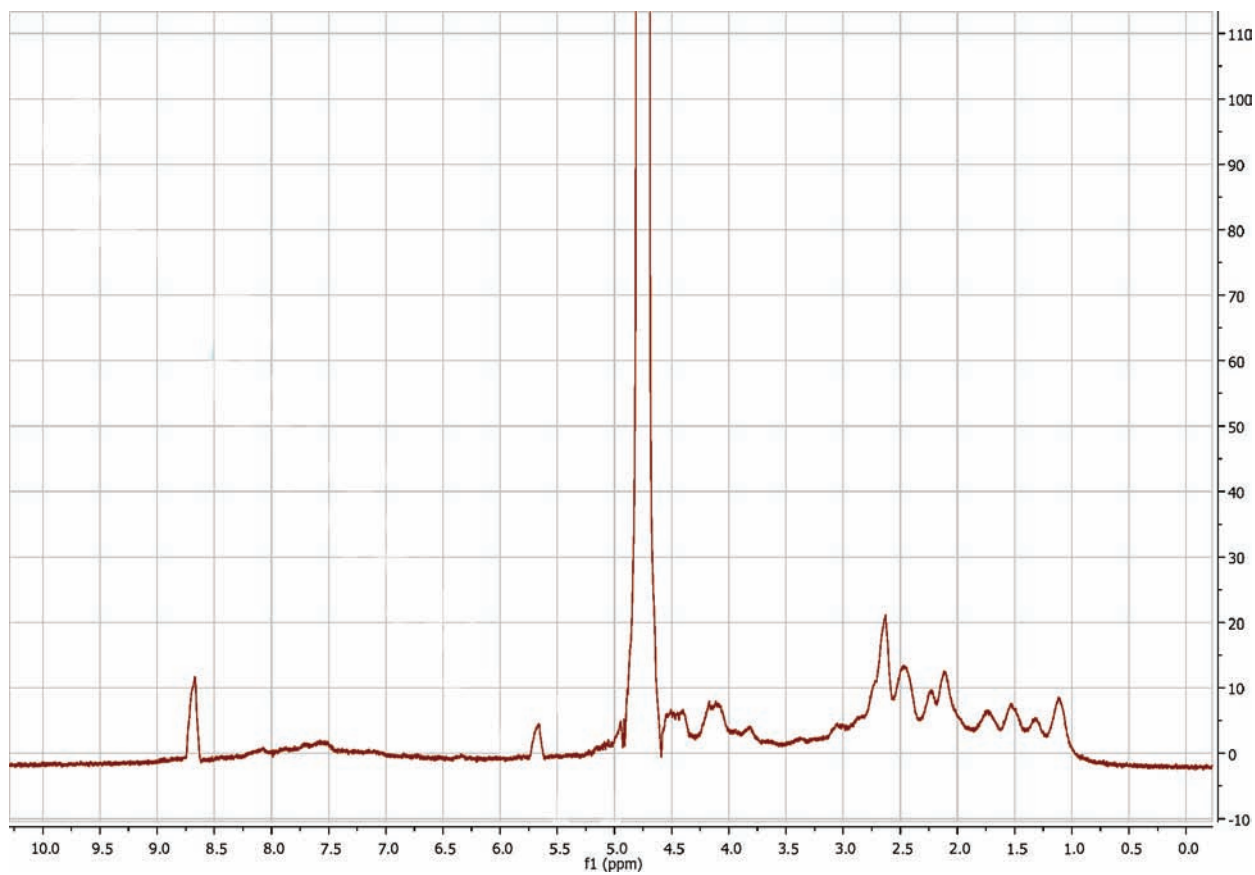
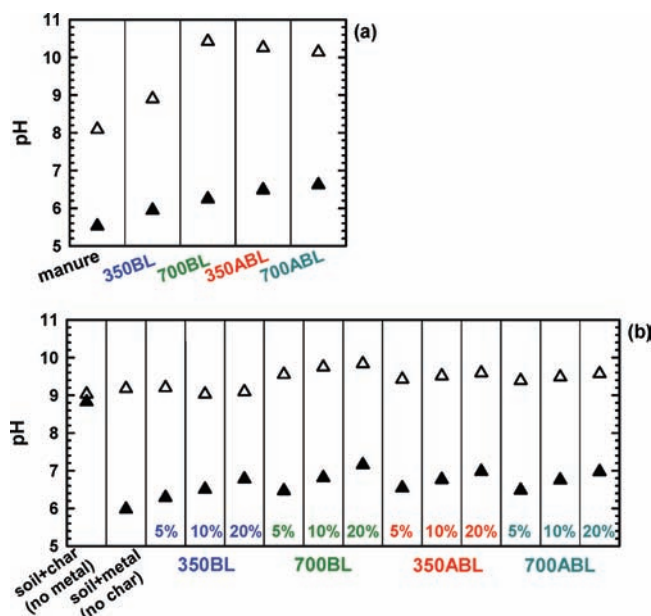
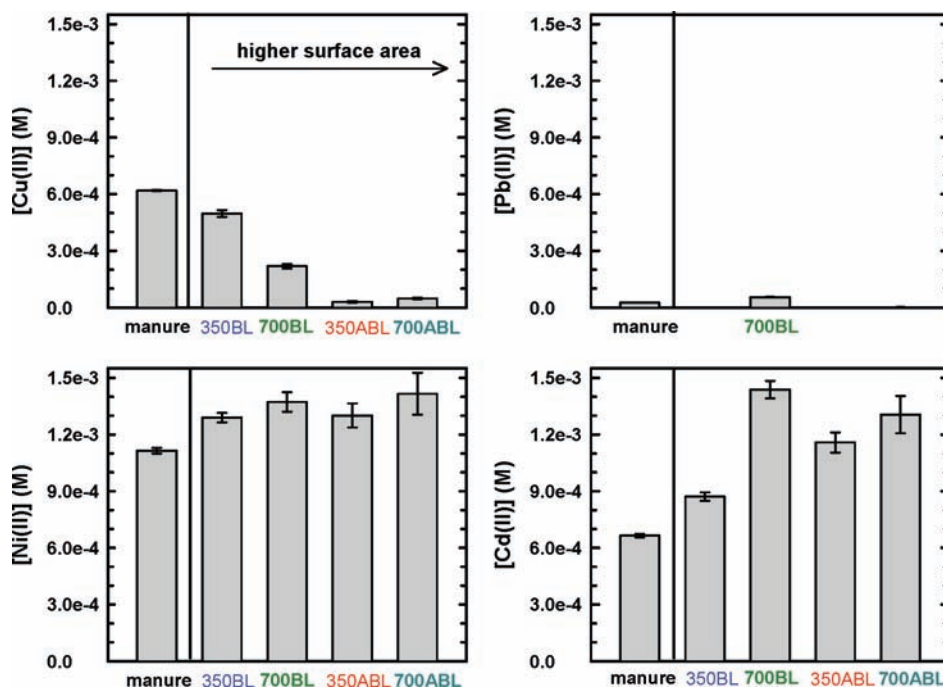


Figure 2. <sup>1</sup>H NMR spectrum for 0.1 M NaOH extract of 350BL.

Information). Similar nonstoichiometric release of protons was observed previously in the sorption of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  on wood chars in the presence of hydrophobic organic compounds and was attributed to the complexation of heavy metals by surface groups that do not involve proton release, such as  $-\text{O}-$ ,  $=\text{O}$ , and  $-\text{CHO}$  (25). In addition, heavy metals may replace alkaline earth metal cations originally present in chars, such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$  (25). A previous paper on  $\text{Pb}^{\text{II}}$  sorption by basic activated carbons postulated the coordination of  $\text{Pb}^{\text{II}}$  by the electron



**Figure 3.** Determined pH before ( $\text{pH}_{t_0}$ , open triangles) and after ( $\text{pH}_{t_{24}}$ , solid triangles) 24 h of equilibration of (a)  $5 \text{ g L}^{-1}$  (in  $0.01 \text{ M NaCl}$ ) biochars or manure with  $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  ( $1.5 \text{ mM}$  each added together at  $t_0$ ) and (b) soil ( $20 \text{ g}$  of soil  $\text{L}^{-1}$ ) and biochars ( $5$ – $20\%$  in  $\text{g}$  of char  $\text{g}^{-1}$  of soil) with  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  ( $1.5 \text{ mM}$  each added together at  $\text{pH}_{t_0}$ ). In (b), control experiments without metal or char are shown (far left).



**Figure 4.** Concentrations of  $\text{Cd}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$  remaining in solution after 24 h of equilibration of each biochar sample ( $5 \text{ g L}^{-1}$  in  $0.01 \text{ M NaCl}$ ) with a mixture of metals ( $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$ ,  $1.5 \text{ mM}$  each added together at  $t = 0$ ). All values are shown as mean  $\pm$  standard deviation for duplicate experiments.

charge density ( $\pi$  electrons of  $\text{C}=\text{C}$ ) of carbon, a process that does not involve proton release, as the predominant sorption mechanism (26).

As shown in **Figure 4**, the sorption capacity of chars strongly depended on the metal ion type, showing the following trend for greater removal from solution:  $\text{Ni}^{\text{II}} < \text{Cd}^{\text{II}} < \text{Cu}^{\text{II}} < \text{Pb}^{\text{II}}$ . This trend was observed for all chars as well as the manure. Considering the alkaline pH of char suspensions prior to the addition of metal ions (**Figure 3a**, open triangles), the formation of solubility-limiting metal (hydr)oxide phases (i.e., precipitation) must be considered as an immobilization mechanism:  $\text{Me}^{2+} + 2\text{OH}^- = \text{Me}(\text{OH})_2(\text{s,amorph})$  (27). Stability constants for the hydrolysis reactions of metal ions (28) were used to determine the concentrations of total soluble metal ions as a function of pH (Figure S2, Supporting Information). Equilibrium calculations were performed separately for each element for  $1.5 \text{ mM}$  total metal ion concentration with  $\text{Me}(\text{OH})_2(\text{s,amorph})$  as the solubility-limiting phase ( $I = 0.01 \text{ M NaCl}$ ). For each metal system, the total dissolved concentration rapidly decreased above a critical pH (Figure S2, Supporting Information): pH 6.0 for  $\text{Cu}^{\text{II}}$ , pH 7.0 for  $\text{Pb}^{\text{II}}$ , pH 8.0 for  $\text{Ni}^{\text{II}}$ , and pH 8.3 for  $\text{Cd}^{\text{II}}$ . The tendency to form  $\text{Me}(\text{OH})_2(\text{s,amorph})$  (Figure S2, Supporting Information) does not directly correlate with the extent of removal observed in **Figure 4** ( $\text{Ni}^{\text{II}} < \text{Cd}^{\text{II}} < \text{Cu}^{\text{II}} < \text{Pb}^{\text{II}}$ ).

Elemental analyses of broiler litter manure (20) and chars (12) indicated significant phosphorus, nitrogen, and sulfur contents. Broiler litter chars contained 3.7% (w/w) phosphorus and 1.7% (w/w) sulfur (12). Broiler manure contained 5.9% (w/w) nitrogen and 0.8% (w/w) sulfur (20). In addition, the viscous portion of bio-oil derived by fast pyrolysis of broiler manure at  $350 \text{ }^\circ\text{C}$  contained 6.3% (w/w) nitrogen, 0.5% (w/w) sulfur, and 0.04% (w/w) phosphorus (20).  $^{31}\text{P}$  NMR and HPLC analyses indicated orthophosphate, orthophosphate esters, and phytate as the primary phosphorus compounds in broiler litter (29). Previous elemental (12, 20), NMR, and HPLC (29) analyses and FTIR results in this study (**Figure 1**) suggest the abundance of organic and inorganic phosphorus functional groups in broiler manure and biochars investigated in this study. To determine

the ability of phosphorus functional groups to bind divalent metal ions, stability constants were obtained for model ligands:  $\text{CH}_3\text{-O-PO}_3^{2-}$ ,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-PO}_3^{2-}$ , cytidine-5'-(dihydrogenphosphate) (CMP-5), and phenyl dihydrogenphosphate (28). The following trend was consistently observed for the affinity of orthophosphate ester ligands for metal ions (Table S2, Supporting Information):  $\text{Ni}^{\text{II}} < \text{Cd}^{\text{II}} < \text{Cu}^{\text{II}} < \text{Pb}^{\text{II}}$ . The trend coincides with the relative extent of removal for the four heavy metal ions observed in this study (Figure 4). The complete removal of  $\text{Pb}^{\text{II}}$  (Figure 4) likely resulted from the high affinity of  $\text{Pb}^{\text{II}}$  for phosphate-based ligands to form  $\text{Pb}$  phosphate precipitates, as observed previously for  $\text{Pb}^{\text{II}}$  immobilization by dairy manure-derived biochars (5).

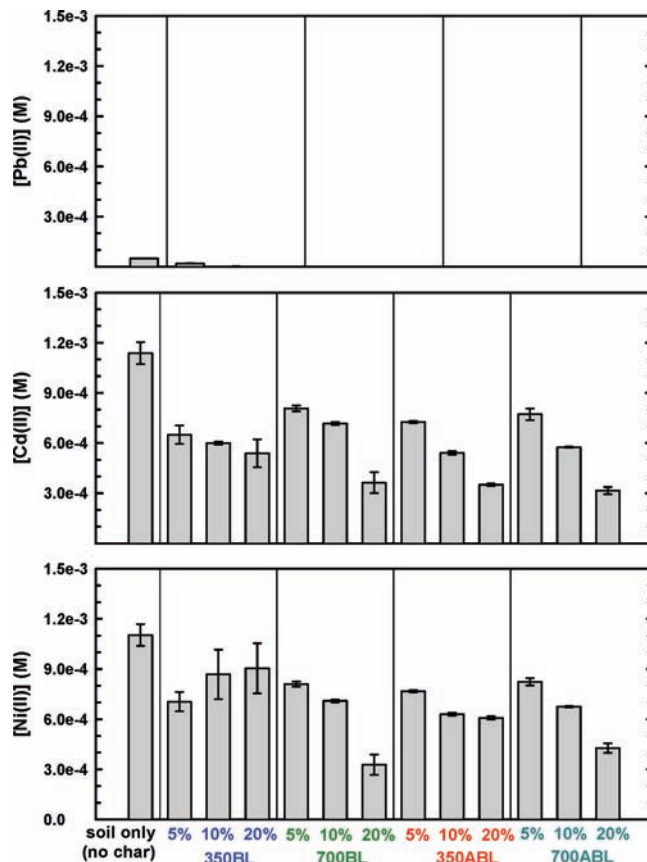
Each plot in Figure 4 represents increasing surface area of chars from left to right of the  $x$ -axis, from 350BL and 700BL to 350ABL and 700ABL (Table 1). The extent of sorption increased with the surface area of char for  $\text{Cu}^{\text{II}}$  (Figure S3, Supporting Information) but not  $\text{Ni}^{\text{II}}$  or  $\text{Cd}^{\text{II}}$ . For  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$ , noncarbonized biomass source (manure) sorbed more than all chars investigated, including 350ABL and 700ABL having high surface areas (Table 1).

#### Effects of Biochars on Retention of $\text{Cd}^{\text{II}}$ , $\text{Ni}^{\text{II}}$ , and $\text{Pb}^{\text{II}}$ in Soil.

Experiments were conducted to test for the effects of char amendment (0–20% in  $\text{g}$  of char  $\text{g}^{-1}$  of soil) on the mobility of a mixture of selected heavy metals ( $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$ , 1.5 mM each added at  $t_0$ ) in soil (20  $\text{g}$  of soil  $\text{L}^{-1}$ ). All experiments involving soil were conducted using SRW to simulate contaminant leaching by percolating rainfall (15). The initial pH of soil with and without biochar (after 24 h of equilibration in SRW) ranged between 9.0 for 10% 350BL and 9.8 for 20% 700BL (Figure 3b, open triangles). After subsequent equilibration with metal ions for 24 h, a dramatic decrease in pH was observed (Figure 3b, solid triangles). The pH both before and after the metal addition increased with the biochar loading, resulting in a positive correlation:  $\text{pH}_{t_{24}} = 0.67(\text{pH}_{t_0}) - 0.39$  ( $R^2 = 0.41$ ) (Figure S1d). In addition, the pH change was less dramatic in the presence of soil ( $\Delta\text{pH} = 2.6\text{--}3.1$ , Figure 3b) than in its absence ( $\Delta\text{pH} = 3.0\text{--}4.2$ , Figure 3a), indicating a buffering capacity of the soil.

A log–log plot of the total amount of metals bound and the protons released showed an inversely linear correlation:  $\log[\text{total metals sorbed (M)}] = -0.17(\log[\text{total proton released}]) - 3.64$  ( $R^2 = 0.81$ ) (Figure S4, Supporting Information). Hence, greater metal immobilization was observed for fewer equivalent protons released. A closer look into individual experiments in Figure 5 indicates the maximum proton release (for the amount of metals bound) in the absence of biochars (soil-only case in Table S1b, Supporting Information). The ratio ( $[\text{total metal bound}]/[\text{proton released}]$ ) decreases with biochar loading (from 5 to 20%) for each char, and of all the chars investigated, the lowest ratio was observed for 350BL (Table S1a,b, Supporting Information). The observed trend suggests that the ionic exchange becomes a less dominant factor for heavy metal immobilization with increasing proportion of carbonized fractions in soil (Table S1b).

As shown in Figure 5, whereas soil alone retained considerable portions of added  $\text{Pb}^{\text{II}}$  (and  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  to a lesser extent), biochar amendment significantly enhanced the metal retention. As was observed in the absence of soil (Figure 4), the majority of  $\text{Pb}^{\text{II}}$  was immobilized under all conditions investigated (Figure 5). An increase in char amendment from 0, 5, 10, to 20% gradually enhanced the retention of  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$ . For 10–20% 350BL, 5–20% 350ABL, and 10–20% 700ABL,  $\text{Cd}^{\text{II}}$  was removed from solution to a greater degree than  $\text{Ni}^{\text{II}}$  (Figure 5). Higher sorption capacity of biochars for  $\text{Cd}^{\text{II}}$  compared to  $\text{Ni}^{\text{II}}$  was also observed in the absence of soils (Figure 4). For 700BL, however, soluble



**Figure 5.** Soluble metal concentrations after 24 h of equilibration of char-amended (0–20% in  $\text{g}$  char  $\text{g}^{-1}$  of soil) soil (20  $\text{g}$  of soil  $\text{L}^{-1}$  in SRW) with a mixture of heavy metals ( $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Pb}^{\text{II}}$ , 1.5 mM each added at  $t_0$ ). All values are shown as mean  $\pm$  standard deviation for duplicate experiments.

$\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  concentrations were within the error range (Figure 5). In the absence of soil, dissolved  $\text{Cd}^{\text{II}}$  concentration increased in the following order (Figure 4): 350BL < 350ABL < 700BL  $\approx$  700ABL. Although the same relative sorption capacity of chars was observed for  $\text{Cd}^{\text{II}}$  in the presence of soil at 5% char amendment (Figure 5), the trend was no longer observed at higher (10–20%) char amendment. For both  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$ , greatest removal was observed for 700BL and 700ABL at the highest (20%) amendment. A log–log plot of soluble  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  concentrations versus  $\text{pH}_{t_{24}}$  showed a linear correlation with negative slopes (Figure S5, Supporting Information), indicating a greater removal of  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  at higher  $\text{pH}_{t_{24}}$ . Hence, an increase in soil pH by char amendment (Figure 3) enhanced the retention of  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  by soil.

The results presented above show that pH rise by the addition of basic char led to an enhanced immobilization of  $\text{Ni}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$ . The effectiveness of char amendment strongly depended upon the type of metal contaminant. Possible mechanisms for the heavy metal retention by chars are (1) the formation of metal (hydr)oxide, carbonate, or phosphate precipitates and/or the activation of surfaces caused by the pH rise, (2) sorptive interactions between d-electrons of metals and aromatic  $\pi$ -electrons of chars (6), and (3) specific metal–ligand complexation involving surface functional groups of chars (particularly oxygen, phosphorus, sulfur, and nitrogen functional groups) that may or may not involve cation exchange. Complexation is likely important for metal ions having high affinity for specific (e.g., phosphate) ligands on the surface of, or released by, chars and can result in precipitation, as was observed previously for  $\text{Pb}^{\text{II}}$  immobilization by dairy manure-derived chars (5). The considerable sorption



capacity of 350BL for heavy metal contaminants, despite low surface areas, highlights the roles of noncarbonized biomass fractions in heavy metal immobilization. Release of functional groups from chars can have an impact on the composition of natural organic matter (NOM) in the surrounding environment. NOM and BC comprise major sorption capacities in soils and sediments (1). NOM is widely recognized for affecting the sorption behaviors of BC (e.g., see ref 30 and references cited therein). Therefore, the impact of leachable functional groups from amended chars on the NOM composition and metal ion speciation in the surrounding environmental media must be addressed. Our subsequent papers in this series will explore the roles of both NOM and leachable organic fraction of chars on the properties of char-amended soils, with particular emphasis on the nutrient (PKS) release and immobilization of Cu<sup>II</sup>.

**Supporting Information Available:** pH change resulting from metal immobilization in char-amended soil and water, equilibrium concentration of total dissolved metal ions for Cu(II), Cd(II), Ni(II), and Pb(II), stability constants for phosphate-based ligands, relationships between the surface area of char and the extent of Cu sorption, and impact of char amendment on soil pH and contaminant immobilization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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