



Screening biochars for heavy metal retention in soil: Role of oxygen functional groups[☆]

Minori Uchimiya^{*}, SeChin Chang, K. Thomas Klasson

USDA-ARS Southern Regional Research Center, 1100 Robert E. Lee Boulevard, New Orleans, LA 70124, United States

ARTICLE INFO

Article history:

Received 18 January 2011

Received in revised form 2 March 2011

Accepted 16 March 2011

Available online 23 March 2011

Keywords:

Biochar

Activated carbon

Heavy metal

Volatile matter

Positive matrix factorization

ABSTRACT

Oxygen-containing carboxyl, hydroxyl, and phenolic surface functional groups of soil organic and mineral components play central roles in binding metal ions, and biochar amendment can provide means of increasing these surface ligands in soil. In this study, positive matrix factorization (PMF) was first employed to fingerprint the principal components responsible for the stabilization of heavy metals (Cu, Ni, Cd, Pb) and the release of selected elements (Na, Ca, K, Mg, S, Al, P, Zn) and the pH change in biochar amended soils. The PMF analysis indicated that effective heavy metal stabilization occurred concurrently with the release of Na, Ca, S, K, and Mg originating from soil and biochar, resulting in as much as an order or magnitude greater equilibrium concentrations relative to the soil-only control. In weathered acidic soil, the heavy metal (especially Pb and Cu) stabilization ability of biochar directly correlated with the amount of oxygen functional groups revealed by the O/C ratio, pH_{pzc} , total acidity, and by the ^1H NMR analysis. Equilibrium speciation calculation showed minor influence of hydrolysis on the total soluble metal concentration, further suggesting the importance of binding by surface ligands of biochar that is likely to be promoted by biochar-induced pH increase.

Published by Elsevier B.V.

1. Introduction

Heavy metal contamination poses a global challenge at shooting range [1,2], mining site [3], and industrially impacted urban soils [4] that represent a wide range of total organic carbon (TOC) content, cation exchange capacity (CEC), and pH. The mobility and bioavailability of heavy metal contaminants are controlled by complex redox and acid–base chemistry and the availability of sorption sites such as the iron and aluminum (hydr)oxides, clay, and natural organic matter [5]. Carboxyl, phenolic hydroxyl, and other oxygen-containing surface functional groups of these soil components play central roles in binding metal ions [5]. In recent years, carbonaceous materials such as activated carbons [6] and char products (biochar) from thermochemical processing (slow/fast pyrolysis and gasification) of biomass for biofuel production purposes [7] have received considerable interests as a waste-derived soil/sediment amendment for *in situ* stabilization of inorganic and organic contaminants. Both biochar and activated carbon can be engineered to have high oxygen-containing surface functional group con-

tents for amendment on soil types that lack sufficient binding sites.

For activated carbons [8,9], chars [10], as well as carbon nanotubes [11], greater amounts of oxygen-containing surface functional groups (especially carboxyl) result in enhanced sorption of metal ions in controlled aqueous media. For example, sorption of Cd^{II} on activated carbon was enhanced by the degree of ozonation (higher ozone flow rate resulting in lower pH_{pzc} of treated activated carbons), suggesting the importance of electrostatic interactions above pH_{pzc} [8]. Similarly, greater degree of air oxidation during the formation of phosphoric acid activated carbon resulted in enhanced Cu^{II} sorption capacity [9]. In addition to the intentional oxidation using HNO_3 , KMnO_4 , H_2O_2 [11], ammonium persulfate [10], air [9], and ozone [8], biochars undergo slower but measurable *in situ* oxidation in soils that results in the formation of carboxylic, phenolic and other oxygen-containing surface functional groups [12]. These oxygen-containing functional groups of biochars are known to increase the CEC of soil [13].

In the presence of soil, the importance of oxygen-containing groups on biochar surfaces strongly depends upon the inherent sorption capacity of soil [14]. Improved copper sorption on activated carbons having higher oxygen functional group content (in acidic aqueous solution) [9] was no longer observed when amended to San Joaquin soil, regardless of the amendment rate (5–20 wt%) [15]. In contrast, clear influence of oxygen-containing functional groups was observed in Norfolk soil amended with cottonseed hull biochars [16]. In addition, biochar impacts complex stabi-

[☆] Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

^{*} Corresponding author. Tel.: +1 504 286 4356; fax: +1 504 286 4367.

E-mail addresses: sophie.uchimiya@ars.usda.gov, uchi982001@yahoo.co.jp (M. Uchimiya).

lization and release of various elements in soil [14,17,18] by (1) the release of native inorganic contents of soil and biochar, (2) buffering of these leachable elements by biochar and soil, and (3) biochar-induced changes in pH and natural organic matter (NOM) composition, and subsequent impact on the metal ion speciation. Principal component analysis (PCA)-based statistical tools should be examined as a way of determining the primary factors that control the equilibrium concentrations of target elements (heavy metals and nutrients) in biochar amended soils.

The objective of this study was to determine the primary factors that control the equilibrium soluble concentrations of added heavy metals (Cu, Ni, Cd, Pb), selected elements originating from biochar and soil (Na, Ca, K, Mg, S, Al, P, Zn), as well as the pH change in biochar amended soils. A PCA-based receptor model called positive matrix factorization (PMF) [19] was employed to resolve complex data sets into distinct fingerprints representative of biochar characteristics and soil property. In order to separately address the roles of biochar and soil, the PMF analysis was first performed on the retention of Cu, Ni, Cd, Pb in Norfolk soil amended with nine biochar samples. Norfolk loamy sand is fine-loamy, kaolinitic, thermic, Typic Kandiuult soil [20]. Norfolk loamy sand is acidic and eroded, low in TOC content, and is estimated to contain 740, 250, and 10 g kg⁻¹ sand, silt, and clay, respectively [21]. Weathering of Norfolk soil at 0–15 cm surface is a result of the past inversion tillage practice that accelerated the decomposition of organic residues [20].

In order to examine the influence of soil property, separate PMF analysis was performed for Cu sorption isotherms on Norfolk and San Joaquin soils amended with one biochar sample that significantly enhanced the heavy metal retention capacity of Norfolk soil. In contrast to Norfolk soil, San Joaquin soil is classified as clay-rich (40–60% clay contents, mainly montmorillonite mineral) cemented Abruptic Durixeralfs [22]. To deduce heavy metal stabilization mechanisms that are responsible for the obtained PMF factors, the PMF results were compared with the parameters pertaining to oxygen-containing surface functional groups of biochars: pH_{pzc}, total acidity, O/C ratio, and ¹H NMR analysis of char extracts.

2. Materials and methods

Detailed biochar preparation and characterization methods, and experimental procedure for sorption studies were provided in previous reports [9,16,23,24] and are summarized below.

2.1. Chemicals

Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (Millipore, Milford, MA) was used for all procedures. Nickel (II) nitrate, copper (II) chloride dihydrate, lead (II) nitrate, and cadmium (II) nitrate tetrahydrate were purchased from Sigma–Aldrich (Milwaukee, WI) and stock solutions (0.2 M) were prepared in DDW.

2.2. Biochars employed

To prepare cottonseed hull biochars [16], cottonseed hulls were obtained from Planters Cotton Oil Mill (Pine Bluff, AK) and were used as received without pretreatments as a mixture of hulls and cottonseeds. Cottonseed hulls were pyrolyzed at 200, 350, 500, 650, and 800 °C for 4 h under 1600 mL min⁻¹ nitrogen flow rate using a box furnace (22 L void volume) with retort (Lindberg, Type 51662-HR, Watertown, WI). The resulting chars (CH200, CH350, CH500, CH650, and CH800) were allowed to cool to room temperature overnight under nitrogen atmosphere.

Broiler litter biochar (700BL) was prepared by pyrolysis at 700 °C for 1 h by the method described above for cottonseed hull

biochars using broiler litter samples obtained from USDA–ARS Poultry Research Unit (Starkville, MS). Prior to pyrolysis, broiler litter samples were milled to less than 1 mm (<25% moisture content) and pelletized to cylinders of approximately 5 mm diameter and 5 mm length [23].

Steam activated carbons from flax shive and cotton (harvested by picker and stripper) gin wastes were prepared by pyrolysis at 700 °C for 1 h under 1600 mL min⁻¹ nitrogen flow rate and subsequent steam activation at 850 °C for 1.5 h under nitrogen atmosphere with 3 mL min⁻¹ water flow rate [24]. To remove excess ash, cottonseed hull chars, 700BL, and steam activated carbons (flax, picker, and stripper) 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.

For pecan shell-derived phosphoric acid activated carbons [9], pecan shells were ground and sieved, soaked in 30 wt% phosphoric acid overnight, and heated at 450 °C for 4 h under 100, 400, 800, 1200, 1600, and 2000 mL min⁻¹ air flow rates. The resulting activated carbons (PS100, PS400, PS800, PS1200, PS1600, PS2000) were washed five times in hot water (90 °C) and oven-dried overnight at 80 °C. All biochars (CH200, CH350, CH500, CH650, CH800, and 700BL) and activated carbons (PS100, PS400, PS800, PS1200, PS1600, PS2000, flax, picker, and stripper) were ground and sieved to less than 44 μm (325 mesh).

2.3. Total acidity, pH_{pzc}, and elemental composition

Total acidity was determined for cottonseed hull chars by Boehm titration method [25]. Briefly, pH of aqueous char suspension (10 g 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 NaOH was added to make 10 g L⁻¹ char suspension. After stirring for 24 h, char suspension was filtered (0.45 μm Millipore Millex-GS; Millipore Corp., Billerica, MA) and 10 mL of 0.1 M HCl was added to 5 mL filtrate. Resulting solution was titrated with 0.1 M NaOH (titrand 835 autotitrator, Metrohm ion analysis, Herisau, Switzerland). Blanks were prepared by adding 5 mL of 0.1 M NaOH to 10 mL of 0.1 M HCl. Surface acidity (in mequiv. g⁻¹) was determined assuming that NaOH neutralizes all organic acids with pK_a less than 12, including high pK_a phenols [25].

Point of zero charge (pH_{pzc}) of PS100, PS2000, flax, picker, and stripper were determined by a previously described pH drift method [26]. Briefly, 5 mM CaCl₂ solution was boiled to remove CO₂ and cooled to room temperature. Sample (0.06 g) was added to 20 mL of resulting CaCl₂ solution pre-adjusted to pH 4, 6, 8, and 10 using 0.5 M HCl or NaOH, and equilibrated for 24 h by constant stirring in capped glass vials prior to pH measurements. The pH_{pzc} was determined as the pH at which the initial pH equals the final pH [26]. The results of pH_{pzc} measurements are presented in Fig. S1, Supporting Information.

Elemental composition (CHNSO) was determined by dry combustion using Perkin–Elmer 2400 Series II CHNS/O Analyzer (Perkin–Elmer, Shelton, CT).

2.4. ¹H NMR analysis of DMSO extracts

In order to understand the changes in volatile matter (VM) composition as a function of pyrolysis temperature, dimethyl sulfoxide (DMSO) extracts of cottonseed hull chars were obtained by shaking char suspension (9.5 g L⁻¹) end-over-end at 85 rpm in DMSO for 24 h and then evaporating DMSO off the decanted supernatant. The resulting extracts were dissolved in DMSO-d₆ and analyzed by ¹H NMR (Varian Unity 400 spectrometer, 400 MHz) at ambient probe temperature. Tetramethylsilane (TMS) was used as the internal reference.

2.5. Retention of Pb, Cu, Ni, and Cd in Norfolk soil

All experiments were conducted using synthetic rain water (SRW) to simulate contaminant leaching by percolating rainfall [27]. The SRW was prepared daily by adding 10 mM H₂SO₄ to DDW until pH 4.5 was attained [28]. Norfolk loamy sand [21] was obtained from USDA-ARS Coastal Plains Soil, Water and Plant Research Center (Florence, SC) and was air dried and sieved (2 mm) prior to use. Separate amber glass batch reactors were prepared for Norfolk soil in SRW (20 g soil L⁻¹) with and without 10% (g biochar g⁻¹ soil) CH350, CH500, CH650, CH800, PS100, PS400, PS800, 700BL, flax, picker, and stripper. The total volume of each reactor was set to 20 mL. Reactors were pre-equilibrated for 48 h by shaking end-over-end at 70 rpm.

After the pH measurement (pH_{t₀}; Orion 3-star plus benchtop pH meter, ThermoScientific, Waltham, MA), Pb^{II}, Cd^{II}, Cu^{II}, and Ni^{II} were added together to each reactor for the final concentration of 300 μM for each metal (i.e., each reactor contained 1.2 mM total added metals at t₀). Reactors were equilibrated for 48 h and, following pH measurement (pH_{t₄₈}), filtered (0.2 μm Millipore Millex-GS). The filtrate was acidified to 4% (v/v) nitric acid (trace metal grade, Sigma–Aldrich) for the determination of soluble Cu, Ni, Cd, Pb, Na, Ca, K, Mg, S, Al, P concentrations using an inductively coupled plasma optical emissions spectrometer (ICP–AES; Profile Plus, Teledyne/Leeman Labs, Hudson, NH). Each sorption experiment was performed in duplicate.

2.6. Statistical analysis

Receptor models such as PMF are powerful statistical tools for quantitatively resolving the number, chemical composition, and spatiotemporal distribution of the chemical fingerprints simultaneously [19]. The receptor models have been widely employed to determine the point source [29,30] and fate [31] of contaminants in sediments. The PMF is a receptor model based on the principal component analysis with nonnegativity constraints that involves solution of quantitative source apportionment equations by the oblique solutions in reduced dimensional space [32]. The following linear algebraic equation addresses PMF [33]:

$$x_{ij} = \sum_{k=1}^p a_{ik}f_{kj} + \varepsilon_{ij} \quad (1)$$

where x_{ij} is the concentration of the j th element in i th sample of the original data set, a_{ik} is the contribution of the k th factor on sample i , f_{kj} is the fraction of the k th factor arising from element j , and ε_{ij} is the residual between x_{ij} and the estimate of x_{ij} using p principal components. The objective of PMF is to minimize Q , the weighted sum of squares of differences between the PMF output and the original data set [33]:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{x_{ij} - \sum_{k=1}^p a_{ik}f_{kj}}{s_{ij}} \right)^2 \quad (2)$$

where s_{ij} is the uncertainty of the j th element in i th sample of the original data set containing m elements and n samples.

A computer software [34] based on Paatero's PMF program [35] was used for all analyses. To ensure that the numerical solutions are found at the global (and not local) minimum, 100 random starting points were selected for each run.

2.7. Pretreatment of data sets

The original data sets (in M) were first converted to % contribution to total concentration of all measured elements in each sample to allow precise recognition of the relative proportions of each

element in the fingerprint. This normalization procedure enables the recognition of samples having significant contribution from a fingerprint regardless of the total concentration of measured elements. Then, values below the detection limit (DL) were replaced with half of DL [19]. Elements with more than 15% below DL values were eliminated.

The PMF analysis was conducted on two separate experimental data sets from heavy metal retention studies. First data set combined the results from this and previous [16] study for screening nine biochars (10 wt% amendment rate) for retention of added Pb, Ni, Cu, Cd, release of Na, Ca, K, Mg, S, and the pH change in Norfolk soil. The final data set contained 100 equilibrium Cu, Ni, Cd, Pb, Na, Ca, K, Mg, S concentrations and the released proton for screening 10 biochar amendment cases (9 biochar samples and the soil-only control). The amount of released proton was calculated from the pH change before and after 48 h equilibration with Cu, Ni, Cd, and Pb. It must be noted that both soil and biochar possess buffering capacity for all released elements and protons. The primary source of Na, Ca, K, Mg, S is expected to be (1) soil and biochar in equilibrium with synthetic rain water and (2) cation exchange and mineral dissolution resulting from Cu, Ni, Cd, Pb addition, while the primary sink is expected to be (3) retention by soil and biochar; the amount of released proton accounts for (1) and is influenced primarily by (2–3).

Second data set was obtained from a previous study [14] on copper sorption isotherms for Norfolk and San Joaquin soils amended with 20 wt% PS800. The final data set contained 234 equilibrium Cu, Na, Al, P, Ca, K, S, Zn concentrations and the released proton in experiments conducted with four (San Joaquin and Norfolk soil-only control) and three (San Joaquin and Norfolk amended with PS800) initial Cu concentrations (each in replicate). The amount of released proton was calculated from the pH change before and after 24 h equilibration with added copper. Because the data sets were normalized to the total concentration of all elements in each sample, the uncertainty of the j th element in i th sample (s_{ij} values in Eq. (2)) was fixed to the standard deviation of the j th element for all samples considered for the PMF analysis.

2.8. Error analysis

The coefficient of determination (COD) was used to evaluate the ability of PMF to reproduce the original data set, and to determine the number of principal components. The COD provides the goodness of fit (r^2) between the observed and predicted concentration of each element and equals to 1.0 for a perfect fit [19].

3. Results and discussion

3.1. Screening biochars for heavy metal retention

Fig. 1 presents soluble Cu, Ni, Cd, Pb concentrations after 48 h equilibration of Norfolk soil (20 g soil L⁻¹ in SRW) amended with 10% (g biochar g⁻¹ soil) CH350, CH500, CH650, CH800, PS100, PS400, PS800, 700BL, flax, picker, and stripper. Except for PS100, PS400, flax, picker, and stripper, all values in Fig. 1 were obtained from our previous report [16]. Values in Fig. 1 are given as mean ± s.d. of duplicate experiments in which Pb^{II}, Cd^{II}, Cu^{II}, and Ni^{II} were added together to each reactor for the final concentration of 300 μM for each metal (i.e., each reactor contained 1.2 mM total added metals at t₀). For all heavy metals considered, CH350 was most effective in lowering soluble concentrations (except for greater lead retention capacities of PS400, PS800, and 700BL in Fig. 1d). Fig. 1f provides pH of soil suspensions after 48 h pre-equilibration of amended soils in SRW (t₀ shown as squares in Fig. 1f) and subsequent 48 h equilibration following the addition

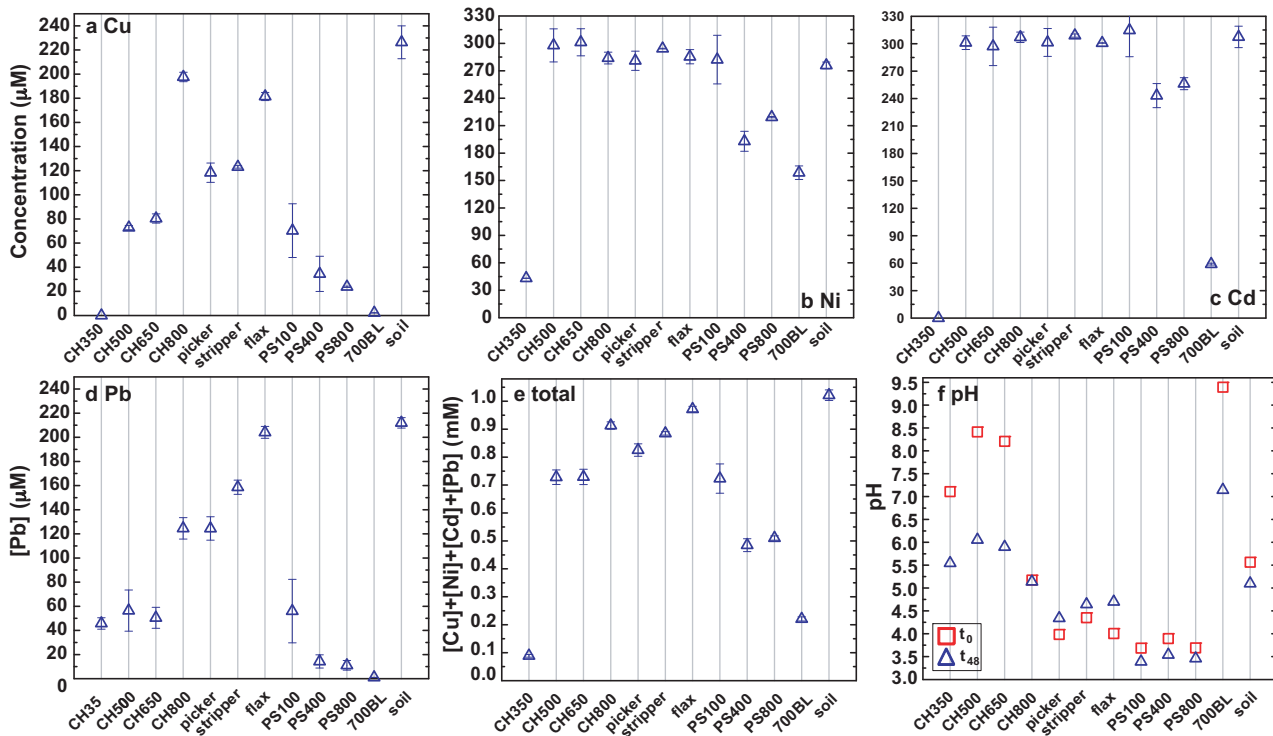


Fig. 1. Equilibrium concentrations of (a) Cu (b) Ni (c) Cd and (d) Pb (300 μM each added together at t_0) after 48 h equilibration in Norfolk soil (20 g soil L^{-1} in SRW) amended with 10% char (g char g^{-1} soil). All values are shown as mean \pm standard deviation for duplicate experiments. The pH before (squares) and after (triangles) 48 h equilibration with added metals are provided in (f). Except for PS100, PS400, flax, picker, and stripper, all values were obtained from Ref. [16].

of Pb^{II} , Cd^{II} , Cu^{II} , and Ni^{II} (t_{48} shown as triangles in Fig. 1f). Depending on the biochar type, the addition of heavy metals resulted in a significant decrease (700BL, CH350, CH500, CH650) and slight decrease (PS100, PS400, PS800) or increase (flax, picker, stripper, CH800) in soil pH (Fig. 1f).

To account for the formation of solubility-limiting metal (hydr)oxide phases as a result of biochar-induced pH change (relative to the soil-only control, Fig. 1f), equilibrium speciation calculation was conducted using HYDRAQL software [36]. Stability constants of the hydrolysis reactions [37] were used to determine

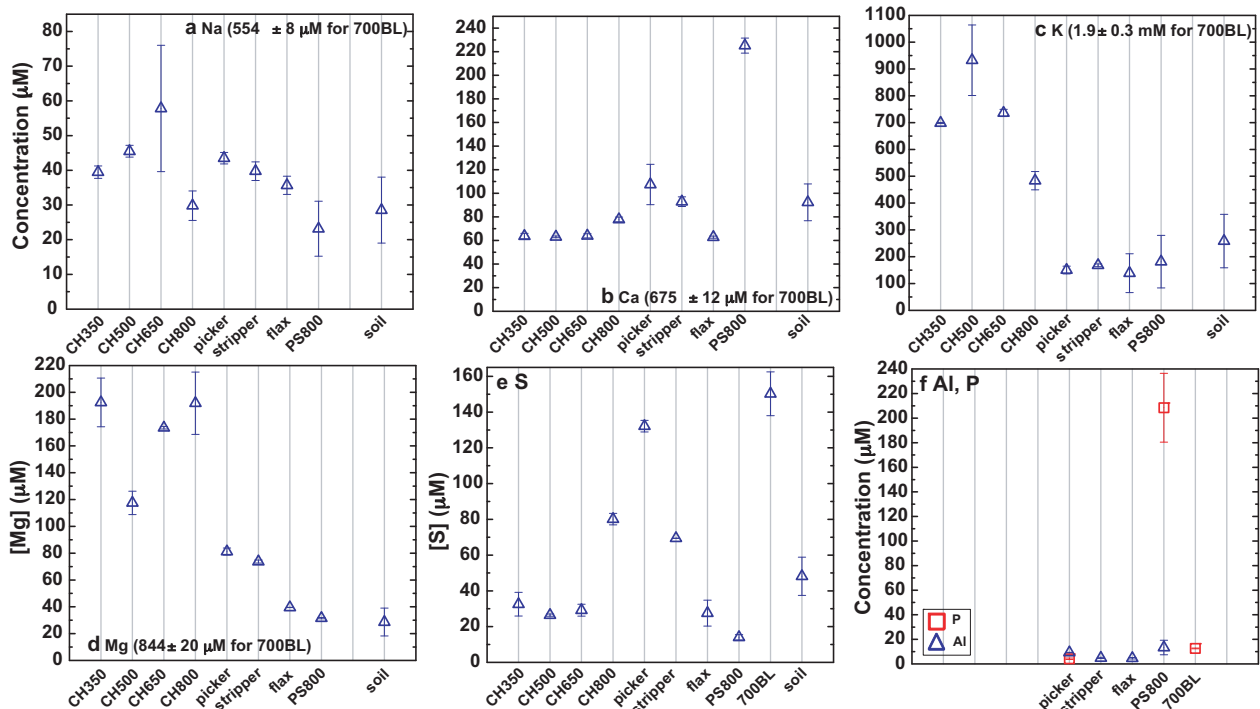


Fig. 2. Equilibrium soluble Na, Ca, K, Mg, S, Al, P concentrations corresponding to Fig. 1. All values above detection limit are presented, as mean \pm standard deviation for duplicate experiments.

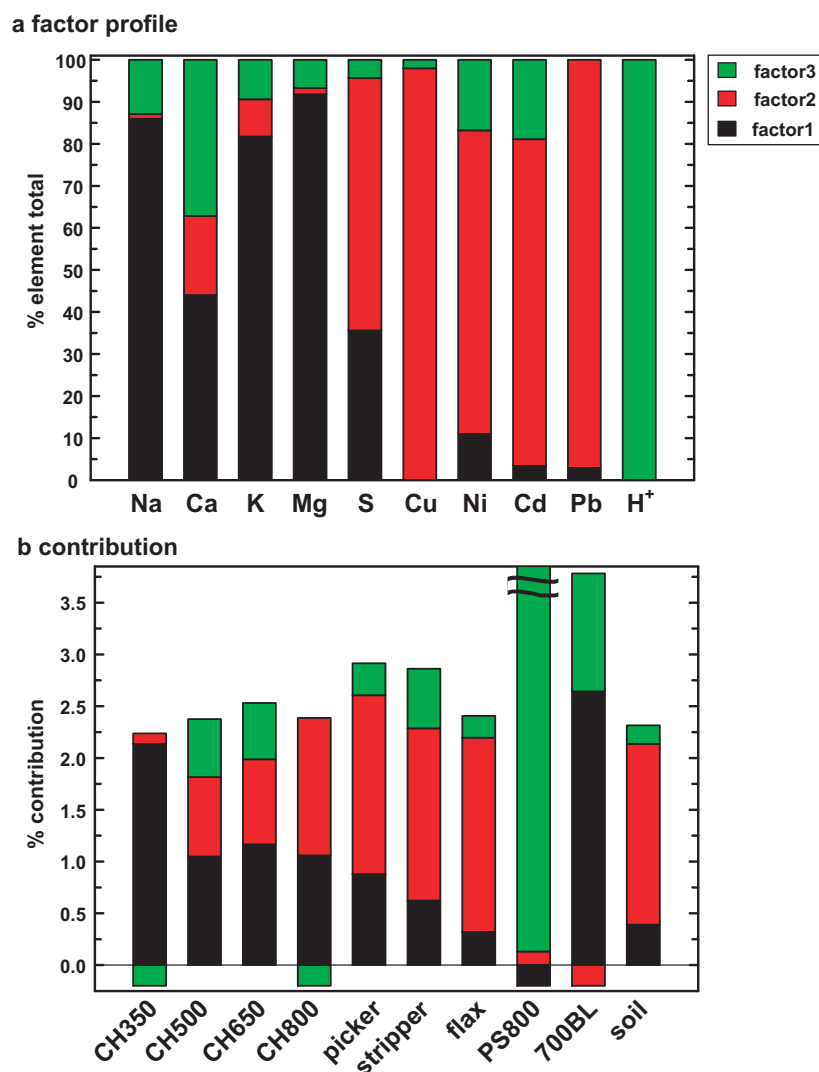


Fig. 3. Chemical fingerprint (a) and contribution (b) of PMF factors obtained from the biochar screening experiment presented in Figs. 1 and 2. In (b), contribution of factor 3 on PS800 is 7.0.

the total soluble metal ion concentrations as a function of pH (Fig. S2, Supporting Information). Equilibrium calculations were performed separately for each element using 300 μM total metal ion concentration with $\text{Me}(\text{OH})_2(\text{s}, \text{amorphous})$ as the solubility-limiting phase ($I=0.01 \text{ M NaCl}$). For each metal ion, the total dissolved concentration rapidly decreased above a critical pH (Fig. S2): pH 6.0 for Cu^{II} , pH 7.5 for Pb^{II} , pH 8.2 for Ni^{II} , and pH 8.7 for Cd^{II} . Therefore, majority of Cu, Ni, Cd, and Pb are expected to be in soluble forms at equilibrium pH (pH_{48} in Fig. 1f) with respect to hydrolysis, except for Cu in the presence of 700BL. Hence, additional heavy metal stabilization mechanisms such as the surface adsorption, cation exchange, and the formation of other solubility-limiting phases should be considered. In particular, the binding of metal ions by surface ligands is strongly pH-dependent [38] and can be promoted by the biochar-induced pH increase. For example, sorption of Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} on ferric hydroxide increases from zero to nearly 100% within 1–2 pH units starting from strongly acidic pH range [38].

Fig. 2 presents equilibrium concentrations of selected elements (Na, Ca, K, Mg, S, Al, P) corresponding to the experiments presented in Fig. 1. Relative to the soil-only control, as much as an order of magnitude greater concentration was observed for Na, Ca, K, and Mg in the presence of 700BL and for P in the presence of PS800 (Fig. 2). However, there is no clear correlation between

the equilibrium concentrations of added heavy metals (Fig. 1) and elements originating from soil and biochar (Fig. 2). For Cu sorption isotherms on biochar amended soils, the release of certain elements correlated with the total Cu sorbed, suggesting the importance of cation exchange mechanism [14]. Additional interpretive tools such as PMF are necessary to understand the factors controlling the equilibrium concentrations of heavy metals and leachable elements.

3.2. Positive matrix factorization

Fig. 3 shows three principal components obtained from the PMF analysis of Figs. 1 and 2. Fig. 3a shows the fingerprint (f_{kj} in Eq. (1)) and Fig. 3b shows the corresponding contribution (contribution of each factor to the total concentration by sample, a_{jk} ; average of all contributions for each factor is 1). The fingerprints are given as % of element total (in M) to recognize the relative proportion of each element in the fingerprint. The results of diagnostic analyses are provided in Table S1 of the Supporting Information.

First factor had among the highest contribution to Na (86%), K (82), Mg (92%), and S (36%), Ca (44%) to a lesser extent, and contributed negligibly to Cu, Ni, Cd, Pb, and the proton release (Fig. 3a). Among nine biochars investigated, factor 1 had the greatest contribution to 700BL, followed by CH350, CH500 \approx CH650 \approx CH800,

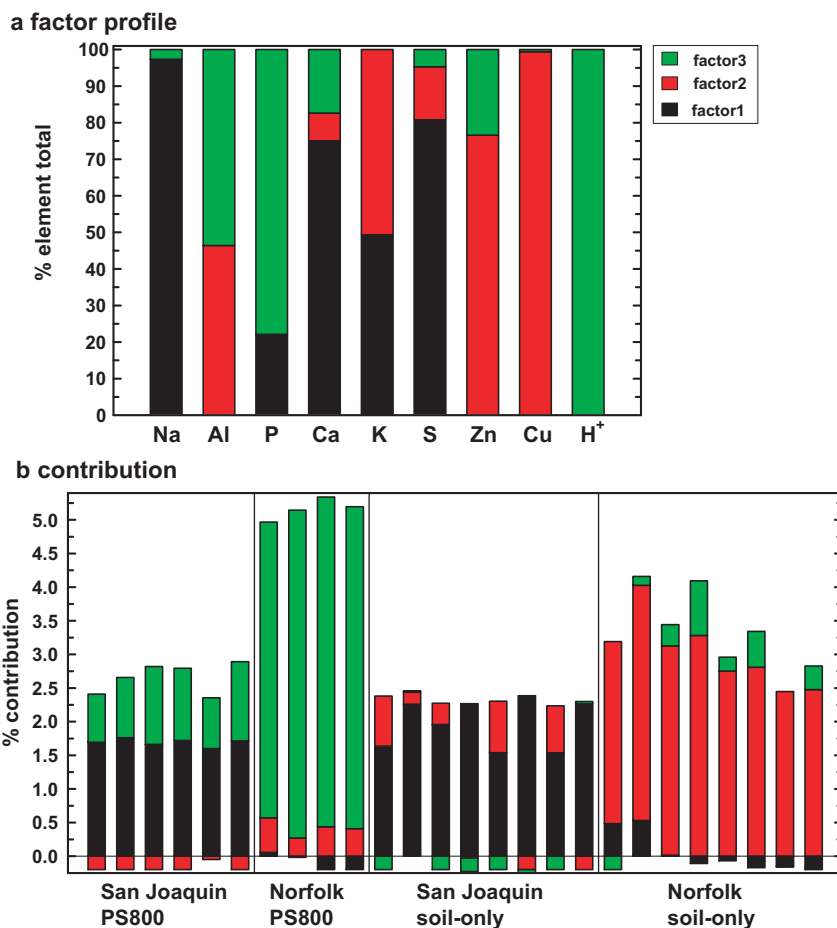


Fig. 4. Chemical fingerprint (a) and contribution (b) of PMF factors obtained from the copper sorption isotherms on Norfolk and San Joaquin soils amended with PS800.

picker, stripper, flax \approx soil-only, and the contribution to PS800 was negligible (Fig. 3b). The trend observed for factor 1 in Fig. 3b correlates with the greater stabilization ability of biochars for Pb, Cu, and total added heavy metals in Fig. 1. Hence, factor 1 fingerprints the heavy metal stabilization ability of biochars with a concurrent release of Na, Ca, S, Mg, and K (Fig. 3a), and is dominated by the cottonseed hull biochar formed at the lowest pyrolysis temperature (CH350) and 700BL (Fig. 3b). Greater equilibrium K concentration and heavy metal retention ability with decreasing pyrolysis temperature (Figs. 1 and 2) are reflected in factor 1 (Fig. 3). Exceptionally high Na, Ca, K, Mg, and S concentrations in the presence of 700BL (Fig. 2) are reflected in the chemical composition of factor 1 (Fig. 3a).

Second factor was the only factor that contributed more than 19% (Cd for factor 3, Fig. 3a) to Cu (98%), Ni (72%), Cd (77%), and Pb (97%). Contributions to the leachable elements were low, except for sulfur (60%, Fig. 3a). The factor 2 showed the greatest contribution in the absence of biochars and in the presence of steam activated carbons (Fig. 3b) having minimal ability to stabilize Cu, Ni, Cd, and Pb (Fig. 1). The contribution trends of factors 1–2 are nearly a complete opposite of one another, and reflect increasing (factor 1) and decreasing (factor 2) heavy metal retention ability of biochars in Norfolk soil, as observed in Fig. 1.

Third factor had 100% contribution to the proton release and much lower contribution ($\leq 37\%$) to all other elements (Fig. 3a). This factor contributed almost solely to PS800 (Fig. 3b) that released the greatest amount of protons in Norfolk soil [14] and had poorer capacity to lower Cd (19% in Fig. 3a) and Ni (17% in Fig. 3a) concentrations relative to Cu and Pb (PS800 in Fig. 1). Therefore, while both factors 1 and 3 represent heavy metal stabilization ability of

biochars, factor 3 is uniquely for the phosphoric acid activated carbon that substantially decreased soil pH (Fig. 1f). In addition to the proton release by cation exchange [14], PS800 contains residual phosphoric acid (15–30% total phosphorus content of PS800) [39] that causes acidic soil pH (Fig. 1f). Released phosphoric acid can (1) promote the dissolution of sorbed metal ions and (2) form anionic species that complexes metal ions.

To investigate the influence of soil property, separate PMF analysis was performed on copper sorption isotherms (0.1–1 mM initial Cu^{II} concentrations) for two soils (Norfolk and San Joaquin) amended with PS800 that showed a particular effective for retaining heavy metals in the biochar screening experiment (Fig. 1). Original data set was obtained from our previous reports [14,18] and fingerprint and contribution for three principal components are shown in Fig. 4. Results of diagnostic analyses are provided in Table S2 of the Supporting Information.

First factor contributed significantly to Na (97%), Ca (75%), S (81%), and P (22%), K (50%) to a lesser extent, while the contribution to Zn, Cu, and the proton release was negligible (Fig. 4a). This factor contributed significantly only to San Joaquin Soil (with and without PS800, Fig. 4b). Hence, factor 1 reflects Cu stabilization and concurrent release of Na, Ca, S, P, and K, similarly to factor 1 obtained from the biochar screening experiment in Norfolk soil (Fig. 3a). Therefore, factor 1 explains substantial Cu retention capacity of San Joaquin soil, regardless of biochar amendment [14]. The sorption of Cu on Norfolk soil was negligible compared to the nonlinear isotherm obtained for San Joaquin soil, and a linear increase in equilibrium Ca, Al concentrations and a decrease in pH were observed as a function of total Cu sorbed on San Joaquin soil, suggesting the contribution of cation exchange mechanism [14].

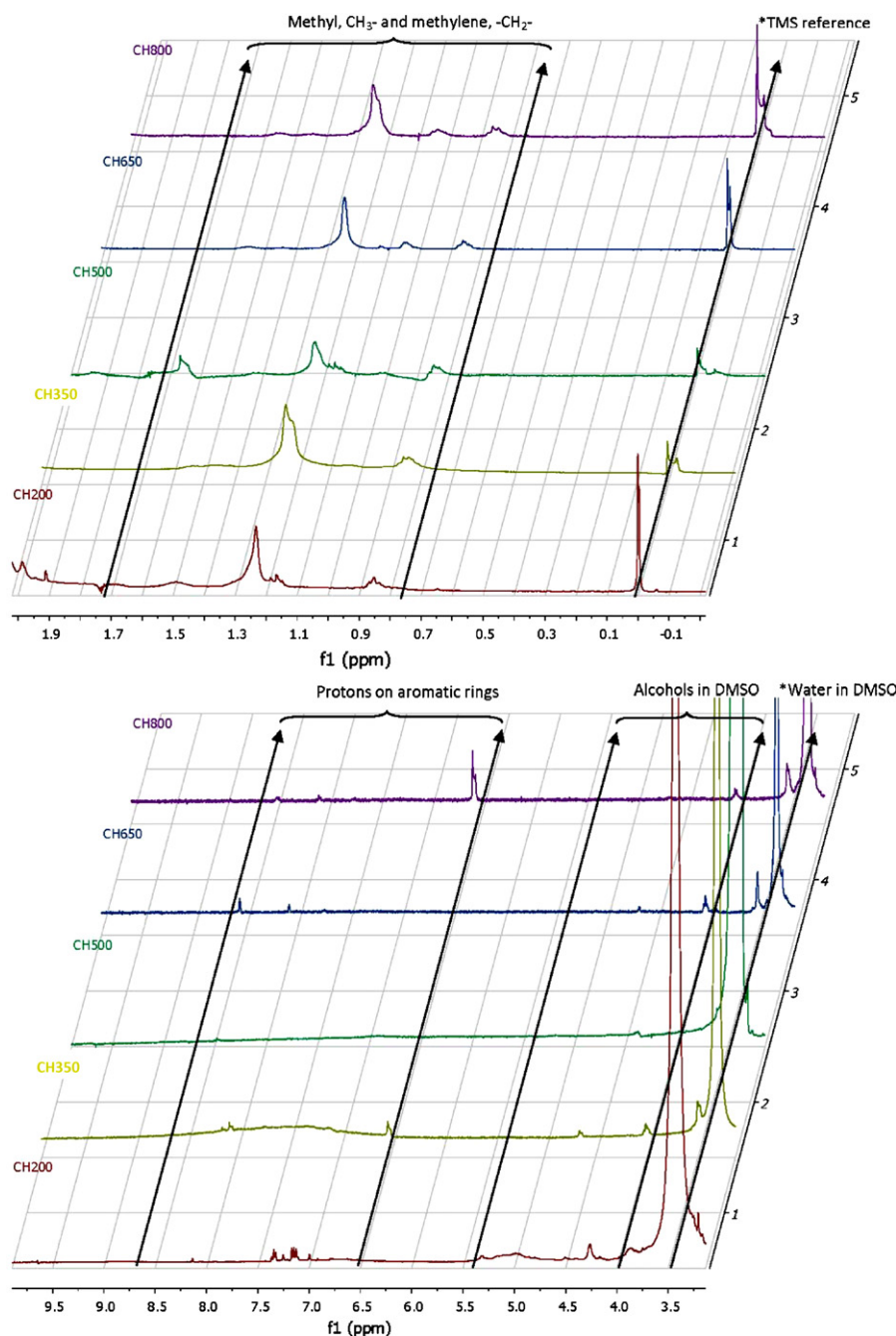


Fig. 5. Proton NMR spectra for DMSO extracts of cottonseed hull chars.

Second factor is attributable to 99% Cu, 77% Zn, 50% K, and 46% Al (Fig. 4a). This factor contributed appreciably only to the Norfolk soil-only case (Fig. 4b) exhibiting negligibly low capacity to retain Cu [14]. Similarly to factor 2 in Fig. 3, this factor represents low capacity of a sorbent (soil or biochar) for heavy metals.

As shown in Fig. 4a, factor 3 is attributable to 100% of proton release, 78% P, and 54% Al. This factor contributed significantly only to Norfolk soil in the presence of PS800 (Fig. 4b). Both the fingerprint composition and contribution (Fig. 4) of factor 3 resemble factor 3 in the biochar screening experiment (Fig. 3). High contribution of factor 3 to P and Al (Fig. 4b) suggests the release of residual phosphoric acid by PS800 and acid dissolution of particulate phases [14]. The existence of principal component for the PS800 amendment on Norfolk (but not San Joaquin) soil suggests that biochar amendment for heavy metal retention is more suitable for low

CEC and TOC sandy (Norfolk) soil having low retention capacity [14].

In conclusion, two separate data sets were analyzed by PMF: (1) experiment designed to screen nine biochars for sorption of Cu, Ni, Cd, and Pb in Norfolk soil and (2) Cu sorption isotherms for PS800 in Norfolk and San Joaquin soils. Both data sets afforded three common principal components attributable to (1) the retention of heavy metals and the concurrent release of Na, Ca, K, Mg, and S, (2) negligible heavy metal stabilization, and (3) the retention of heavy metals and the pH decrease in the presence of acidic activated carbon. Subsequent sections aim to determine the properties that make biochar an effective heavy metal sorbent (revealed as the PMF factor 1 in Figs. 3 and 4) in highly weathered soils that are mostly likely to be subjected to biochar amendment for heavy metal sequestration purposes (Fig. 1).

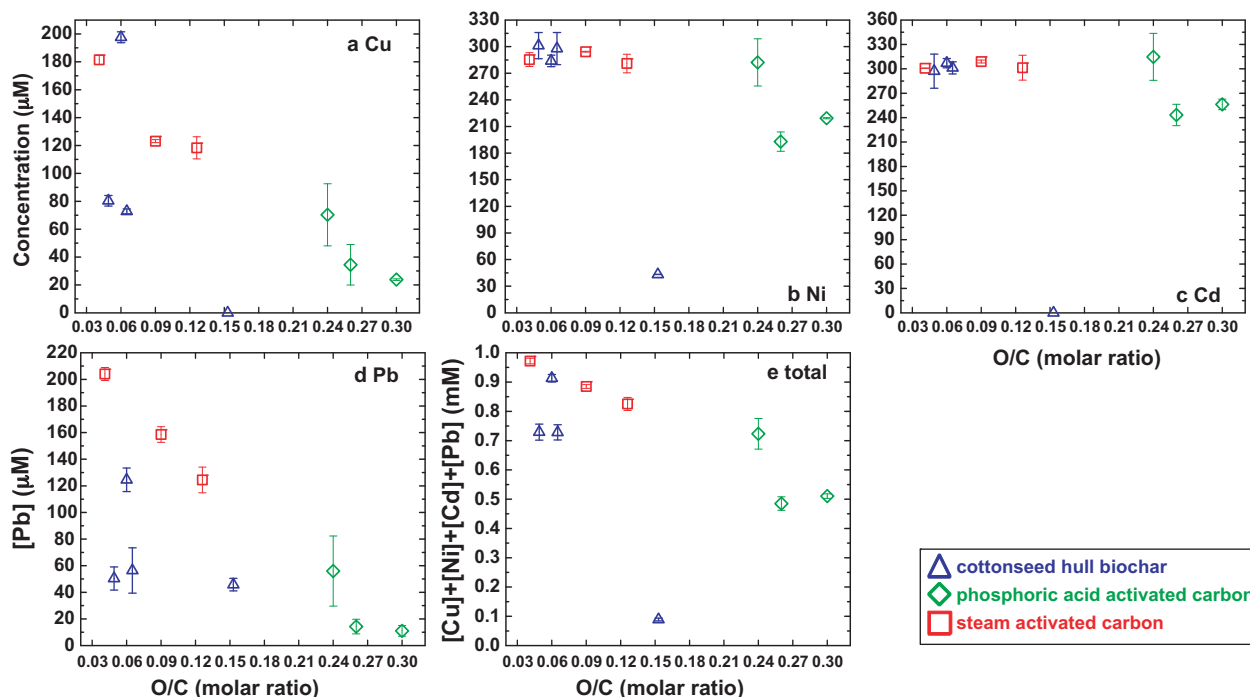


Fig. 6. Equilibrium Cu, Ni, Cd, Pb concentrations (obtained from Fig. 1) as a function of molar O/C ratio of biochar (obtained from Table 1).

3.3. Proton NMR analysis of DMSO extracts for cottonseed hull chars

The DMSO extracts of cottonseed hull chars showed darker brown coloration with decreasing pyrolysis temperature (Fig. S3, Supporting Information) suggesting a complex VM composition that can influence the ability of biochars to sorb heavy metals [16]. Cottonseed hulls are composed primarily of cellulosic materials with small amounts of lignin and phenolics [40]. Cottonseed, which was present in the source material, can contain nearly 30 wt% protein [41]. Fig. 5 presents the ^1H NMR spectra for the DMSO extract of cottonseed hull chars. In Fig. 5 (TOP), the peaks at 0.7–1.7 ppm arise from the chemical shifts of the aliphatic proton groups such as $\text{M-CH}_2\text{R}$ ($\text{M}=\text{methyl}$, methylene or methane ; $\text{R}=\text{alkyl}$ group), M-Ph ($\text{Ph}=\text{phenyl}$), M-C(=O)R , M-C(=O)OR , M-C(=O)NR_2 , M-NR_2 , and M-CN [42]. In Fig. 5 (BOTTOM), the peaks at 6.5–8.8 ppm are attributable to the chemical shifts of protons on monosubstituted benzene rings [43]. The peaks at 8.2 and 8.7 ppm may arise from the chemical shifts of protons on nitrogen-containing heteroaromatic groups such as pyridine, pyrrole, and indole [43]. A broad peak was observed at 7.0–8.4 ppm for CH350 and indicates significant steric hindrance [42]. Cottonseed hull biochars presented in Fig. 5 showed an increase (200–350 °C) and subsequent decrease (350–500 °C) of FTIR peaks attributable to carboxyl C=O and aromatic C=C , C=O stretching of conjugated ketones and quinones [16]. These and other oxygen-containing functional groups observed in Fig. 5 can translate into the ability of CH350 to complex and retain metal ions (Fig. 1).

3.4. Oxygen functional groups

Elemental analysis and the determination of total acidity and pH_{pzc} are useful approaches for quantifying oxygen-containing functional groups observed in ^1H NMR analyses of char extracts (Fig. 5). In Table 1, total acidity (in mequiv. g^{-1}) was determined assuming that NaOH neutralizes all organic acids with pK_a less than 12, including high pK_a phenols [25]. The pH_{pzc} and O/C for cotton-

seed hull chars and PS800 [16] and total acidity of phosphoric acid activated carbons [9] are the literature values.

Examination of Table 1 for each category (cottonseed hull char, phosphoric acid activated carbon, and steam activated carbon) indicates the following consistent trend: a decrease in pH_{pzc} with an increase in total acidity and the molar O/C ratio of biochar. A plot of equilibrium Cu, Ni, Cd, Pb concentrations (Fig. 1) as a function of molar O/C ratio (Table 1) will provide a quantitative assessment for the influence of oxygen functional groups. As shown in Fig. 6, for each category (cottonseed hull biochar, phosphoric acid activated carbon, and steam activated carbon), the equilibrium concentration consistently decreases as a function of O/C ratio, and the greatest influence of the O/C ratio is observed for Cu, Pb and

Table 1

Determined pH_{pzc} , total acidity, and molar O/C ratio of chars^a. Ultimate analysis results are given as mean \pm standard deviation for triplicate measurements on a moisture- and ash-free basis.

Char	pH_{pzc}	Total acidity (mequiv. g^{-1})	O/C (molar ratio)
<i>Cottonseed hull chars</i>			
CH200	3.5	1.63	0.59 ± 0.01
CH350	7.0	1.47	0.153 ± 0.001
CH500	10.1	0.21	0.065 ± 0.002
CH650	9.9	0.18	0.049 ± 0.003
CH800	9.2	0.26	0.06 ± 0.01
<i>Phosphoric acid activated carbons^b</i>			
PS100	3.14	1.7 ± 0.1	0.24 ± 0.01
PS400		2.5 ± 0.3	0.26 ± 0.02
PS800	3.07	2.9 ± 0.3	0.30 ± 0.01
PS1200		3.74 ± 0.02	0.30 ± 0.03
PS1600		3.1 ± 0.5	0.27 ± 0.04
PS2000	3.04	3.6 ± 0.1	0.30 ± 0.02
<i>Steam activated carbons</i>			
Flax	4.1		0.041 ± 0.003
Picker	3.8		0.126 ± 0.004
Stripper	4.0		0.09 ± 0.02

^a pH_{pzc} and O/C for cottonseed hull chars and PS800 were obtained from Refs. [14,16].

^b Total acidity of phosphoric acid activated carbons were obtained from Ref. [9].

total concentrations. For cottonseed hull chars, CH350 (having the highest oxygen content of all cottonseed hull chars employed in Figs. 1 and 6, Table 1) showed a disproportionately high effectiveness for sorption of all heavy metals examined (Cu, Ni, Cd, Pb) [16]. For phosphoric acid activated carbons, the ability to sorb each heavy metal (Fig. 1) linearly increased with the oxygen functional group content (PS100 < PS400 < PS800, Table 1). For steam activated carbons, despite minimal heavy metal retention capacity, higher O/C ratio of picker (Table 1) correlated with the greatest ability to retain Cu, Pb (and total in Fig. 1), and the lowest O/C ratio of flax correlated with the lowest heavy metal retention capacity of all biochars investigated in Fig. 1e.

In conclusion, biochars containing high oxygen functional groups are expected to be most effective for stabilizing heavy metals, especially softer acids (Pb²⁺, Cu²⁺) [44] in acidic, low CEC, low TOC soils. The PMF analyses in this study indicated that heavy metal stabilization by biochar amendment occurred with a concurrent release of various elements such as Na, Ca, K, Mg, P, and S originating from soil and biochar. Both soil and biochar possess buffering capacity and can serve as the source and sink of all elements considered in the PMF analyses.

For a long-term stabilization of Pb and Cu at target sites such as shooting range [1], biochars should be engineered to have (1) high stability (high fixed carbon content) and (2) high metal ion-coordinating functional group content. With increasing pyrolysis temperature, recalcitrance of biochar towards microbial and chemical degradation increases [45] while the O/C ratio decreases [16]. Oxidation of biochar [10] formed at high pyrolysis temperature is a way of engineering biochar to have high stability and high oxygen content. Similarly, steam activated carbons that showed minimal heavy metal retention capacity can be oxidized to improve their metal ion-coordinating ability. For agricultural usage, biochars having high ash contents are known to induce pH increase and release elements having nutrient values (P, K, N) [46]. However, care must be taken to assess the potential release of undesirable elements [17], especially the oxoanions of Sb and As [27].

Supporting Information Available

Diagnostic tools for the PMF analysis, determination of pH_{pzc} for steam- and phosphoric acid-activated carbons, equilibrium concentration of total dissolved divalent metal ions for Cu, Cd, Ni, and Pb, and DMSO extracts of cottonseed hull chars. This materials is available free of charge online.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.063.

References

- [1] D.I. Bannon, J.W. Drexler, G.M. Fent, S.W. Casteel, P.J. Hunter, W.J. Brattin, M.A. Major, Evaluation of small arms range soils for metal contamination and lead bioavailability, *Environ. Sci. Technol.* 43 (2009) 9071–9076.
- [2] X.D. Cao, L.Q. Ma, M. Chen, D.W. Hardison, W.G. Harris, Weathering of lead bullets and their environmental effects at outdoor shooting ranges, *J. Environ. Qual.* 32 (2003) 526–534.
- [3] F. Monna, C. Petit, J.P. Guillaumet, I. Jouffroy-Bapicot, C. Blanchot, J. Dominik, R. Losno, H. Richard, J. Leveque, C. Chateau, History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat bog (Morvan, France), *Environ. Sci. Technol.* 38 (2004) 665–673.
- [4] C. Adams, E.C. Witt, J.M. Wang, D.K. Shaver, D. Summers, Y. Filali-Meknassi, H.L. Shi, R. Luna, N. Anderson, Chemical quality of depositional sediments and associated soils in New Orleans and the Louisiana peninsula following Hurricane Katrina, *Environ. Sci. Technol.* 41 (2007) 3437–3443.
- [5] G. Sposito, *The Chemistry of Soils*, Oxford University Press, New York, NY, 1989.
- [6] Y.M. Cho, U. Ghosh, A.J. Kennedy, A. Grossman, G. Ray, J.E. Tomaszewski, D.W. Smithenry, T.S. Bridges, R.G. Luthy, Field application of activated carbon amend-

- ment for in-situ stabilization of polychlorinated biphenyls in marine sediment, *Environ. Sci. Technol.* 43 (2009) 3815–3823.
- [7] C.E. Brewer, K. Schmidt-Rohr, J.A. Satrio, R.C. Brown, Characterization of biochar from fast pyrolysis and gasification systems, *Environ. Prog. Sustainable Energy* 28 (2009) 386–396.
- [8] M.S. Polo, J.R. Utrilla, Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons, *Environ. Sci. Technol.* 36 (2002) 3850–3854.
- [9] K.T. Klasson, L.H. Wartelle, J.E. Rodgers, I.M. Lima, Copper(II) adsorption by activated carbons from pecan shells: Effect of oxygen level during activation, *Ind. Crop. Prod.* 30 (2009) 72–77.
- [10] L.A. Langley, D.H. Fairbrother, Effect of wet chemical treatments on the distribution of surface oxides on carbonaceous materials, *Carbon* 45 (2007) 47–54.
- [11] H.-H. Cho, K. Wepasnick, B.A. Smith, F.K. Bangash, D.H. Fairbrother, W.P. Ball, Sorption of aqueous Zn(II) and Cd(II) by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphenic carbon, *Langmuir* 26 (2010) 967–981.
- [12] C.H. Cheng, J. Lehmann, J.E. Thies, S.D. Burton, M.H. Engelhard, Oxidation of black carbon by biotic and abiotic processes, *Org. Geochem.* 37 (2006) 1477–1488.
- [13] J.W. Lee, M. Kidder, B.R. Evans, S. Paik, A.C. Buchanan, C.T. Garten, R.C. Brown, Characterization of biochars produced from cornstovers for soil amendment, *Environ. Sci. Technol.* 44 (2010) 7970–7974.
- [14] M. Uchimiya, K.T. Klasson, L.H. Wartelle, I.M. Lima, Influence of soil properties on heavy metal sequestration by biochar amendment: 1. copper sorption isotherms and the release of cations, *Chemosphere* 82 (2011) 1431–1437.
- [15] M. Uchimiya, I.M. Lima, K.T. Klasson, L.H. Wartelle, Contaminant immobilization and nutrient release by biochar soil amendment: roles of natural organic matter, *Chemosphere* 80 (2010) 935–940.
- [16] M. Uchimiya, L.H. Wartelle, K.T. Klasson, C.A. Fortier, I.M. Lima, Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil, *J. Agr. Food Chem.* 59 (2011) 2501–2510.
- [17] L. Beesley, E. Moreno-Jimenez, J.L. Gomez-Eyles, Effects of biochar and green-waste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil, *Environ. Pollut.* 158 (2010) 2282–2287.
- [18] M. Uchimiya, K.T. Klasson, L.H. Wartelle, I.M. Lima, Influence of soil properties on heavy metal sequestration by biochar amendment: 2. copper desorption isotherms, *Chemosphere* 82 (2011) 1438–1447.
- [19] G.W. Johnson, R. Ehrlich, W. Full, Principal components analysis and receptor models in environmental forensics, in: B.L. Murphy, R.D. Morrison (Eds.), *An Introduction to Environmental Forensics*, Academic Press, San Diego, 2002, pp. 461–515.
- [20] J.M. Novak, W.J. Busscher, D.W. Watts, D.A. Laird, M.A. Ahmedna, M.A.S. Nandou, Short-term CO₂ mineralization after additions of biochar and switchgrass to a Typic Kandiodult Geoderma 154 (2010) 281–288.
- [21] J.M. Novak, P.J. Bauer, P.G. Hunt, Carbon dynamics under long-term conservation and disk tillage management in a Norfolk loamy sand, *Soil Sci. Soc. Am. J.* 71 (2007) 453–456.
- [22] G. Schoups, J.W. Hopmans, C.A. Young, J.A. Vrugt, W.W. Wallender, K.K. Tanji, S. Panday, Sustainability of irrigated agriculture in the San Joaquin Valley, California, *Proc. Natl. Acad. Sci. U.S.A.* 102 (2005) 15352–15356.
- [23] I.M. Lima, A.A. Boateng, K.T. Klasson, Pyrolysis of broiler manure: char and product gas characterization, *Ind. Eng. Chem. Res.* 48 (2009) 1292–1297.
- [24] K.T. Klasson, L.H. Wartelle, I.M. Lima, W.E. Marshall, D.E. Akin, Activated carbons from flax shive and cotton gin waste as environmental adsorbents for the chlorinated hydrocarbon trichloroethylene, *Bioresour. Technol.* 100 (2009) 5045–5050.
- [25] H.P. Boehm, Chemical identification of surface groups, *Adv. Catal.* 16 (1966) 179–274.
- [26] Y.N. Yang, Y. Chun, G.Y. Sheng, M.S. Huang, pH-dependence of pesticide adsorption by wheat-residue-derived black carbon, *Langmuir* 20 (2004) 6736–6741.
- [27] K. Hooper, M. Iskander, G. Sivia, F. Hussein, J. Hsu, M. Deguzman, Z. Odion, Z. Ileyay, F. Sy, M. Petreas, B. Simmons, Toxicity characteristic leaching procedure fails to extract oxoanion-forming elements that are extracted by municipal solid waste leachates, *Environ. Sci. Technol.* 32 (1998) 3825–3830.
- [28] R.J. Kieber, S.A. Skrabal, C. Smith, J.D. Willey, Redox speciation of copper in rainwater: temporal variability and atmospheric deposition, *Environ. Sci. Technol.* 38 (2004) 3587–3594.
- [29] N. Barabas, P. Goovaerts, P. Adriaens, Modified polytopic vector analysis to identify and quantify a dioxin dechlorination signature in sediments. 2. Application to the passaic river, *Environ. Sci. Technol.* 38 (2004) 1821–1827.
- [30] M. Uchimiya, M. Arai, S. Masunaga, Fingerprinting localized dioxin contamination: ichihara anchorage case, *Environ. Sci. Technol.* 41 (2007) 3864–3870.
- [31] P.A. Bzdusek, J.H. Lu, E.R. Christensen, PCB congeners and dechlorination in sediments of Sheboygan River, Wisconsin, determined by matrix factorization, *Environ. Sci. Technol.* 40 (2006) 120–129.
- [32] G.W. Johnson, R. Ehrlich, State of the art report on multivariate chemometric methods in environmental forensics, *Environ. Forensics* 3 (2002) 59–79.
- [33] P. Paatero, U. Tapper, Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics* 5 (1994) 111–126.
- [34] G. Norris, R. Vedantham, K. Wade, S. Brown, J. Prouty, C. Foley, EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals and User Guide; EPA 600/R-08/108, in, U.S. Environmental Protection Agency, Research Triangle Park, NC, 2008.

- [35] P. Paatero, Least squares formulation of robust non-negative factor analysis, *Chemom. Intell. Lab.* 37 (1997) 23–35.
- [36] C. Papelis, K.F. Hayes, J.O. Lechkie, HYDRAQL: A Program for the Computation of Chemical Equilibrium Composition of Aqueous Batch Systems, Version 1.0 (1988).
- [37] Critically Selected Stability Constants of Metal Complexes Database, in: V. 8. 0, in: A.E. Martell, R.M. Smith, R.J. Motekaitis (Eds.), U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD, 2004.
- [38] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, Wiley-Interscience, NY, 1996.
- [39] H.N. Cheng, L.H. Wartelle, K.T. Klasson, J.C. Edwards, Solid-state NMR and ESR studies of activated carbons produced from pecan shells, *Carbon* 48 (2010) 2455–2469.
- [40] D.S. Himmelsbach, J.W. Hellgeth, D.D. McAlister, Development and use of an attenuated total reflectance/fourier transform infrared (ATR/FT-IR) spectral database to identify foreign matter in cotton, *J. Agric. Food Chem.* 54 (2006) 7405–7412.
- [41] S.A. Berberich, J.E. Ream, T.L. Jackson, R. Wood, R. Stipanovic, P. Harvey, S. Patzer, R.L. Fuchs, The composition of insect-protected cottonseed is equivalent to that of conventional cottonseed, *J. Agric. Food Chem.* 44 (1996) 365–371.
- [42] M.I. Schnitzer, C.M. Monreal, G.A. Facey, P.B. Fransham, The conversion of chicken manure to biooil by fast pyrolysis I. Analyses of chicken manure, biooils and char by C-13 and H-1 NMR and FTIR spectrophotometry, *J. Environ. Sci. Health. B* 42 (2007) 71–77.
- [43] R.M. Silverstein, G.C. Bassler, T.C. Morrill, *Spectrometric Identification of Organic Compound*, fifth ed., John Wiley & Sons, Inc., New York, 1991.
- [44] G. Wulfsberg, *Inorganic Chemistry*, University Science Books, Sausalito, CA, 2000.
- [45] A.R. Zimmerman, Abiotic and microbial oxidation of laboratory-produced black carbon (biochar), *Environ. Sci. Technol.* 44 (2010) 1295–1301.
- [46] K.Y. Chan, L. Van Zwieten, I. Meszaros, A. Downie, S. Joseph, Using poultry litter biochars as soil amendments, *Aust. J. Soil Res.* 46 (2008) 437–444.