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Retention of Heavy Metals by Carboxyl Functional Groups of Biochars in Small Arms Range Soil

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S *Supporting Information*

ABSTRACT: Long-term effectiveness of biochar for heavy metal stabilization depends upon biochar's sorptive property and recalcitrance in soil. To understand the role of carboxyl functional groups on heavy metal stabilization, cottonseed hull biochar and flax shive steam-activated biochar having a low O/C ratio (0.04−0.06) and high fixed carbon content (∼80% dry weight basis) were oxidized using concentrated H_2SO_4/HNO_3 and 30% HNO_3. Oxidized and unoxidized biochars were characterized for O/C ratio, total acidity, pH, moisture, ash, volatile matter, and fixed carbon contents, Brunauer−Emmett−Teller surface area, and attenuated total reflectance Fourier transform infrared spectral features. Characterized biochars were amended (2%, 5%, 10%, and 20% in grams of biochar per gram of soil) on a sandy, slightly acidic (pH 6.27) heavy metal contaminated small arms range soil fraction (<250 μm) having low total organic carbon (0.518%) and low cation exchange capacity (0.95 cmol$_c$ kg^{-1}). Oxidized biochars rich in carboxyl functional groups exhibited significantly greater Pb, Cu, and Zn stabilization ability compared to unoxidized biochars, especially in pH 4.9 acetate buffer (standard solution for the toxicity characteristic leaching procedure). Oppositely, only oxidized biochars caused desorption of Sb, indicating a counteracting impact of carboxyl functional groups on the solubility of anions and cations. The results suggested that appropriate selection of biochar oxidant will produce recalcitrant biochars rich in carboxyl functional groups for a long-term heavy metal stabilization strategy in contaminated soils.

KEYWORDS: *biochar, surface functional group, oxidation, heavy metal, soil*

INTRODUCTION

There are approximately 3000 Department of Defense small arms ranges (SARs) in the United States[1] and many thousands more used by police and civilians. On range soils, metallic Pb in spent bullets undergoes a slow and strongly pH dependent oxidation to form lead carbonate, lead sulfate, and lead (hydr)oxide phases that are mostly confined to the top few inches of soil.[1,2] While additional elements such as Cu, Sb, As, and Zn used to manufacture bullets are found in SAR soils, Pb is by far the major risk driver at ranges because of high concentration and toxicity.[3] Various removal (phytoremediation, soil washing, electrokinetics)[4] and nonremoval (solidification/stabilization) remediation technologies have been proposed as an alternative to costly soil excavation and disposal.[4] The long-term effectiveness of heavy metal stabilizing agents is strongly influenced by the amendment-induced changes in pH and dissolved organic carbon (DOC) content.[2,5]

Phosphate amendment is demonstrated as an effective chemical stabilization approach in shooting range soils.[5] In addition to hydroxyapatite ($Ca_5(PO_4)_3OH$) and rock phosphate ($Ca_5(PO_4)_3F$), cost-effective, waste-derived phosphorus sources such as poultry manure, incinerated poultry litter, biosolid compost, fly ash,[5] and bone char[6] have shown utility as the soil amendment for Pb stabilization. The primary mechanism of Pb stabilization by phosphate amendment is considered to be the rapid formation of thermodynamically stable solubility-limiting pyromorphite phases.[2] During 1 year of incubation of shooting range soils, relative proportions of Pb species evolved from 32% organic, 22% PbO, 28% $PbCO_3$, and

8% $Pb(CO_3)_2(OH)_2$ in unamended soil to as much as 31% chloropyromorphite in the presence of the following amendments: calcium phosphate, incinerated poultry litter, and hydroxyapatite synthesized from ceramic waste.[2] However, organically complexed Pb persisted in amended soils and likely inhibited the formation of pyromorphite.[2] Biochar has been investigated for heavy metal stabilization in mine tailings (for Cd, Cr, Cu, Ni, Pb, and Zn)[7] and urban soils (for As, Cd, Cu, and Zn).[8] To our knowledge, no prior report is available on the stabilization of heavy metals by biochar amendment in shooting range soils.

A previous study showed controlling roles of surface functional groups (attributable to volatile matter and oxygen contents of biochar) on heavy metal retention[9] in sandy acidic (Norfolk) soil having a low cation exchange capacity (CEC; 2−8 cmol$_c$ kg^{-1}) and total organic carbon (TOC; 6.3−9.2 g kg^{-1} at 0−15 cm depth) content.[10] Biochars having a higher O/C ratio showed progressively greater ability to retain Pb, Cu, Ni, and Cd in Norfolk soil.[11] Because the O/C ratio decreases as a function of the pyrolysis temperature, biochars formed at lower pyrolysis temperature exhibited greater heavy metal stabilization.[9] The long-term effectiveness of biochar as a heavy metal sorbent must be considered in conjunction with the recalcitrance in soil that increases as a function of the pyrolysis

temperature.[12] Biochars formed at high pyrolysis temperatures (650−800 °C) that are post-treated by acids and other oxidants will possess oxygen-containing surface functional groups[13] as well as recalcitrance toward biotic and abiotic degradation pathways.[12]

This is the first in a series of papers investigating the factors controlling heavy metal stabilization by biochars in SAR soils. Particular focus was given to the carboxyl surface functional groups by employing two biochars having a low O/C ratio and high fixed carbon content[9,11] as well as oxidized analogues. The objective of this study was to understand (1) how different oxidants (concentrated H_2SO_4/HNO_3 and 30% HNO_3) influence the carboxyl content and stability (fixed carbon content) of unactivated and steam-activated biochars and (2) the role of carboxyl 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. To understand the relative importance of cation exchange, acid dissolution,[14] and other processes[15] controlling the fate of Pb, the following additional selected elements were quantified at each equilibration step: Cu, P, K, Na, Ca, Mg, Zn, and Sb.

MATERIALS AND METHODS

Detailed biochar production and characterization methods are available in previous reports[9,16] and are summarized below. Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (Millipore, Milford, MA) was used for all procedures. Elliott soil humic acid (ESHA; 1S102H) and reference Suwannee River natural organic matter (SRNOM; 1R101N) were obtained from the International Humic Substance Society (IHSS; St. Paul, MN).

Biochar Production and Oxidation. Cottonseed hulls were obtained from the 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 800 °C for 4 h under a 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 char (CH800) was allowed to cool to room temperature overnight under a nitrogen atmosphere.

Steam-activated biochar from flax shive (hereby denoted flax) was prepared by pyrolysis at 700 °C for 1 h under a 1600 mL min^{-1} nitrogen flow rate and subsequent steam activation at 850 °C for 1.5 h under a nitrogen atmosphere with a 3 mL min^{-1} water flow rate.[16] To remove excess ash, CH800 and flax were washed with 0.1 M HCl (27 g of char L^{-1}) by constant stirring for 1 h, rinsed three times with DDW, and dried overnight at 80 °C.

A mixture of concentrated H_2SO_4 and HNO_3 was selected to oxidize CH800 and flax, because this treatment was previously shown to increase the carboxyl content of multiwalled carbon nanotubes (MWCNTs) to a greater extent than other oxidants such as nitric acid and $KMnO_4$.[17] The char sample (5 g) was immersed in 400 mL of a 3:1 (v/v) H_2SO_4/HNO_3 mixture. The reaction was highly exothermic, was allowed to cool, and was maintained at 70 °C for 6 h. To remove residual acid, oxidized chars were first drained through a 325 mesh sieve and were repeatedly washed with 1 L of DDW for 1 h until the pH stabilized (Figure S1, Supporting Information). The resulting oxidized char samples are hereby denoted flax-ox and CH800-ox.

Separate, milder oxidation of flax and CH800 was carried out using 30% (v/v) nitric acid. Nitric acid is commonly employed to oxidize activated carbon.[18,19] A char sample (5 g) was immersed in 125 mL of 30% nitric acid and was heated to 70 °C for 1 h. The resulting oxidized chars are hereby denoted flax-30% and CH800-30%. Immediately following the oxidation, flax-30% and CH800-30% were repeatedly washed as described above for flax-ox and CH800-ox until the pH stabilized to 3.7 (flax-30%) and 4.4 (CH800-30%).

Surface Area and Elemental Composition. Surface areas were measured in duplicate by nitrogen adsorption isotherms at 77 K using a NOVA 2000 surface area analyzer (Quantachrome, Boynton Beach, FL). Specific surface areas were determined from adsorption isotherms using the Brunauer−Emmett−Teller (BET) equation. The micropore area was calculated using t-plots derived from the AS1WIN software. The elemental composition (CHNSO) was determined by dry combustion using a Perkin-Elmer 2400 series II CHNS/O analyzer (Perkin-Elmer, Shelton, CT).

Total Acidity. Total acidity was determined using the modified Boehm titration method.[20] Briefly, 10 g L^{-1} char suspension was prepared in 0.1 M NaOH. After being stirred for 24 h, the char suspension was filtered (0.45 μm Millipore Millex-GS, Millipore Corp., Billerica, MA), and 9 mL of 0.1 M HCl was added to 4.5 mL of filtrate. The resulting solution was N_2 sparged for 2 h and then titrated with 0.1 M NaOH (Titrando 835 autotitrator, Metrohm ion analysis, Herisau, Switzerland). Blanks were prepared by adding 4.5 mL of 0.1 M NaOH to 9 mL of 0.1 M HCl. Surface acidity (mequiv g^{-1}) was determined assuming that NaOH neutralizes all organic acids with a pK_a of less than 12, including high-pK_a phenols.[20]

ATR-FTIR. Fourier transform infrared (FTIR) spectra were obtained for triplicate subsets of each sample using a Bruker Vertex 70 spectrometer (Bruker Optics, Billerica, MA) fitted with a Pike Technologies MIRacle attenuated total reflectance (ATR) accessory (Madison, WI) with a diamond crystal plate. The spectra were obtained at 8 cm^{-1} resolution from 650 to 4500 cm^{-1} with 128 scans. First derivatives of the FTIR spectra were obtained using OPUS 6.5 software with nine-point Savitzky−Golay smoothing.[21]

Proximate Analysis. Moisture, ash, volatile matter, and fixed carbon contents of biochars and selected soil, natural organic matter (NOM), and biomass feedstock samples were determined in duplicate by following American Society for Testing and Materials (ASTM) method D5142[22] using a LECO thermogravimetric analyzer (TGA701, LECO, St. Joseph, MI). Moisture was determined as the weight loss after the char was heated in an open crucible to 107 °C and held at this temperature until the sample weight stabilized. Volatile matter was determined as the weight loss after the char was heated in a covered crucible to 950 °C and held for 7 min. Ash was defined as the remaining mass after the char was subsequently heated in an open crucible to 750 °C and held at this temperature until the sample weight stabilized. After the determination of moisture, ash, and volatile matter, fixed carbon was calculated by difference. Proximate analyses were not performed for CH800-ox and flax-ox because of limited sample quantity.

Soil Incubation Experiment. As described in detail in a previous report,[1] the top few inches of small arms range soil sample from Maryland (MD1) was obtained from Aberdeen Proving Ground, air-dried, and sieved (<250 μm). Detailed collection, handling, and characterization of MD1 were described previously.[1] MD1 was characterized as a sandy, slightly acidic (pH 6.27) soil containing low TOC (0.518%) and low CEC (0.95 cmol$_c$ kg^{-1}).[1] Total metal concentrations were determined by nitric acid/hydrofluoric acid digestion of MD1 followed by inductively coupled plasma mass spectrometry (ICP-MS) and were (μg g^{-1} for 3−5 subsamples) 14847 ± 193 for Pb, 1419 ± 31 for Cu, 205 ± 4.3 for Zn, and 33 ± 0.5 for Sb.[1] 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 high concentration and toxicity.[1] In MD1, Pb existed primarily (~80% by electron microprobe) in highly bioavailable $PbCO_3$ phases.[1] Minor Pb fractions (<10%) were associated with TiO_2, FeOOH, or clay or were in PbOOH, PbO, and $PbSO_4$ phases.[1]

Batch equilibration experiments were conducted using a standard weak acid solution prepared by adding 10 mM H_2SO_4 to DDW until a pH of 4.5 was attained. This solution was often employed in experiments designed to simulate element leaching due to rainfall.[23] Separate reactors were prepared in polypropylene centrifuge tubes (50 mL nominal volume, Thermo Fisher Scientific, Waltham, MA) for MD1 (20 g of soil L^{-1}) with and without 2%, 5%, 10%, and 20% (g of biochar g^{-1} of soil) flax, CH800, flax-ox, and CH800-ox. The total volume of each reactor was set to 30 mL. The reactors were equilibrated for 1 week by being shaken end-over-end at 70 rpm. Each equilibration experiment was performed in duplicate.

Table 1. O/C Ratio, Moisture, VM, Fixed Carbon, and Ash Contents, pH, Total Acidity, BET Surface Area (SA), and Micropore Area of Unactivated (CH800) and Steam-Activated (Flax) Biochars before and after Oxidation Using Concentrated H_2SO_4/HNO_3 (Flax-ox, CH800-ox) and 30% HNO_3 (Flax-30%, CH800-30%)[a]

char	O/C ratio	moisture content, % (w/w)	VM_{db} content, % (w/w)	fixed C_{db} content, % (w/w)	ash_{db} content, % (w/w)	pH	total acidity, mequiv g^{-1}	BET SA, m^2 g^{-1}	micropore area, m^2 g^{-1}
flax	0.041 ± 0.003[b]	15.9 ± 0.1	9.0 ± 0.3	89.1 ± 0.2	1.9 ± 0.3	3.7	0	650 ± 11	515 ± 8
flax-30%	0.29 ± 0.02	14.1 ± 0.8	29.0 ± 0.9	70.2 ± 0.8	0.8 ± 0.1	3.7	1.2	580 ± 11	443 ± 12
flax-ox	0.39 ± 0.01	N/A	N/A	N/A	N/A	3.7	3.3	182 ± 4	145 ± 11
CH800	0.06 ± 0.01[c]	9.92 ± 0.05	12.7 ± 0.1	77.14 ± 0.04	10.2 ± 0.1	7.7	0	322 ± 1	274 ± 1
CH800−30%	0.21 ± 0.01	12.2 ± 0.2	22.6 ± 0.6	75.3 ± 0.6	2.09 ± 0.02	4.4	0.1	184 ± 46	157 ± 42
CH800-ox	0.31 ± 0.02	N/A	N/A	N/A	N/A	4.3	2.7	282 ± 5	258 ± 4

[a]Values are given as the mean ± standard deviation for duplicate (BET and proximate analysis) or triplicate (O/C ratio) measurements. Proximate analysis results are given on a dry weight basis (db). [b]From ref 11. [c]From ref 9.

After 1 week of equilibration, the pH of the soil suspension was measured (Orion 3-star plus benchtop pH meter, ThermoScientific, Waltham, MA). 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 26 reactors determined gravimetrically) was carefully decanted into a clear glass vial and filtered (0.2 μm Millipore Millex-GS, Millipore, Billerica, MA) 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 inductively coupled plasma atomic emission spectrometry (ICP-AES; Profile Plus, Teledyne/Leeman Laboratories, Hudson, NH). 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 procedure (TCLP).[23] The reactors were equilibrated for 1 week by being shaken 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 analysis as described above for the weak acid extraction. The second equilibration step is hereby denoted "acetate buffer extraction".

■ RESULTS AND DISCUSSION

Impact of Biochar Oxidation on the Surface Area and Functional Group. Table 1 presents the O/C ratio, moisture, VM_{db} (VM = volatile matter, db = dry weight basis), fixed C_{db}, and ash_{db} contents, pH, total acidity, BET surface area, and micropore area for flax, flax-30%, flax-ox, CH800, CH800-30%, and CH800-ox. In Table 1, the pH values of flax and CH800 were determined after a 0.5 g sample was stirred in 50 mL of DDW for 24 h. For oxidized samples, Table 1 provides the final pH from the washing procedure (Figure S1, Supporting Informaiton). Table 1 shows 10-fold (flax) and 5-fold (CH800) increases in O/C ratios of biochars as a result of oxidation using concentrated H_2SO_4/HNO_3. Milder oxidation using 30% HNO_3 resulted in 7-fold (flax) and 4-fold (CH800) increases in O/C ratios relative to those of the biochars before oxidation. Correspondingly, the total acidity of flax increased from 0 (before oxidation) to 1.2 (30% HNO_3) and 3.3 (H_2SO_4/HNO_3); a similar trend was observed for CH800 (Table 1). Both the O/C ratio and total acidity indicate that flax, despite an initially lower O/C ratio than that of CH800, was oxidized to a greater extent than CH800 by H_2SO_4/HNO_3 as well as 30% HNO_3. The surface acidity in Table 1 was determined assuming that NaOH neutralizes all organic acids with a pK_a of less than 12, including high-pK_a phenols.[20] Although acid-oxidized biochars were repeatedly washed with

DDW until the pH stabilized (Figure S1), residual acid can contribute to the total acidity in Table 1.

Table 1 indicates a decrease in BET surface area as a result of oxidation for both flax and CH800. Before oxidation, flax had a higher surface area (650 ± 11 m^2 g^{-1}) than CH800 (322 ± 1 m^2 g^{-1}) because of steam activation. While 30% HNO_3 treatment of flax caused a minor decrease (580 ± 11 m^2 g^{-1}), H_2SO_4/HNO_3 decreased the surface area to 182 ± 4 m^2 g^{-1}. The BET surface area of almond-shell-derived steam-activated carbon showed a similar decrease as a result of oxidation using concentrated HNO_3.[19] Greater reduction in BET surface area was observed for activated carbons that were exposed to steam for a longer period of time (1−8 h) and had a higher surface area prior to oxidation.[19] Activated carbon is often treated with nonoxidizing acids such as HCl and HF to reduce mineral contents.[18] This treatment results in a higher BET surface area of biochars initially containing a large fraction of ash.[24] In contrast, oxidizing acids such as HNO_3 are useful for adding oxygen-containing surface functional groups but can also "mechanically destroy pores by creating a surface tension".[18] In Table 1, greater reduction in the surface area of flax by H_2SO_4/HNO_3, compared to CH800, suggests a greater susceptibility of activated biochar (pyrolysis followed by steam activation) toward pore destruction.[19] Overall, steam-activated biochar (flax) showed a greater sensitivity to oxidation than the biochar without activation (CH800) and resulted in a greater decrease in BET surface area and a greater increase in O/C ratio and total acidity (Table 1).

A similar decrease in BET surface area was observed when MWCNTs were oxidized using H_2SO_4/HNO_3, but not other oxidants such as $KMnO_4$.[17] In addition to the decrease in BET surface area, nitric acid oxidation at elevated temperature partially digested MWCNTs, generating functionalized amorphous carbon, and resulted in higher solubility of MWCNTs.[25]

In 0.1 M NaOH suspension (10 g L^{-1}, used to determine the total acidity in Table 1), flax-ox and CH800-ox formed a darkly colored suspension that passed through a 0.2 μm filter. This darkly colored filtrate was not observed for flax, CH800, flax-30%, or CH800-30%. These observations and Table 1 corroborate previous reports on activated carbons[18] and MWCNTs[25] and suggest that H_2SO_4/HNO_3 treatment of flax and CH800 causes physical changes such as the destruction of pores and formation of amorphous carbon, in addition to increases in oxygen-containing surface functional groups.

Table 1 shows proximate analysis results (wt % on a dry weight basis) for flax and CH800 with and without oxidation using 30% HNO_3. As a result of oxidation, the VM content increased 3-fold (flax) and 2-fold (CH800) while the ash

content decreased. The oxidation decreased the moisture content of flax and increased that for CH800 (Table 1). The fixed carbon content was calculated by difference after the determination of moisture, VM, and ash contents. Oxidation slightly decreased the fixed carbon content of flax and did not significantly change that of CH800 (Table 1). Although proximate analysis results are not available for flax-ox and CH800-ox due to limited sample quantity, Table 1 indicates that mild oxidation (30% HNO_3) of biochar increased the surface functional groups (O/C ratio and total acidity) while maintaining the stability (fixed carbon content) of biochar.

Fixed Carbon Content of Biochar, Biomass, NOM, and Soil. To illustrate the fixed carbon content of soil components, Figure 1 presents proximate analysis results for biochars (Table
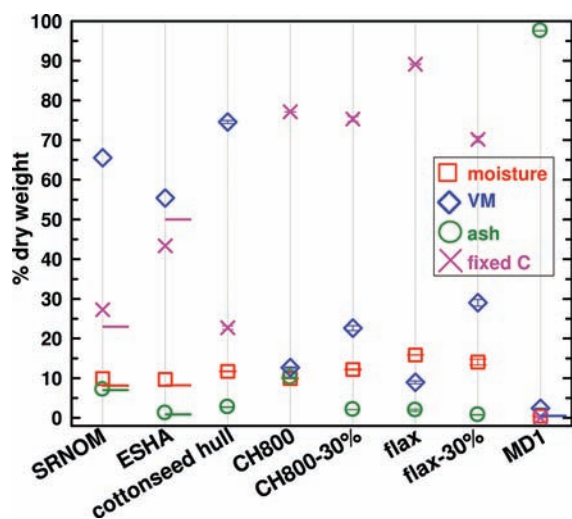

Figure 1. Proximate analysis results for ESHA and reference SRNOM, soil (MD1), biomass feedstock (cottonseed hull), and unactivated (CH800) and steam-activated (flax) biochars before and after oxidation using 30% HNO_3 (flax-30%, CH800-30%). For SRNOM and ESHA, horizontal lines represent moisture, ash, and aromatic carbon (for fixed C) values obtained from the International Humic Substance Society Web site (http://www.humicsubstances.org). For MD1, the horizontal line represents the total organic carbon value obtained from ref 1.

1) without (CH800, flax) and with (CH800-30%, flax-30%) oxidation, soil (MD1), biomass used to make CH800 (cottonseed hull), and model NOM samples (SRNOM, ESHA). Values in Figure 1 are given in weight percent on a dry weight basis. Pyrolysis of cottonseed hulls at 800 °C increased the fixed carbon content from 21% to 77% (Figure 1). As described in the previous section, oxidation (30% HNO_3) did not significantly decrease the fixed carbon content of biochars, and the fixed carbon content was greater than 70% for four biochar samples in Figure 1. Soil (MD1) consisted primarily of mineral (97.55% ± 0.02% ash) with a minimal fixed carbon content (0.05% ± 0.03%). The horizontal blue line for MD1 indicates the TOC of MD1[1] and was close to the VM content of MD1. Similarly to biomass (cottonseed hull), NOM consisted primarily of VM and had a much lower fixed carbon content than biochars (Figure 1). Horizontal lines for SRNOM and ESHA represent moisture (red) and ash (green) contents reported by IHSS and show a close agreement with the present study (Figure 1). Horizontal pink lines for SRNOM and ESHA represent aromatic carbon contents reported by IHSS and show

a trend similar to that for the fixed carbon content. Humic acid is a portion of humic substance that precipitates after acidification (pH 1) of organic materials solubilized by mixing soil with 0.5 M NaOH.[26] Relative to humic acid (ESHA) that represents the advanced stage of humification,[26] SRNOM contains a much greater amount of aliphatic components.[27] Overall, Figure 1 indicates the following increasing order of fixed carbon content for model soil components/amendments: soil (MD1) ≪ NOM ≈ biomass ≪ biochar. The significantly greater fixed carbon content of biochars (regardless of oxidation) relative to SRNOM and ESHA indicates the ability of biochars to serve as a recalcitrant carbon sink in sandy soil (MD1) having a low fixed carbon content. A minimal influence of biochar oxidation on the fixed carbon content suggests that a careful selection of biochar oxidation method will allow us to increase the metal ion coordinating surface functional groups (O/C ratio and total acidity in Table 1) while maintaining the stability of biochar (Figure 1). Although there is an active debate on the use of thermal stability and chemical structure as a measure for the stability of NOM,[28,29] laboratory experiments showed a greater stability of biochar toward microbial and abiotic degradation (which results in CO_2 release) as a function of the pyrolysis temperature,[12] and a higher pyrolysis temperature results in a higher fixed carbon content of biochar.[30,31] In addition, the stability of charred biomass (via formation of stable complexes with Al, Fe, and other mineral components) is well described for Andosol[32,33] and various other soils globally.[34]

FTIR. Figure 2 presents the first derivatives (with nine-point Savitzky−Golay smoothing) of FTIR spectra for flax, flax-ox,
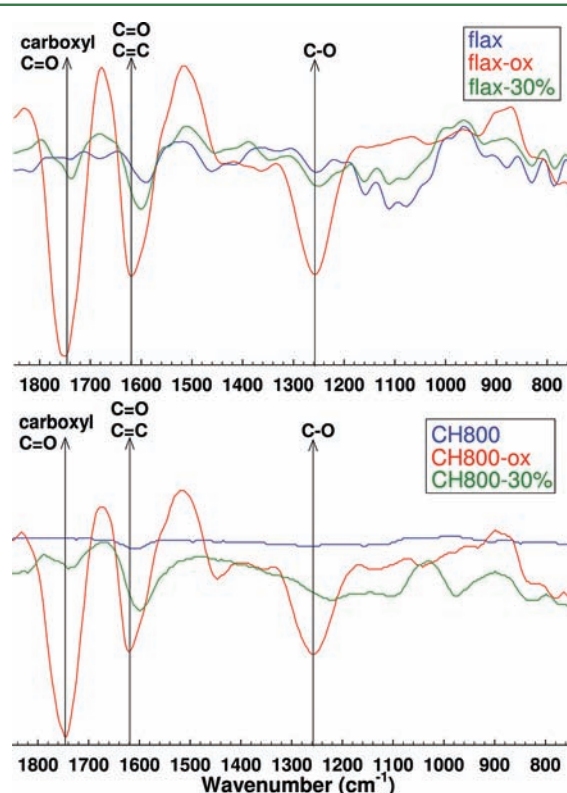
Figure 2. First derivatives of ATR-FTIR spectra for unactivated (CH800) and steam-activated (flax) biochars before and after oxidation using concentrated H_2SO_4/HNO_3 (flax-ox, CH800-ox) and 30% HNO_3 (flax-30%, CH800-30%).
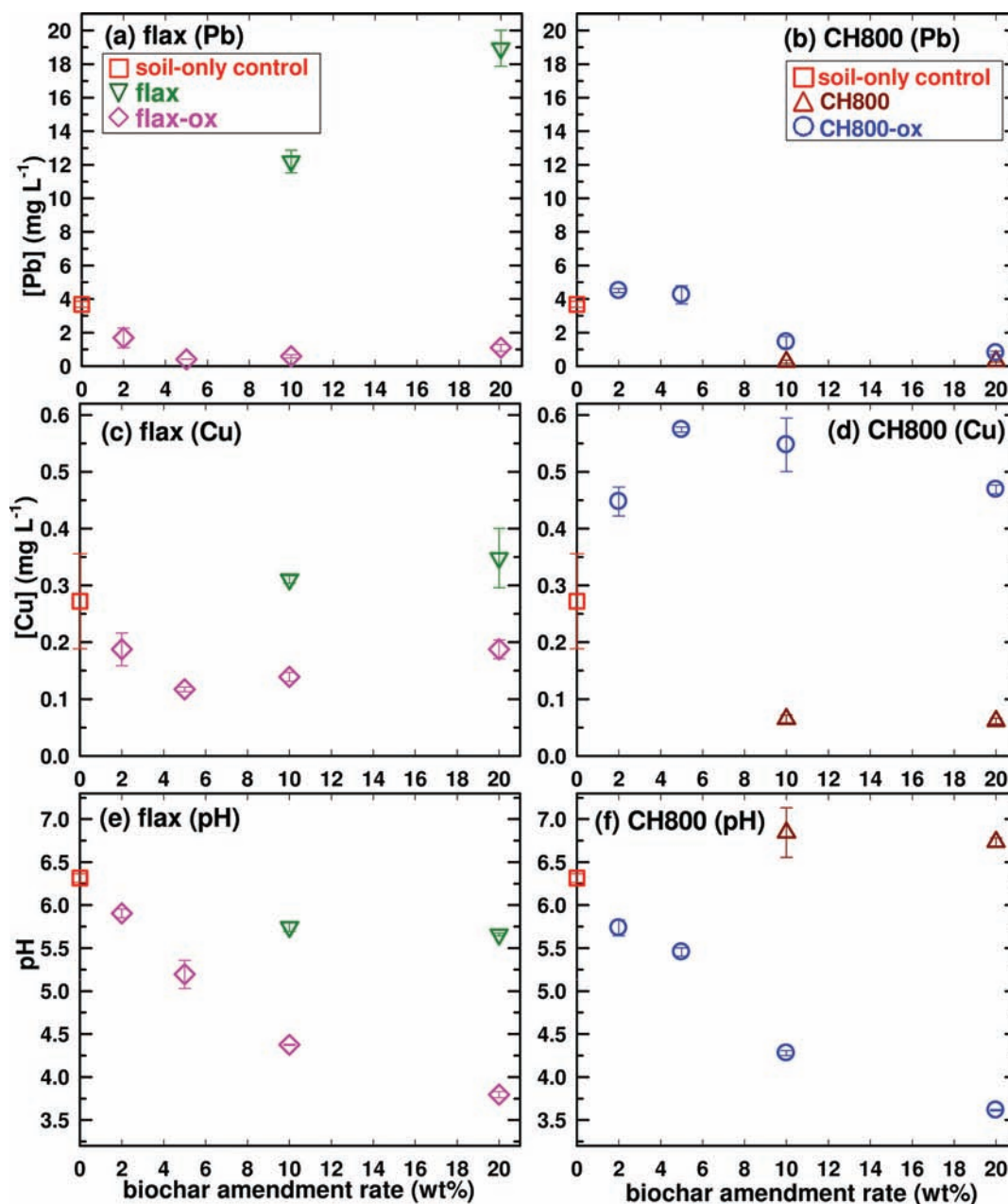
Figure 3. Soluble Pb and Cu concentrations and pH after 1 week of equilibration in pH 4.5 sulfuric acid solution (weak acid extraction) for MD1 (20 g of soil L^{-1}) amended with 2%, 5%, 10%, and 20% (g of biochar g^{-1} of soil) flax (left) and CH800 (right) biochars with and without oxidation. All values are given as the mean ± SD for duplicate experiments.

flax-30%, CH800, CH800-ox, and CH800-30%. Prior to oxidation, biochars, particularly CH800, lacked spectral features and indicated minimal surface functional group contents. For both CH800 and flax, the H$_2$SO$_4$/HNO$_3$ treatment resulted in a sharp increase in a peak attributable to C=O stretching of carboxyl functional groups.[35] Two additional peaks showed a significant increase and were attributable to C=O stretching of conjugated ketone and quinone[35] and C−O stretching of phenol.[36] The 30% HNO$_3$ treatment enhanced peaks at these regions to much lesser extent compared to H$_2$SO$_4$/HNO$_3$. Trends in Figure 2 agree with higher O/C ratio and total acidity as a result of biochar oxidation (Table 1). A subsequent heavy metal stabilization study will focus on the role of carboxyl functional groups by comparing biochars with low (flax, CH800) and high (flax-ox, CH800-ox) carboxyl contents

(Figure 2). Results for flax-30% and CH800-30% will be presented in future reports.

Equilibration 1: Weak Acid Extraction. Figure 3 presents the soluble Pb and Cu concentrations and pH in MD1 amended with 2−20 wt % biochar with and without oxidation (flax on left and CH800 on right) after 1 week of equilibration without buffer (pH 4.8 sulfuric acid solution). All values in Figure 3 are given as the mean ± SD for duplicate experiments. Squares in Figure 3 represent the soil-only control (without biochar amendment). The amendment of flax progressively increased the Pb concentration by as much as 4.5-fold at 20 wt %, compared to the soil-only control. In contrast, flax-ox gradually decreased the Pb concentration as a function of the amendment rate (Figure 3a). Both CH800 and CH800-ox retained Pb at 10−20 wt % (Figure 3b). While flax-ox (Figure
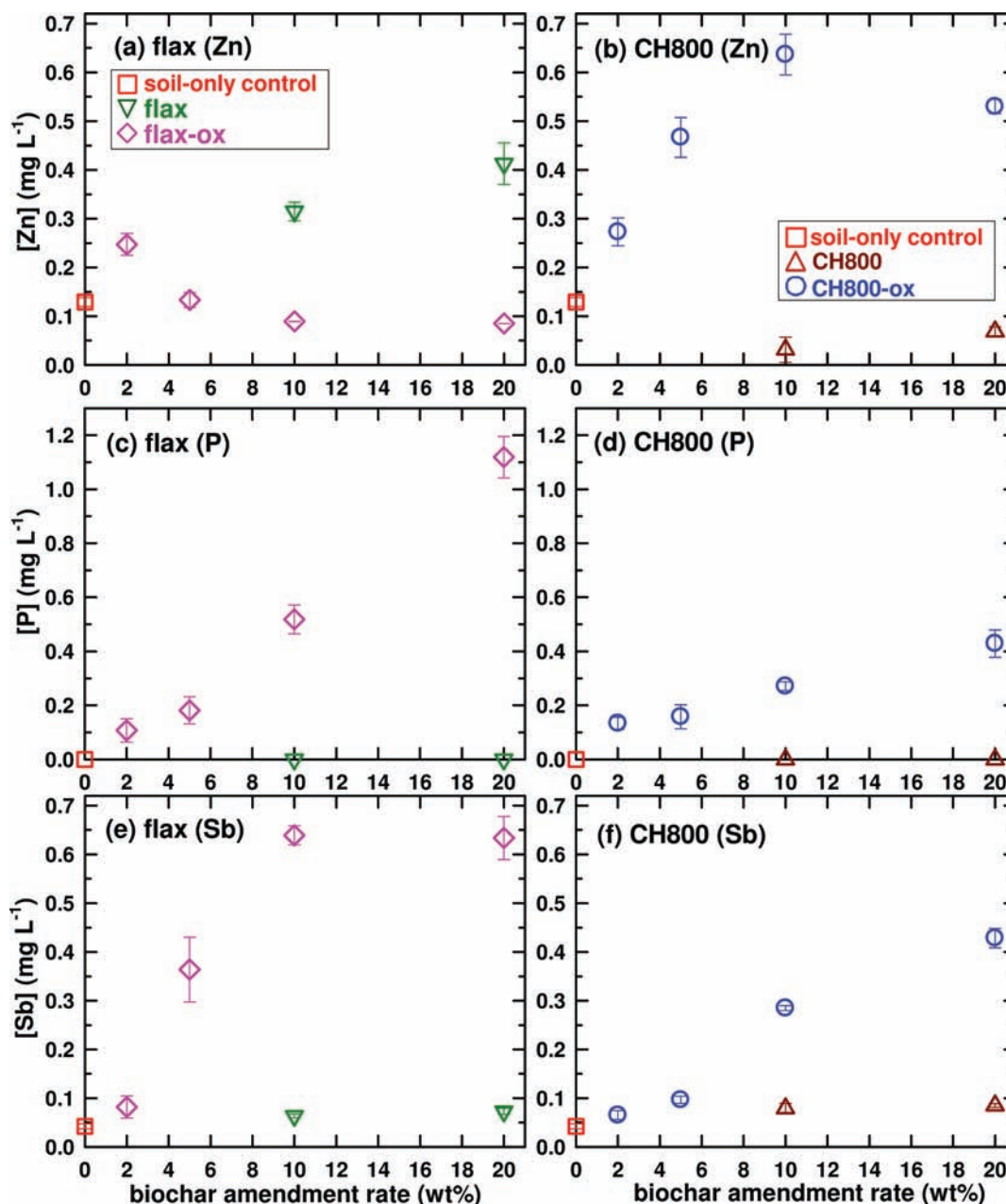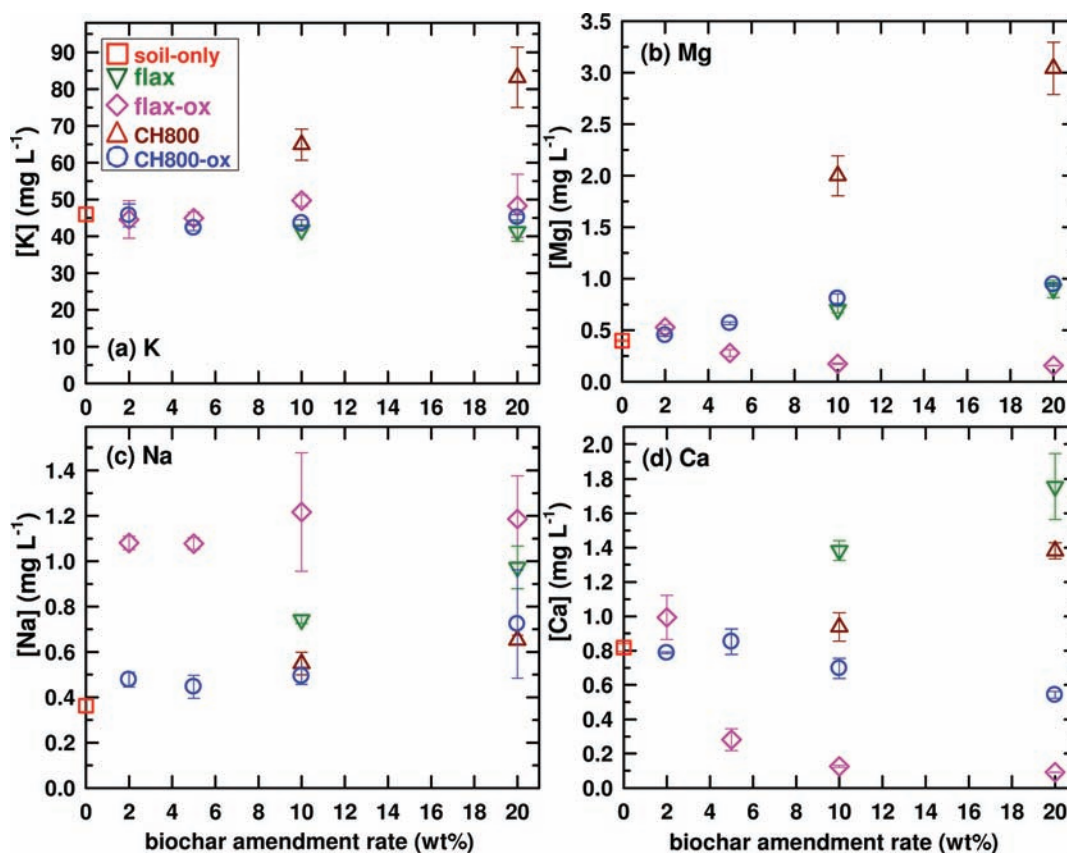
Figure 4. Soluble Zn, P, and Sb concentrations after weak acid extraction (1 week) of MD1 (20 g of soil L^{-1}) amended with 2%, 5%, 10%, and 20% (g of biochar g^{-1} of soil) flax (left) and CH800 (right) biochars with and without oxidation. All values are given as the mean ± SD for duplicate experiments.

3c) and CH800 (Figure 3d) were able to retain Cu, CH800-ox slightly increased the Cu concentration relative to that of the soil-only control (Figure 3d).

Parts e and f of Figure 3 provides the pH corresponding to Figure 3a−d. Although oxidized chars were thoroughly washed with DDW until the pH stabilized (Figure S1, Supporting Information), flax-ox (pH 3.7, Table 1) and CH800-ox (pH 4.3, Table 1) linearly decreased the pH of MD1 as a function of the amendment rate to as low as 3.6 for 20 wt % (Figure 3e,f). The observed pH decrease likely resulted from the release of residual acid and/or the pH buffering ability of oxidized biochars rich in carboxyl functional groups (Figure 2). The 10−20 wt % amendment of CH800 (pH 7.7, Table 1) slightly increased the pH of MD1, while flax (pH 3.7, Table 1) slightly decreased the pH of MD1 (Figure 3e,f).

Comparison of flax and CH800 systems shows confounding effects of pH and biochar oxidation. Parts a and c of Figure 3 indicate lower soluble Pb and Cu concentrations in the presence of flax-ox, despite acidic conditions (Figure 3e). In contrast, a slight pH decrease by flax (Figure 3e) resulted in Pb desorption (Figure 3a). Unlike flax-ox (which stabilized Pb and Cu, Figure 3a,c), CH800-ox decreased the Pb concentration only at high (10−20%) amendment rates and slightly increased the Cu concentration relative to those of the soil-only control (Figure 3b,d). In addition, CH800 showed greater Pb and Cu stabilization ability than CH800-ox. Comparison of flax and CH800 systems indicates similar impacts of biochar oxidation on the pH of amended soil (Figure 3e,f). In contrast, oxidation impacted the Pb and Cu stabilization abilities of flax and CH800 differently, resulting in the following increasing order of

Figure 5. Soluble K, Mg, Na, and Ca concentrations after weak acid extraction (1 week) of MD1 (20 g of soil L^{-1}) amended with 2%, 5%, 10%, and 20% (g of biochar g^{-1} of soil) flax (left) and CH800 (right) biochars with and without oxidation. All values are given as the mean ± SD for duplicate experiments.

stabilization: flax < control < CH800-ox < CH800 ≈ flax-ox (for Pb, Figure 3a,b); control ≈ CH800-ox ≈ flax < flax-ox ≈ CH800 (for Cu, Figure 3c,d). A generally higher soluble Pb concentration, relative to that of Cu in Figure 3, likely resulted from an order of magnitude higher total Pb content of MD1 soil (14847 ± 193 $\mu g\ g^{-1}$), compared to the Cu content (1419 ± 31 $\mu g\ g^{-1}$).[1]

Figures 4 and 5 present the soluble concentrations of additional selected elements (Zn, P, Sb, K, Na, Mg, Ca) corresponding to Figure 3. In Figure 4, the Zn, P, and Sb concentrations increased as a function of the flax-ox and CH800-ox amendment rate, except for Zn in the presence of flax-ox (Figure 4a). Because H_2SO_4/HNO_3 treatment is not likely to increase the Zn, P, and Sb contents of flax and CH800, the results indicate dissolution and/or desorption of Zn, P, and Sb from soil components under acidic conditions induced by oxidized biochars (Figure 3e,f). Acid dissolution of Zn and P was observed in a previous biochar amendment study.[37]

Under oxic conditions, Sb(V) predominates as $Sb(OH)_6^-$, sorbs on iron and manganese hydroxides (especially under acidic conditions), and forms Sb_2O_5.[38] When structurally incorporated in goethite and other mineral phases, Sb becomes much less sensitive to solubilization by changes in pH and ionic strength.[39] Despite a low total content (33 ± 0.5 $\mu g\ g^{-1}$) in MD1, desorption of Sb oxanions by oxidized biochars (and not by unoxidized biochars, Figure 4) suggests the displacement of Sb oxanions by cations (Pb and Cu) at soil and biochar surfaces. A previous biochar amendment study showed a biochar-induced increase in soluble As (which exists

predominantly in anionic forms) concentration by as much as 30-fold, concurrently with the stabilization of Cd and Zn.[40] In Figure 4f, however, CH800 did not increase the Sb concentration, despite the greater Pb and Cu stabilization ability of CH800 than CH800-ox (Figure 3b,d).

An additional cause of Sb desorption is likely to be the large amount of carboxyl surface functional groups in oxidized biochars (Figure 2). Antimony oxanions cannot form complexes with negatively charged carboxyl functional groups of oxidized biochars (above the point of zero charge, pH_{pzc}). Repulsive electrostatic interactions[41] between anions and biochar/soil surfaces can result in desorption of Sb. Oxanions are stabilized by positively charged surface functional groups, e.g., amine,[42] and carboxyl ligands such as acetate and citrate are suitable for extracting Pb, but not Sb and other elements that form oxanions.[23]

Compared to Zn, P, and Sb (Figure 4), alkali and alkaline-earth metals (K, Mg, Na, and Ca in Figure 5) did not show a clear influence of biochar type or amendment rate, except for (1) higher K, Mg, and Ca with a higher CH800 amendment rate, (2) higher Na and Ca with a higher flax amendment rate, (3) consistently higher Na in the presence of flax-ox, and (4) a gradual decrease in Ca and Mg as a function of the flax-ox amendment rate. The concentrations of K, Mg, Na, and Ca (Figure 5) are expected to show a trend with the biochar amendment rate if Pb and Cu are stabilized primarily by cation exchange[26] and as a result of pH buffering.[43] In Figure 5, only unoxidized biochars increased the K, Mg, Ca (CH800), and Na (flax) concentrations as a function of the amendment rate (note
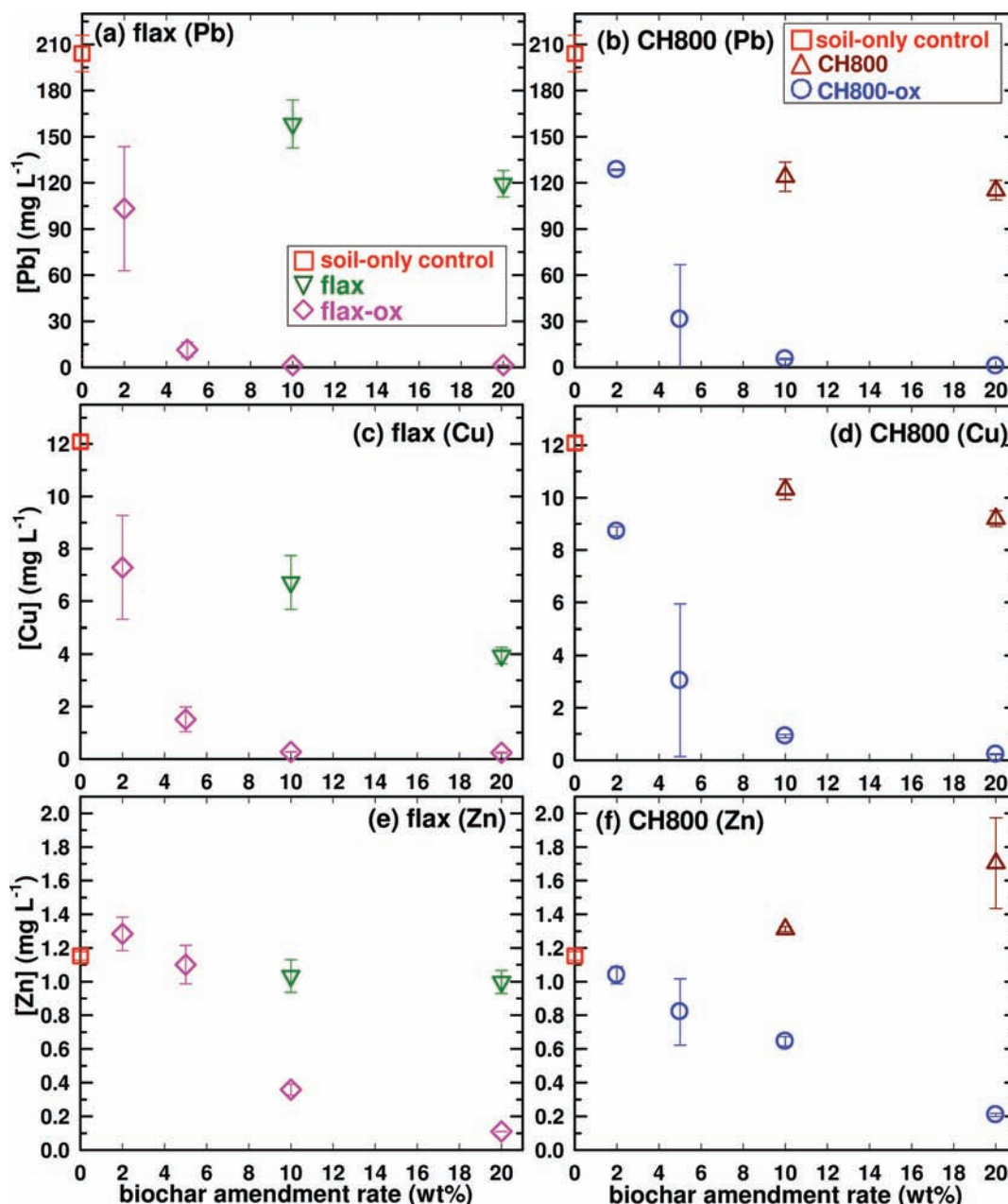
Figure 6. Soluble Pb, Cu, and Zn concentrations after 1 week of equilibration in acetate buffer (pH 4.9) for MD1 (20 g of soil L^{-1}) amended with 2%, 5%, 10%, and 20% (g of biochar g^{-1} of soil) flax (left) and CH800 (right) biochars with and without oxidation.

that the pH changes by flax and CH800 were minor compared to those of the oxidized analogues in Figure 3e,f). In contrast, flax-ox gradually decreased the Ca and Mg concentrations as a function of the amendment rate, despite Pb and Cu stabilization ability similar to that of CH800 (Figure 5; note that flax-ox progressively decreased the pH in Figure 3e). In Cu sorption−desorption isotherm experiments on Norfolk soil, the equilibrium Ca concentration was higher when sorbed Cu was higher.[37] Although the results are not directly comparable with those of the present study because the isotherms were obtained by adding Cu to Norfolk soil,[37] a greater Cu content of soil (by higher Cu addition[37] or lower biochar amendment, Figure 3c for flax-ox) may cause greater Ca release in the desorption step.

In Figure 5, opposite trends for unoxidized (CH800 and flax that increased K, Mg, Ca, and Na) and oxidized (flax-ox that decreased Mg and Ca) biochars suggest different contributions

of the cation exchange mechanism. Softer acids such as Pb[44] form weakly hydrated cations that bind electrostatically to negatively charged surfaces of clay minerals and NOM that can be readily displaced by background cations such as Ca^{2+} and Na^{+}.[45] Specific (covalent and inner-sphere) binding on reactive sites of surface functional groups makes metal cations less sensitive to background electrolyte concentrations.[46] In addition, a higher Ca concentration enhances the aggregation of DOC[15,47] and decreases the concentration of organically bound Cu.[15] The cation exchange mechanism will be explored in more detail in our future biochar amendment studies employing six additional SAR soils of known CEC values.[1]

Equilibration 2: Acetate Buffer Extraction. Figure 6 presents the Pb, Cu, and Zn concentrations after subsequent 1 week equilibration in pH 4.9 acetate buffer (0.1 M). The results in Figure 6 were obtained using the TCLP extraction fluid;
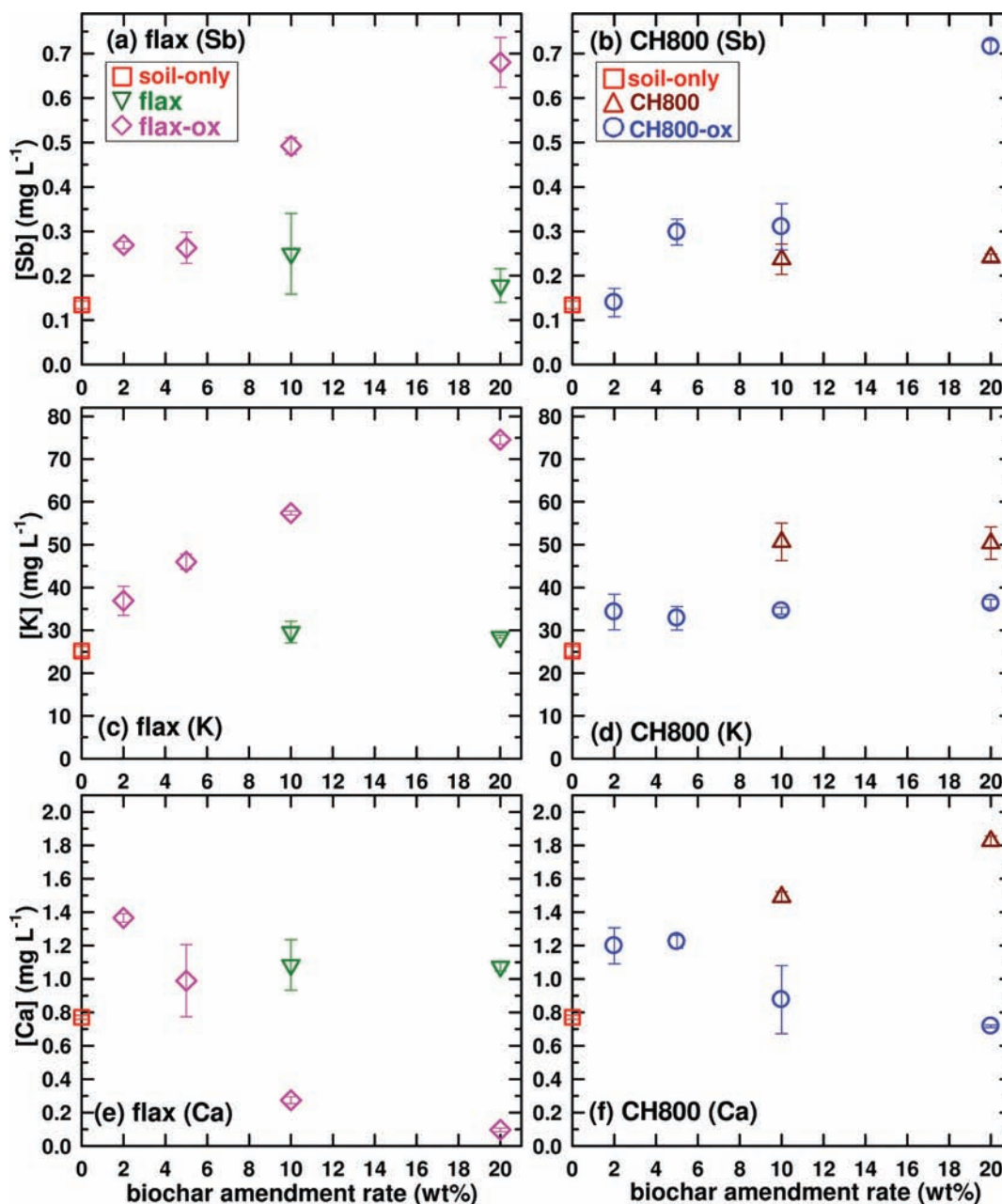
Figure 7. Soluble Sb, K, and Ca concentrations after 1 week of equilibration in acetate buffer (pH 4.9) for MD1 (20 g of soil L^{-1}) amended with 2%, 5%, 10%, and 20% (g of biochar g^{-1} of soil) flax (left) and CH800 (right) biochars with and without oxidation.

however, the standard TCLP procedure (18 h mixing period at a liquid-to-solid ratio of 20)[48] was not employed. The regulatory limit for Pb by TCLP extraction is 5 mg L^{-1}. The pH of the soil suspension was 5.0 ± 0.2 for 26 batch experiments presented in Figure 6. In acetate buffer (Figure 6), the soluble concentrations of Pb and Cu in the soil-only control were several orders of magnitude higher than in the case without buffer (Figure 3). Acetate, like other organic ligands (especially at high concentration), causes Pb desorption from soil with[37] and without[49] biochar amendment. Similarly to the case without buffer (Figures 3 and 4), the relative scale of soluble Pb, Cu, and Zn concentrations in Figure 6 followed that of the total Pb (14847 ± 193 $\mu g\ g^{-1}$), Cu (1419 ± 31 $\mu g\ g^{-1}$), and Zn (205 ± 4.3 $\mu g\ g^{-1}$) contents in MD1 soil.[1] In a striking contrast to weak acid extraction (Figure 3), all biochars stabilized Pb and Cu in acetate buffer (Figure 6). In addition,

the heavy metal retention ability of biochar showed a clear impact of the oxidation and amendment rate in a fashion distinct from that of weak acid extraction. That is, the Pb and Cu concentrations progressively decreased when the flax-ox and CH800-ox amendment rates were increased from 0 to 2 and 5 wt % and nearly reached the detection limit by 10 wt % (Figure 6a–d). For both Pb and Cu, the following increasing order of stabilization was observed: control < flax ≈ CH800 ≪ flax-ox ≈ CH800-ox (Figure 6). A similar influence of the biochar oxidation and amendment rate was observed for Zn (Figure 6e,f).

Figure 7 presents additional elements that, like Pb, Cu, and Zn (Figure 6), showed a clear dependence on the amendment rate: Sb, K, and Ca. The concentrations of other measured elements (P, Mg, and Na) did not show a dependence on the biochar amendment rate and are provided in Figure S2,

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Supporting Information (note that the majority of Na in Figure S2 resulted from 0.1 M sodium acetate). Similarly to the weak acid extraction (Figure 4e,f), a greater amount of oxidized biochars (flax-ox and CH800-ox) resulted in a progressively higher Sb concentration, whereas unoxidized biochars (flax and CH800) did not influence the Sb concentration (Figure 7a,b). Trends for the K and Ca concentrations were also similar for two extraction steps (Figures 5 and 7), except for a gradual increase in the K concentration with the flax-ox amendment rate in acetate buffer (Figure 7c). Overall, regardless of biochar amendment, the Sb, K, Ca, P, and Mg concentrations did not significantly differ between weak acid (Figures 4 and 5) and acetate buffer (Figures 7 and S2) extractions. Biochars employed in this study contained low ash fractions (Table 1), compared to manure biochars containing as much as 50 wt % ash[50] that released significantly greater P, K, and other elements in acetate buffer than in weak acid.[14,37]

Oxidized biochars (flax-ox and CH800-ox) decreased the concentrations of cations (Pb, Cu, and Zn) to a much greater extent than unoxidized biochars (flax and CH800, Figure 6). Oppositely, only oxidized biochars increased the oxoanion (Sb) concentration (Figure 7). These trends were consistently observed for two extraction steps and likely resulted from different amounts of carboxyl functional groups on oxidized and unoxidized biochars. Cations are able to form complexes with carboxyl functional groups on the surface of oxidized biochars.[41] For anions, surface interactions are suppressed by repulsive interactions with negatively charged carboxyl functional groups of oxidized biochar.

This study employed a wide range (0, 2, 5, 10, and 20 wt %) of biochar amendment rates for end-users to select the appropriate rate. When oxoanion-forming elements such as Sb and As are not a potential risk driver, carboxyl-rich biochars can be used to stabilize Pb, Cu, and Zn at a practical ($\leq$5 wt %) amendment rate (Figure 7). The carboxyl content (FTIR spectral feature, O/C ratio, and total acidity) will provide an initial screening parameter for utilizing biochars to stabilize Pb, Cu, and Zn. For a large-scale soil amendment, alternative oxidation methods should be explored for preparing carboxyl-rich biochars that are more cost-competitive than acid oxidation. Various other oxidants for activated carbons and biochars have been reported in the literature, e.g., $KMnO_4$, H_2O_2,[17] ammonium persulfate,[51] air,[52] and ozone.[41] Controlling the roles of carboxyl functional groups (flax-ox and CH800-ox) in Pb, Cu, and Zn stabilization suggests that slow in situ oxidation of biochars (which results in the formation of carboxylic, phenolic, and other oxygen-containing surface functional groups[53]) may result in a greater ability to stabilize heavy metals in soils. However, the effects of biochar aging should be fully addressed by considering additional processes such as the coating of the biochar surface by mineral, organic, clay, and silt components of soil, root penetration,[54] and transport.[55] Our future studies on additional shooting range soil samples[1] as well as field trials will provide additional information necessary for implementing a large-scale biochar soil amendment.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Oxidized biochar washing procedure and P, Mg, and Na concentrations for the acetate buffer extraction step. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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