



Physical and chemical characterization of waste wood derived biochars



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ABSTRACT

Biochar, a solid byproduct generated during waste biomass pyrolysis or gasification in the absence (or near-absence) of oxygen, has recently garnered interest for both agricultural and environmental management purposes owing to its unique physicochemical properties. Favorable properties of biochar include its high surface area and porosity, and ability to adsorb a variety of compounds, including nutrients, organic contaminants, and some gases. Physical and chemical properties of biochars are dictated by the feedstock and production processes (pyrolysis or gasification temperature, conversion technology and pre- and post-treatment processes, if any), which vary widely across commercially produced biochars. In this study, several commercially available biochars derived from waste wood are characterized for physical and chemical properties that can signify their relevant environmental applications. Parameters characterized include: physical properties (particle size distribution, specific gravity, density, porosity, surface area), hydraulic properties (hydraulic conductivity and water holding capacity), and chemical and electrochemical properties (organic matter and organic carbon contents, pH, oxidation–reduction potential and electrical conductivity, zeta potential, carbon, nitrogen and hydrogen (CHN) elemental composition, polycyclic aromatic hydrocarbons (PAHs), heavy metals, and leachable PAHs and heavy metals). A wide range of fixed carbon (0–47.8%), volatile matter (28–74.1%), and ash contents (1.5–65.7%) were observed among tested biochars. A high variability in surface area (0.1–155.1 g/m²) and PAH and heavy metal contents of the solid phase among commercially available biochars was also observed (0.7–83 mg kg⁻¹), underscoring the importance of pre-screening biochars prior to application. Production conditions appear to dictate PAH content – with the highest PAHs observed in biochar produced via fast pyrolysis and lowest among the gasification-produced biochars.

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1. Introduction

Recent innovations in environmental applications have focused on improving environmental accountability, either through the use of more sustainable materials or better management practices, into project design and implementation. Biochar has been a widely researched material for its ability to be used in environmental management and soil improvement, and has shown promise as a sorbent for some environmental contaminants, including heavy metals (Park et al., 2011; Mohan et al., 2011; Reddy et al., 2014a), polycyclic aromatic hydrocarbons (Chen and Yuan, 2011; Chen et al., 2012), and other organic contaminants (Cao et al., 2009; Sun et al., 2011; Reddy et al., 2014a). Ongoing research indicates biochar may be a favorable landfill cover amendment for

enhanced microbial methane oxidation due to its high internal microporosity, sorption properties, and stability in soil (Yaghoubi, 2011; Reddy et al., 2014b). Because biochar is often produced from waste biomass such as agricultural residues (e.g. corn stover, rice husks), scrap wood or other feedstocks (e.g. sewage sludge, poultry litter, dairy manure), biochar production and application is considered a sustainable process (Laird, 2008). Biochar amendment to soil is often deemed “carbon negative” as it can be considered as a mechanism to sequester organic carbon in vegetative biomass that would otherwise be discarded and released into the atmosphere as carbon dioxide (Spokas, 2010; Enders et al., 2012); thus the organic carbon is moved to a more slowly cycling reservoir (biochar) potentially for centuries.

Biochar has recently gained considerable interest for its potential use as a carbon sequestration agent and as a soil amendment for improved agricultural productivity (Lehmann et al., 2006; Shackley et al., 2013). Though demand for biochar in agricultural and environmental applications has increased in recent years, the

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use of carbonized biomass (or ‘black carbon’) in agriculture is not new, with archaeological and geological evidence pointing to the use of charcoal for soil improvement by indigenous people several centuries earlier in the Amazon basin of Brazil (Glaser et al., 2001) and ancient Egyptian culture (Lucas et al., 1962). The Amazonian soils, known as Terra Preta, are rich in charred biomass and as a consequence have much higher fertility than surrounding soils lacking charred material, suggesting that the char may improve plant growth by furnishing the soil with additional organic matter and nutrients (Glaser et al., 2001). However, attempts to recreate these soils have largely been unsuccessful (Kookana et al., 2011), and results from field and laboratory studies on effects of biochars on agricultural productivity have been highly variable, with some studies reporting minimal and even negative effects from biochar addition (Spokas et al., 2012). To date, there is no known correlation between biochar properties and crop yield improvements (Crane-Droesch et al., 2013).

Given the many sources of feedstock that can be used to produce biochar and the availability of multiple production technologies, the physical and chemical properties of biochars used in these studies can vary tremendously, likely leading to the high variability observed in terms of their effects on soil fertility. Accordingly, attempts have been made to characterize the physical and chemical properties of biochars that are relevant for the targeted application in order to relate the type of source material and production method to the properties of the resultant char (Brewer et al., 2009, 2011; Singh et al., 2010; Peng et al., 2011; Fabbri et al., 2012; Kloss et al., 2012). Previous work has found that the physical and chemical properties of the source material, as well as the production conditions and post-production treatments applied, play a notable role in governing key functional properties of the resultant biochar, such as sorption characteristics, surface area, porosity and structural arrangement, surface charge and alkalinity, and organic carbon content (Brewer et al., 2009; Spokas et al., 2011; Uchimiya et al., 2011; Kloss et al., 2012). The amount of toxic constituents contained in biochars has also recently been investigated by several authors (Hale et al., 2012; Lucchini et al., 2013; Oleszczuk et al., 2013). In particular, PAHs are produced during incomplete combustion of biomass, and thus are inherently generated during biochar production. Due to their known toxicity and carcinogenic traits, the risk of leaching these toxins to the surrounding environment requires careful scrutiny prior to actual field application of biochars (Oleszczuk et al., 2014).

In addition to the original feedstock composition, key production parameters governing the resulting elemental composition are the temperature and duration of heat treatment. With increasing heat treatment temperatures, the degree of carbonization of biochar increases, resulting in decreasing H:C and O:C ratios and amorphous organic matter contents (Uchimiya et al., 2011; Spokas, 2010; Beesley et al., 2011). Increases in treatment temperature from 300 to 500 °C are also associated with a rapid loss of volatile matter (Keiluweit et al., 2010; Spokas, 2010). Volatile organic compounds tend to form cyclic, aromatic molecules as pyrolysis temperature increases, with condensation of smaller aromatics also occurring to generate larger aromatic structures (Keiluweit et al., 2010; Spokas, 2010). Once biomass is heated to approximately 400 °C, most oxygenated aliphatic functional groups are thermally degraded; at 500 °C, condensation reactions begin to take place (Keiluweit et al., 2010). High heat treatment temperatures as well as chemical activation of charred materials both increase the degree of aromatic condensation on the char surface (McBeath and Smernik, 2009). An increase in surface area with increasing pyrolysis temperature is also typically observed (Downie et al., 2009). Higher surface area in biochar has been associated with improved sorption of organic chemicals, such as pesticides and herbicides (Cabrera-Mesa and Spokas, 2011; Kasozi et al., 2010; Yu et al., 2009). By these

mechanisms, bioavailability of these toxins can be reduced (Yu et al., 2009), which is one application of biochar for environmental remediation. However, strong sorption properties may be less desirable if biochar is applied for agricultural use, as herbicide efficiency may be impacted (Spokas et al., 2009; Nag et al., 2011; Graber et al., 2012). For example, Sun et al. (2011) found that biochars with the greatest amount of amorphous carbon (production temperature of 400 °C) also had the highest sorption affinities for fluorinated herbicides fluridone and norflurazon. They attribute the considerable increase in herbicide sorption from low to high temperature biochars to a concomitant increase in amorphous carbon content (Sun et al., 2011). Nag et al. (2011) also observed reduced herbicide effectiveness (by up to 3.5 times for atrazine) in soils amended with wheat straw biochar produced at 450 °C, indicating that increased herbicide application rates may be needed for biochar-amended soils. As a result of the varying properties and end uses of biochar, it is essential to characterize biochar properties prior to selecting a particular char for a specific application.

Research regarding the physical and chemical properties of biochars has responded to increased interest in biochar amendments for environmental applications. Design of biochars for targeted applications calls for employing suitable feedstock and conversion technologies that are capable of producing biochars with desired physical–chemical properties. Several researchers have characterized the physicochemical properties of laboratory-produced biochars with respect to source materials and pyrolysis technology employed (Brewer et al., 2009; Lee et al., 2010; Koide et al., 2011; Kloss et al., 2012). However, limited studies have emphasized characterizing commercially-available biochars, which often have distinct properties from those that have been produced under controlled laboratory conditions (Spokas and Reicosky, 2009). In this study, six biochars produced commercially using waste wood are characterized relative to a manufactured granular activated carbon (GAC) to provide further insight on the effects of production and post-production processes on relevant physicochemical properties of commercial, wood-derived biochars in order to assess their suitability for use in environmental applications.

2. Materials and methods

Six different wood-derived biochars and granular activated carbon (GAC) were obtained from commercial vendors and selected for detailed characterization tests as outlined in Fig. 1. Biochars were selected based on local availability and potential for use in large-scale applications; a photo of each tested biochar is shown in Fig. 2. Table 1 summarizes the feedstock sources, production processes and conditions, and type of post-treatment applied (if any) for each of the studied biochars. In addition to physical and chemical characterization, both the total and leachable PAHs and heavy metals of biochars and GAC were determined in order to assess the total and leachable amounts of toxic constituents in the selected wood-derived biochars. All characterization tests were performed using each biochar obtained as received from the vendor unless otherwise stated.

2.1. Particle size distribution, specific gravity and dry density

Particle size distribution and specific gravity of dry biochar samples were characterized according to ASTM D 422 and ASTM D 854, respectively. Dry density was determined using the Harvard miniature compaction test setup (Humboldt Mfg. Co.) according to the suggested test method described by Wilson (1970). After weighing the empty Harvard miniature mold, it was filled with the dry biochar sample in three uniformly spaced layers with five compaction strokes per layer. Once filled, the biochar samples

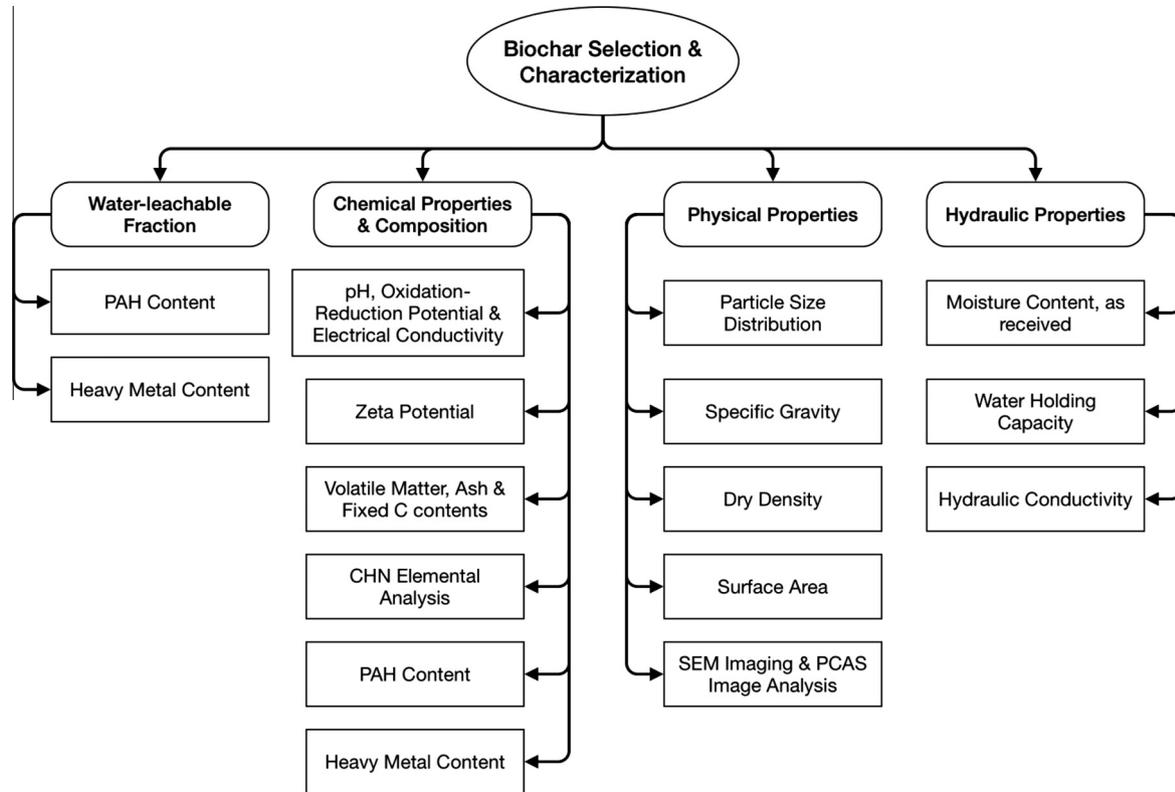


Fig. 1. Graphical overview of characterization tests performed on selected biochars and GAC.

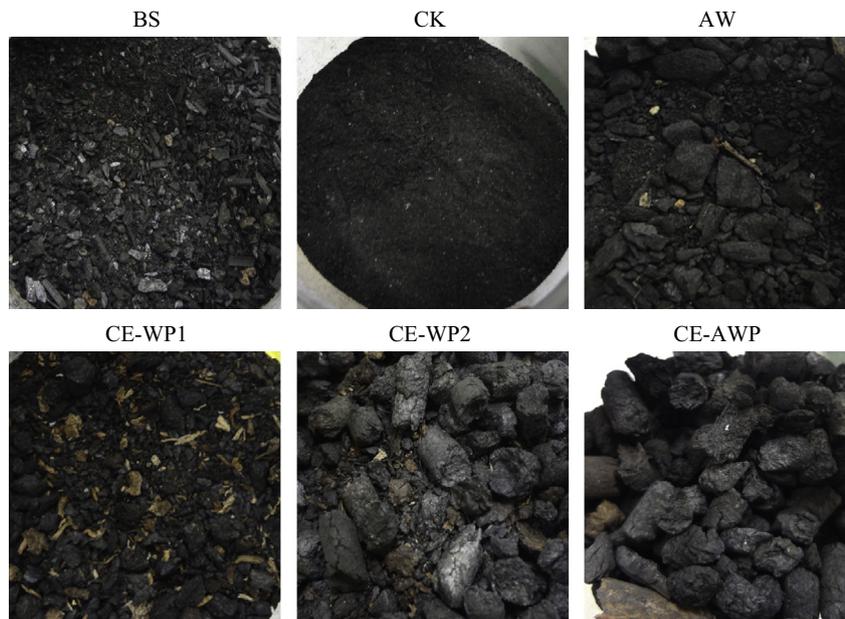


Fig. 2. Photographs of biochars tested in this study.

were leveled on the surface of the mold and the weight of the mold with biochar was noted. The dry densities of the biochars were computed based on the weight of biochar compacted into the mold and the volume of the mold.

2.2. Hydraulic properties and leachability testing

Prior to testing the biochar samples for field capacity, or water holding capacity (WHC), they were oven-dried overnight at 60 °C

to remove any residual absorbed water. The WHC of the biochars was determined by placing a known weight of biochar material in a ceramic Buchner funnel lined with filter paper (size P8; Fisherbrand). A known amount of deionized water was added to biochar slowly until the biochar was saturated and the water was allowed to drain by gravity from the biochar for approximately 3 h. The final moisture content of the biochar was determined gravimetrically as per ASTM D2216. WHC was determined by calculating the moisture content of the saturated sample and the

Table 1

Production conditions and source materials of biochars used in this study. In addition to the biochars listed below, granular activated carbon (GAC) obtained from Fisher Scientific was also used. NR: not reported.

Sample ID	Feedstock	Treatment process	Treatment temp.	Residence time	Post-treatment
GAC	Coconut charcoal	<i>Proprietary information not available</i>			High-temperature steam activation
BS	Pine wood	Slow pyrolysis	350–600 °C	6 h	Screened through 3 mm mesh
CK	90% pine; 10% fir wood	Fast pyrolysis	>500 °C	<1 h	Activated with O ₂
AW	Aged oak and hickory wood biochar	Pyrolysis – Missouri type concrete kiln	~500 °C	NR	Mixed with proprietary inocula blend and sieved (1/4")
CE-WP1	Pinewood pellets	Gasification	~520 °C	NR	Fine ash retained
CE-WP2				NR	Fine ash sieved
CE-AWP				NR	None (aged for 2 years under laboratory conditions)

relative proportion of water passing through the biochar sample after correcting for the moisture absorbed by the filter paper. This procedure was also previously adopted by a study pertaining to biochar characterization and proved to be effective in quantifying the field capacity of biochars (Kinney et al., 2012).

Hydraulic conductivity was determined via the constant-head test method as per ASTM D2434. For each biochar, 3 different constant head levels were used and the results averaged to determine the hydraulic conductivity (k) of the material. Deionized water was used during the first pore volume so that leachate could be collected and analyzed for leachable contaminants, namely PAHs and heavy metals.

2.3. Surface area measurements

Surface areas were determined on dry biochar samples via N₂ adsorption at 77 K on a Surface Area Analyzer (Micromeritics ASAP 2020 BET). BET and Langmuir adsorption isotherms were generated to determine the single-point surface area.

2.4. SEM imaging and image analysis

Samples were first coated with 3–6 nm of Pt/Pd coating using a sputter coater (Cressington HR208) in order to minimize sample charging. Images were captured using a Hitachi S-3000N Variable Pressure Scanning Electron Microscope (SEM) operated in high vacuum mode with 2–10 kV accelerating voltage (voltage applied varied based on extent of sample charging) using a secondary electron detector. Images were taken at several magnifications ranging from 50× to 4000×.

The micro-porosities of biochars and GAC were quantified using the image processing software, Pores (Particles) and Cracks Analysis System (PCAS), which was developed and validated by Liu et al. (2011). The SEM images are imported into the software which then converts them into equivalent binary forms based on the gray-level threshold values (T) entered. The microporous regions in the binary images are distinguished by segmenting the image into black and white regions representing solid surfaces and void spaces, respectively. The average T values used for this study ranged from 107 to 138 for the biochars and GAC. Error analysis was conducted for individual biochars by varying the T values from $T - 4$ to $T + 4$ at two-step intervals. The minimum pore area (S_0) was set to a default value of 50 pixels and the division radius (r) was set to 2.1 pixels. The segmentation process for the SEM images was repeated for each threshold value prior to the auto analysis. The statistical parameters corresponding to a pre-set probability range number ($n = 7$) was extracted from the software for the pore area range analyzed. The average porosity value is then recorded from the resulting tabular output along with other micropore characteristics corresponding to pore geometry.

2.5. Organic matter, ash, volatile matter, and fixed carbon contents

Organic matter was determined according to ASTM D 2947 via loss on ignition (LOI) at 440 °C. This test is typically applied to determine organic matter in soils, and thus may underestimate the actual organic content of charred materials due to the high recalcitrance of carbonaceous residues. Consequently, standard chemical analyses for wood charcoal as per ASTM D 1762-84 were also performed to determine the volatile matter, ash, and fixed carbon contents of air-dried biochar samples. Moisture content was determined gravimetrically as per ASTM D2216 prior to these tests.

2.6. pH, oxidation–reduction potential and electrical conductivity

Biochar samples (10 g) were soaked in 1:1 slurry of 0.01 M CaCl₂ solution for 2 h prior to measurement of pH, ORP and EC (Orion720A Model pH meter) as per ASTM D4972. The pH meter was calibrated with standard pH buffers at pH 4, 7 and 10 prior to analysis. All analyses were performed in triplicate and the results averaged.

2.7. Zeta potential measurements

Zeta potential (ZP) was determined for each sample in duplicate using a Zeta-Meter 3.0+ system (Zeta Meter Inc., VA). All samples were dried and passed through a No. 200 sieve prior to measurement. A solution of 0.05 g biochar in 50 mL deionized water (sample concentration of 1 g/L) was prepared in clean 50-mL vials. A small amount of the solution was placed into the sample well in the Zeta-Meter System. The velocity of particles moving toward a positively charged electrode is then measured to compute the ZP of each sample using the Zeta Meter. This measurement was taken 5–6 times per trial and averaged, with duplicate samples for each biochar tested.

2.8. CHN elemental analysis

Samples were first air-dried at 60 °C and placed into glass vials. At least two subsamples (2.0–3.0 mg each) from these sample vials were analyzed using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer operated in CHN mode. The CHN mode utilizes the Pregl-Dumas method in which samples are combusted in a pure O₂ atmosphere, and the resultant combustion gases are automatically measured and quantified to determine initial elemental concentrations of C, H and N. The reported values are averaged results from each set of duplicate samples.

2.9. Polycyclic aromatic hydrocarbons (PAHs) analysis

The concentrations of 16 USEPA Priority Pollutant PAHs were determined in all solid biochar samples. Analyses of the PAHs within

the leachate were undertaken if amounts detected in the solid char were above the detection limits of the analytical instruments used. PAHs were extracted from the biochars using an ultrasonic extraction and subsequently quantified via gas chromatography–mass spectrometry (GC/MS) according to EPA Method SW8270C. Leachate samples were generated by percolating one pore volume of deionized water through a packed column of solid biochar during hydraulic conductivity testing via the constant-head method (ASTM D2434).

2.10. Trace metal analysis

Metal content of the solid biochars was determined via inductively coupled plasma mass spectrometry (ICP/MS) according to EPA Method SW6020 for all metals tested (Al, As, Ba, Be, Ca, Cd, Cu, Cr, Co, Fe, K, Mg, Mn, Na, Ni, Pb, Se, Ag, Tl, V, Zn) except for mercury and cyanide, which were analyzed according to EPA Methods SW 7471A and SW9012A, respectively. The total metal concentrations in the leachate of biochars were also determined according to EPA Method SW6020.

3. Results

3.1. Particle size distributions

Fig. 3 shows the particle size distribution curves for biochars. The percentage of particles greater than 4.75 mm and 0.075 mm, as well as the average and effective grain sizes (D_{50} and D_{10} , respectively), for each biochar type are shown in Table 2. Based on visual interpretation of the particle size distribution curves, the percentage of fine particles (<0.075 mm) varies considerably among commercially-available biochars. As anticipated, the pelleted CE biochars typically had a lower fraction of small particles

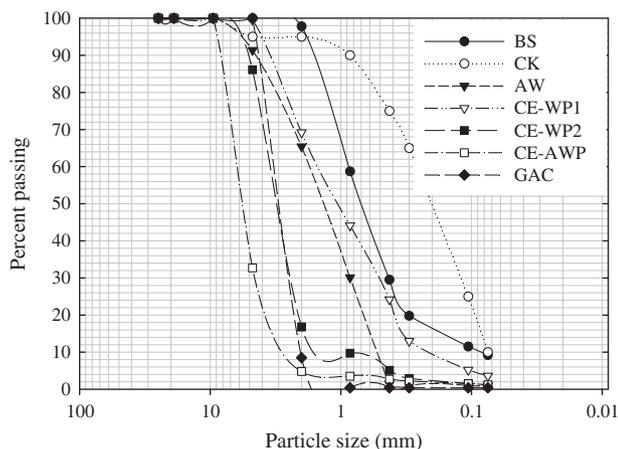


Fig. 3. Particle size distributions of tested biochars and GAC.

than the finer grained chars (i.e. CK, BS and AW). Though these biochars were produced via gasification, which tends to generate chars with smaller particles (Brewer et al., 2009), the pre-treatment pelleting (and in the case of CE-WP2, post-production sieving) removed many of the smaller particles, effectively changing the physical attributes of the biochar. This likely impacted the effective surface areas of the biochars, given that finer-textured biochars typically had higher measurable surface areas as compared to the pelleted chars (Table 2).

3.2. Dry density and specific gravity

For all tested biochars and GAC, the average dry bulk density values were less than 1 g cm^{-3} (Table 2). The low densities observed likely reflect the high internal porosities of biochars. Specific gravities of the biochars varied between 0.59 and 1.51 (Table 2), with the highest specific gravity for the biochar with lowest H:C ratio (i.e. CK biochar). Since H:C can be an indication of charring intensity (Ameloot et al., 2013), this was likely due to the concentration of heavier biomass components (e.g. ash, metals) due to greater extent of pyrolysis.

3.3. Surface area

Surface areas for the biochars were low relative to GAC, which had a surface area of $611.87 \text{ m}^2 \text{ g}^{-1}$ (Table 2). Single point surface areas for biochars ranged from $0.095 \text{ m}^2 \text{ g}^{-1}$ (CE-WP2 biochar) to $155.1 \text{ m}^2 \text{ g}^{-1}$ (CK biochar; refer to Table 2). The relatively low surface area values reported for the CE biochars are thought to be underestimates of the actual surface area due to difficulty in obtaining accurate measurements for the CE biochars. This may be attributed to the presence of pore constrictions smaller than 0.5 nm, which can lead to underestimates of surface area during N_2 adsorption, especially for coal and carbonaceous materials (De Jonge and Mittelmeijer-Hazeleger, 1996). Because of these limitations, these low surface area values are not considered to be entirely representative of the actual surface areas of the CE biochars.

3.4. SEM image analysis

SEM images were taken at several magnifications ranging from $50\times$ to $4000\times$; Fig. 4 shows representative images of each of the biochars at $250\times$ magnification. Visual inspection of these images illustrates the differences in microstructure among the chars, with distinct micropores observable, especially in the CK and BS biochars. The SEM images for all samples captured at a magnification of $2000\times$ were used for PCAS analysis. Data on microporosity obtained from PCAS analyses for all biochars and GAC are shown in Fig. 5. The results of error analysis using PCAS (provided in Supplementary Information, Table S3) indicated that the error values corresponding to average porosity of samples were within the acceptable range of 5% (Liu et al., 2011). The average porosity of biochars and GAC range from as low as 30% for AW up to 60% for GAC (Fig. 5). The porosity values corresponding to CE-biochars

Table 2
Physical properties of biochars as determined from analysis of grain size, dry density, specific gravity and surface area.

Biochar	% >4.75 (mm)	% >0.075 (mm)	D_{10} (mm)	D_{50} (mm)	Avg. dry density, ρ_d (g/cm^3)	Avg. specific gravity, G_s	Surface area ($\text{m}^2 \text{ g}^{-1}$)
BS	0.0	90.8	0.09	0.71	0.73	1.36	40.63
CK	3.8	73.0	0.08	0.22	0.54	1.51	155.1
AW	6.6	90.1	0.33	0.89	0.48	1.19	5.41
CE-WP1	0.4	96.1	0.24	1.13	0.56	0.77	0.38
CE-WP2	13.9	85.2	1.29	3.15	0.52	0.59	0.10
CE-AWP	67.3	31.5	2.68	5.75	0.53	0.91	–
GAC	0.0	91.1	1.18	2.97	0.67	1.65	611.87

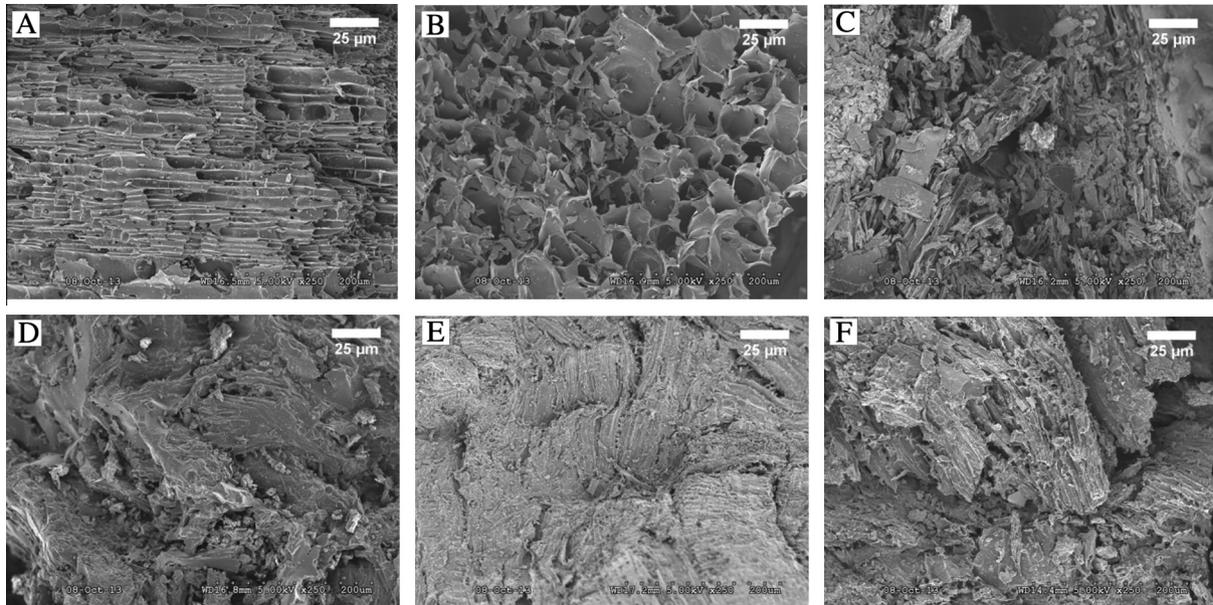


Fig. 4. SEM images of biochars tested in this study at 250× magnification. A: BS; B: CK; C: AW; D: CE-WP1; E: CE-WP2; F: CE-AWP.

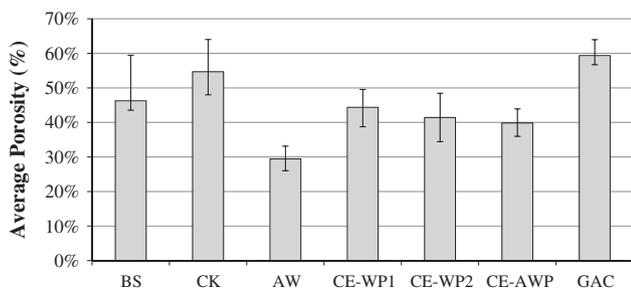


Fig. 5. Average porosity of biochars and GAC from PCAS analysis.

ranged closely from 36% to 44%. The SEM image identification results for CE-WP2 and GAC are shown in Figs. 6a and 6b, respectively. The porosity of GAC is higher than the wood-derived biochars tested for this study. CK biochar had the second highest porosity, with a value of approximately 55%. These results are in agreement with previous studies which reported an increase in porosity and surface area of biochars with increasing treatment temperatures and activation (Brown et al., 2006). Moreover, the presence of micropores in biochars makes it highly preferable for gas adsorption, which will also aid gas retention within a gas treatment system.

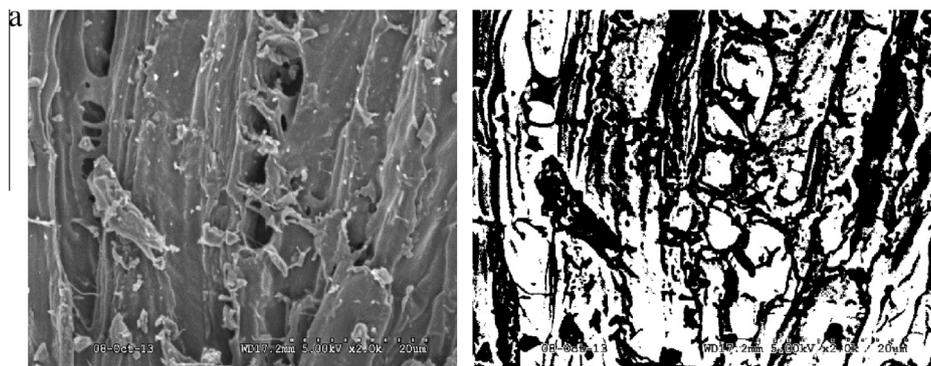


Fig. 6a. SEM image segmentation for CE-WP2 using PCAS.

3.5. Hydraulic properties

Hydraulic properties determined for each biochar and GAC include hydraulic conductivity and water-holding capacity (WHC), shown along with the initial moisture content of the samples as received from the vendors in Table 3. WHC of the tested biochars varied from 32.9% to 63.9% on a wet weight basis, or 50.6–179.4% on a dry weight basis, with the finer-grained biochars generally having higher WHC. This effect may be due to higher void ratios in finer grained biochars, in addition to stronger capillary forces among fine particles, and was especially notable in the increased WHC of the pinewood biochar with ash retained (CE-WP1) relative to the same type of pinewood biochar with the fine ash removed (CE-WP2), with WHC values of 58.7% and 32.9% on a wet mass basis, respectively. Hydraulic conductivities of the biochars are given in Table 3. As expected, finer-grained biochars also tended to have lower hydraulic conductivities, with the lowest values for CK and AW (7.9×10^{-4} and 4.2×10^{-4} cm/s, respectively).

3.6. Organic matter, volatile matter, ash and fixed carbon content

Gravimetric analysis of biochar is used to assess the relative fractions of fixed and labile organic matter, which can be represented by the volatile matter component. Ash content refers to

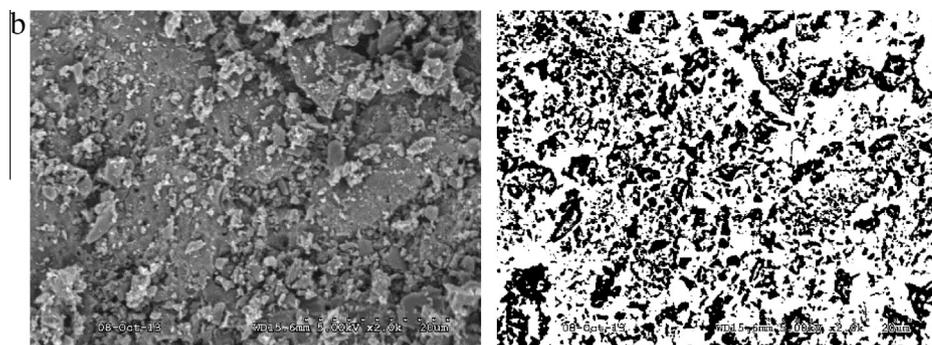


Fig. 6b. SEM image segmentation for GAC using PCAS.

Table 3

Hydraulic properties of tested biochars. Moisture content is reported as received from the vendor.

Sample	Moisture content (%)	Water holding capacity		Hydraulic conductivity, K_T (cm/s)
		% dry wt.	% total mass	
BS	0.33	120.6	54.7	1.7×10^{-3}
CK	5.66	179.4	63.9	7.9×10^{-4}
AW	66.2	113.8	50.0	4.2×10^{-4}
CE-WP1	1.38	142.4	58.7	1.1×10^{-3}
CE-WP2	2.15	50.6	32.9	3.9×10^{-3}
CE-AWP	1.98	80.8	44.5	2.7×10^{-2}
GAC	17.02	96.4	49.1	7.2×10^{-3}

the inorganic, non-combustible portion of biochar that remains after volatile matter is removed via heating at 950 °C. Though originally intended for analysis of coal and charcoal, gravimetric analysis as per ASTM D1762 has been used by several researchers to investigate the chemical properties of biochars as the relative proportions of ash and volatile matter will impact both chemical and physical properties of the biochar (e.g. Spokas and Reicosky, 2009; Brewer et al., 2009; Lee et al., 2010; Keiluweit et al., 2010). Percentages of volatile matter, ash, and fixed and organic carbon are given in Table 4 and also represented in Fig. 7.

From Fig. 7, it can be seen that biochars with higher fractions of ash content generally have the lowest values of fixed carbon and vice versa. This trend has been noted previously in many studies of biochar and charcoal (Spokas, 2010; Lee et al., 2010). The CE biochars, which were all produced from the same feedstock type and pyrolysis technology, clustered together in terms of relative abundance of ash (1.5–4.6%), volatile matter (61.8–93.6%) and fixed carbon (33.2–47.8%). By contrast, biochars from other ven-

dors (AW, BS, CK) all had distinct chemical compositions, reflecting the inherent variability in biochar chemistry that is reflective of feedstock and production conditions. Thus these wood-derived biochars have relatively low ash content as compared to previously studied biochars derived from corn stover, which can have ash contents in the range of 54–74% (Spokas and Reicosky, 2009; Lee et al., 2010). Grasses have also been known to have relatively high ash contents (e.g. ~20%; Keiluweit et al., 2010), due to the lower abundance of lignin as compared to woody feedstocks. The fixed carbon content of GAC was found to be within the range observed for the biochars at ~18%, though the GAC had a higher volatile matter content (64%). The low ash content of GAC was similar to that observed in CE biochars at ~2.8% ash by weight.

3.7. pH, ORP, EC and zeta potential

Table 4 presents pH, oxidation–reduction potential (ORP), electrical conductivity (EC), and zeta potential values of all biochars and GAC. Among the tested biochars, pH values ranged from slightly acidic to alkaline [pH = 6.24 (CE-WP2) to 8.77 (CK)]. The pH of GAC was higher than all tested biochars at 8.86. Significant differences in ORP, a measure of redox activity, were also noted among the biochars. Only 2 of 6 commercial biochars, along with GAC, displayed negative ORP values, indicating a higher reductive potential (i.e. a tendency to become oxidized through loss of electrons via reduction of another compound). This likely reflects the chemistry of sorbed cationic metals on the biochar surface or in the ash since these were biochars produced at higher temperatures with lower H:C ratios. The EC of the solid biochars varied from 0.007 to 8.33 mS cm⁻¹, with higher EC values in the lower pH biochars (pH 6.24–6.78), which also corresponded to biochars with

Table 4

Chemical properties for biochars and GAC investigated. BDL: below detection limit. ND: not determined.

Property	BS	CK	AW	CE-WP1	CE-WP2	CE-AWP	GAC
LOI organic matter content (%)	33.9	32.3	74.5	96.0	97.5	87.8	91.4
Volatile matter content (%)	28.0	28.1	74.1	61.8	62.7	55.4	64.2
Ash content (%)	65.7	61.6	25.4	4.6	1.5	4.3	2.9
Fixed C content (%)	4.6	3.7	ND	33.2	35.0	40.3	17.9
<i>Elemental analysis</i>							
C (%)	53.2	23.5	51.9	70.7	74.0	78.1	76.5
H (%)	1.6	0.4	2.2	3.8	3.8	1.8	0.8
N (%)	0.4	0.01	0.4	0.3	0.3	0.4	0.2
<i>Molar ratios</i>							
H:C	0.35	0.18	0.51	0.63	0.61	0.27	0.12
C:N	143.4	5513.9	151.9	290.7	293.9	261.5	426.6
pH	8.47	8.77	7.88	6.24	6.78	7.64	8.86
ORP	74.2	-116.1	-63.5	35.1	2.3	-48.7	-120.8
EC	0.04	0.007	0.14	4.15	1.1	0.54	0.01
Zeta potential (mV)	-23.7	-15.8	-15.4	-25.6	-24.4	-18.6	-31.0
ΣPAHs (mg kg ⁻¹)	16.9	83.0	0.68	BDL	BDL	BDL	BDL

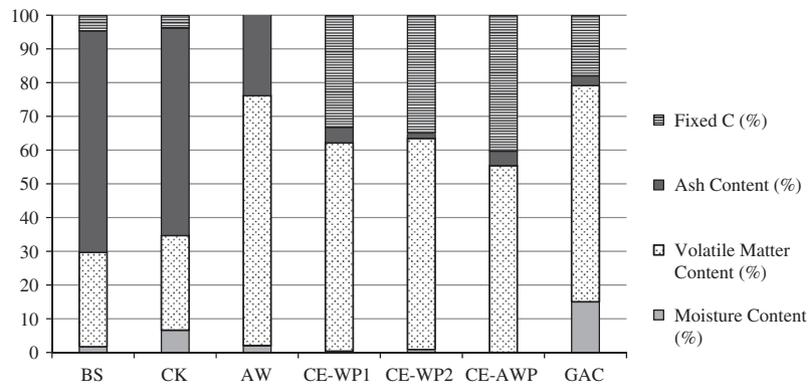


Fig. 7. Moisture, volatile matter, ash and fixed C contents of tested biochars and GAC as determined via ASTM D1462.

positive ORP values. Zeta potential values, which reflect surface charge of the material, were all negative for the tested biochars, varying from -25.6 (CE-WP1) to -15.4 mV (AW) for the biochars. Zeta potential of GAC was significantly more negative than all tested biochars (-31.0 mV), likely as a result of surface activation.

A lower fraction of cationic metals may also contribute to the lower ZP of GAC relative to the biochars, considering that CK biochar was also activated, but had a ZP of only -15.8 mV as compared to -31.0 mV for GAC, in addition to a higher concentration of cationic metals.

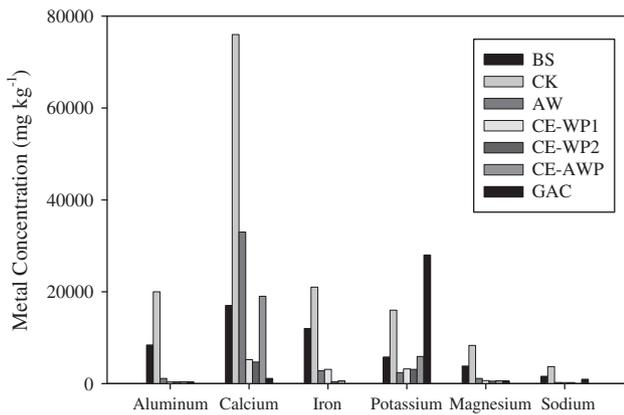


Fig. 8. Nontoxic metal concentrations in biochars and granular activated carbon (GAC) in mg kg^{-1} .

3.8. Elemental composition

The elemental composition of solid biochars was assessed by measurement of C, H and N in the solid biochars as received from the vendors; percentages by weight of C, H and N for each dry biochar are given in Table 4. Overall, the chemical composition of tested biochars varied significantly, with C, H and N contents ranging from 23.5% to 78.1%, 0.35% to 3.8% and 0.005% to 0.4%, respectively. Molar ratios of H:C and C:N are also presented as they provide indications of the extent of biomass carbonization (Table 4). Chars with higher C:N and lower H:C ratios likely underwent greater thermal alteration due to the greater loss of H and N relative to C. Of the biochars included in this study, both the lowest H:C ratio and highest C:N ratio was observed in the CK biochar. As with other properties, these data suggest that a greater extent of carbonization occurred in this biochar. However, the elemental C content of CK biochar is relatively low at 23.5%, indicating the presence of a significant amount of inorganic minerals in the ash fraction of the char.

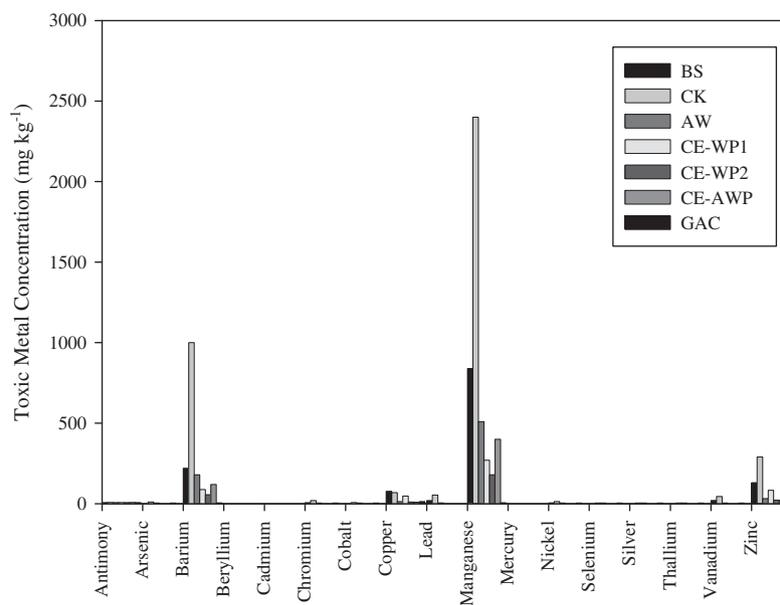


Fig. 9. Toxic metal concentrations in biochar and granular activated carbon in mg kg^{-1} .

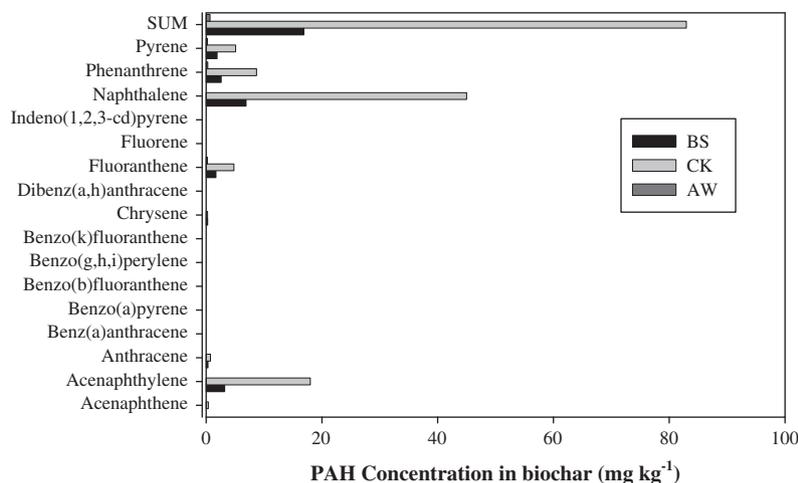


Fig. 10. PAH concentrations detected in biochars in this study in mg kg^{-1} .

3.9. PAH and metal content

For the GAC, all PAHs were below the detection limits. PAHs were only detected in three of six tested biochars (AW, BS, and CK) and ranged from a total content of 0.7 (AW) to 83 mg kg^{-1} (CK); by contrast, none of the CE biochars had detectable PAHs. Naphthalene, a low-weight and highly volatile PAH, constituted the majority (approximately 54%) of detected PAHs in the CK biochar with a concentration of 45 mg kg^{-1} in the solid char. This observation is consistent with previous studies, who also observed a dominance of naphthalene in wood-derived chars, especially at shorter pyrolysis times (Kloss et al., 2012; Hale et al., 2012). Metal concentrations varied significantly among the tested biochars, with the highest total metal content found in CK biochar ($\Sigma\text{Metals} = 148.9 \text{ g kg}^{-1}$). Overall, metal contents of the CE biochars were generally lower than AW, BS or CK chars. Figs. 8 and 9 show the concentrations of toxic and nontoxic metals, and Fig. 10 shows the PAH concentrations for biochars and GAC.

3.10. Leachability of metals and PAHs

Leachability potential for metals and PAHs was assessed upon analyzing the effluent samples (one pore volume) collected during testing of hydraulic conductivity. It was found that the risk of leaching of potentially toxic contaminants was low for the studied biochars, as all tested metals and PAHs in the leachate were below the detection limits of the analytical instruments used (provided in Tables S1 and S2, Supp. Info). In only two instances metal constituents in the biochar leachate were found in concentrations greater than Class I groundwater remediation objectives in Illinois, USA

Table 5

Metal concentrations in biochar leachate compared to residential (Class I) remedial groundwater standards in Illinois. All other metals tested (Sb, As, Be, Cd, Cr, Co, Hg, Ni, Se, Ag, Tl, V, Zn) were below the detection limits.

	Units	Class I GW	BS	CK	AW
Aluminum	mg L^{-1}	–	0.62	<0.4	1.5
Barium	mg L^{-1}	2.0	0.065	0.064	0.12
Calcium	mg L^{-1}	–	16	25	54
Copper	mg L^{-1}	0.65	<0.1	0.12	<0.1
Iron	mg L^{-1}	5.0	<1	<1	1.7
Lead	mg L^{-1}	0.0075	<0.02	<0.02	0.038
Magnesium	mg L^{-1}	–	11	5.9	7.3
Manganese	mg L^{-1}	0.15	0.077	<0.04	0.28
Potassium	mg L^{-1}	–	94	260	72
Sodium	mg L^{-1}	–	11	53	5.6

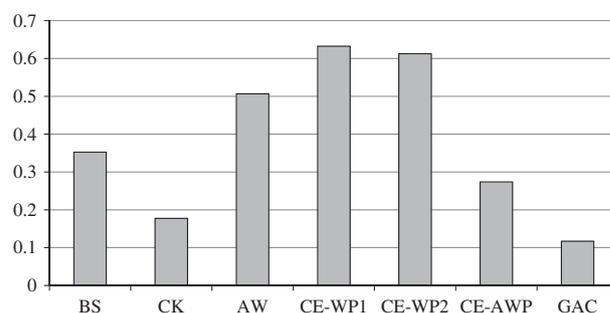


Fig. 11. H:C molar ratios as calculated from CHN elemental analysis of solid biochars and GA. Lower H:C ratios indicate a greater degree of carbonization or thermal alteration of the original biomass.

(i.e. Mn and Pb in CK leachate; see Table 5). Even in these cases, the exceedance is relatively minor and concentrations are low enough to satisfy water quality remediation objectives for industrial/commercial uses for contaminated sites in Illinois (i.e. Class II groundwater remediation objectives; 35 IAC Part 742). These standards were developed as remediation objectives for polluted sites undergoing assessment and cleanup in Illinois; additional regulations govern protected water bodies and drinking water and may be more stringent. Given the generally low metal concentrations and the absence of detectable PAHs in the leachate, the leachability of toxic constituents from the tested biochars is considered negligible for most applications (see Fig. 10).

4. Discussion

4.1. Physical properties of biochars

A number of differences in the physical properties of the tested biochars and GAC were apparent from visual observation alone, most notably whether biochars were in a loose, granular (AW, BS, CK) or pelleted form (CE-WP1, CE-WP2, CE-AWP). Generally, the pelleted biochars incorporated less of the finer ash particles (fine ash was separated from CE-WP2 biochar by sieving). These differences will impact how well biochar can be mixed into soils (demonstrated in an incubation study of biochar-amended soils by Zimmerman, 2010), as well as a number of key physical parameters including: specific surface area and surface charge, particle size distribution, porosity and thus also bulk density and specific

gravity, water-holding capacity, and hydraulic conductivity. Considering the practicality for direct application to soil (e.g. for agriculture or soil remediation) pelleted biochars may be more favorable than fine-grained biochars due to lower dust generation during application to soils. Inhalation of charcoal dust can be a human health issue (Nadel, 1968; Kato et al., 2004). However, given the past utility of fine powders in environmental remediation, methods to reduce dust generation during application of fine powders have been developed to minimize this issue (e.g. application with a wet solution as slurry or high-pressure injection). Achieving homogenous mixing with pelleted biochars may be considerably more difficult than amending soil with a finer texture biochar. This can introduce spatial heterogeneity over small scales in a soil–biochar mixture, potentially creating pockets of anoxic and oxic conditions in the soil matrix.

The particle size distributions clearly impacted hydraulic properties, with the finer biochars having generally lower hydraulic conductivities due to smaller pore spaces. At the same time, higher water holding capacities were generally observed in finer biochars or those with fine ash retained (i.e. CE-WP1). These properties are both considered favorable for soil improvement; however, higher ash content chars generally have lower fixed carbon contents and relatively high volatile matter contents, which would lower their resistance to biotic degradation and thus reduce their carbon sequestration potential (Brewer et al., 2011). There is also the hypothesis that metal oxides found in the ash fraction can react with the biochar to further accelerate its degradation (Huisman et al., 2012). As a result, high ash biochars likely have shorter lifetimes in natural soil systems due to higher degradation rates.

Given the relatively high hydraulic conductivities of some biochars, their use as filter media in environmental applications may be feasible depending upon the type of contamination and the required residence times. Other proposed uses of biochars for climate change mitigation, such as a landfill cover amendment, may require a certain low hydraulic conductivity to be maintained as otherwise it can pose a risk of excessive rainwater percolation and generation of leachate (Farquhar, 1989). An important consideration in biochar application in these scenarios will be the hydraulic conductivity of the biochar–soil mixture, both initially and over time as biochar is subject to ageing effects (e.g. surface oxidation).

4.2. Chemical properties of biochars

Overall, biochars made via pyrolysis exhibited a wide range of physical and chemical properties, and those produced via gasification (CE biochars) tended to have distinct properties from chars obtained from different vendors. As observed in previous studies, the fast pyrolysis biochars not only have finer textures due to more rapid conversion in a fast pyrolysis reactor, but also exhibited a higher degree of thermal alteration as indicated by its low H:C ratio than the slow pyrolysis or gasification biochars (see Fig. 11). Other properties, such as elevated pH and surface area, were also apparently related to this rapid rate of carbonization, consistent with observations in prior biochar characterization studies (Bruun et al., 2011; Brewer et al., 2009, 2011).

The pH values of biochars with a greater extent of carbonization reflected by their relatively lower H:C ratios were slightly alkaline, with the highest pH values observed in the biochar with the greatest degree of thermal alteration (CK), consistent with prior reports documenting a liming effect as biomass is pyrolyzed (Cantrell et al., 2012). This is in contrast to the CE biochars, which had pH values closer to 6.5 (ranging from pH 6.24 to 6.78). Again it is observed that biochars from the same vendor cluster together, likely because the extent of biomass pyrolysis is controlling the development of alkaline pH due to the formation of insoluble salts

(i.e. alkali metals), which are more typically more abundant in hardwood ash (Brewer et al., 2009). However, this also could suggest specific chemistries as a function of a particular pyrolysis reaction design, which has been observed for sorbed organics (Spokas et al., 2011). The highest pH values for commercial biochar are also associated with the highest elemental fractions of metals, such as K and P (i.e. CK and BS biochars), reinforcing the hypothesis that biochar pH and metal salt content are directly related and resultant from the degree of biomass carbonization. Further evidence for this phenomenon is illustrated by the slight negative correlation ($R^2 = 0.78$) observed between pH and H:C content of the studied chars (Fig. 12).

Surface chemical properties of the biochars were also affected by the extent of thermal alteration, primarily as a result of enrichment in various ionic species, such as alkali metals, on the biochar surface as labile organic carbon and volatile matter are removed during pyrolysis (Keiluweit et al., 2010; Brewer et al., 2011). All biochars had negative zeta potential, indicating a negative surface charge for all tested samples. This is consistent with prior reports which document negative surface charge in biochar (e.g. Liang et al., 2006; Cheng et al., 2006, 2008; Mukherjee et al., 2011). This negative charge is the primary mechanism by which cationic nutrients are adsorbed and retained by the biochar, a process believed to lead to improved soil fertility in biochar-amended soils (Glaser et al., 2001; Lehmann et al., 2006). Thus, it would appear these evaluated biochars have favorable surface characteristics for application as an agricultural amendment, or for sorption of cationic nutrients and metals. Additionally, biochars with a higher portion of fine particles (AW, CK) typically had a higher (i.e. less negative) zeta potential than the pelleted CE biochars, with the exception of BS biochar. Differences can also arise due to variations in the amount of sorbed cations (e.g. K^+ , Ca^{2+}), which is a plausible explanation for the relatively higher (less negative) zeta potentials observed in those higher cation containing biochars.

The chemical compositions and properties of the biochars reflect both the chemical attributes of the source materials and the extent of thermal alteration of the original biomass. Moreover, differences in the relative amounts of volatile matter and ash also have implications for biotic and abiotic interactions in biochar-amended soil systems, namely the biochars' long-term stability and the extent of microbial utilization of the carbon in biochar (Spokas, 2010). Though not specifically addressed in this study, it is likely that the biochars with low fixed carbon (e.g. CK and BS) biodegrade more readily in soil (Zimmerman, 2010), thus requiring their more frequent application to maintain a targeted carbon content, for example. Moreover, because complete graphitization requires temperatures in excess of 1000 °C, the biomass often is not completely or uniformly charred, leading to highly variable chemical properties within the same biochar batch (McBeath and Smernik, 2009; Spokas, 2010; Harvey et al., 2011). Incomplete combustion of feedstock biomass likely contributed to variations

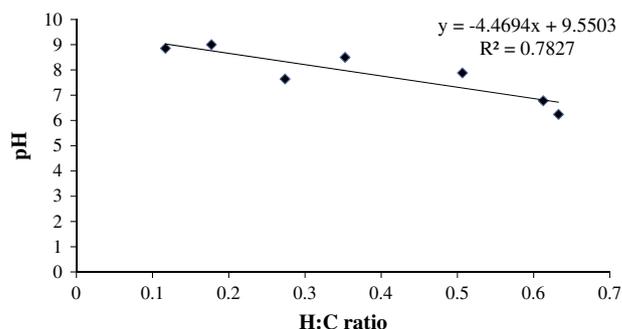


Fig. 12. Relationship between biochar pH and H:C content.

in biochar properties tested in this study, as evidence of incomplete charring was noted in some of the larger biochar particles (i.e. CE-WP1 and 2). Though the fast pyrolysis char (CK) included in this study had a fairly high degree of thermal alteration as indicated by H:C ratios, other researchers have noted that fast pyrolysis can sometimes lead to incomplete biomass combustion due to the very short residence times employed (Bruun et al., 2011). The significance of this issue should be evaluated on a case-by-case basis as it can result in decreased stability in soil due to microbial degradation of readily bioavailable organic carbon, as well as affect the biochars' sorption properties.

4.3. Role of production conditions on toxin content

Previous work has not found any strong correlations with process conditions and heavy metal content of biochars (Koppolu et al., 2003; Lucchini et al., 2013). Rather, metal content appears to reflect that of the source materials, though generally at higher concentrations due to the loss of organic carbon and volatile matter during pyrolysis. Overall, in this study, heavy metal contents of the biochars were fairly low, though higher than in GAC, as seen in Figs. 8 and 9, showing similar trends as with PAH content (Fig. 10).

Several researchers have concluded that slow pyrolysis times, high treatment temperatures (i.e. 400–600 °C), and woody source materials generally result in biochars with minimal PAHs (Hale et al., 2012; Keiluweit et al., 2012; Kloss et al., 2012; Oleszczuk et al., 2013). Both longer residence times employed in slow pyrolysis and high treatment temperatures allow PAHs generated at the initial stages of carbonization to be later burned off. Though it is not possible to discern differences due to feedstock from this study (all biochars were wood-based), clear differences due to production processes are observed. All three of the biochars produced via gasification (CE biochars) had PAH concentrations below the detection limit for all 16 PAHs tested. This result differs from the findings of Hale et al. (2012), in which the highest PAH content was found in a gasification-produced biochar. It was speculated that gasification may actually lead to higher PAH contents due to a higher rate of PAH forming reactions taking place (Hale et al., 2012). However, it is possible that the incorporation of a greater amount of O₂ during gasification led to more complete organic matter combustion to CO₂, thereby reducing the formation of semivolatile aromatic hydrocarbons, such as PAHs (Spokas et al., 2011). It is important to note that previous investigations by Spokas et al. (2011) on sorbed volatile organic compounds on biochar have found high variability in the amount and composition of aromatic products generated, with no consistent relationship of chemical characteristics with temperature or pyrolysis conditions observed, especially among the slow pyrolysis biochars. Such variability may explain the lack of consensus among the results from this study and earlier biochar characterization studies regarding the role of production technology on PAH content.

Though Spokas et al. (2011) did not include all PAHs in their study (i.e. only naphthalene was included), it is thought that similar processes are responsible for the formation of semi-volatile species during combustion, namely through the accumulation of single aromatic rings to form polycyclic species. It was also found that post-production treatment processes (e.g. activation, storage and handling) can have a significant impact on the quantity of sorbed volatile species (Spokas et al., 2011); however, the extent to which this impacts semi-volatile species requires further research. CK biochar was the only biochar included in this study that was subjected to activation with O₂ following pyrolysis, which may have led to increased sorption of PAHs to its surface due to a greater functional surface area. However, GAC was also subjected to activation and did not contain detectable PAHs, indicating that activation in itself is not a cause for elevated PAH levels in charred

materials. The implications of post-treatment processes on PAH sorption should be further investigated to better understand the mechanisms of PAH sorption to biochars and to determine whether these sorbed species can be readily mobilized into solution.

Earlier work has noted that fast pyrolysis may lead to higher PAH concentrations due to the condensation of generated PAHs on the biochar surface during production, rather than being burned off later as during slow pyrolysis (Hale et al., 2012). This finding is supported to a certain extent by the results of this study, as the fast-pyrolysis biochar (CK) had significantly greater total PAHs than any of the other studied biochars produced via slow pyrolysis or gasification. This is also a promising finding for the development of production guidelines for minimal toxin content in commercial biochars, as the heating times can simply be increased to burn off PAHs that may be generated and subsequently sorbed to the biochar. However, further research is strongly recommended to determine the minimum residence times and temperatures necessary to eliminate sorbed PAHs from the variety of source materials commonly used to produce biochar.

5. Implications

Overall, a high variability in biochar properties was observed among wood-derived biochars. Many properties, such as pH and PAH and metal contents, appear to be related to the extent of thermal alteration of the original biomass, which is often investigated by determining molar ratios of H:C and O:C. In this study, the biochar with the lowest H:C ratios typically had higher surface area, porosity, pH, and concentrations of toxic constituents (metals and PAHs) than the other chars. Many of the findings from this study are consistent with prior studies that have highlighted the importance of heat treatment temperature and residence time, as well as any post-processing treatments and effects of storage, on the surface chemistry and physical properties of biochar (Brewer et al., 2009; Keiluweit et al., 2010; Lee et al., 2010; Mukherjee et al., 2011). The desired qualities will depend on the end use of the biochar (i.e. energy use, agricultural amendment, or carbon sequestration), which will dictate the choice of production technology and feedstocks. For carbon sequestration purposes, including as a landfill cover amendment for enhanced microbial CH₄ oxidation, it appears that woody feedstocks are more favorable given their higher fixed carbon content and thus greater stability in soil and biocover systems. Whatever the intended application, pre-screening of biochars for key functional properties is highly recommended given the variability observed in commercially available, wood-derived biochar properties.

6. Conclusions

In this study, physical and chemical properties of six different types of waste wood-derived biochars were characterized and results were compared with those of activated carbon and those of biochars reported in literature. Physical properties characterized included particle size distribution, dry density, specific gravity, surface area, hydraulic conductivity, and water-holding capacity. SEM imaging and image analysis were also conducted to characterize the physical properties of the biochar surfaces. Chemical properties tested included pH, ORP, EC, PAH and metal content, CHN elemental compositions, relative fractions of organic and fixed carbon, ash and volatile matter, and leachate properties. From these results, the following conclusions can be drawn:

- Biochar pH varied from 6.24 to 8.77 and was negatively correlated with H:C ratio, indicating the degree of carbonization of the biochar directly relates to its alkalinity.

- Biochar surface areas were inversely related to fixed carbon content, with the highest surface areas in biochars correlating with higher degree of carbonization (i.e. low fixed carbon content and H:C ratios). Surface porosity determined via SEM image analysis also followed a similar trend, with the highest porosity among biochars belonging to the biochar with the lowest amount of fixed C (CK biochar).
- Biochars with high ash contents also tended to have greater amounts of PAHs and trace metals, indicating the ash fraction of biomass is largely responsible for the presence of these constituents.
- PAH content of solid biochars was highest in the fast pyrolysis biochar (up to 83 mg/kg in CK biochar) and below detection limits for biochars produced via gasification. However, the mobility of these PAHs appears to be very low as no PAHs could be detected in the leachate.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2014.10.029>.

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