1 Phenolic acid sorption to biochars from mixtures of feedstock materials

2
3
4 K. E. Hall¹, M. J. Calderon², K. A. Spokas^{3*}, L. Cox², W. C. Koskinen³, J. Novak⁴, K. Cantrell⁴

5
6 ¹ Department of Soil Water & Climate, University of Minnesota, 1991 Upper Buford Circle; St.
7 Paul, MN USA 55108

8 ² CSIC-IRNAS, Avda. María Luisa s/n. Pabellón de Perú; 41013 Sevilla, Spain

9 ³ USDA-Agricultural Research Service, 1991 Upper Buford Circle; St. Paul, MN USA 55108

10 ⁴ USDA-Agricultural Research Service, 2611 West Lucas Street; Florence, SC USA 29501

11
12 *Corresponding author:

13 K. A. Spokas

14 USDA-ARS, Soil and Water Management Unit

15 1991 Upper Buford Circle, 439 Borlaug Hall, St. Paul, MN 55108

16 Email: kurt.spokas@ars.usda.gov ; phone 612-626-2834

17
18
19 **Abstract**

20
21 In an effort to customize biochars for soil amendments, multiple feedstocks have been combined
22 in various ratios prior to pyrolysis at 350°C. The resulting variation in the chemistry and structure
23 can affect the adsorption capacity of biochar and thus influence the bioavailability of many
24 chemical compounds in the soil system including phenolic acids. This study examines the
25 sorption of ¹⁴C-labeled ferulic acid, syringic acid, and chlorocatechol to four biochars prepared
26 from individual feedstocks and four biochars produced from mixed feedstocks using batch
27 equilibration. Pure feedstock biochar sorption followed switchgrass< swine solids< poultry litter<
28 pine chip for both ferulic ($K_d = 1.4\text{--}75 \text{ L kg}^{-1}$) and syringic acid ($K_d = 0.07\text{--}6.03 \text{ L kg}^{-1}$). Sorption
29 appeared to be influenced by the properties of the biochars as well as the structure of the
30 chemicals. All biochar K_d values, except pine chip, were consistently lower than that of the
31 reference silt loam soil. The sorptive properties of biochars produced from combined feedstocks
32 could not be predicted from their pure feedstock components and sorption coefficients were both
33 higher and lower than the individual parent materials' biochars. Further research is necessary to
34 understand the characteristics of these combination biochars, particularly their sorption, which
35 this study has shown is not merely an average of its components.

36
37 **Keywords** syringic acid, ferulic acid, sorption, allelopathy, feedstock, soil organic matter

1 Introduction

Biochar, a carbon-rich product of biomass pyrolysis, is defined primarily by its intended use in carbon sequestration and as a soil amendment (Lehmann and Joseph 2009). Incorporation of biochar as a soil additive has been associated with numerous benefits including increased crop yield, plant growth, nutrient retention, water holding capacity, and enhanced biological activity (Chan et al. 2007; Graber et al. 2010). On the other hand, neutral and negative effects (e.g. plant growth suppression, decreased arbuscular mycorrhizal fungi) have also been observed (Deenik et al. 2010; Gundale and DeLuca 2007; Rajkovich 2010; Warnock et al. 2010).

Remarkable diversity exists among the chemical and physical properties of different biochars, mainly as a result of variation in feedstock materials and pyrolysis conditions (Kookana et al. 2011), as well as post-production factors (Azargohar and Dalai 2008). Because quality issues vary from soil to soil, Novak et al. (2013b) proposed the use of what has been termed "designer biochars"- biochars tailored to meet the needs of specific soils. Altering the original feedstock produces numerous unique biochars (Mukome et al., 2013; Novak et al., 2013a), and mixing these carbonaceous materials in various ratios (prior to pyrolysis) further enhances the diversity and potential customization of properties (Novak et al., 2013b). For example, mixing nutrient-rich poultry litter with carbon-enriched pine chips may produce a biochar which improves soil fertility and sequesters carbon without disturbing the phosphorus balance or pH (Novak et al. 2013b). The properties of these combination biochars cannot be predicted based on the characteristics of the individual parent material biochars (Zhao et al., 2013a; Zhao et al., 2013b). They have been observed to have unique chemistries different from their original components, with organic chemical sorption capacities controlled by the resulting surface chemistry differences (Mukherjee et al., 2011; Shafeeyan et al., 2011; Uchimiya et al., 2011) and/or associated mineral oxide forms (Long et al., 2011; Yao et al., 2011).

When studying the impacts of biochar as a soil amendment, it is critical to recognize that the term "biochar" encompasses a range of heterogeneous materials with non-uniform effects and behaviors (Antal and Gronli 2003; Lehmann and Joseph 2009; Ronsse et al. 2013). Variability in characteristics such as specific surface area (SSA), aromaticity, and microporosity of biochars, for example, affect their sorption capacity, which in part governs the bioavailability of many chemical compounds in soil (Kookana et al. 2011). To date, research on the sorptive properties of biochar has focused heavily on the sorption of pesticides (Spokas et al. 2009; Yu et al. 2009; Sun et al. 2011a) and environmental contaminants (Cao et al. 2011; Chen and Chen 2009; Chen and Yuan 2011; Sun et al. 2011b). However, naturally occurring compounds such as aromatic acids (i.e. phenolic acids) from root exudates and vegetative material in the rhizosphere would also be

subject to potential immobilization by biochar sorption (Jones et al., 2012). Phenolic acids released into the soil system influence a number of processes including nutrient uptake, protein synthesis, humus formation, plant signaling, development of mutualistic relationships, and allelopathy (Dalton et al. 1989; Mersie and Singh 1993). The allelopathic effects of phenolic acids make them compounds of interest for their potential use in weed management in agroecosystems ((Bhadoria, 2011; Pandino et al., 2011; WONA et al., 2013). Simple phenolic acids such as *p*-hydroxybenzoic, vanillic, *p*-coumaric, syringic, and ferulic acids in wheat (*Triticum vulgare* L.) and its residues, for example, are known to contribute to its allelopathic action (Lodhi et al. 1987).

The phytotoxicity of phenolic acids is affected by their bioavailability, persistence, and fate in the soil (Tharayil et al. 2006). Because phenolic acids are effective as allelopathic agents only when they are in their free form (unbound) (Blum et al. 1999), studies on the sorption of these compounds in soil are required to determine potential biological availability and, in turn, efficacy (e.g. Dalton et al. 1989). The sorption-desorption of five phenolic acids on soils of varying physicochemical properties has previously been characterized (Cecchi et al. 2004) as well as the preferential sorption of phenolic phytotoxins on soil (Tharayil et al. 2006). However, information concerning the sorption of these allelopathic compounds by biochar is lacking.

Some of the initial reported effects of biochar on allelochemicals are from plant growth studies and those investigating the influence of biochar on mycorrhizal associations. Assorted biochars have been found to greatly differ in their ability to disrupt the function of allelopathic chemicals leached from corn residues (*Zea mays* L.) (assumed via adsorption) and thus reduce their inhibitory effect on corn seedling growth (Rogovska et al. 2012). Asparagus (*Asparagus officinalis* L.) similarly releases phenolic acid allelochemicals that suppress seedling growth, which is thought to be partly due to their negative effects on arbuscular mycorrhizal (AM) root colonization (Yeasmin et al., 2013). Warnock et al. (2007) proposed four mechanisms by which biochar impacts mycorrhizal abundance and/or functioning, one being through the detoxification of allelochemicals or the alteration of plant-fungus signaling, although no specific data was presented on their sorption potential. Elmer and Pignatello (2011) found that allelochemicals added to soil without biochar significantly suppressed AM root colonization in asparagus; however, an increase in AM colonization with the addition of biochar was observed in both the presence and absence of allelochemicals.

Although the research on the effects of biochar on allelopathy frequently discusses the potential sorption of phytotoxins by biochar, studies actually characterizing the sorption of allelochemicals are scant, and ones accounting for the physicochemical variability of biochars are

fewer still. Of the limited available studies, one by Ni et al. (2012) describes the mechanism of allelopathic aromatic acid adsorption to biochar and reports isotherms for cinnamic and coumaric acids, which could not be fit to Freundlich or Langmuir models.

The objectives of this study were to examine the sorption of two phenolic acids, ferulic acid (3-(4-hydroxy-3-methoxy-phenyl)prop-2-enoic acid) and syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid), and chlorocatechol (4-chlorobenzene-1,2-diol) on a variety of biochars and to determine how the sorption by biochar prepared from mixtures of feedstock materials differs from those prepared from the pure feedstocks. Ferulic and syringic acid were selected based on their ubiquity and known allelopathic properties. Chlorocatechol was included to compare the reactivity of more complex aromatic compound with substituted moieties on the aromatic ring as well as its importance as a degradation intermediate of chlorinated aromatic species (Schlomann, 1994).

2 Materials and Methods

2.1 Biochar and soil

Eight low temperature (350°C, 2 h residence time) biochars prepared from different feedstock/ feedstock mixtures were selected for this experiment. The feedstock materials used in the pure feedstock biochars include switchgrass (SG), swine solids (SS), poultry litter (PL), and pine chips (PC). These same feedstocks were mixed in measured ratios (w/w%) to create 4 additional biochars. The SG:SS (80:20) biochar, for example, was prepared from the same switchgrass and swine solids that were used to create SG and SS biochars. The parent materials were mixed prior to pyrolysis and prepared under conditions identical to the singular feedstock biochars. Properties of these biochars are listed in Table 1. The lignocellulosic-based and manure-based feedstock mixtures in this study were designed to rebalance soil phosphorus concentrations and improve moisture retention (Novak et al. 2013b). As these are common soil quality issues, use of similar mixtures may be widely adopted and are therefore important to study. A Waukegan silt loam soil (fine-silty, mixed, mesic Typic Hapludoll; Rosemount, MN) (6.0 pH/H₂O, 2.5 % organic carbon (OC), 15% clay, and 33% sand) was included for comparison.

2.2 Chemicals

¹⁴C-ring labeled ferulic acid, syringic acid, 4-chlorocatechol acid were synthesized and provided by Dr. Konrad Haider, Deisenhofen, Germany. The chemicals were purified by thin-layer chromatography using Si250-F-PA plates (J.T. Baker Chemical Co., Phillipsburg, NJ) with

a toluene, ethyl acetate, formic acid (30:25:5) mixture acting as the liquid phase. Chemical structures for the polyphenols used in this study appear in Fig. 1.

2.3 Sorption

Sorption studies were performed in duplicate using the batch equilibration method. Biochar or soil (0.5 g) was weighed into 35 mL glass centrifuge tubes with Teflon lined caps and 5 mL of a 1 $\mu\text{g mL}^{-1}$ phenolic acid ($>17 \text{ Bq mL}^{-1} \text{ }^{14}\text{C}$) in 0.005 M CaCl_2 solution was added. A blank tube containing solution with no soil or biochar was included as a method blank. The tubes were oriented horizontally on a shaker and subsequently shaken approximately 18 h, which is considered to be sufficient time for equilibration on soil (Cecchi et al. 2004). Samples were centrifuged for 30 min at 1280xg and the supernatants collected using disposable glass pipettes. Duplicate 1-mL aliquots were combined with 5 mL scintillation cocktail (EcoLite(+)TM, MP Biomedicals, LLC, Solon, OH) in 7 mL vials and thoroughly mixed. After sitting overnight, the solutions were analyzed for ^{14}C by liquid scintillation counting with a Packard 1500 counter (Packard Tri-Carb, Downers Grover, IL). No chemiluminescence was observed.

The amount of chemical sorbed was calculated as the difference between the amount of chemical in the initial solution and amount of chemical in the final supernatant solution after equilibration. The sorption distribution coefficient, $K_d (\text{L kg}^{-1})$, was determined from the concentration sorbed (C_s) and the concentration remaining in solution after equilibration (C_w) according to the following relationship: $K_d = C_s/C_w$. K_d values were calculated to compare sorption of the phenolic acids to biochars at the single concentration used. Sorption normalized to OC was calculated: $K_{\text{OC}} = (K_d/\% \text{OC}) \cdot 100, (\text{L kg}^{-1})$. Measured total carbon (C) values of the biochars (Table 1) were used for this calculation since the biochars in this study are known to contain <1% inorganic carbon. Reported K_d and K_{OC} values are the averages of the duplicate samples.

2.4 Statistical analysis

The average of two independent replicates is shown in the Figures and Tables ($n=2$). The calculation of the standard deviation (SD) from the replicated samples was used as an assessment of the reproducibility of the measurements (Jones and Payne 1997). The data was analyzed with the analysis of variance (ANOVA) procedure for independent samples to test for statistically significant differences using MINITAB (Minitab, Inc., State College, PA). A P-value of 0.05 was assumed to indicate statistical significance.

3 Results and Discussion

3.1 Phenolic acid/ pure feedstock biochar sorption

Biochars prepared from a single feedstock had sorption distribution coefficients, K_d , ranging from 1.4 to 75 for ferulic acid and from 0.07 to 6.03 for syringic acid (Table 2). Chlorocatechol was completely sorbed on all biochars except the poultry litter ($K_d = 25$). Sorption of the three compounds consistently increased in the following order: syringic acid < ferulic acid < chlorocatechol, a trend which could be related to the chemistries of the compounds (Fig. 1).

According to previous studies, sorption is influenced by the phenolic acid structure. One reported observation is that cinnamic acid derivatives sorb more to soil as compared to benzoic acid derivatives (Dalton et al. 1989). Dalton et al. (1989) and Lehman et al. (1987) found that methoxy substitution and longer carboxyl-containing side-chains increased the reactivity of phenolic acids. If the carboxyl group, a ring deactivator, is directly bonded to the aromatic ring (as is the case for benzoic acid derivatives) the phenolic group is less reactive, therefore less susceptible to oxidation (Lehman et al. 1987). The results from this study appear to be in accordance with this finding; ferulic acid (a cinnamic acid derivative) showed greater sorption to both the soil and biochars than syringic acid (a benzoic acid derivative). A study by Cecchi et al. (2004) found that chemicals having free phenolic groups displayed greater sorption, consistent with our data. Chlorocatechol, which has two highly reactive phenolic groups, had the highest sorption of the three chemicals followed by ferulic acid and lastly, syringic acid. Although ferulic and syringic acid each have a single phenolic group, steric hindrance from the two methoxy groups on syringic acid may lessen its reactivity as compared to ferulic acid.

Whether phenolic acids exist as ions or neutral compounds can also affect sorptive behavior; neutral compounds can more readily sorb to organic matter (Weed and Weber 1974) and anions to oxides (Green 1974). The negative surface charge of the biochars would sorb chemicals in their molecular form more so than their anionic species (Moreno-Castilla 2004). At the pHs of the biochars in this study (pH=6.4-9.4), ferulic ($pK_a=4.58$) and syringic acid ($pK_a=4.34$) exist predominantly as anions (although ferulic acid would have a slightly higher proportion of its molecular form than syringic), while chlorocatechol, assuming a pK_a similar to that of catechol (9.48), remains neutral.

The pure feedstock biochars had K_d and K_{oc} values increasing in the following order: SG < SS < PL < PC for both ferulic and syringic acid. Because this order is the same for both chemicals, certain characteristics of the biochars must also be affecting sorption. Correlations have been found between phenolic acid sorption and OC, pH, and clay content in a soil matrix,

although no single variable could be used singularly to predict sorption (Cecchi et al. 2004). In the present study, no such correlations between measured biochar properties and sorption were observed. The order of sorption magnitude did not correlate to any of the chemical and physical properties listed in Table 1 including pH, total C, and ash content. A distinct increase in sorption with an increase in OC was not observed and correcting for OC content did not reduce the variability among biochars.

The PC biochar had a notably higher sorption coefficient than the other three biochars with both ferulic and syringic acid. Efforts have been made to identify trends in biochar characteristics associated with feedstock materials and these are typically discussed in terms of general groups, mainly wood and non-wood, or subgroups of hard-wood, soft-wood, grass, and manure (Mukome et al. 2013). Based on this broad division, wood biochars are found to have a lower ash content, lower pH, higher C/N, and higher SSA than non-wood chars (Mukome et al. 2013; Singh et al. 2010). The pine chip biochar did in fact have a lower % ash and pH than the switchgrass, swine solids, and poultry litter in this study; however the lack of correlation between these characteristics and sorption suggests others are exerting a greater influence.

Sorption is typically reported to increase with SSA of biochars. However, PC biochar possessed the lowest SSA ($<0.1 \text{ m}^2\text{g}^{-1}$) of all biochars studied, as measured by BET nitrogen adsorption (Brunauer et al. 1938). The low observed SSA may be due to resins, tars, or oils blocking sorption in pore spaces, since pine chips are a particularly oil rich biomass (Conner and Rowe, 1975). Additionally, the resins in the wood may alter the surface properties of the pores and in turn the adsorption capacity (Keech et al. 2005). Biochars are known to maintain relic structures of the parent material; therefore pore distribution can vary among them (Keech et al. 2005). Warnock et al. (2007) states that feedstock materials with large diameter cells can result in biochars with more macropores, which can adsorb large molecules such as phenolic compounds (Keech et al. 2005). Measurements of SSA, however, do not account for differences in the size and shapes of pores, which may be influential. SSA and feedstock material do not have a transparent relationship beyond the general wood/ non-wood distinction and SSA is found to be largely temperature dependent (Brown et al. 2006; Chun et al. 2004; Ronsse et al. 2013).

Pyrolysis temperature is known to be a principal factor influencing biochar characteristics. Increasing production temperatures has been shown to increase SSA, microporosity, and decrease the H/C ratio (i.e. aromaticity), cation exchange capacity, and % volatile matter (Kookana et al. 2011; Mukherjee et al. 2011; Mukome et al. 2013). The biochars in this experiment were prepared at a single temperature (350°C) to strictly compare sorption differences from feedstock variability, however the capacity of high temperature biochars to sorb

phenolic acids merits further study. A high temperature (550°) olive mill waste biochar, for example, had a greater sorption coefficient than the soil for syringic acid ($K_d=14.58$ vs. 12.04) and well above the soil and PC biochar for ferulic acid ($K_d=236$ vs. 29 and 75, respectively) (unpublished data). This may be related to the higher SSA of this biochar ($9.82 \text{ m}^2\text{g}^{-1}$).

Our assumption that sorption is the sole mechanism responsible for removing the chemicals from solution in this study cannot be made with absolute certainty. The removal of metal oxides from soils largely decreased sorption (Cecchi et al. 2004), although the influence of metal oxides may go beyond sorption alone. The two phenolic acids examined here have been observed to react with iron and manganese oxides very rapidly, with 70% of ferulic and 90% of the syringic acid disappearing in 4 hours (Lehmann et al., 1987). Biochars and the soil evaluated here do contain both of these metals, and therefore could provide pathways for abiotic interactions with the metal oxides. The extent of this influence was not analyzed here.

3.2 Phenolic acid/ combination biochar sorption

The K_d values of the four mixed biochars [SG:SS(80:20), PC:PL(90:10), PC:PL(80:20), and PC:PL(50:50)] differed from their components for both phenolic acids. An 80:20 blend of switchgrass and swine solids feedstocks, had a *higher* K_d value than either of its constituent biochars (SG, SS) (Fig. 2). A similar counterintuitive effect was observed with the 90:10 mixture of pine chip and poultry litter. Unlike the SG:SS(80:20) biochar, this feedstock combination led to a biochar with a K_d value *lower* than either of its individual components (PC, PL). The weighted averages of the amount sorbed to the pure feedstock components failed to predict the amount sorbed of the blended biochar. This clearly shows that extreme caution needs to be used when predicting the sorptive behavior of mixed feedstock biochars.

The sorption differences between biochars prepared from a known mixture of feedstock materials and those from the individual components could arise from physicochemical alterations to the biochar during pyrolysis. Variation in trace metal constituents, which may act as catalysts during pyrolysis (Agblevor and Besler, 1996), can lead to differences in observed surface chemistries of the biochar. The surface properties are the primary factor determining sorption characteristics. While it may be possible to estimate the chemical properties of biochars based on trends relating to chemical and physical characteristics of a single feedstock (Mukome et al. 2013), sorption properties of combination biochars have proven more challenging to predict. Further research on the sorptive behaviors of these combination biochars is necessary before customization can be achieved based on feedstocks.

3.3 Soil

The silt loam soil in this study sorbed syringic acid to a greater extent than the biochars (both pure and mixed feedstock). Ferulic acid also sorbed more strongly to the soil than the biochars with the exception of the PC biochar. The normalization of the K_d values to OC provided K_{oc} values that remained relatively low for the majority of the biochars (Table 2). However, when the soil K_d was adjusted for its OC content, which was much lower than that of the biochars, the resulting K_{oc} drastically increased, with the highest biochar K_{oc} value (PC) being over an order of magnitude less for ferulic acid and syringic acid. The generally higher sorption of the phenolic acids to soil may also result from mineral interactions (Cecchi et al. 2004; Tharayil et al. 2006).

3.4 Impacts

Because the majority of the biochars have sorption coefficient values below that of the soil, if they were incorporated into this silt loam soil, their impact on the sorption of the phenolic acids would be inconsequential. However, the addition of these biochars to soils with lower sorptive capacities or in the presence of other phenolic acids with different chemistries (eg. more free phenolic groups) may have greater impacts on the immobilization of these compounds and interfere with their allelopathic effects. Biochars prepared with different feedstocks, feedstock mixtures, higher pyrolysis temperatures, or activation may sorb phenolic acids to a larger degree and must also be studied.

4 Conclusion

All of the biochars examined in this study, with the exception of the pure pine chip biochar, sorbed ferulic and syringic acid less than the reference soil and therefore would not likely alter the bioavailability of these chemicals in the soil environment to a large degree. It was observed that the structure of the phenolic acid, particularly the hydroxyl group, may impact its sorption to biochar. Chlorocatechol showed the greatest sorption with two available hydroxyl groups followed by ferulic acid with one and lastly syringic acid, whose single hydroxyl group is less accessible due to steric hindrance. Sorption did not appear to be correlated with biochar pH, OC, % ash, or SSA and the sorption of the phenolic acids to the mixed feedstock biochars could not be predicted from the behavior of their pure feedstock components.

Coinciding with previous research, the physicochemical variability among the biochars in this study affected their sorptive behavior and reinforced the importance of acknowledging the diverse effects a biochar amendment may have. While feedstock materials, pyrolysis conditions, and post-production factors are well known to create the observed variability, the interaction of

316 multiple feedstock materials during pyrolysis is not well understood. What is unique to this study
317 is that it demonstrates the counterintuitive effects combining feedstock materials can have on the
318 sorption characteristics of the resulting biochar.
319

References

- Agblevor, F., & Besler, S. (1996). Inorganic compounds in biomass feedstocks .1. Effect on the quality of fast pyrolysis oils. *Energy & Fuels*, 10(2), 293-298.
- Antal, M., & Gronli, M. (2003). The art, science, and technology of charcoal production. *Industrial & Engineering Chemistry Research*, 42(8), 1619-1640.
- Azargohar, R., & Dalai, A. K. (2008). Steam and KOH activation of biochar: Experimental and modeling studies. *Microporous and Mesoporous Materials*, 110(2-3), 413-421.
- Bhadoria, P. B. S. (2011). Allelopathy: A natural way towards weed management. *American Journal of Experimental Agriculture*, 1(1), 7-20.
- Blum, U., Shafer, S., & Lehman, M. (1999). Evidence for inhibitory allelopathic interactions involving phenolic acids in field soils: Concepts vs. an experimental model. *Critical Reviews in Plant Sciences*, 18(5), 673-693.
- Brunauer S., Emmett P. H., & Teller E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60, 309-319.
- Brown, R., Kercher, A., Nguyen, T., Nagle, D., & Ball, W. (2006). Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Organic Geochemistry*, 37(3), 321-333.
- Cao, X., Ma, L., Liang, Y., Gao, B., & Harris, W. (2011). Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environmental Science & Technology*, 45(11), 4884-4889.
- Cecchi, A., Koskinen, W., Cheng, H., & Haider, K. (2004). Sorption-desorption of phenolic acids as affected by soil properties. *Biology and Fertility of Soils*, 39(4), 235-242.
- Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A., & Joseph, S. (2007). Agronomic values of greenwaste biochar as a soil amendment. *Australian Journal of Soil Research*, 45(8), 629-634.
- Chen, B., & Chen, Z. (2009). Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, 76(1), 127-133.
- Chen, B., & Yuan, M. (2011). Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. *Journal of Soils and Sediments*, 11(1), 62-71.
- Chun, Y., Sheng, G., Chiou, C., & Xing, B. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental Science & Technology*, 38(17), 4649-4655.

351 Conner, A. H., & Rowe, J.B. (1975). Neutrals in southern pine tall oil. *Journal of the American*
352 *Oil Chemists Society* 52(9), 334-338.

353 Dalton, B. R., Blum, U., & Weed, S. B. (1989). Differential sorption of exogenously applied
354 ferulic, p-coumaric, p-hydroxybenzoic, and vanillic acids in soil. *Soil Science Society of*
355 *America Journal*, 53(3), 757-762.

356 Deenik, J. L., McClellan, T., Uehara, G., Antal, M. J., Jr., & Campbell, S. (2010). Charcoal
357 volatile matter content influences plant growth and soil nitrogen transformations. *Soil*
358 *Science Society of America Journal*, 74(4), 1259-1270.

359 Elmer, W. H., & Pignatello, J. J. (2011). Effect of biochar amendments on mycorrhizal
360 associations and fusarium crown and root rot of asparagus in replant soils. *Plant Disease*,
361 95(8), 960-966.

362 Graber, E. R., Harel, Y. M., Kolton, M., Cytryn, E., Silber, A., David, D. R., et al. (2010).
363 Biochar impact on development and productivity of pepper and tomato grown in fertigated
364 soilless media. *Plant and Soil*, 337(1-2), 481-496.

365 Green, R. E. (1974). Pesticide-clay-water interactions. In W. D. Guenzi (Ed.), *Pesticides in soil*
366 *and water* (pp. 3-38). Madison: Soil Sci. Soc. Amer. Inc.

367 Gundale, M. J., & DeLuca, T. H. (2007). Charcoal effects on soil solution chemistry and growth
368 of koeleria macrantha in the ponderosa pine/Douglas-fir ecosystem. *Biology and Fertility of*
369 *Soils*, 43(3), 303-311.

370 Jones, R., Payne, B. (1997). *Clinical investigation and statistics in laboratory medicine*. London:
371 *ACB Venture Publications*.

372 Jones, D. L., Rousk, J., Edwards-Jones, G., DeLuca, T. H., & Murphy, D. V. (2012). Biochar-
373 mediated changes in soil quality and plant growth in a three year field trial. *Soil Biology &*
374 *Biochemistry*, 45, 113-124.

375 Keech, O., Carcaillet, C., & Nilsson, M. C. (2005). Adsorption of allelopathic compounds by wood-derived
376 charcoal: the role of wood porosity. *Plant and Soil*, 272(1-2), 291-300.

377 Kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E., & Singh, B. (2011). Biochar
378 application to soil: Agronomic and environmental benefits and unintended consequences.
379 *Advances in Agronomy, Vol 112, 112*, 103-143.

380 Lehmann, R., Cheng, H., & Harsh, J. (1987). Oxidation of phenolic-acids by soil iron and
381 manganese oxides. *Soil Science Society of America Journal*, 51(2), 352-356.

382 Lehmann, J., & Joseph, S. (Eds.). (2009). *Biochar for environmental management: science and*
383 *technology*. Earthscan.

384 Lodhi, M., Bilal, R., & Malik, K. (1987). Allelopathy in agroecosystems - wheat phytotoxicity
385 and its possible roles in crop-rotation. *Journal of Chemical Ecology*, 13(8), 1881-1891.

386 Long, J. W., Laskoski, M., Peterson, G. W., Keller, T. M., Pettigrew, K. A., & Schindler, B. J.
387 (2011). Metal-catalyzed graphitic nanostructures as sorbents for vapor-phase ammonia.
388 *Journal of Materials Chemistry*, 21(10), 3477-3484. doi:10.1039/c0jm03167d

389 Mersie, W., & Singh, M. (1993). Phenolic-acids affect photosynthesis and protein-synthesis by
390 isolated leaf-cells of velvet-leaf. *Journal of Chemical Ecology*, 19(7), 1293-1301.

391 Moreno-Castilla, C. (2004). Adsorption of organic molecules from aqueous solutions on carbon
392 materials. *Carbon*, 42(1), 83-94. doi:10.1016/j.carbon.2003.09.022

393 Mukherjee, A., Zimmerman, A. R., & Harris, W. (2011). Surface chemistry variations among a
394 series of laboratory-produced biochars. *Geoderma*, 163(3-4), 247-255.

395 Mukome, F. N. D., Zhang, X., Silva, L. C. R., Six, J., & Parikh, S. J. (2013). Use of chemical and
396 physical characteristics to investigate trends in biochar feedstocks. *Journal of Agricultural
397 and Food Chemistry*, 61(9), 2196-2204.

398 Ni, J., Pignatello, J. J., & Xing, B. (2012). Adsorption of aromatic carboxylate ions to charcoal
399 black carbon is accompanied by proton exchange with water (vol 45, pg 9240, 2012).
400 *Environmental Science & Technology*, 46(10), 5633-5633.

401 Novak, J., Cantrell, K., Watts, D., & Johnson, M. (2013a). Designing relevant biochars to
402 revitalize soil quality: Current status and advances. In *Functions of Natural Organic Matter
403 in Changing Environment* (pp. 955-958). Springer Netherlands.

404 Novak, J. M., Cantrell, K. B., Watts, D. W., Busscher, W. J., & Johnson, M. G. (2013b).
405 Designing relevant biochars as soil amendments using lignocellulosic-based and manure-
406 based feedstocks. *Journal of Soils and Sediments*, 1-14.

407 Okuno, T., Sonoyama, N., Hayashi, J. I., Li, C. Z., Sathe, C., & Chiba, T. (2005). Primary release
408 of alkali and alkaline earth metallic species during the pyrolysis of pulverized
409 biomass. *Energy & fuels*, 19(5), 2164-2171.

410 Pandino, G., Lombardo, S., Mauromicale, G., & Williamson, G. (2011). Profile of polyphenols
411 and phenolic acids in bracts and receptacles of globe artichoke (*cynara cardunculus* var.
412 scolymus) germplasm. *Journal of Food Composition and Analysis*, 24(2), 148-153.

413 Rajkovich, S. (2010). Biochar as an amendment to improve soil fertility. Research Honors thesis,
414 Cornell University, Ithaca, NY.

415 Rogovska, N., Laird, D., Cruse, R. M., Trabue, S., & Heaton, E. (2012). Germination tests for
416 assessing biochar quality. *Journal of Environmental Quality*, 41(4), 1014-1022.

- 417 Ronsse, F., van Hecke, S., Dickinson, D., & Prins, W. (2013). Production and characterization of
418 slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *Global Change*
419 *Biology Bioenergy*, 5(2), 104-115.
- 420 Shafeeyan, M. S., Daud, W. M. A. W., Houshmand, A., & Arami-Niya, A. (2011). Ammonia
421 modification of activated carbon to enhance carbon dioxide adsorption: Effect of pre-
422 oxidation. *Applied Surface Science*, 257(9), 3936-3942.
- 423 Singh, B., Singh, B. P., & Cowie, A. L. (2010). Characterisation and evaluation of biochars for
424 their application as a soil amendment. *Australian Journal of Soil Research*, 48(6-7), 516-
425 525.
- 426 Spokas, K. A., Koskinen, W. C., Baker, J. M., & Reicosky, D. C. (2009). Impacts of woodchip
427 biochar additions on greenhouse gas production and sorption/degradation of two herbicides
428 in a minnesota soil. *Chemosphere*, 77(4), 574-581.
- 429 Sun, K., Keiluweit, M., Kleber, M., Pan, Z., & Xing, B. (2011a). Sorption of fluorinated
430 herbicides to plant biomass-derived biochars as a function of molecular structure.
431 *Bioresource Technology*, 102(21), 9897-9903.
- 432 Sun, K., Ro, K., Guo, M., Novak, J., Mashayekhi, H., & Xing, B. (2011b). Sorption of bisphenol
433 A, 17 alpha-ethinyl estradiol and phenanthrene on thermally and hydrothermally produced
434 biochars. *Bioresource Technology*, 102(10), 5757-5763.
- 435 Tharayil, N., Bhowmik, P., & Xing, B. (2006). Preferential sorption of phenolic phytotoxins to
436 soil: Implications for altering the availability of allelochemicals. *Journal of Agricultural and*
437 *Food Chemistry*, 54(8), 3033-3040.
- 438 Uchimiya, M., Wartelle, L. H., Klasson, K. T., Fortier, C. A., & Lima, I. M. (2011). Influence of
439 pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil.
440 *Journal of Agricultural and Food Chemistry*, 59(6), 2501-2510.
- 441 Warnock, D. D., Lehmann, J., Kuyper, T. W., & Rillig, M. C. (2007). Mycorrhizal responses to
442 biochar in soil - concepts and mechanisms. *Plant and Soil*, 300(1-2), 9-20.
- 443 Warnock, D. D., Mummey, D. L., McBride, B., Major, J., Lehmann, J., & Rillig, M. C. (2010).
444 Influences of non-herbaceous biochar on arbuscular mycorrhizal fungal abundances in roots
445 and soils: Results from growth-chamber and field experiments. *Applied Soil Ecology*, 46(3),
446 450-456.
- 447 Weed, S. B., & Weber, J. B. (1974). Pesticide-organic matter interactions. In W. D. Guenzi (Ed.),
448 Pesticides in soil and water (pp. 39-68). Madison: Soil Sci. Soc. Amer. Inc.
- 449 Weston, L. (1996). Utilization of allelopathy for weed management in agroecosystems.
450 *Agronomy Journal*, 88(6), 860-866.

451 Won, O. J., Uddin, M. R., Park, K. W., Pyon, J. Y., & Park, S. U. (2013). Phenolic compounds in
452 sorghum leaf extracts and their effects on weed control. *Allelopathy Journal*, 31(1), 147-155.

453 Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., & Yang, L.
454 (2011). Removal of phosphate from aqueous solution by biochar derived from anaerobically
455 digested sugar beet tailings. *Journal of hazardous materials*, 190(1), 501-507.

456 Yeasmin, R., Motoki, S., Yamamoto, S., & Nishihara, E. (2013). Allelochemicals inhibit the
457 growth of subsequently replanted asparagus (*asparagus officinalis* L.). *Biological*
458 *Agriculture & Horticulture*, 29(3), 165-172.

459 Yu, X., Ying, G., & Kookana, R. S. (2009). Reduced plant uptake of pesticides with biochar
460 additions to soil. *Chemosphere*, 76(5), 665-671.

461 Zhao, L., Cao, X., Masek, O., & Zimmerman, A. (2013a). Heterogeneity of biochar properties as
462 a function of feedstock sources and production temperatures. *Journal of Hazardous*
463 *Materials*, 256, 1-9.

464 Zhao, L., Cao, X., Wang, Q., Yang, F., & Xu, S. (2013b). Mineral constituents profile of biochar
465 derived from diversified waste biomasses: Implications for agricultural applications. *Journal*
466 *of Environmental Quality*, 42(2), 545-552.

467

468

Table 1 Biochar properties

feedstock	pyrolysis temp (°C)	pH ^a	ash %	VC ^b %	FC ^c %	C %	H %	N %	O %	S %	SSA ^d (m ² g ⁻¹)
Pure feedstock (100%)											
switchgrass (Florence)	350	7.4	3.21	41.4 0	55.3 9	75.5 3	4.5 5	0.5 2	16.1 5	0.04	0.500
swine solids (Florence)	350	6.5	34.9 7	37.6 1	27.4 2	51.0 2	3.6 8	5.9 4	3.19	1.21	1.008
poultry litter	350	9.4	32.0 6	36.1 5	31.8 0	51.5 0	3.5 6	5.1 3	6.86	0.89	1.937
pine chip (loblolly) (Lt 4mm)	350	7.1	1.79	40.4 1	57.8 0	78.6 8	4.8 7	0.3 7	14.2 8	0.02	< 0.100
Feedstock mixtures (w:w ratios)											
<i>Swine solids : switchgrass</i>											
SG:SS(80:20)	350	6.5	7.29	33.7 4	58.9 7	75.8 5	4.5 5	1.3 2	10.7 8	0.22	1.351
<i>Pine chips : poultry litter</i>											
PC:PL(90:10) (Lt 4mm)	350	6.4	4.36	37.1 8	58.4 5	78.1 3	4.8 3	0.8 9	11.7 0	0.08	1.115
PC:PL(80:20) (<4mm)	350	7.5	7.3	33.7 4	58.9 7	75.8	4.5 5	1.3	10.7 8	0.22	1.089
PC:PL(50:50) (Lt 4mm)	350	7.4	18.5	31.5 5	50.1 6	63.7	3.8 0	3.4	10.2 7	0.38	1.139

^apH was measured in a 1 g biochar/10 mL DI water slurry after 5 min settling time^bvolatile compounds^cfixed carbon^dSpecific surface area as measure by BET nitrogen adsorption

Table 2 Sorption distribution coefficient (K_d) and organic C K_{oc} value

	K_d (L kg ⁻¹) ^a			K_{oc} (L kg ⁻¹) ^a		
	ferulic acid	syringic acid	chloro-catechol	ferulic acid	syringic acid	chloro-catechol
soil	29 ± 0.50 a	12.04 ± 0.76 a	56 ± 4.00 a	1160 ± 20 a	482 ± 30.4 a	2240 ± 160 a
Pure feedstock						
SG	1.4 ± 0.18 b	0.07 ± 0.10 b	*	1.85 ± 0.24 b	0.09 ± 0.13 b	*
SS	1.6 ± 0.15 b	0.41 ± 0.02 c	*	3.14 ± 0.29 c	0.80 ± 0.04 c	*
PL	3.1 ± 0.40 c	0.43 ± 0.00 c	25 ± 0.25 b	6.02 ± 0.78 d	0.83 ± 0.00 c	49 ± 0.49 b
PC	75 ± 8.00 d	6.03 ± 0.06 d	*	95.32 ± 10.17 e	7.66 ± 0.08 d	*
Feedstock mixtures (w:w ratios)						
SG:SS (80:20)	9 ± 0.35 e	1.03 ± 0.04 d	*	11.87 ± 0.46 f	1.36 ± 0.05 e	*
PC:PL (90:10)	1.8 ± 0.35 b	0.31 ± 0.14 c	*	2.30 ± 0.45 c	0.40 ± 0.18 f	*
PC:PL (80:20)	3.1 ± 0.13 c	0.40 ± 0.10 c	*	4.09 ± 0.17 g	0.53 ± 0.13 f	*
PC:PL (50:50)	8.2 ± 0.40 f	1.02 ± 0.09 d	*	12.87 ± 0.63 f	1.60 ± 0.14 g	*

*Chemical was sorbed completely- K_d could not be calculated

^a Average of 2 replicates ± standard deviation

Values with different letters are significantly different (Tukey's HSD; $P < 0.05$), compared by K_d and K_{oc} by compound.

Fig. 1 Chemical structures of polyphenols used in this study

(Created using ChemSketch)

Fig. 2 Sorption coefficients, K_d (L kg^{-1}), of combination biochars compared to their pure feedstock component biochars; K_d values are averages of 2 replicates and error bars represent 1 standard deviation.

(Created using SigmaPlot10.0)

Agblevor, F.A., Besler, S., 1996. Inorganic compounds in biomass feedstocks. 1. Effect on the quality of fast pyrolysis oils. *Energy Fuel*. 10, 293-298.

Bhadoria, P., 2011. Allelopathy: a natural way towards weed management. *American Journal of Experimental Agriculture* 1, 7-20.

Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H., Murphy, D.V., 2012. Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biol. Biochem.* 45, 113-124.

Lehmann, R.G., Cheng, H.H., Harsh, J.B., 1987. Oxidation of Phenolic Acids by Soil Iron and Manganese Oxides. *Soil Sci. Soc. Am. J.* 51, 352-356.

Long, J.W., Laskoski, M., Peterson, G.W., Keller, T.M., Pettigrew, K.A., Schindler, B.J., 2011. Metal-catalyzed graphitic nanostructures as sorbents for vapor-phase ammonia. *J. Mater. Chem.* 21, 3477-3484.

Mukherjee, A., Zimmerman, A.R., Harris, W., 2011. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma* 163, 247-255.

Mukome, F.N., Zhang, X., Silva, L.C., Six, J., Parikh, S.J., 2013. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *J. Agric. Food Chem.* 61, 2196-2204.

Novak, J., Cantrell, K., Watts, D., Johnson, M., 2013a. Designing relevant biochars to revitalize soil quality: Current status and advances. *Functions of Natural Organic Matter in Changing Environment*. Springer, pp. 955-958.

Novak, J.M., Cantrell, K.B., Watts, D.W., Busscher, W.J., Johnson, M.G., 2013b. Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks. *J. Soils Sed.*, 1-14.

Pandino, G., Lombardo, S., Mauromicale, G., Williamson, G., 2011. Profile of polyphenols and phenolic acids in bracts and receptacles of globe artichoke (*Cynara cardunculus* var. *scolymus*) germplasm. *Journal of Food Composition and Analysis* 24, 148-153.

Schlomann, M., 1994. Evolution of chlorocatechol catabolic pathways. Conclusions to be drawn from comparisons of lactone hydrolases. *Biodegradation* 5, 301-321.

Shafeeyan, M.S., Daud, W.M.A.W., Houshmand, A., Arami-Niya, A., 2011. Ammonia modification of activated carbon to enhance carbon dioxide adsorption: Effect of pre-oxidation. *Appl. Surf. Sci.* 257, 3936-3942.

Uchimiya, M., Wartelle, L.H., Klasson, K.T., Fortier, C.A., Lima, I.M., 2011. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. *J. Agric. Food Chem.* 59, 2501-2510.

WONa, O., Uddin, M., Park, K., Pyon, J., Park, S., 2013. Phenolic compounds in sorghum leaf extracts and their effects on weed control. *Allelopathy Journal* 31, 147-155.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. *J. Hazard. Mater.* 190, 501-507.

Yeasmin, R., Motoki, S., Yamamoto, S., Nishihara, E., 2013. Allelochemicals inhibit the growth of subsequently replanted asparagus (*Asparagus officinalis* L.). *Biological Agriculture & Horticulture*, 1-8.

Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013a. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. *J. Hazard. Mater.*

Zhao, L., Cao, X., Wang, Q., Yang, F., Xu, S., 2013b. Mineral Constituents Profile of Biochar Derived from Diversified Waste Biomasses: Implications for Agricultural Applications. *J. Environ. Qual.* 42, 545-552.