

Phenolic Acid Sorption to Biochars from Mixtures of Feedstock Materials

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Abstract In an effort to customize biochars for soil amendments, multiple feedstocks have been combined in various ratios prior to pyrolysis at 350 °C. The resulting variation in the chemistry and structure can affect the adsorption capacity of biochar and thus influence the bioavailability of many chemical compounds in the soil system including phenolic acids. This study examines the sorption of ¹⁴C-labeled ferulic acid, syringic acid, and chlorocatechol to four biochars prepared from individual feedstocks and four biochars produced from mixed feedstocks using batch equilibration. Pure feedstock biochar sorption followed switchgrass < swine solids < poultry litter < 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 appeared to be influenced by the properties of the biochars as well as the structure of the chemicals. All biochar K_d values, except pine chip, were consistently lower than that of the

reference silt loam soil. The sorptive properties of biochars produced from combined feedstocks could not be predicted from their pure feedstock components, and sorption coefficients were both higher and lower than the individual parent materials' biochars. Further research is necessary to understand the characteristics of these combination biochars, particularly their sorption, which this study has shown is not merely an average of its components.

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 & 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 & 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

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factors (Azargohar & 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 & Gronli 2003); (Lehmann & 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 & Chen 2009); (Chen & 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 & 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); (Weston 1996); (Won 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, as well as the preferential sorption of phenolic phytotoxins on soil, has previously been characterized ((Cecchi et al. 2004); (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). Turner (1955) first suggested that biochar (charcoal) was sorbing inhibitory compounds in the soil. 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 & 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 their known allelopathic properties (Blum 1996). Chlorocatechol was included to compare the reactivity of another complex aromatic compound with substituted moieties on the aromatic ring as well as its importance as a degradation intermediate of chlorinated aromatic species (Schlömman 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 four 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, and 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, and formic acid (30:25:5) mixture acting as the liquid phase. Chemical structures for the polyphenols used in this study are shown 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 μg mL⁻¹ phenolic acid (>17 Bq mL⁻¹ ¹⁴C) in 0.005-M CaCl₂ 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 1,280×*g* 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 ¹⁴C 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 (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: $K_{oc} = (K_d/\%OC) \times 100$,

Table 1 Biochar properties

Feedstock	Pyrolysis temperature (°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	41.40	55.39	75.53	4.55	0.52	16.15	0.04	0.500
Swine solids (Florence)	350	6.5	34.97	37.61	27.42	51.02	3.68	5.94	3.19	1.21	1.008
Poultry litter	350	9.4	32.06	36.15	31.80	51.50	3.56	5.13	6.86	0.89	1.937
Pine chip (loblolly) (<4 mm)	350	7.1	1.79	40.41	57.80	78.68	4.87	0.37	14.28	0.02	< 0.100
Feedstock mixtures (w/w ratios)											
Swine solids/switchgrass											
SG/SS (80:20)	350	6.5	7.29	33.74	58.97	75.85	4.55	1.32	10.78	0.22	1.351
Pine chips/poultry litter											
PC/PL (90:10) (<4 mm)	350	6.4	4.36	37.18	58.45	78.13	4.83	0.89	11.70	0.08	1.115
PC/PL (80:20) (<4 mm)	350	7.5	7.3	33.74	58.97	75.8	4.55	1.3	10.78	0.22	1.089
PC/PL (50:50) (<4 mm)	350	7.4	18.5	31.55	50.16	63.7	3.80	3.4	10.27	0.38	1.139

^a pH was measured in a 1-g biochar/10-mL DI water slurry after 5-min settling time

^b Volatile compounds

^c Fixed carbon

^d Specific surface area as measured by BET nitrogen adsorption

(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 & 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.

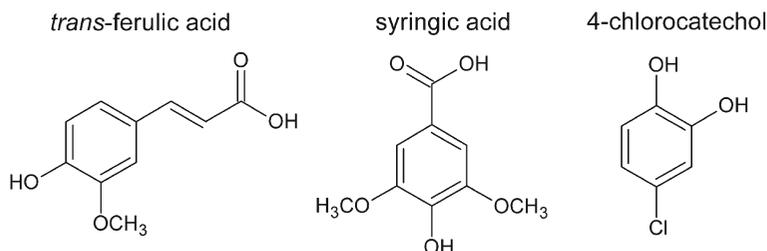
3 Results and Discussion

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 Lehmann et al. (1987)

Fig. 1 Chemical structures of polyphenols used in this study (created using ChemSketch)



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 (Lehmann 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 & 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 one 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 sub-groups 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 that 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 & 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

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	Chlorocatechol	Ferulic acid	Syringic acid	Chlorocatechol
Soil	29±0.50 a	12.04±0.76 a	56±4.00 a	1,160±20 a	482±30.4 a	2,240±160 a
Pure feedstock						
SG	1.4±0.18 b	0.07±0.10 b	b	1.85±0.24 b	0.09±0.13 b	b
SS	1.6±0.15 b	0.41±0.02 c	b	3.14±0.29 c	0.80±0.04 c	b
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	b	95.32±10.17 e	7.66±0.08 d	b
Feedstock mixtures (w/w ratios)						
SG/SS (80:20)	9±0.35 e	1.03±0.04 d	b	11.87±0.46 f	1.36±0.05 e	b
PC/PL (90:10)	1.8±0.35 b	0.31±0.14 c	b	2.30±0.45 c	0.40±0.18 f	b
PC/PL (80:20)	3.1±0.13 c	0.40±0.10 c	b	4.09±0.17 g	0.53±0.13 f	b
PC/PL (50:50)	8.2±0.40 f	1.02±0.09 d	b	12.87±0.63 f	1.60±0.14 g	b

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

^a Average of two replicates±standard deviation

^b Chemical was sorbed completely— K_d could not be calculated

sorb phenolic acids merits further study. A high-temperature (550 °C) 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 m² 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 h (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 solid

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 ((Aglevor & Besler 1996); (Okuno et al. 2005)), 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.

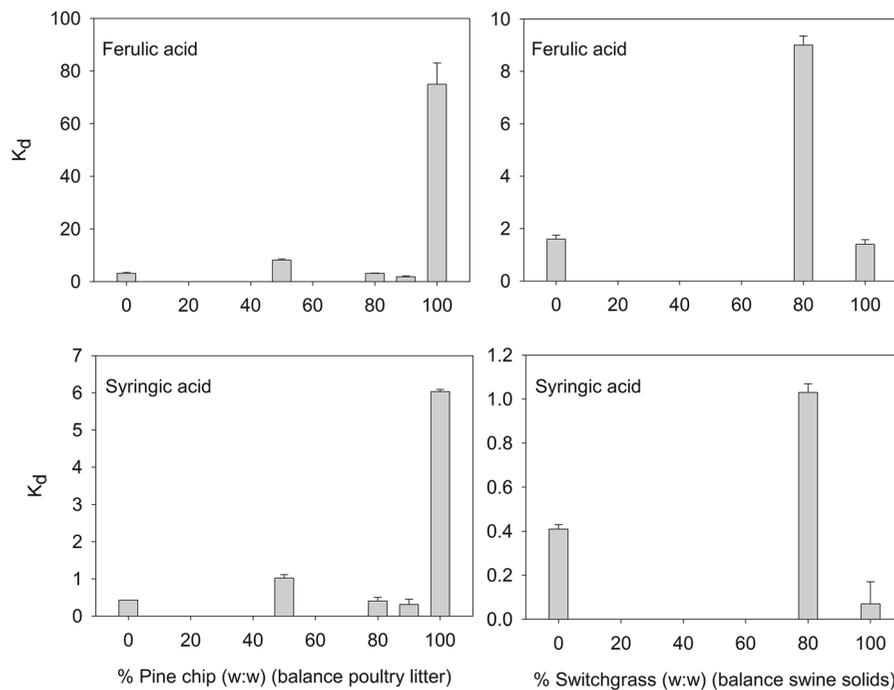


Fig. 2 Sorption coefficients, K_d (L kg⁻¹), of combination biochars compared to their pure feedstock component biochars; K_d values are averages of two replicates, and *error bars* represent the standard deviation (created using SigmaPlot 10.0)

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 (e.g., 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 100 % 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. Furthermore, sorption of the

phenolic acids evaluated here to the mixed feedstock biochars could not be predicted from the behavior of biochars of their individual 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 multiple feedstock materials during pyrolysis is not well understood. What is unique to this study is that it demonstrates the counterintuitive effects combining feedstock materials can have on the sorption characteristics of the resulting biochar.

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