5-2016

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Recommended Citation

Sharon A. Clay, Kaitlynn K. Krack, Stephanie A. Bruggeman, Sharon Papiernik & Thomas E. Schumacher (2016) Maize, switchgrass, and ponderosa pine biochar added to soil increased herbicide sorption and decreased herbicide efficacy, Journal of Environmental Science and Health, Part B, 51:8, 497-507, DOI: 10.1080/03601234.2016.1170540

JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH, PART B
2016, VOL. 51, NO. 8, 497–507
http://dx.doi.org/10.1080/03601234.2016.1170540

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Maize, switchgrass, and ponderosa pine biochar added to soil increased herbicide sorption and decreased herbicide efficacy

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ABSTRACT

Biochar, a by-product of pyrolysis made from a wide array of plant biomass when producing biofuels, is a proposed soil amendment to improve soil health. This study measured herbicide sorption and efficacy when soils were treated with low (1% w/w) or high (10% w/w) amounts of biochar manufactured from different feedstocks [maize (*Zea mays*) stover, switchgrass (*Panicum vigatum*), and ponderosa pine (*Pinus ponderosa*)], and treated with different post-processing techniques. Twenty-four hour batch equilibration measured sorption of ^{14}C-labelled atrazine or 2,4-D to two soil types with and without biochar amendments. Herbicide efficacy was measured with and without biochar using speed of seed germination tests of sensitive species. Biochar amended soils sorbed more herbicide than untreated soils, with major differences due to biochar application rate but minor differences due to biochar type or post-process handling technique. Biochar presence increased the speed of seed germination compared with herbicide alone addition. These data indicate that biochar addition to soil can increase herbicide sorption and reduce efficacy. Evaluation for site-specific biochar applications may be warranted to obtain maximal benefits without compromising other agronomic practices.

ARTICLE HISTORY
Received 27 February 2015

KEYWORDS
2,4-D; Atrazine; herbicide efficacy; sorption; speed of germination

Introduction

Biochar is the by-product of a thermal process conducted under low oxygen or oxygen-free conditions (pyroytic process) to convert vegetative biomass to biofuel.[1] The wide variety of feedstocks and pyrolysis processing parameters including temperature, heating rate, processing time, and pressure can influence the end-products and recovery amounts, energy values of bio-oils, and properties of the remaining biochar.[2,3] Biochar is not a precisely defined material but can vary widely in properties depending on parent material type and quality,[4,5] manufacturing process,[6–13] and post-process handling or chemical activation. Biochar is a microbial recalcitrant form of carbon[14] and land-spreading these carbon-rich products is recommended for recycling of nutrients and sequestering of carbon.

Biochar applications, based on types and rates can produce diverse benefits including increased plant available water,[15–17] increased soil organic matter; enhanced nutrient cycling; reduced soil compaction, higher soil pH, higher base saturation, and greater nutrient availability.[18–21] These factors often lead to enhanced seed germination and positive impacts on plant growth and development.[21–23] Biochars have been shown to sorb high amounts of pesticides and nutrients,[13,24,25] reducing potential movement to offsite areas, with concomitant improvement of water quality.

However, biochar can reduce agronomic productivity by at least three mechanisms. First, biochar may negatively impact seed germination and early seedling growth of some species.[26] Reduced germination is attributed to the release of a wide variety of volatile organic compounds.[27] Second, biochar may reduce plant uptake of nutrients because of extreme affinity for these nutrients.[28] Third, biochar may reduce herbicide or other agrichemical efficacy due to high sorption rates [13,29–32] reducing pest control.

Biochars are highly diverse, may be highly reactive, and have long soil residence times. The challenge is to identify the benefits that biochar can provide (e.g., fertility, increased water holding capacity)[33] and balance these against any negative effects (e.g., toxicity to seed germination,[26,27] interference with agrichemical application,[13,29–32] negative impact on microbial activity[5]). Much biochar research has been based on the assumptions that biochar will improve soil fertility, water holding capacity, or mitigate greenhouse gas emissions. The greatest positive impacts have been observed on degraded soils and those with low fertility, whereas applications on highly productive soils have been reported to have low or minimal impacts.[34] Therefore, the selection of specific biochar types that have the desired properties, which are a function of production and processing criteria,[5,13] need to be carefully considered to match with desired outcomes on a site-specific application basis.

The null hypotheses of these experiments were that biochar addition to soil would not: (1) influence soil pH or electrical conductivity (EC); (2) influence herbicide sorption to soil; nor (3) influence herbicide efficacy. Biochars from three parent feedstock materials (maize, switchgrass, or ponderosa pine)

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and two post-processing methods (allowed to cool to ambient air temperature with no intervention or water-cooled soon after pyrolysis to accelerate cooling and reduce fire hazards) were used. We quantified the effect of biochar applications at two rates (1% and 10% w/w) to two soils (one highly productive and the other degraded) on soil pH, EC, and the sorption of two herbicides (2, 4-D, an acidic herbicide and atrazine, a basic herbicide). To examine herbicide efficacy and possible biochar toxicity,[27] we evaluated speed and percent of seed germination of several indicator species, described below, with and without herbicide or biochar addition.

Materials and methods

Biochar and soil description

Ponderosa pine biomass (wood chips and shavings) was collected from sawmill waste from a mill near Carbondale, CO, USA (N 39°23′41/W 107°12′52). After grain harvest, maize stover was obtained in late fall 2012 from a field site near Brookings, SD (N 44°18′23/W 96°47′17) that had been managed for optimal yield by cutting about 6 cm above the soil and baling the materials. Physiologically mature switchgrass was harvested and baled in late fall from sites near Brookings, SD. The baled biomass was then pelletized to an average pellet size of 6 mm diameter by 15 cm length (Iowa Biofiber, Harlan, IA, USA) to produce a more uniform feedstock. All materials were processed by the patented carbon optimized gasification process which is a two stage continuous process where the reactor temperature ramps from 150 to 850 C with a material residence time of about 4 h (Biochar Solutions, Inc., Carbondale, CO, USA). The oxygen-free condition was maintained by flushing with nitrogen gas.

The gasification process was conducted at two different times with two different post-process handling techniques. The first batch of biochar was close to 0% water after processing and was allowed to air-cool to ambient temperature prior to shipping. Biochars from this batch were sieved to obtain two size fractions, <2-mm and 2–4-mm, which were expected to have different reactivity in soil.[35,36]

The second batch of biochar was doused with water to cool immediately after gasification to prevent smoldering and fire hazards. These water-cooled biochars were used as mixed size blend. The percent water of these biochars was determined and ranged from 30 to 70% water. The biochar amendments were added based on their calculated dry weight. Specific surface area, electrical conductivity (EC), and cation exchange capacity (CEC) for bulk samples of each biochar are reported in Table 1, more detailed information, including nutrient composition, can be obtained from Chintala et al.[5]

The A horizon soils for these studies were: a Brookings silty clay loam (Fine-silty, mixed, superactive, frigid Pachic Hapludoll) [37] from a footslope position in the landscape with 60% sand, 16% clay, 24% silt, 34 g kg^{-1} organic matter, pH of 6.1, and total C of 20.1 g kg^{-1}; and a Maddock loamy fine sand (Sandy, mixed frigid Entic Hapludoll) [37] from a summit position with 72.4% sand, 8.5% clay, 19.0% silt, 16 g kg^{-1} organic matter, pH of 5.2, and 10 g kg^{-1} of total C.

Biochar effect on soil pH and EC

The maize, switchgrass, and ponderosa pine biochars were used alone or mixed with the soils at 1 or 10% (w/w) to examine the biochar influence on solution pH, EC, and atrazine and 2,4-D sorption. To maximize homogeneity, each soil/biochar combination was individually mixed by adding air-dry soil and biochar (dry if allowed to cool naturally, or wet if water-cooled) to each individual tube.

The pH of the biochar, soil or biochar/soil mix was determined by adding 0.01 M $CaCl_2$ to the solid at 1:2 w/v creating a slurry, and shaking the slurry for 30 min. After settling for 30 min, the pH was measured with a standardized pH electrode (Thermo Fisher Scientific, Waltham, MA, USA) and recorded after the reading on the probe had stabilized (about 15 s). Electrical conductivity (EC) was determined on the same slurry using a commercially available EC electrode (Thermo Fisher Scientific). Experimental treatments were done in triplicate and the experiments were repeated in time. Data were combined for the studies due to similarity of means and homogeneity of variance among the repetitions. Means for pH, and EC are the average of six replicates per treatment. The 95% confidence intervals are reported for each parameter.

Biochar effect on herbicide sorption

Atrazine (technical grade, >99% purity, Sigma Chemical Co., St. Louis, MO, USA) was weighed and dissolved in a small amount of methanol (~1 ml) and then 0.01 M $CaCl_2$ was added to make a final concentration of 13μM atrazine. Serial dilutions from this concentration were made to obtain solutions of 13, 6.5, 3.25, and 1.625 μM atrazine. Each solution was spiked with about 0.4 kBq of uniformly-ring-labeled [^{14}C] atrazine (specific activity of 1000 MBq mmol^{-1} with >99% purity; Sigma Chemical Co.) with a final specific activity from 0.03 to 0.25 kBq μM^{-1}. The 2,4-D solution was made in a similar

Table 1. Selected properties of bulk corn stover, switchgrass, and ponderosa pine biochars, one set that was allowed to air-cool after pyrolysis and the other water cooled and allow to air-dry (data modified from Chintala et al.).[5]

	Corn stover		Switchgrass		Ponderosa pine	
Property	Air-dried	Water-cooled	Air-dried	Water-cooled	Air-dried	Water-cooled
Specific surface area(m^2 g^{-1})	196 (3)[a]	176 (1)	260 (2)	188 (1)	296 (4)	233 (2)
EC (uS cm^{-1})	773 (46)	800 (21)	516 (20)	550 (11)	106 (6)	120 (14)
CEC (Cmol kg^{-1})	468 (9)	459 (11)	447 (6)	458 (9)	406 (8)	397 (5)

[a]Numbers in parentheses are standard errors based on four replications.

manner with about 13 μM of technical grade 2,4-D added to 0.01 M $CaCl_2$. Serial dilutions from this concentration were made to obtain solutions of 13, 6.5, 3.25, and 1.625 μM 2,4-D. Each solution was spiked with uniformly-ring-labeled [^{14}C]-2,4-D (specific activity of 1000 MBq $mmol^{-1}$ with > 99% purity; Sigma Chemical Co.) with final specific activities from 0.03 to 0.25 kBq μM^{-1}.

The batch equilibration method was used to examine herbicide sorption to soil.[13] A 4-mL aliquot of herbicide solution containing the appropriate radioactive chemical was added to 2 g soil or soil amended with 1 or 10% 2–4 mm, <2 mm, or wet mixed-sized biochars (final slurry solution 2:1 v/w) in glass centrifuge tubes sealed with a Teflon-lined cap. Herbicide sorption to biochar alone was evaluated by adding a 5 ml aliquot of each herbicide solution to 0.5 g of each biochar resulting in a final solution/biochar ratio was 10:1 v/w, due to the highly solution-sorbent characteristics of the biochar. After solution addition, the mixtures were vortexed for about 10 s to create a slurry. Tubes containing the slurries were shaken for 24 h, centrifuged at 7000 g for 30 min, and a 250-μL aliquot of supernatant removed. The amount of ^{14}C remaining in the supernatant solution was determined by liquid scintillation counting (Beckman LS6500, Fullerton, CA, USA) after the addition of scintillation cocktail (Thermo Fisher Scientific). The amount of radioactivity sorbed was determined by comparing the counts in the supernatant samples with counts recorded from the original soil and biochar-free blank solution samples.

Sorption was calculated as L kg^{-1} correcting for the differences in volume added per g of material. The Freundlich isotherm (except for maize biochar treated with a single 2,4-D solution containing 13 μM) often is used to describe nonidealized heterogeneous surface sorption[38,39] and was used to compare sorption by treatments across concentrations. The Freundlich isotherm[38]

$$x/m = K_f C^{1/n},$$

where x/m = weight of absorbate per unit weight of absorbent (μmol kg^{-1}); C = the absorbate concentration in solution (μmol L^{-1}); and K_f and n are empirical constants was used to describe sorption isotherms for each treatment and herbicide. The log-log transformation of this equation:

$$\text{Log}\ x/m = \log K_f + 1/n\ (\log C)$$

provides the linearized form so that the intercept (K_f) and the slope ($1/n$) of the isotherm lines are easily compared. The regression equations for isotherms were compared within a biochar feedstock and application rate across post-handling treatments. Individual isotherms and combined isotherms within a feedstock type were calculated. Regressions were compared using an F-test and the P value determined.[40] If the $P >$ 0.05, indicating no significant difference among the regression equations, data were combined, as appropriate, and a single isotherm reported.

Biochar effect on speed of seed germination

The speed of seed germination (see calculation below) using water and herbicide solutions, with and without biochar, and with and without soil, was evaluated. Based on herbicide labels, species sensitivity,[41,42] and seed availability, Daikon radish (*Raphanus sativus*) and black-seeded Simpson lettuce (*Lactuca sativa*) were selected as indicator species for 2,4-D. Daikon radish and winter wheat (*Triticum aestivum*) were used as indicator species for atrazine. Twenty seeds of each species were placed in an 8-mm petri dish with a filter paper placed above the seeds. The 2–4-mm size of maize, switchgrass, or Ponderora pine biochar (0.1, or 0.5 g) or 5 g of Brookings or Maddock A horizon soil alone or mixed with 0.1 or 0.5 g each biochar was spread atop the filter paper. Five-ml of deionized water, atrazine solution (0.5, 1.0, 2.0, or 2.5 g atrazine L^{-1}), or 2,4-D solution (0.02, 0.05, 0.1, or 0.2 g $L^{-1}$of 2,4-D) was distributed evenly over the top. A water-only treatment was used as a control. Dishes were covered, and germinated seeds were counted daily and removed, for 10 days. Germination percent was calculated by: total number of seeds germinated during the 10 d test/total number of test seeds.

Germination speed was calculated by:[43]

$$\begin{aligned} Speed = \sum\nolimits_{1}^{10} & (\#\ \text{seed germinated day}\ 1/1) \\ & + (\#\ \text{seed germinated on day}\ 2/2) \\ & + (\#\ \text{seed germinated on day}\ n/n). \end{aligned}$$

The greatest speed of germination = 20, if all seeds germinated on day 1. These studies were conducted twice with three replications per treatment and repeated in time, with data combined across the repeated studies.

Results

Biochar materials

Initial feedstock and post-process handling had the greatest influence on biochar specific surface area, moderate influence on EC values, and no influence on CEC values (Table 1). In general, surface areas were greater for air-dried compared with water-cooled biochars. The influence of initial feedstock on surface area from greatest to least was ponderosa pine>switchgrass>maize (Table 1) whereas EC was lowest for biochars of ponderosa pine (110 μS cm^{-1}), and greatest for maize biochars (775 μS cm^{-1}). The pH of maize and switchgrass biochar types were greater than > 9.5 (Fig. 1) whereas the pH of ponderosa pine biochar ranged from 7.8 (2–4 mm and water-cooled) to about 9.5 (<2mm).

Biochar effect on soil EC and pH

Unamended Brookings soil samples had an average pH of 6.74 (95% CI = 0.55) (Fig. 1) and an average EC of 2070 (95% CI = 30) μS cm^{-1}. Unamended Maddock soil samples had a pH of 5.24 (CI = 0.58) and an average EC of 2110 (95% CI = 160) μS cm^{-1}. A 1% biochar addition did not influence either soil's EC

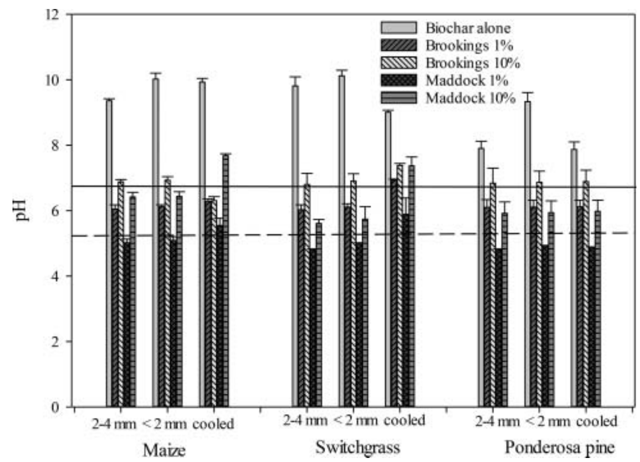

Figure 1. The pH of maize, switchgrass, and ponderosa pine biochars of two sizes of dry material (2–4 mm and <2 mm) and water cooled post-pyrolysis alone, and soil amended pH with 1 or 10% biochar (w/w). The Brookings unamended soil pH is represented by the solid line, whereas the Maddock unamended soil pH is represented by the dashed line.

value whereas a 10% addition of maize biochars increased the EC value of the Maddock soil by about 23%.

Although biochars had much higher pHs than either soil (Fig. 1), the addition of 1% biochar to the Brookings soil decreased the soil pH by about 0.4 pH units in eight of the nine treatments (Fig. 1). Brookings soil amended with 10% of any of the biochar types had pH values similar to unamended soil. The 1% biochar addition did not change the Maddock soil pH. However, the 10% addition of ponderosa pine and switchgrass biochars increased the Maddock soil pH by about 0.5 pH units and maize biochar raised the pH by about 1 pH unit.

Biochar influence on atrazine sorption

About 90% of the Freundlich atrazine sorption isotherms for biochar, soil, or soil amended with biochar, had a goodness of fit (adjusted r^2 value) of >0.73. The sorption isotherms had $1/n$ values that ranged from 0.44 to 1.4 (Table 2) with values <1 indicating that sorption to the matrix was greater when the initial atrazine concentration was low and less sorbed when the initial concentration was high. Atrazine sorption to the Brookings soil was greater than sorption to the Maddock soil (Fig. 2 and Table 2) with *Kf* values of 10 and 6.8 $\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$, respectively. The slopes ($1/n$) of these isotherms were 0.83 for the Brookings soil and 0.92 for the Maddock soil.

Atrazine sorption to biochars ranged from 7 to 90X greater than to either soil alone (Fig. 2 and Table 2). *Kf* values ranged

Table 2. Atrazine sorption isotherms[a] with adjusted R^2 values, coefficients for log Kf, *Kf*, and slope ($1/n$) of the Fruendlich isotherms for each biochar type and soil alone and 1% or 10% of the biochar added to soil.

Soil	Species	Amount of biochar added	Post-process treatment	Adj r^2	Log Kf	*Kf* $\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$	$1/n$
None	Maize	100%	<2 mm	0.72	2.96	912 (477–1746)[b]	1.4 (0.26)
		100%	2–4 mm	0.45	2.32	209 (109–400)	0.86 (0.28)
		100%	wet	0.86	2.18	151 (126–182)	0.98 (0.12)
None	Switchgrass	100%	<2 and 2–4 mm	0.9	2.20	159 (138–182)	0.79 (0.08)
		100%	wet	0.93	1.87	74 (67–82)	0.74 (0.08)
None	Ponderosa pine	100%	<2 and 2–4 mm	0.53	2.35	224 (141–356)	0.78 (0.20)
		100%	wet	0.58	2.72	525 (201–1368)	0.83 (0.31)
Maddock		0%		0.97	0.83	6.8 (6.5–7.0)	0.92 (0.04)
	Maize	1%	All	0.95	0.99	9.8 (9.4–10.2)	0.79 (0.04)
		10%	<2 mm	0.89	1.48	30 (24–38)	0.73 (0.10)
		10%	2–4 mm	0.78	1.14	14 (11–17)	0.44 (0.10)
		10%	wet	0.86	1.30	20 (17–24)	0.76 (0.15)
	Switchgrass	1%	<2 and 2–4 mm	0.96	0.90	7.9 (7.6–8.3)	0.88 (0.06)
		1%	wet	0.95	0.99	9.8 (8.9–10.7)	1.0 (0.10)
		10%	<2 mm	0.97	1.40	25 (22–28)	0.79 (0.04)
		10%	2–4mm	0.86	1.25	18 (15–22)	0.67 (0.12)
		10%	wet	0.83	1.23	17 (14–21)	0.84 (0.17)
	Ponderosa pine	1%	All	0.73	1.00	10 (9–11)	0.58 (0.08)
		10%	<2 and 2–4 mm	0.58	1.36	23 (17–30)	0.46 (0.12)
		10%	wet	0.71	2.01	102 (47–224)	1.07 (0.36)
Brookings		0%		0.98	0.91	8.1 (7.9–8.4)	0.83 (0.04)
	Maize	1%	<2mm	0.93	1.00	10.0 (9–11)	0.98 (0.12)
		1%	2–4 mm	0.88	1.08	12 (10–14)	1.23 (0.19)
		1%	wet	0.95	0.99	9.8 (9.3–10.2)	0.94 (0.08)
		10%	<2 mm	0.87	1.67	47 (35–62)	0.98 (0.17)
		10%	2–4 mm	0.44	1.38	24 (14–43)	0.79 (0.37)
		10%	wet	0.92	1.39	25 (20–30)	0.83 (0.12)
	Switchgrass	1%	All	0.96	0.99	9.8 (9.4–10.1)	0.83 (0.04)
		10%	<2mm	0.96	1.41	26 (22–30)	0.76 (0.06)
		10%	2–4 mm and wet	0.85	1.28	19 (17–22)	0.77 (0.10)
	Ponderosa pine	1%	<2 mm	0.96	1.06	12 (11–12)	0.8 (0.08)
		1%	2–4 mm	0.84	1.02	11 (9–12)	0.57 (0.10)
		1%	wet	0.86	1.06	12 (10–13)	0.63 (0.10)
		10%	<2 mm	0.85	1.58	38 (29–51)	0.77 (0.15)
		10%	2–4 mm and wet	0.79	1.63	43 (32–56)	0.68 (0.10)

[a]Isotherms for different biochar types within a biochar species and amount were tested for homogeneity and if not significantly different using the F statistic and a $P \leq 0.05$, the regression was developed using appropriate combined datasets.
[b]Numbers in parentheses for the log Kf and $1/n$ values are confidence intervals for the given parameters.

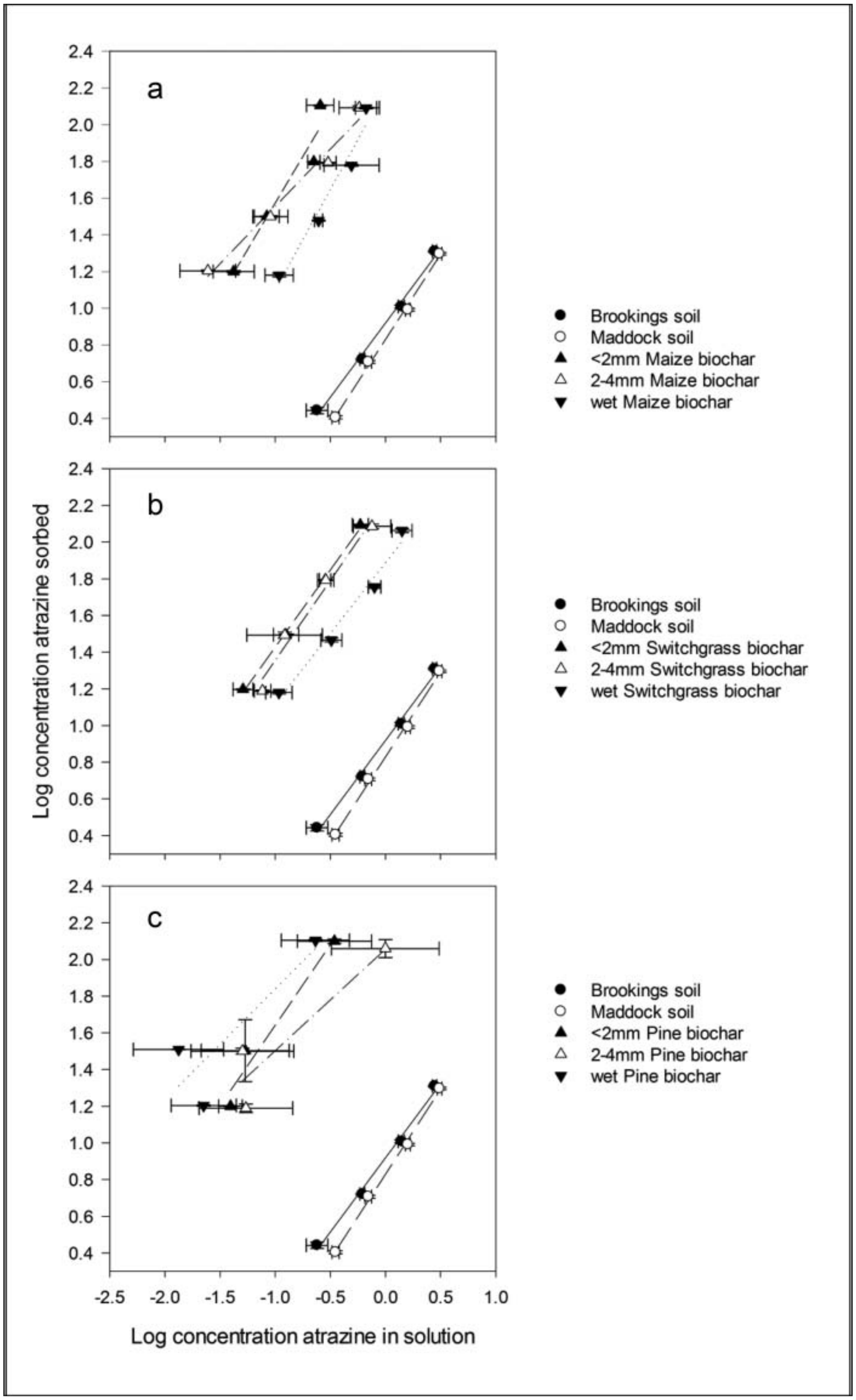

Figure 2. Freundlich isotherms for atrazine sorption to unamended Brookings and Maddock soil and for (a) maize biochars; (b) switchgrass biochars; and (c) ponderosa pine biochars. The points are the treatment mean and the bidirectional lines for each point are confidence intervals for amount in solution (horizontal) and sorbed (vertical). Fitted parameters are provided in Table 2.

from 74 to 912 $\mu mol^{1-1/n}$ $L^{1/n}$ kg^{-1} and were influenced by the initial feedstock material and, to a lesser extent, post-process handling. Biochar made from ponderosa pine had the greatest variability for atrazine sorption, with low adjusted r^2 values (<0.6), and the water-cooled biochar had slightly greater sorption than either of the dry biochar types. Switchgrass had adjusted r^2 values >0.9. Water-cooled maize and switchgrass biochars had lower *Kf* values compared with the <2-mm or 2–4-mm biochars (Fig. 2).

Soil amended with 1% biochar increased atrazine sorption (Fig. 3 and 4 and Table 2). The 1% addition of most biochars increased atrazine *Kf* values for the Maddock soil by about 45% and for the Brookings soil about 25%. Post-processing technique of maize and ponderosa pine biochar did not influence the atrazine sorption isotherm in the Maddock soil (Fig. 3a and c). However, Maddock soil amended with water-cooled switchgrass biochar had greater atrazine sorption than soils amended with the air-dried

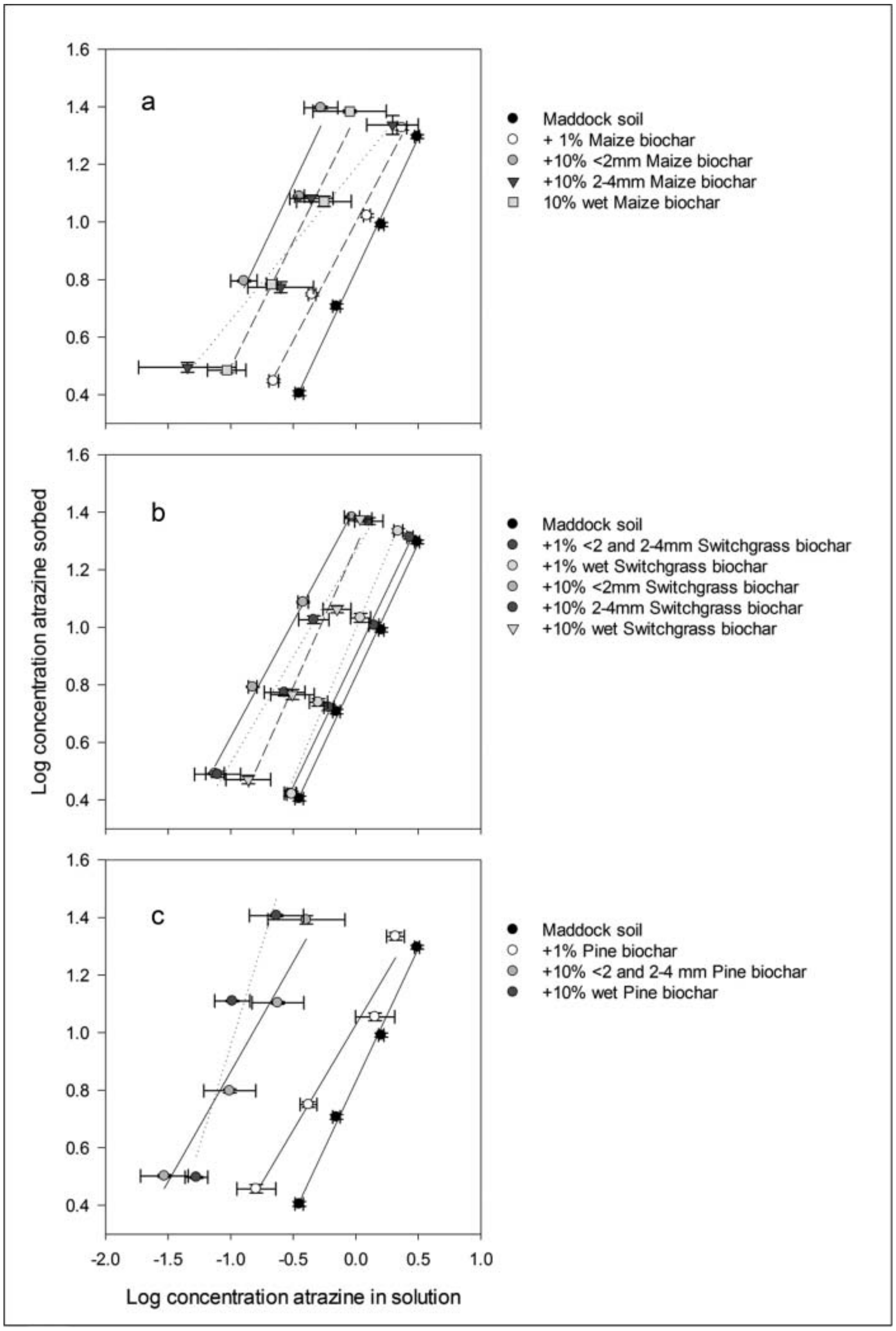

Figure 3. Freundlich isotherms for atrazine sorption to unamended Maddock soil and amended with 1 and 10% additions of (a) maize biochars; (b) switchgrass biochars; and (c) ponderosa pine biochars. The points are the treatment mean and the bidirectional lines for each point are confidence intervals for amount in solution (horizontal) and sorbed (vertical). Fitted parameters are provided in Table 2.

switchgrass biochar (Fig. 3b). Post-processing of maize and ponderosa pine biochars when added at 1% influenced sorption isotherms, with different *Kf* values but similar 1/n values for the three types of maize biochar (Fig. 4a) and similar *Kf* values but different $1/n$ values for the three types of ponderosa pine biochar (Fig. 4c). The 1% switchgrass addition had similar sorption isotherm regardless of post-process handling and was described using a single isotherm (Fig. 4b).

The 10% addition of biochar increased sorption to both soils compared with unamended or 1% biochar amended soils (Table 2 and Figs. 3 and 4). Sorption isotherms generally differed among feedstock materials and post-process handling. The addition of 10% <2-mm biochar size of maize or switchgrass feedstock to either soil had higher *Kf* values than the 2–4-mm and the wet biochars. The wet ponderosa pine biochar had a higher atrazine sorption *Kf* value than the <2-mm or 2–4-mm biochars.

Biochar influence on 2,4-D sorption

2,4-D sorption to maize biochars was evaluated at one initial concentration (13 μmol L^{-1}). The sorption coefficient (K_d) averaged 240 L μmol^{-1} kg^{-1}, and was similar among all post-processing treatments. The 2,4-D sorption isotherms for switchgrass and ponderosa pine biochars had adjusted r^2

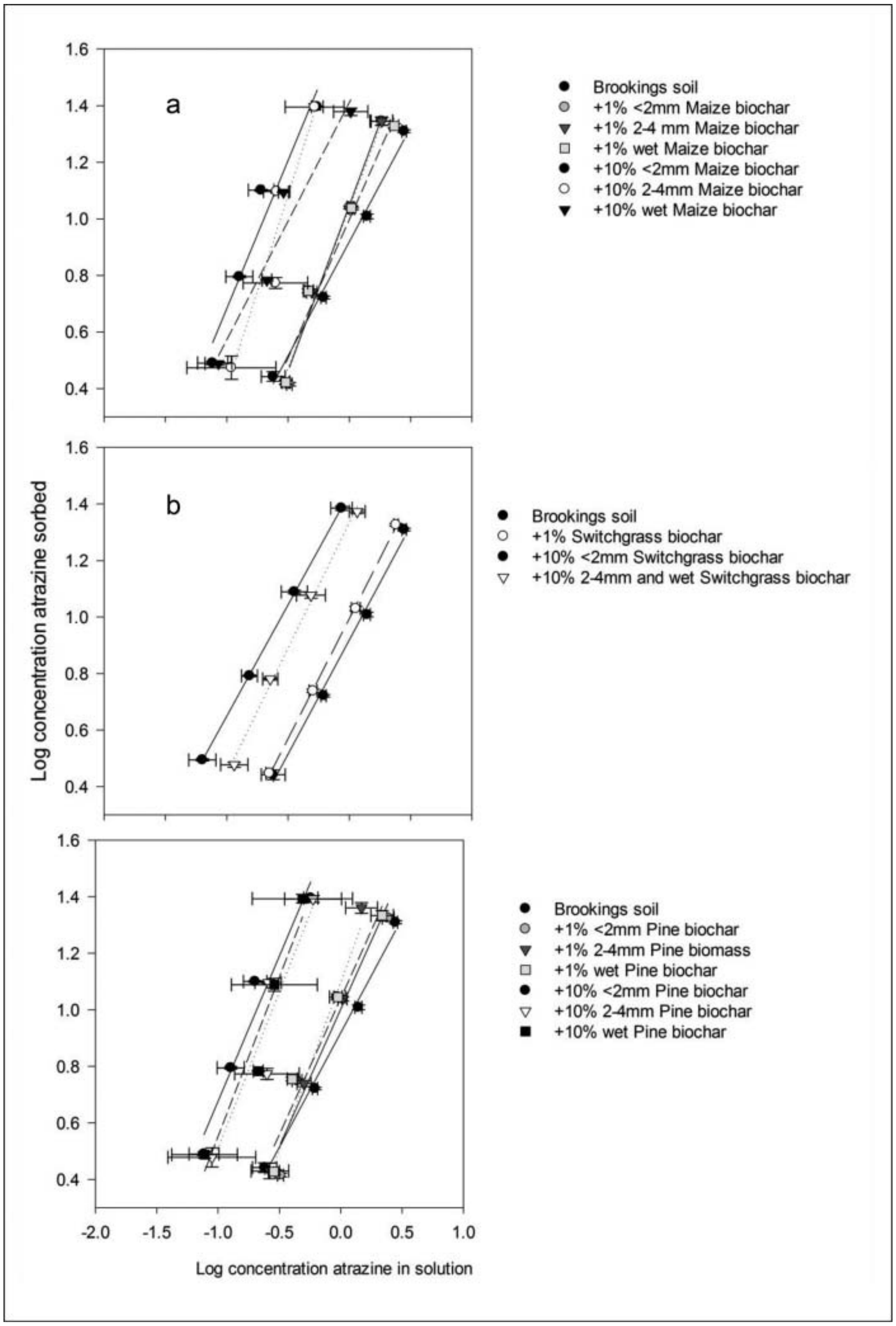

Figure 4. Freundlich isotherms for atrazine sorption to unamended Brookings soil and amended with 1 and 10% additions of (a) maize biochars; (b) switchgrass biochars; and (c) ponderosa pine biochars. The points are the treatment mean and the bidirectional lines for each point are confidence intervals for amount in solution (horizontal) and sorbed (vertical). Fitted parameters are provided in Table 2.

values, that were greater than 0.84 (Table 3). The 1/n values for the 2,4-D sorption isotherms were much lower than atrazine values, indicating less 2,4-D sorption from solution at higher concentrations compared with atrazine.

The 2,4-D sorption *Kf* values for unamended Maddock and Brookings soils were 0.22 and 0.60 $\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$, respectively (Table 3). When compared with the atrazine isotherms, the 2,4-D isotherms generally had lower adjusted r^2 values, indicating that the isotherms were less good fits to the data, most likely due to high variability in sorption data (Figs. 5–7). The addition of 1% biochar increased *Kf* values of 2,4-D sorption markedly [from 10X (ponderosa pine added to Brookings soil) (Fig. 7) to 136X (switchgrass added to Maddock soil) (Fig. 6)].

In both soils, post-processing techniques within a feedstock had little influence the sorption parameters. For example, post-processing treatment was only found to be significant in two cases. The first was ponderosa pine added to Maddock soil with <2-mm having a similar *Kf* value but higher $1/n$ value than the 2–4-mm and wet biochar isotherms. The other exception was maize added to the Brookings soil with <2-mm biochar having both a higher $1/n$ value and greater *Kf* value than the 2–4-mm and wet biochar isotherms. Biochars made from maize and switchgrass

Table 3. The parameters for the 2,4-D sorption isotherms[a] with coefficients for the log Kf, *Kf*, and slope (1/*n*) of the isotherm lines for switchgrass and ponderosa pine biochars and soil alone and 1% or 10% of the biochar added to soil.

Soil type	Species	Amount of biochar added	Post-process treatment	Adj r^2	Log Kf	*Kf* $\mu mol^{1-1/n} L^{1/n} kg^{-1}$	1/*n*
None	Switchgrass	100%	<2mm	0.90	2.60	398 (299 – 529)[b]	0.64 (0.08)
		100%	2–4 mm	0.84	2.28	190 (150 – 242)	0.35 (0.06)
		100%	wet	0.85	2.07	117 (93–149)	0.63 (0.10)
	Ponderosa pine	100%	<2 mm	0.88	2.29	195 (169–225)	0.33 (0.04)
		100%	2–4 mm	0.90	2.63	427 (354–514)	0.59 (0.06)
		100%	wet	0.93	1.65	45 (41–49)	0.58 (0.06)
Maddock		0%		0.45	−0.66	0.22 (0.1–0.4)	0.93 (0.39)
	Maize	1%	All	0.75	1.32	21 (17–25)	0.63 (0.10)
		10%	All	0.78	1.55	35 (28–45)	0.85 (0.12)
	Switchgrass	1%	All	0.61	1.48	30 (23–40)	0.96 (0.18)
		10%	All	0.73	1.44	28 (23–33)	0.49 (0.08)
	Ponderosa pine	1%	All	0.73	0.62	4.0 (3.6–4.8)	0.44 (0.10)
		10%	<2mm	0.62	1.45	28 (19–41)	0.85 (0.34)
		10%	2–4 mm and wet	0.74	1.45	28 (22–36)	0.63 (0.12)
Brookings	0%			0.76	−0.23	0.6 (0.5–0.8)	0.79 (0.21)
	Maize	1%	All	0.76	1.33	21 (19–25)	0.63 (0.08)
		10%	<2 mm	0.75	1.99	98 (47–203)	1.27 (0.38)
		10%	2–4 mm and wet	0.78	1.56	36 (28–48)	0.88 (0.15)
	Switchgrass	1%	All	0.62	1.48	30 (23–40)	0.96 (0.19)
		10%	All	0.71	1.50	32 (31–33)	0.61 (0.12)
	Ponderosa pine	1%	All	0.75	0.79	6.2 (5.6–6.8)	0.48 (0.08)
		10%	All	0.62	1.47	30 (22–40)	0.62 (0.12)

[a]Isotherms for different biochar post-processing treatments within a biochar species and amount were tested for homogeneity and if not significantly different using the F statistic and a $P \leq 0.05$, the regression was developed using appropriate combined datasets.
[b]Numbers in parentheses for the log Kf and 1/*n* values are confidence intervals for the given parameters.

feedstocks had increased sorption by about 5X compared with biochar made from ponderosa pine feedstock. The 10% addition of biochar increased 2,4-D sorption compared with unamended soils and soils amended with 1% biochar.

Biochar influence on speed of seed germination

The percent of germinable seeds and the speed of germination [43,44] were compared among treatments. Germination percentages for radish, lettuce, and wheat were generally similar and greater than 90% (data not shown). Adding any of the biochars at either a low or high rate increased the speed of germination (Figs. 8 and 9). These data also indicated that the biochars did not adversely affect germination

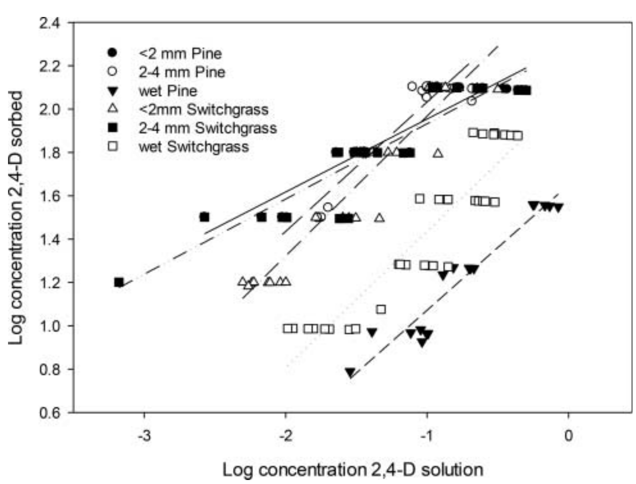

Figure 5. Freundlich isotherms for 2,4-D sorption to switchgrass and ponderosa pine biochars. The points represent individual replications of treatments. Fitted parameters are provided in Table 3.

speed. As herbicide rate increased the speed of germination decreased. The addition of biochar to radish (atrazine and 2,4-D) and wheat (atrazine) seeds counteracted the herbicide addition, with faster germination speeds when compared within a herbicide rate (Fig. 8). The larger seed size and the herbicide sorption by the biochars most likely contributed to these results. Speed of germination for the maize and switchgrass biochars at either rate were similar across atrazine rates. The 10% rate of ponderosa pine biochar for the radish-atrazine assay was more effective in protecting against phytotoxic effects than the 1% rate when atrazine was applied at 1.0 g L^{-1} or higher (Fig. 8).

The addition of high or low rates of biochar for the lettuce assay with 2,4-D present decreased speed of germination when compared with 2,4-D solutions with no biochar present (Fig. 9). The small seed size of lettuce may be a contributing factor to this result.

Discussion

The 1% biochar addition to either of the two soil types did not impact soil pH or EC. Several prior studies [45–47] have noted increased EC and pH with biochar amendments as low as 2%. The 10% maize biochar addition increased the Maddock soil EC value. The Maddock soil has less buffering capacity than the Brookings soil due to the high sand content (724 g kg^{-1}) and lower clay and organic matter contents (85 and 16 g kg^{-1}, respectively) compared with a higher clay and organic matter content (310 and 34 g kg^{-1}, respectively). If biochars would be applied in high amounts or frequently, the EC values should be monitored to avoid salt problems as eastern South Dakota has soil parent materials and hydrologic cycles that promote saline conditions, and crop injury may occur in soils >4000 uS cm^{-1}.[48]

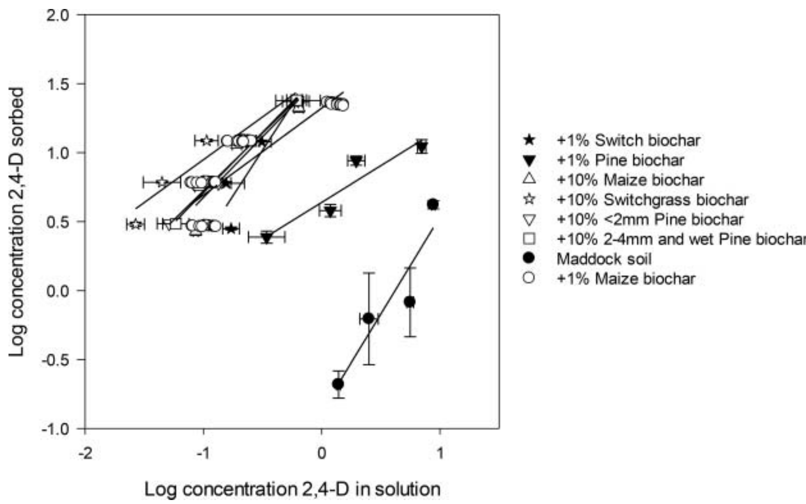

Figure 6. Freundlich isotherms for 2,4-D sorption to Maddock soil alone or amended with 1 or 10% maize, switchgrass or ponderosa pine biochars. The points are the treatment mean and the bidirectional lines for each point are confidence intervals for amount in solution (horizontal) and sorbed (vertical). Fitted parameters are provided in Table 3.

In this study, all biochar types had high sorption values for both atrazine, a basic herbicide (Fig. 2) and 2,4-D, an acidic herbicide (Fig. 5). Post-processing handling also influenced herbicide sorption. Clay and Malo [13] and Deng et al.[49] also reported atrazine sorption differed among different processing types within a feedstock species. Higher heat, longer processing times, and particle size have been reported to influence sorption. In addition, other post-processing treatments of biochars, for example the addition of ammonium dihydrogen phosphate, have been reported to increase atrazine sorption by increasing the specific area of sorption on char produced from corn stover.[50]

Sorption to soil was much lower than to biochar alone. Based on past atrazine sorption studies of soils with high sand and low clay and organic matter content vs soils with high clay and organic matter,[30,39] the sorption differences between the unamended Maddock and Brookings soils were expected.

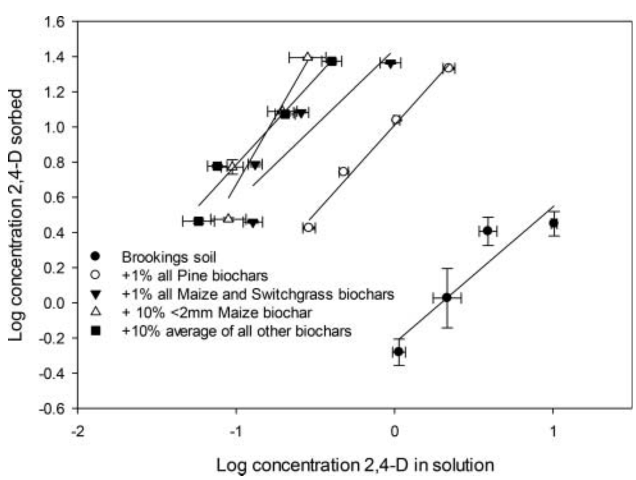

Figure 7. Freundlich isotherms for 2,4-D sorption to Brookings soil alone or amended with 1 or 10% maize, switchgrass or ponderosa pine biochars. The points are the treatment mean and the bidirectional lines for each point are confidence intervals for amount in solution (horizontal) and sorbed (vertical). Fitted parameters are provided in Table 3.

The overriding factor for both atrazine and 2,4-D sorption to soil was the amount of biochar added, with 10% amendment have greater sorption than 1%. Feedstock type and post-processing technique had more limited influences on herbicide sorption. Organic carbon content and pH are known to

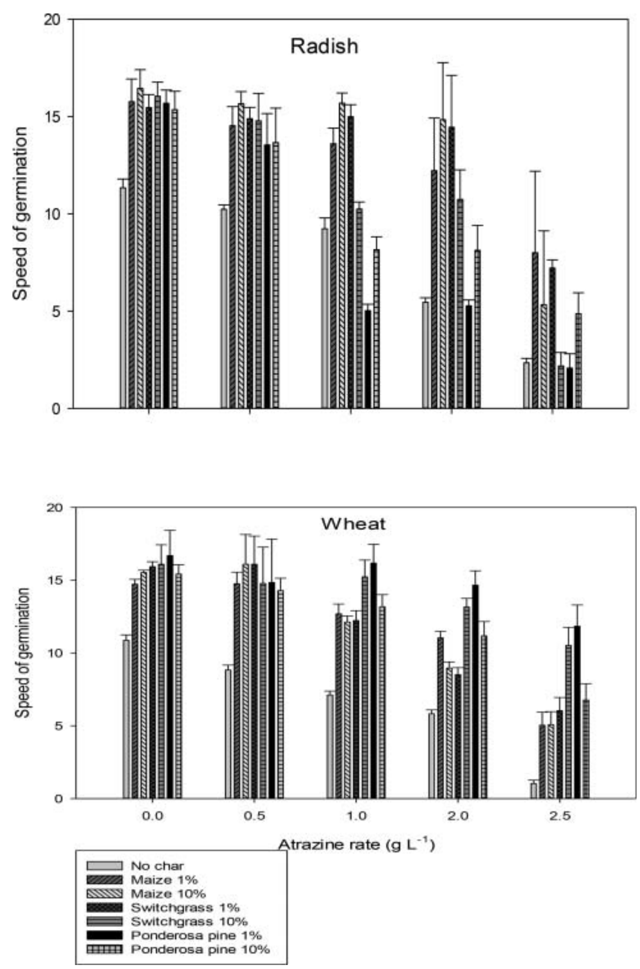

Figure 8. Speed of germination of radish and wheat treated with differing amounts of atrazine and differing amounts of biochar derived from pyrolysis of three feedstock materials.

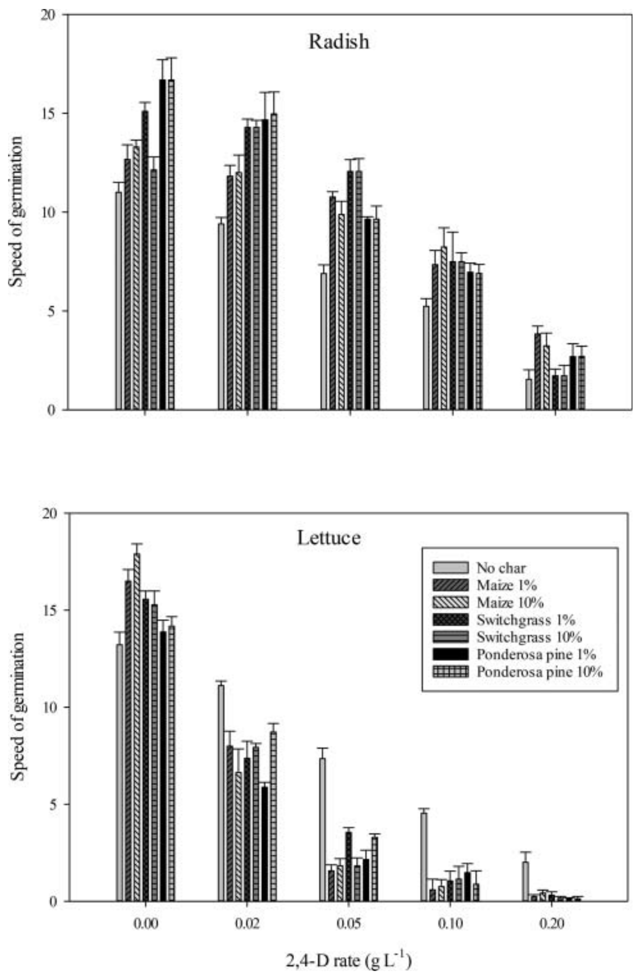

Figure 9. Speed of germination of radish and lettuce treated with differing amounts of 2,4-D and differing amounts of biochar derived from pyrolysis of three feedstock materials.

influence triazine herbicide sorption.[39] Increased atrazine sorption to biochar amended soil has been reported in many studies.[13,30,49] Other studies have shown higher sorption of neutral herbicides (treflan and pendimethalin).[32,51] Acidic herbicides, like 2,4-D, are less sorbed to soil when compared with slightly positively charged herbicides like atrazine, but sorption also is influenced by soil organic matter content and pH.[52] Kearns et al.[53] reported that 2,4-D sorption to biochar (feedstocks of bamboo, pine, or corn cobs) depended on initial biochar production temperature, with greater sorption to biochars produced at higher temperatures or undergoing longer pyrolysis times.

In speed of seed germination assays, germination in herbicide treatments was similar to untreated controls when biochar was present. These results are in line with the Mesa and Spokas [25] review where they reported that biochar (regardless of type) application to soils increased herbicide sorption, decreased dissipation (i.e., the half-life of the chemical was longer in the environment), but also, in general, decreased herbicide bioavailability. Our germination assay results also are similar to previous studies that reported reduced herbicide uptake or weed efficacy when soils were amended with biochar.[31,32,51] For example, Nag et al.[32] reported that straw biochar applied at 0.5 or 1% decreased bioavailability of atrazine and trifluralin in calcarosol and ferrosol soils types. Soni et al.[51] reported a 75% reduction in weed control in the field studies with atrazine applied preemergence to soils amended with 0.5 kg m^{-2} biochar.

While herbicide sorption was increased and efficacy decreased, biochar effect on the ultimate environmental fate of herbicides is not straightforward. Typically, increased herbicide sorption in A horizon soils is reported to reduce leaching through the soil profile.[54] However, Delwiche et al.[55] reported that while biochar addition to a soil surface reduced peak flow of atrazine leachate in homogeneous packed columns, the flow of atrazine through undisturbed soil was more influenced by soil heterogeneity and marcopore flow than by the addition of biochar.

Summary

Biochars that were manufactured from different types of feedstocks under different post-production handling conditions had slightly different baseline properties. Biochars used in this study had different specific surface areas,[5] EC, and CEC values. Herbicide sorption and, as a consequence, herbicide efficacy were influenced by biochar addition to soil, with greater amounts increasing the effects.

Overall, our results suggest that biochar applications to soils should be done in a deliberate, well planned manner. General addition of biochars to soil increased herbicide sorption and reduced herbicide efficacy, which may result in the need for greater herbicide application rates, additional application times, or more weed control operations required for controlling problem weeds. However, biochar additions to waterways may help reduce pesticides in runoff waters, although not necessarily leaching waters, from field sites before reaching off-site areas as a result of increased sorption to the amended soil.

Funding

Funding provided by Agriculture and Food Research Initiative Competitive Grant no. 2011-67009-30076 from the USDA National Institute of Food and Agriculture and South Dakota Agricultural Experiment Station.

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