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# The Influence of Biochar Production on Herbicide Sorption Characteristics

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## 1. Introduction

Biochar is the by-product of a thermal process conducted under low oxygen or oxygen-free conditions (pyrolysis) to convert vegetative biomass to biofuel (Jha et al., 2010). There are a wide variety of end-products that can be manufactured depending on processing parameters and initial feedstocks (Bridgewater, 2003). The pyrolytic process parameters such as temperature, heating rate, and pressure can change the recovery amounts of each end-product, energy values of the bio-oils, and the physico-chemical properties of biochar (Yaman, 2004).

Biochars are recalcitrant forms of carbon and, depending on properties, can remain in the soil for greater than 1000 years (Skjemstad et al., 2002). The long-term persistence of this carbon form is due to slow microbial degradation and chemical oxidation rates (Sanchez et al., 2009). In addition, biochar interacts with soil materials such as ions, organic matter, and clays that generally increase the persistence of biochar within the soil. However, biochars, unlike commercial fertilizers, are not precisely defined materials and vary widely in properties depending on organic material source and manufacturing process (Karaosmanoglu et al., 2000; McHenry, 2009; Sohi et al., 2010). Increasing pyrolytic temperature decreases biochar recovery but increases C concentration of the char compared with char recovered at lower temperatures (Daud et al., 2001; Katyal et al., 2003). For example, as temperature increased from $300^0$ to $800^0$ C, biochar C content increased from 56 to 93% whereas biochar yield decreased from 67 to 26% (Okimori et al., 2003). Other pyrolytic parameters, such as sweep gas flow, can influence biochar particle size with higher flows reducing the particle size but increasing heating values (Katyal et al., 2003; Demirbas, 2004). Biochar also can be influenced by reactor design and other reaction parameters including heating rate, residence time, pressure, and catalyst used. Feedstock type, quality, and initial physical characteristics of the material (e.g. particle size, shape, and structure) can impact the bio-oil yield and properties, as well as the type and amounts of biochar formed (Bridgewater et al., 1999).

Landspreading biochar for a soil amendment is suggested to improve crop production efficiency because regardless of the initial manufacturing process, biochars have a high charge density and surface area. The use of biochar as a soil amendment is not a new concept. Dark earths (terra preta) discovered in the Amazon Basin were found to have

received deliberate land applications of charred materials and residues of biomass burning by Amer-indian populations before European arrival (Erickson, 2003; Sombroek et al. 2003). Pyrogenic C in terra preta is very resistant to microbial decay over centuries due to its complex aromatic structure and acts as a significant C sink (Glaser et al., 2001).

The benefits of biochar application have been hypothesized to include: increasing plant available soil water; building soil organic matter; enhancing nutrient cycling; lowering soil bulk density; acting as a liming agent if high in pH; and reducing transfer of pesticides and nutrients to surface and ground water (Laird, 2008) thereby improving water quality. The application of biochar to soil has been reported to have a positive impact on physical properties such as soil water retention and aggregation (Piccolo et al., 1996) and may decrease erosion potential. Glaser et al. (2002) observed an increase in field water holding capacity by 18% in charcoal enriched Anthrosol due to an increase in surface area. Biochar application has been shown to improve other soil physical, chemical, and biological properties (Glaser et al., 2002; Lehmann and Rondon, 2006) leading to positive impacts on plant growth and development. For example, Chidumayo (1994) observed enhanced seed germination (30%), shoot height (24%), and biomass production (13%) of seven indigenous woody crops with the application of charcoal compared with the crops on undisturbed Zambian Alfisols and Ultisols. Kishimoto and Sugiura (1985) also found increases in height (26 to 35%) and biomass (2.3 X greater) production of sugi trees (*Cryptomeria japonica L.*). Similar enhancement was observed in yields of annual crops such as maize (*Zea mays L.*) on Nigerian Alfisols and Inceptisols with the application of charcoal (Mbagwu and Piccolo, 1997) due to an increase of soil pH that resulted in greater micro-nutrient availability and decreased deficiencies. However, biochars also have been shown to have an extreme affinity for essential plant nutrients (Sanchez et al., 2009) that can provide a slow release mechanism.

Some biochars that have high pH (e.g. >9.5) can provide liming capacity and increase the soil pH (Sanchez et al., 1983; Mbagwu and Piccolo, 1997). For example, application of coal ash at the rate of 110 Mg $ha^{-1}$ increased the pH of an eroded Palouse soil from 6.0 to 6.8 (Cox et al., 2001). Exchangeable bases also were observed to increase in sandy and loamy soils with the additions of hardwood and conifer charcoals (Tryon, 1948). Application of charcoal to highly weathered soils with low-ion retention capacities increased the cation exchange capacity (CEC) by 50% compared to unamended soil (Mbagwu and Piccolo, 1997). Oguntunde et al. (2004) reported a significant increase in soil pH, base saturation, electrical conductivity (EC), exchangeable Ca, Mg, K, Na, and available P in charcoal kiln sites and reported an increase in grain and biomass yield of maize of 91% and 44% respectively, with a coal char application. Leaching of $NH_4^+$ from an unfertilized Ferralsol was reduced with the application of charcoal due to its high C content, although the retention properties of chars may differ for other ionic species (e.g. K, Ca, Mg) if the char already contains high concentrations of the ion of interest (Lehmann et al., 2002). Because of biochar's diverse properties and potential for high reactivity in soils, a 'one-recommendation-fits-all situations' mentality for the use as of biochar as a soil amendment needs to be avoided. To date, the greatest positive impacts of biochar have been primarily observed on degraded soils and those with low fertility whereas applications on highly productive soils have been reported to have low or minimal impacts (Woolf et al., 2010).

Agrichemicals such as pesticides, growth regulating chemicals, and nutrients are applied to crops to control pests and increase yield potential. Depending on the type and amount of

biochar applied, the changes in soil properties associated with the application (e.g. soil pH, EC) as well as the physio-chemical properties of the char itself, may impact the use, rates, efficacious properties, and fates of agrichemicals used in agronomic management. The environmental fate (e.g. leachability, rate of decomposition, etc.) and efficacy of soil applied pesticides are influenced strongly by their reaction and retention with soil particles and organic matter (Brown et al., 1995). Agrichemical molecules can be removed from soil solution through attraction or attachment to the surfaces of organic materials and soil particles (adsorption) or movement into the matrix (like water into a sponge) (absorption). Often, experiments cannot distinguish between these processes so that the general term sorption is used.

Sorption is controlled by properties of the chemical of interest including the water solubility, pH, dissociation constant (pKa), octanol/water partition coefficient, and other factors (Weber, 1995) and can be used to help describe the fate of an herbicide in the environment (Wauchope et al., 2002). The sorption of the chemical also is affected by soil properties including water, organic matter, clay, sand, and oxide contents, and soil pH (Koskinen and Clay, 1997; Laird and Koskinen, 2008). Soils high in sand generally sorb much less chemical than loamy or clay type soils. Agricultural practices that involve modifying soil organic matter content often increase chemical retention. Indeed, studies have shown that adding biochar to soil can result in greater sorption of pesticides (Cao et al., 2009; Spokas et al., 2009; Yu et al., 2009). The distribution of chemical between a solution and solid phase gives an indication of the amount of chemical available in solution and is defined using a sorption coefficient ($K_d$) where:

$$K_d = \frac{\text{mass of herbicide sorbed per g of solid}}{\text{amount of chemical remaining in solution at equilibrium}} \quad (1)$$

Large $K_d$ values (typically over 100) indicate that a high amount of the chemical originally in solution is sorbed to the solid interface, with low amounts of chemical remaining in solution. Sorption of a chemical from the liquid phase of soil may result in the chemical being: 1) less available to plants, so there may be less uptake; 2) less available to soil organisms, thereby increasing the chemical's residence time and slowing degradation; and 3) less available to leach with water percolating through the soil, which could result in improved groundwater quality.

The biochar source-processing combination provides a rich diversity of biochars to evaluate for soil amendment use (Lehmann et al., 2009). The potential of a specific biochar for a specific use will depend on the physical and chemical properties of the biochar, as well as soil characteristics. The challenge of amending soil with biochar is to identify the benefits that biochar can provide (e.g. fertility, increased water holding capacity) (Lehmann, 2007) and balance these against any negative effects that the char may have. Site-specific application recommendations of specific biochars require an examination of the products of different production and processing scenarios. Much of the biochar research has been based on slow pyrolysis with a goal to optimize biochar properties for a specific goal such as improved soil fertility, greenhouse gas mitigation, or heating value. Little work has been done with biochar produced from fast pyrolysis processes and even less with biochar produced from microwave pyrolysis reactors.

Feedstock is a key factor governing the status of physio-chemical properties of biochar. All types of materials including, but not limited to, palm shells, rapeseed (*Brassica rapa*) stems, sunflower (*Helianthus annuus*), and wood have been used or are being proposed as potential feedstock sources for use in the biofuel industry. In the Midwestern U.S., maize stover and switchgrass (*Panicum virgatum*) biomass are feedstocks that bioenergy companies are exploring for use.

## 2. Biochar influence on herbicide sorption to soil

This study examined atrazine and 2,4-D sorption to several biochars that were the result of microwave pyrolysis using varying temperatures and processing times of maize and switchgrass biomass. In addition, sorption characteristics of these two chemicals to soil amended with these biochars at two application rates were determined.

### 2.1 Materials and methods

#### 2.1.1 Biochar and soil

Biochar was produced from maize stover (stalks and other residues remaining after maize grain harvest) and switchgrass biomass collected from fields near Brookings, South Dakota, USA (44.31, -96.67). Briefly, the material was dried at room temperature and pulverized mechanically using a Thomas-Wiley laboratory mill (Model No. 3375-E15, Thomas Scientific, USA) to pass through a 4 mm screen. The ground materials were processed by microwave pyrolysis using the SDSU Ag and Biosystem Eng. Dept. microwave system (specific processing methods reported in Lei et al., 2009). Processing temperatures ranged from $530^0$ to $670^0$ C and microwave residence times ranged from 8 to 24 minutes with seven maize and nine switchgrass biochars produced (Table 1 and Figures 1 and 2). The energy output, product types, particle size distribution, and elemental analysis of the biochar recovered from maize stover using these processing conditions are reported in Lei et al. (2009).

For this study, the maize biochars were used alone or mixed with the A horizon soil of a Brandt silty clay loam (Fine-silty, mixed, superactive, frigid Calcic Hapludoll, [Soil Survey Staff, 2011]) soil at 1 or 10% (w/w) to examine their effect on solution pH, EC, and atrazine and 2,4-D $K_d$s (sorption coefficients) for each biochar and biochar/soil combination. For switchgrass biochars, the 1 or 10% amendments to soil were used for pH and EC measurements, however, for herbicide sorption studies only biochar alone or soil mixed with 10% biochar were used, due to limited biochar supply. To maximize homogeneity, each soil/biochar combination was individually mixed by adding air-dry soil and biochar to each individual tube.

#### 2.1.2 Solution characteristics

Biochars, soil, and soil with biochar amendments were analyzed for pH using a 0.01 *M* $CaCl_2$ slurry (1:1 w/v) and a standardized pH electrode. The solution pH was recorded after the reading had stabilized. Electrical conductivity (EC) was determined on a slurry that was mixed 1:1 (v/w) with 0.01 *M* $CaCl_2$ and biochar, soil, or soil amended with biochar. The slurry was shaken for 0.5 hr and EC measured using a commercially available EC electrode.

### 2.1.3 Herbicide sorption

Atrazine solution was diluted to a final concentration of 13 µM in 0.01 $CaCl_2$ using technical grade atrazine. This 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., St. Louis, MO). The 2,4-D solution was made in a similar manner, with technical grade 2,4-D added to 0.01 M $CaCl_2$ to have a final concentration of 13 µM. This 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., St. Louis, MO).

A 4-mL aliquot of herbicide solution was added to 2 g soil or soil amended with 1 or 10% biochar (final slurry solution 2:1 v/w) in glass centrifuge tubes sealed with a Teflon-lined cap. A 5-mL aliquot of herbicide solution was added to 0.5 g biochar when biochar was used as the sorbent, with the final solution/biochar ratio of was 10:1 v/w, due to the highly sorbent characteristics of the biochar.

After solution addition, the mixtures were shaken or vortexed to form a slurry. Tubes containing the slurries were shaken for 24 hr, centrifuged, and a 250-µL aliquot of supernatant removed. The amount of $^{14}$C remaining in the supernatant solution was determined by liquid scintillation (Packard Model 1600TR) counting after the addition of scintillation cocktail. The amount of radioactivity sorbed was determined by comparing the counts in the supernatant samples with counts recorded from the original soil-free blank solution samples. The sorption coefficients (Kd) of the samples were then calculated as L kg$^{-1}$, correcting for the differences in volume added g$^{-1}$ of material.

### 2.1.4 Statistical analysis

Experimental treatments were run in triplicate and studies were repeated in time. Results were combined for the studies due to similarity of means and homogeneity of variance between studies. Means presented were averaged over all treatment replicates and statistically separated by least significant difference calculation at $P \leq 0.05$.

## 2.2 Results

### 2.2.1 Biochar pH and EC values

The biochars produced in this study ranged in pH from acidic (4.06) to alkaline (9.88), and were dependent on feedstock, pyrolysis temperatures, and processing times (Table 1). Differences were observed among maize and switchgrass feedstocks. For maize stover, three of the microwave pyrolysis reactions at high temperatures ($\geq$650$^{o}$C), regardless of processing time, resulted in biochars that were very alkaline (pH>9). Two processes at lower temperatures (530$^{o}$C and a processing time of 16 min or 550$^{o}$C with a processing time of 10 min) resulted in biochars with pH <5. The 22 min processing time at 550$^{o}$C resulted in a biochar with a more neutral (7.6) pH. For switchgrass, four processes resulted in biochars that were acidic (pH < 4.6) and the biochars were more acidic than biochars from maize at the same time and temperature. The acidic biochars were formed from processes that had low temperatures (<600$^{o}$C) or shorter times at 600$^{o}$C (8 min), or 10 min at 650$^{0}$C. The most alkaline switchgrass biochar was the result of processing at 670$^{o}$C for 16 min. This biochar had a pH of ~9.1, which was lower than the alkaline maize biochars that ranged in pH from

| Pyrolysis parameters | | Maize (*Zea mays*) | | | | | |
|---|---|---|---|---|---|---|---|
| | | pH | | | EC | | |
| Temp | time | Biochar | soil + 1% biochar | soil + 10% biochar | Biochar | soil + 1% biochar | soil + 10% biochar |
| °C | min | | | | | mS cm$^{-1}$ | |
| 530 | 16 | 4.59 | 6.39 | 5.85$^{-}$ | 0.3 | 2.4 | 1.4 |
| 550 | 10 | 4.77 | 6.38 | 6.04$^{-}$ | 2.3 | 1.8 | 2.2 |
| | 22 | 7.60 | 6.47 | 6.61$^{+}$ | 1.9 | 1.8 | 1.8 |
| 600 | 8 | 5.68 | 6.44 | 6.44 | 2.1 | 1.8 | 2.0 |
| 650 | 10 | 9.88 | 6.46 | 6.75$^{+}$ | 2.0 | 1.9 | 1.9 |
| | 22 | 9.43 | 6.43 | 6.76$^{+}$ | 2.0 | 1.8 | 1.9 |
| 670 | 16 | 9.65 | 6.43 | 6.73$^{+}$ | 1.1 | 1.9 | 1.9 |
| | | Switchgrass (*Panicum virgatum*) | | | | | |
| 530 | 16 | 5.32 | 6.17 | 6.70 | 0.3 | 1.80 | 1.67 |
| 550 | 10 | 4.12 | 6.49 | 5.67$^{-}$ | 2.1 | 2.13 | 1.97 |
| | 22 | 4.06 | 6.49 | 5.71$^{-}$ | 1.5 | 1.87 | 2.13 |
| 600 | 8 | 4.15 | 6.60 | 5.90$^{-}$ | 1.9 | 1.80 | 1.83 |
| | 16 | 6.47 | 6.45 | 6.76$^{+}$ | 1.7 | 1.30 | 1.33 |
| | 24 | 5.60 | 6.61 | 6.44 | 1.8 | 1.67 | 1.87 |
| 650 | 10 | 4.57 | 6.44 | 6.11$^{-}$ | 2.0 | 2.07 | 2.20 |
| | 22 | 8.28 | 6.48 | 6.80$^{+}$ | 2.9 | 1.97 | 2.37$^{+}$ |
| 670 | 16 | 9.10 | 6.48 | 6.85$^{+}$ | 2.5 | 1.67 | 1.90 |

Table 1. The influence of seven maize stover and nine switchgrass biochars produced with microwave pyrolosis with different processing times and temperature conditions on 100% biochar and soils amended with 1% or 10% (w/w) biochar. The soil used for this study was the A horizon of a Brandt silty clay loam (Fine-silty, mixed, superactive, frigid Calcic Hapludoll, [Soil Survey Staff, 2011]) from Aurora, SD (44.31, -96.67) with an unamended pH in a 1:1 solution of 0.01 *M* $CaCl_2$ of about 6.40 and an EC value of 1.63 mS cm$^{-1}$. A '-' sign indicates significantly lower value and a '+' sign indicates significantly higher value compared with unamended soil.

~9.4 to 9.9. The pH of these biochars can be compared with other biochar data. A wood ash/biochar that was the by-product of a commercial ethanol plant (Chippewa Valley Ethanol Company, Benson, MN) was obtained and used for comparison purposes. The wood ash had a pH of over 11. In comparison, broiler litter biochar obtained from pyrolysis reactions at either 350 or 700°C was found to have a fairly uniform acidic pH (5.5) (Uchimiya et al., 2010). These data indicate that the pH of different types of biochar are dependent on processing time, temperature, and initial feedstock material.

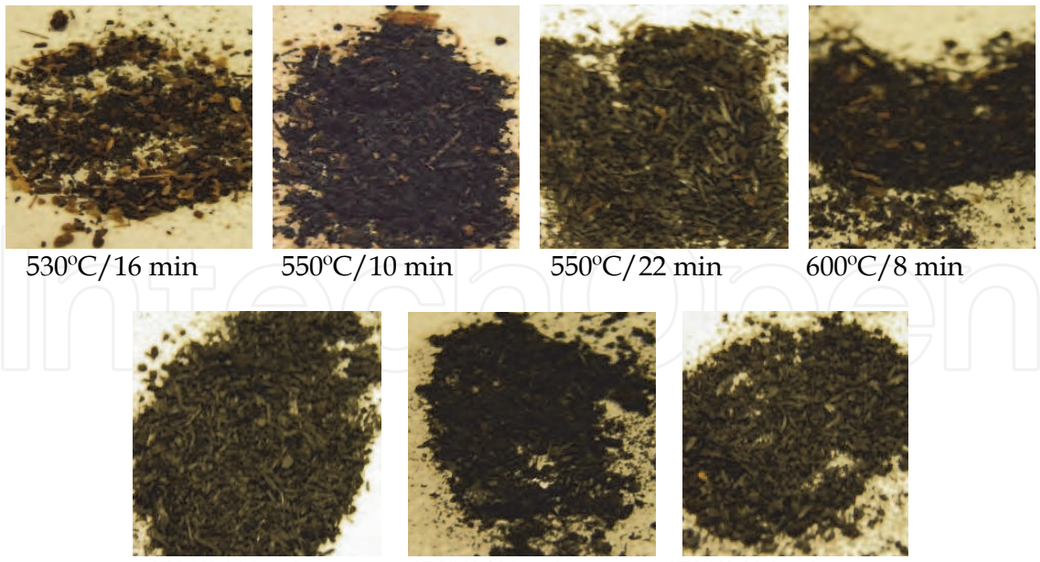


Fig. 1. Examples of biochars formed after exposure of maize (*Zea mays*) stover feedstocks to microwave pyrolosis at varying temperatures and times (see Lei et al., 2009).

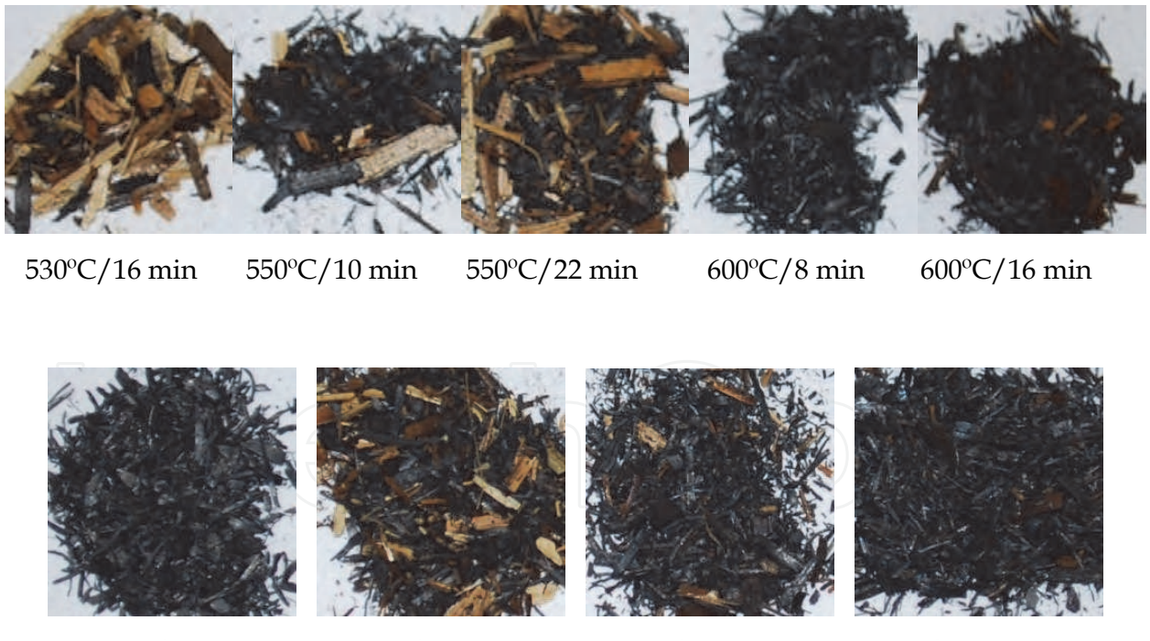


Fig. 2. Examples of biochars formed after exposure of switchgrass (*Panicum virgatum)* feedstocks to microwave pyrolosis at varying temperatures and times.

Electrical conductivity provides an indication of the amount of neutral soluble salts in the material or its salinity. High soil salinity often impedes the growth of most agricultural plants. Adding amendments that increase soil salinity, even though other beneficial

properties such as water holding capacity would increase, would be counterproductive. Saline soils are recognized worldwide (Food and Agriculture Organization, FAO) as soils with an EC reading of >4 mS $cm^{-1}$ (Richards, 1954; Abrol et al., 1988). In the U.S., the Soil Science Society of America (SSSA) uses a value of >2 mS $cm^{-1}$ boundary for the saline classification. Woodchip biochar had an EC value of 3.6 mS $cm^{-1}$. Biochar produced from maize stover had EC values ranging from 1.1 to 2.3 mS $cm^{-1}$ with five out of the seven >1.9 mS $cm^{-1}$. The switchgrass biochars had EC values ranging from 1.5 to 2.9 mS $cm^{-1}$ with the highest EC when materials were processed at 650° C for 22 min.

### 2.2.2 Influence on biochar amendment on soil pH and EC properties

The Brandt soil chosen for this study was a silty clay loam with a pH of 6.4. Due to the inherent soil properties and buffering capacity of this soil, it was expected that even high applications of the most acidic or alkaline biochar would have minimal impact on soil pH. When 1% maize or switchgrass biochars were added to soil, pH changes were minimal (generally <3%) (Table 1). When soils were amended with 10% biochar, pH was influenced to a greater extent. The slurry pH decreased from 4 to 8% when low pH biochars were added and increased a maximum of 9% when high pH biochars were added.

Soil EC was 1.63 mS $cm^{-1}$, well below the salinity values for saline soil. Adding either maize or switchgrass biochar to soil at 1% increased soil salinity, but with the exception of one switchgrass sample, did not increase the salinity to >2 mS $cm^{-1}$. Amending soil with 10% with the maize biochar that had the greatest EC value (2.3 mS $cm^{-1}$) was the only maize biochar that increased soil salinity above 2 mS $cm^{-1}$. Adding switchgrass biochar at 10% had greater impact than maize stover biochar and increased EC values an average of 11% when compared with ECs of unamended soil. Three switchgrass biochars increased EC values from 23 to 36% (Table 1) with final soil slurry EC values above 2 mS $cm^{-1}$, the SSSA value for saline soil classification. However, even with a 10% amendment, all final EC values were well below the FAO saline soil value of 4 mS $cm^{-1}$. If significant amounts of these biochars were applied frequently to the same field, managers must be cognizant of the potential for changes to EC values. Saline soil remediation can be expensive and often requires long-term management interventions, rather than short-term programs.

### 2.2.3 Atrazine sorption to biochar and soils amended with biochar

Atrazine is a chemical in the triazine family and has a slightly positive charge in soil solutions (Laird and Koskinen, 2008). The positive charge on the molecule, when in solutions above its $pK_a$, causes the molecule to be sorbed to materials that have a negative charge. Atrazine sorption to soil is considered moderate with $K_d$ values ranging from 1 to 5 (Koskinen and Clay, 1997). The value is dependent on many soil properties including pH, organic matter, and clay content (Koskinen and Clay, 1997). In this study, atrazine sorption to biochar ranged from 7 to 92 L $kg^{-1}$ (Figure 3). The sorption was dependent on feedstock type and processing method. These values ranged from 200 to 2300% greater than sorption to soil.

In general, the biochars from maize had much more variability in $K_d$ values than switchgrass biochar (Figure 3). Three of the seven maize biochars had $K_d$s less than 20 L $kg^{-1}$ whereas the other four had values of 55 L $kg^{-1}$ or greater. In general, the switchgrass biochars had lower

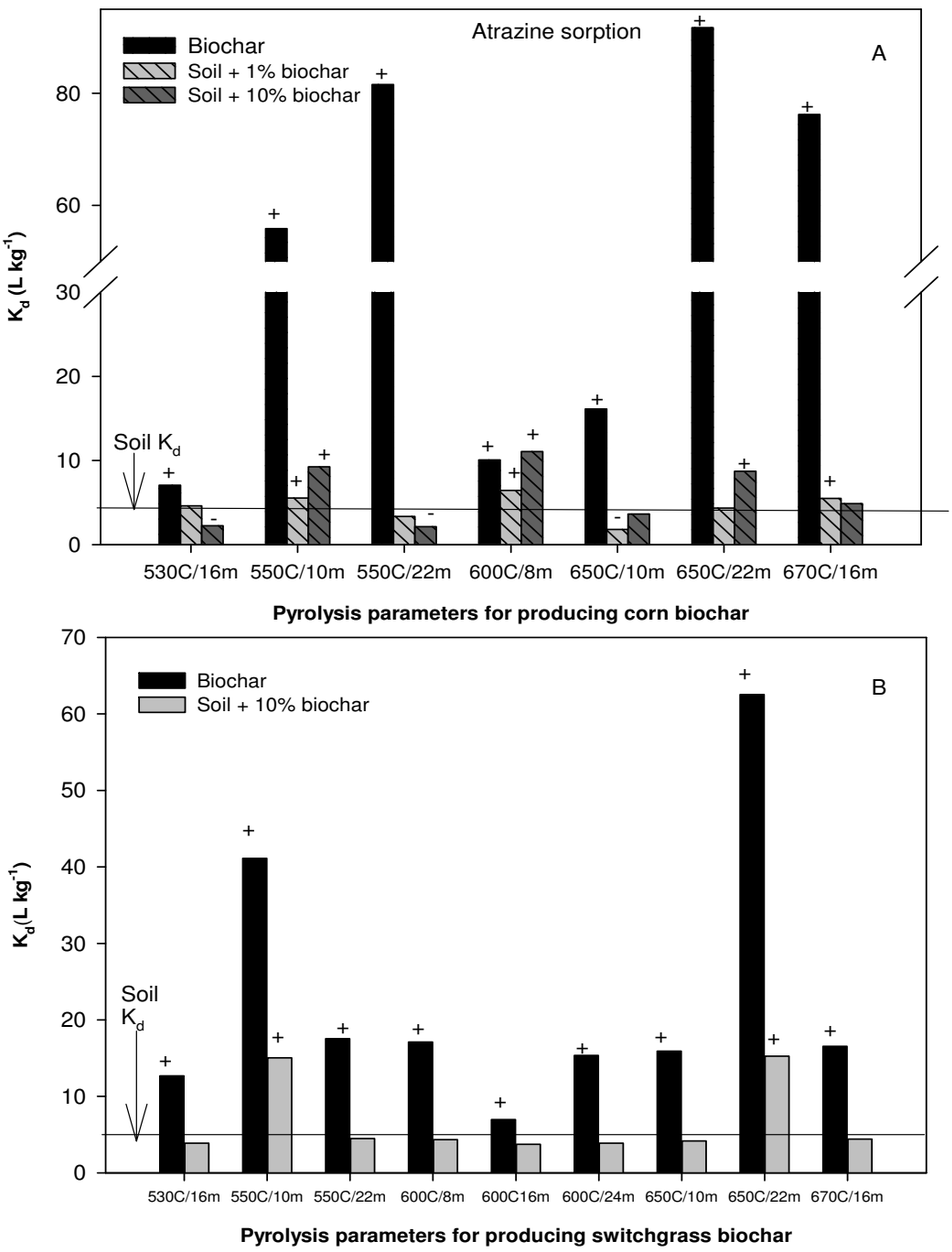


Fig. 3 A and B. Atrazine sorption ($K_d$) values to biochar from maize (*Zea mays*) stover (A) and switchgrass (*Panicum virgatum*) (B) produced by microwave pyrolysis at various processing times and temperatures. $K_d$ values of sorption for the A horizon of a Brandt silty clay loam (Fine-silty, fmixed, superactive, frigid Calcic Hapludoll, [Soil Survey Staff, 2011]) soil when amended with 1 or 10% maize biochar or 1% switchgrass biochar. $K_d$ sorption value of atrazine to unamended soil averaged about 3.86 L kg$^{-1}$. A "–" sign indicates lower sorption at $P \leq 0.05$ and a "+" sign indicates greater sorption at $P \leq 0.05$ than unamended soil.

$K_d$ values for atrazine than maize, with only two of the nine samples having sorption values >18 L $kg^{-1}$. Correlation analysis was conducted to examine pH of biochar vs $K_d$ but these parameters were poorly to moderately correlated for maize (r = 0.4) and not correlated for switchgrass.

Amending soil with maize biochar at 1% increased the $K_d$ with three biochars and decreased the $K_d$ for one biochar. The maximum increase was 66% more sorbed than unamended soil. The 10% additions decreased the amount sorbed by soil in two samples by about 43%. This was surprising as one of the biochars alone had double the $K_d$ of soil ($K_d$ = 7 L $kg^{-1}$) and a pH of 4.5 and the other had very high sorption ($K_d$ = 82 L $kg^{-1}$) value and pH of 7.6. It is unclear what properties of this biochar would result in lower atrazine sorption. The soil amended with three maize biochars used at 10% amendment had nearly 3 times as much atrazine sorbed ($K_d$s ranging from 8.7 to 11.0 L $kg^{-1}$) when compared with soil alone. Two switchgrass biochars with the highest atrazine sorption also increased atrazine sorption when added as a 10% soil amendment, and raised the $K_d$s nearly 4-fold, with a $K_d$ of about 15 L $kg^{-1}$. Other switchgrass biochars had no or only a slight influence on atrazine sorption.

### 2.2.4 2,4-D sorption to biochar and soils amended with biochar

Unlike atrazine which has a positive charge in most soils, 2,4-D with a pKa of 2.8 is a weak acid in most soil solutions (Wauchope et al., 1992). This chemical was chosen as a model compound to explore the effect of biochar on these types of compounds. The negative charge on the 2,4-D, as well as other chemicals in this auxin-type chemistry, often results in low or no sorption to soil (Clay et al., 1988). If these types of chemicals have a long residence time in soil (e.g. picloram), there is a high potential for leaching, although, because 2,4-D often is reported to have a ½ life of 10 d or less, leaching of this chemical is not usually considered a problem.

The $K_d$ sorption value of 2,4-D to unamended Brandt soil was about 1 L $kg^{-1,}$ a four-fold lower sorption than atrazine to this soil. All biochar samples had much greater sorption coefficients than soil alone (Figure 4), with switchgrass biochars generally sorbing more 2,4-D than maize biochars. The $K_d$ values for all biochars, regardless of feedstock type ranged from about 3 to >80 L $kg^{-1}$ and was much greater than soil. $K_d$ values for soil amended with 1% maize biochars were similar to $K_d$ of unamended soil (Figure 4). Amending soil with 10% biochar (either maize or switchgrass) resulted in a few treatment combinations that had increased sorption compared to soil. Maize biochar resulting from processing stover at 600°C for 8 min increased 2,4-D sorption 3.3 times over unamended soils, whereas maize biochar formed from processing at 650°C for 22 min increased 2,4-D sorption by 4.5 times. Switchgrass biochar added at 10% to soil had little impact on 2,4-D sorption with two exceptions. The first was the biochar formed when processed at 550°C for 10 min where a 9.4- fold sorption increase was measured and the second when switchgrass was processed at 650°C for 22 min where a 15-fold sorption increase was measured. These two switchgrass biochars also dramatically increased atrazine sorption. The char produced at the higher temperature did influence soil EC values at 10% addition (Table 1), however, it is not known what the exact properties of these biochars or their interactions with soil/solution resulted in these increased sorption amounts.

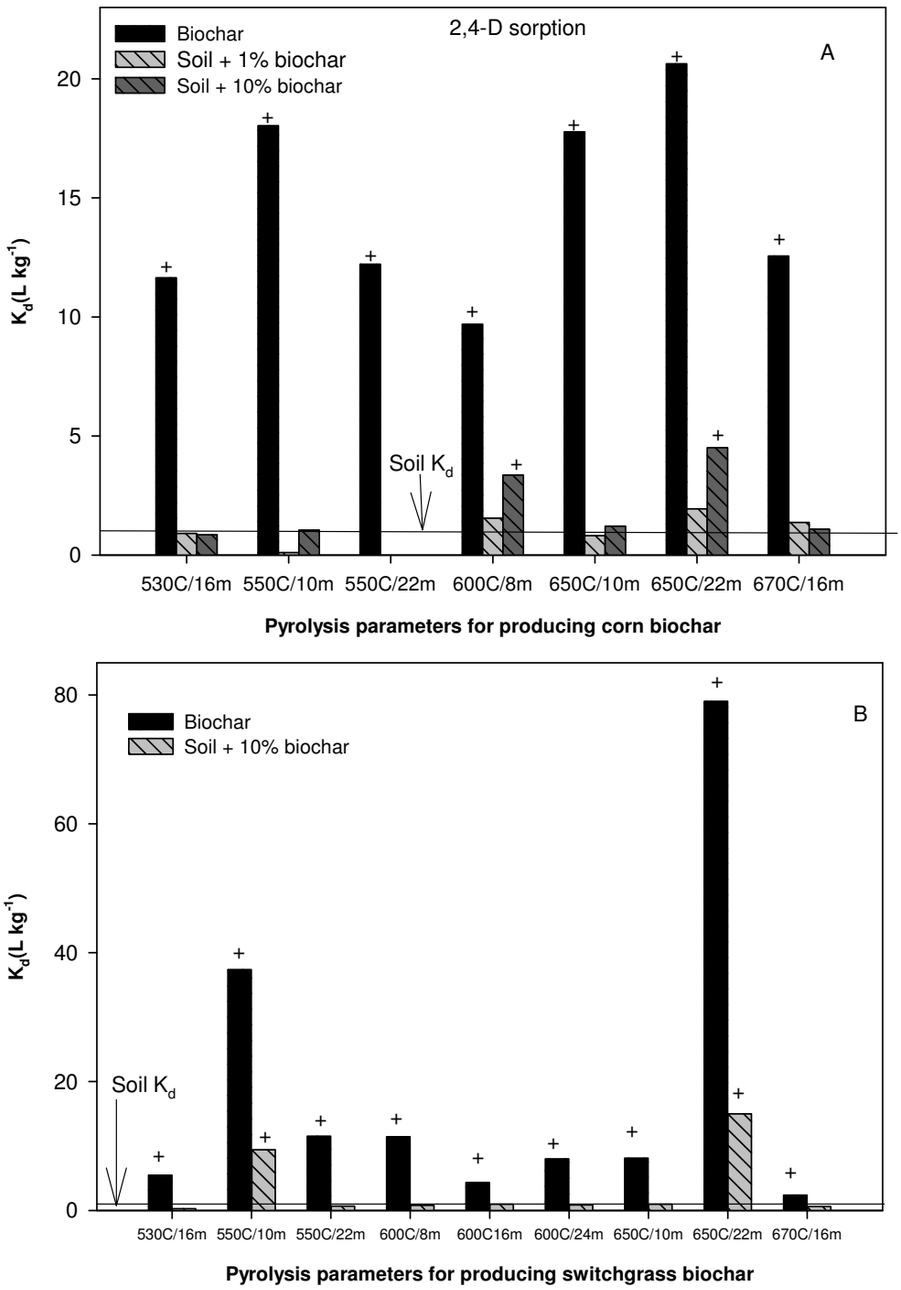


Fig. 4 A and B. 2,4-D sorption ($K_d$) values to biochar from maize (*Zea mays)*stover and switchgrass (*Panicum virgatum*) produced by microwave pyrolysis at various processing times and temperatures; $K_d$ values of sorption for the A horizon of a Brandt silty clay loam (Fine-silty, mixed, superactive, frigid Calcic Hapludoll, [Soil Survey Staff, 2011]) soil when amended with 1 or 10% maize biochar or 10% switchgrass biochar. $K_d$ sorption value of unamended soil averaged about 1.0 L kg$^{-1}$. A "+" sign indicates greater sorption at $P \leq 0.05$ than unamended soil.

## 3. Conclusion

Biochars, the by-products of pyrolitic conversion processes of vegetative biomass to gas, bio-oil, or other fuels, are proposed soil amendments for many diverse purposes. Biomass feedstocks and production processes vary depending on the desired end-products. This study measured the influence of several microwave pyrolitic conversion processes, which varied temperature and residence time, on pH and EC characteristics of the resulting biochars produced from maize stover and switchgrass. These biochars were used to amend a silty clay loam soil and examined the solution pH, EC, and sorption properties of a weakly cationic herbicide, atrazine, and an anionic herbicide, 2,4-D.

The microwave pyrolysis parameters of processing time and temperature of maize stover and switchgrass produced biochars that had a range of characteristics, with enough variation that they should not be thought of as a single entity with uniform properties. Short processing times (<10 min) of either feedstock at high (650$^{o}$C) or low (550$^{o}$C) temperature resulted in biochar with a pH < 4.5. Biochars produced with processing times >15 min at high temperature resulted in materials with pHs >8. Processing at intermediate temperatures and times resulted in char pHs ranging from 5.6 to 6.5. Adding 1% char to soil did not impact soil pH (6.4) whereas adding 10% biochar decreased soil pH a maximum of 12% when low pH biochars were used or increased soil pH up to 7% when high pH biochars were applied. "Native" soil EC was 1.63 mS/cm. Soils amended with 1% or 10% biochar ranged from -20% lower up to 39% higher EC values depending on biochar type and amount added. The biochars used in this study would be considered 'fresh', and not aged or post-process treated. Aging biochar or treating with steam or oxygen has been reported to dramatically change pH and other properties. Studies on these materials would need to be conducted to determine if results are similar to those reported for this study.

In a 2010 literature review, Kookana (2010) stated that there were limited published studies on the effect of biochars on pesticide efficacy and fate in soil, although in the few studies where sorption is reported, the sorption coefficients could be as high as >2000 times those of soil. Results from our study confirmed that when biochars were used as a single sorption material very high sorption amounts could be observed for both a cationic and an anionic compound. Herbicide sorption $K_d$ to all biochars alone was very high compared with soil but varied among biochar types. Soil amended with 1% maize stover biochar had herbicide sorption values similar to unamended soil. However, adding 10% biochar amendment increased both atrazine and 2,4-D sorption coefficients by many-fold. A neutral herbicide, alachlor, has also been shown to have increased sorption in soils amended with woodchip biochar addition (Spokas et al., 2009). If biochars are applied to production fields, biochars may reduce atrazine preemergence weed control due to decreased availability to emerging seedlings. Kookana (2010) also discussed the possibility of longer residence time of pesticides due to reduced bioavailability, which may influence further the impact of a pesticide on ecotoxicology and potential accumulation. Indeed, Jones et al. (2011) reported biochar addition suppressed simazine biodegradation due to limiting availability to soil microbes through increased sorption, although leaching potential was reduced simultaneously.

The results of this study along with other reports have implications on best use of biochar in agricultural fields. If biochar has no or little effect on pesticide sorption, efficacy, or EC values, then the material may be suitable for general application in agricultural fields and

highly desirable if it can be used to increase water holding capacity or as a nutrient source. Biochars, if high in sorption capacity, may be applied strategically and could accomplish important roles in ecosystem health and environmental quality. Biochar, added in filter strips and waterways, eroded landscapes, or other areas where increased sorption is desired, may aid in cleaning water running off fields by sorbing undesirable contaminants. Increased sorption may also slow or stop herbicides from leaching, so highly sorbent biochar types may be desired over shallow aquifers or in areas low in native organic matter (Wang et al., 2010). Herbicide bioavailability in some cases may be reduced, protecting sensitive plants.

Conversely, the effect of spreading biochars across entire fields may have negative results and be undesirable. One consequence may be that the materials increase soil EC values to saline levels. In addition, if the biochar reduces the efficacy of soil-applied herbicides or other pesticides this may have negative impacts. Reduced pesticide efficacy would require higher herbicide application rates to be as effective as lower rates. This would have monetary implications for growers and field managers by increasing management costs. Increased sorption, in some cases, also may increase the recalcitrance of pesticides leading to longer residence times in the environment. The occurrence of greater recalcitrance may be desirable if bioactivity was still acceptable and longer activity of the pesticide was desired to control the pest of interest. However, longer residence time may lead to other long-term environmental problems, such as greater leaching potential or carry-over problems into the following season.

Prior to any regular field applications of any biochar, the biochar properties must be examined to determine the suitability of the material for the long-term management of a particular site. The reasons for the application should be defined clearly and the outcomes closely monitored to determine if expectations and results are synonymous.

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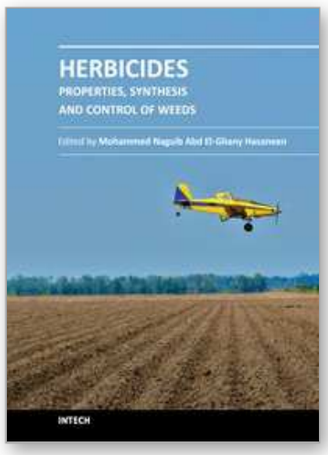


**Herbicides - Properties, Synthesis and Control of Weeds**
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This book is divided into two sections namely: synthesis and properties of herbicides and herbicidal control of weeds. Chapters 1 to 11 deal with the study of different synthetic pathways of certain herbicides and the physical and chemical properties of other synthesized herbicides. The other 14 chapters (12-25) discussed the different methods by which each herbicide controls specific weed population. The overall purpose of the book, is to show properties and characterization of herbicides, the physical and chemical properties of selected types of herbicides, and the influence of certain herbicides on soil physical and chemical properties on microflora. In addition, an evaluation of the degree of contamination of either soils and/or crops by herbicides is discussed alongside an investigation into the performance and photochemistry of herbicides and the fate of excess herbicides in soils and field crops.



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