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Evaluating Agricultural Management Effects on Alachlor Availability: Tillage, Green Manure, and Biochar

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Abstract: Agricultural and soil management practices have been reported to affect alachlor sorption–desorption and degradation rates. Though alachlor has been banned in the E.U. since 2006, it is still used in U.S. corn and soybean production. The objectives of this study were to: (a) assess differences in alachlor sorption due to tillage treatments (chisel plow and ridge tillage) on soils from three midwestern U.S. locations; and (b) determine the effect of various soil amendments on the sorption–desorption and mineralization of alachlor. Soils were amended at a rate of 10% (*w/w*) with biochars derived from soybean stover, sugarcane bagasse, and wood chips, as well as the uncharred feedstock materials. Sorption–desorption studies were performed using the batch equilibration method, and alachlor mineralization was evaluated in a 30-day incubation. Tillage management did not affect alachlor sorption to soil across the three sites, despite the fact that the tillage operations were imposed for 4 years ($p > 0.05$). While the sorption coefficient (K_d) values for alachlor were relatively low in the three unamended soils ($K_d = 1.76, 1.73, \text{ and } 1.15 \text{ L}\cdot\text{kg}^{-1}$ for IL, MN, and PA soils, respectively), biochar amendments increased alachlor sorption between $4\times$ and $33\times$ compared to the unamended soil. The amendments also affected alachlor mineralization such that degradation was slower in both biochar- and raw feedstock-amended soils. Based on these results, biochar additions are expected to affect the availability of alachlor for transport and degradation. Furthermore, this study highlights the larger impact of biochar addition than tillage practices on altering immediate alachlor sorption capacities.

Keywords: black carbon; herbicide; tillage; management practices

1. Introduction

Agricultural management practices are continually evolving to optimize crop yields and improve soil quality. Over the past few decades, there has been a shift toward conservation tillage and a growing interest in the application of soil amendments (e.g., compost, biochar). Such changes in management alter the soil environment, which in turn may influence the efficacy, leaching risk, and persistence of herbicides in agricultural soils [1–5].

Alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) is a chloroacetanilide herbicide used to control annual grasses and broad-leaved weeds, primarily in corn and soybeans. Alachlor can be applied to soil alone or as a mixture (e.g., with atrazine) for pre-emergent weed control at rates up to 4 lb ai/acre [6]. Degradation of this herbicide in soils occurs predominantly through

microbial processes, with a half-life ($t_{1/2}$) of 23–66 days [7–9]. Alachlor has a high solubility ($242 \text{ mg}\cdot\text{L}^{-1}$ at $25 \text{ }^\circ\text{C}$) and sorption on soils is limited (average $K_d \sim 2.1 \text{ L}\cdot\text{kg}^{-1}$, $n = 20$ [10]), which favors its offsite transport. Alachlor has been banned in the E.U. since 2006 [11] due to its adverse human health effects (i.e., potential carcinogen) and widespread groundwater contamination (e.g., [12]); however, alachlor is still registered as a restricted-use herbicide in the U.S. [13]. While the quantity of applied alachlor has decreased over the past few decades, contamination from leaching and runoff remains an issue (e.g., [14]). To predict and mitigate alachlor contamination, it is necessary to understand which factors influence its sorption and bioavailability in soil, such as soil organic carbon (SOC) [15]. Therefore, it is critical to also understand how agricultural practices alter these factors to protect water quality and human health.

Conservation tillage practices, such as no-till or ridge-till, have been found to alter a host of soil physical and chemical properties. By definition, conservation tillage leaves at least 30% of plant residue cover on the soil surface [16], which can result in higher levels of soil organic carbon (SOC) and elevated soil moisture compared to conventional tillage systems. Cooler soil temperatures have also been reported in fields under no-till management (e.g., [1]), as well as decreases in soil pH following surface application of nitrogen fertilizers [17]. It is well-known that the aforementioned soil characteristics can influence herbicide sorption/desorption processes, and, in doing so, alter herbicide mobility and bioavailability in the environment [18]. For example, increased sorption of herbicides on surface soils with conservation tillage has often been attributed to SOC (e.g., [19]). However, plant residues left on the field with conservation tillage management may also impact herbicide fate by directly intercepting the applied chemicals before reaching the soil itself [20].

In addition, conservation tillage can influence herbicide fate and transport in the soil environment through its effects on herbicide degradation. For microbial degradation to occur, it is imperative that degrading organisms are present and the herbicide is bioavailable (i.e., not adsorbed). While the increased SOC and moisture associated with conservation tillage favor increased microbial activity, cooler temperatures and lower pH typically reduce activity. Despite the contrasting effects of these changes on microbial activity, Doran [21] reported greater activity with conservation tillage, which may favor a more rapid transformation of microbe-degraded herbicides. Abiotic degradation (e.g., photolysis) and volatilization are also affected by temperature, moisture, and pH, all of which, as previously stated, can vary under different tillage management. Additional factors, including alterations in water flow patterns [22] and the depth of herbicide incorporation in soils, can further modify herbicide behavior in disparately managed systems.

The addition of soil amendments (e.g., compost, biochar) is another increasingly popular management practice that can affect herbicide sorption and degradation in soil. Akin to conservation tillage, the incorporation of amendments can indirectly influence herbicide fate through changes in soil properties and microbial activity. Amendments, like plant residues, can also sorb the herbicide directly, thereby limiting its mobility and bioavailability to degrading organisms. For example, Guo et al. [23] observed increased sorption of alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetanilide) with the addition of three carbon-rich wastes: municipal sewage, bovine manure, and waste-activated carbon. Biochar has likewise been found to increase herbicide sorption when added to soil as an amendment to sequester carbon and increase soil fertility [24]; however, the effects of biochar on herbicide fate in the field are not well-understood in relation to other management practices.

Previous studies have focused on the influence of individual management changes, as compared to conventional tillage, on herbicides in agricultural systems, but little work has been done comparing the effects these different strategies have. Both tillage [25,26] and soil amendments [23,27] have independently been found to affect alachlor behavior in agricultural soils. The aim of this study was to comparatively analyze the effects of multiple management strategies on alachlor fate in soil. Our objectives were to: (a) determine whether tillage management (ridge tillage versus chisel plow)

affects alachlor sorption on three midwestern U.S. soils; and (b) contrast the influence of biochar and unprocessed soil amendments on the sorption–desorption and mineralization of alachlor in soil.

2. Materials and Methods

2.1. Soil Characterization and Experimental Design

Three midwestern U.S. soils were selected for this study: silt loams from Minnesota (MN) (fine-silty, over sandy, mixed, mesic Typic Hapludoll) and Pennsylvania (PA) (fine, mixed, semiactive, mesic Typic Hapludalf), and a silty clay loam from Illinois (IL) (fine-silty, mixed, superactive, mesic Typic Endoaquoll). Soils from these locations are under corn and soybean production and represent typical midwestern soils to which alachlor is applied. At each location, the experiment was established as a randomized complete block design with four replicates (blocks). Within each block, there were four plots: two ridge tillage (RT) and two chisel plough (CP). Field plots were established in 2011 and initially planted with corn; crops were rotated between corn and soybeans annually.

Prior to 2011, all soils were managed under conventional tillage with corn–soybean rotations on the IL and MN soils and sorghum (*Sorghum bicolor* (L.) Moench) cultivation on the PA soil. Beginning in 2012, the tillage treatments were established and managed under the annual corn–soybean rotation. Thus, the RT plots are in an early stage of transition from conventional to reduced tillage. Permanent ridges were formed in RT, and in both rotations corn and soybean were planted at the center of the ridge tops. Crop residues were concentrated onto the soil surface of furrows during planting. RT ridges were re-ridged (furrow surface soil scraped back onto a ridge [28]) shortly after the corn six leaf stage (V6). In CP, corn and soybean were planted into level, cultivated soil, i.e., no ridges, and crop residues were ripped and incorporated into the soil during CP cultivation. In both tillage systems, weeds were sprayed with glyphosate three weeks prior to planting. Row/ridge widths varied by site, being 30 cm at IL, 25 cm at MN, and 30 cm at PA. Management varied at each site in accordance with local best management practices, as outlined in Williams et al. [29].

From each plot, soil samples were collected from the upper 10 cm of ridges and furrows in the RT soils and from the upper 10 cm of the CP plots. Five soil cores were taken from each plot, and mixed to give a homogenous sample. Soils were air-dried and passed through a 2-mm sieve; visible roots and plant matter were removed by hand. Selected soil properties are listed in Table 1. Analysis of soil texture and chemical composition was performed by a commercial laboratory (Waypoint Analytical, Memphis, TN, USA) using standard reference methods.

Table 1. Physical and chemical properties of Minnesota (MN), Pennsylvania (PA), and Illinois (IL) soils under ridge till (RT) and chisel plow (CP) management.

Location	Tillage	Position	Organic Matter (%)	Cation Exchange Capacity (meq·g ⁻¹)	pH	P (mg·kg ⁻¹)	K (mg·kg ⁻¹)	Ca (mg·kg ⁻¹)	Mg (mg·kg ⁻¹)	Texture		
										Sand (%)	Silt (%)	Clay (%)
MN	RT	Ridge	4.47 (0.38)	14.87 (0.51)	6.27 (0.53)	26.33 (6.22)	129.33 (34.2)	1865.83 (184.51)	409 (46.52)	28	56	16
	RT	Furrow	4.28 (0.35)	15.1 (0.77)	6.25 (0.6)	25.5 (7.37)	115.67 (42.34)	1921.00 (253.82)	400 (59.77)			
	CP		4.4 (0.68)	14.65 (0.85)	6.15 (0.28)	26.67 (6.74)	134.00 (26)	1810.83 (169.67)	398 (53.24)			
PA	RT	Ridge	3.2 (0.17)	7.73 (1.8)	6.13 (0.25)	26.33 (4.16)	72 (21.7)	1148.33 (270.3)	84.33 (11.68)	10	35	25
	RT	Furrow	3 (0.2)	8.27 (1.27)	6.13 (0.06)	21.33 (1.53)	63.33 (19.76)	1232.33 (207.1)	92.67 (16.8)			
	CP		3.2 (0.26)	7.67 (1.42)	6.03 (0.15)	27 (7.81)	90.33 (57.83)	1121 (231.14)	81.33 (9.5)			
IL	RT	Ridge	4.9 (0.61)	16.62 (3.51)	5.77 (0.24)	26.5 (12.99)	201.5 (66.36)	2389.67 (552.08)	428.83 (112.23)	17	56	27
	RT	Furrow	4.9 (0.61)	16.62 (3.51)	5.77 (0.24)	26.5 (12.99)	201.5 (66.36)	2389.67 (552.08)	428.83 (112.23)			
	CP		4.77 (0.47)	15.92 (2.93)	5.95 (0.4)	19.83 (6.31)	176.67 (19.54)	2412.17 (415.04)	423.83 (80.26)			

Soil properties listed are for the 1–10 cm depth interval. Values are the average of 12 replicates and standard deviations appear within the parentheses.

2.2. Chemical

Alachlor solutions were prepared in 0.01 M CaCl₂ using radiolabeled (UL-ring-¹⁴C) alachlor (1 GBq mmol⁻¹; 97% purity) (Pathfinder Laboratories, St. Louis, MO, USA). A 1.2 mg·L⁻¹ alachlor spiking solution was made with a radioactivity level of ~4.5 kBq·mL⁻¹, and was then used in both sorption and mineralization experiments.

2.3. Soil Amendments

Three biochars were prepared from soybean stover (SS), sugarcane bagasse (SB), and wood chips (W) by heating at 500 °C, 350 °C, and 500 °C, respectively, in a Lindberg box programmable furnace equipped with an airtight retort (model 5116HR; Lindberg, Watertown, WI, USA) pyrolysis system (2 h residence time) (Table 2). The selection of soybean stover as a feedstock was based on previous reports of high sorption by soybean-derived biochar [30] and its availability in regions where alachlor is used. While sugarcane bagasse is not readily available in the midwestern U.S., its total biomass production is 4× higher than other row crops; therefore, the sheer volume of sugarcane residue merits its investigation as a feedstock. Moreover, alachlor is a commonly used herbicide in sugarcane production [31]. Grape wood chips were chosen to represent woody biomass feedstock sources for comparative purposes.

Both the biochar and the uncharred “raw” feedstock were evaluated as amendments. The addition of unprocessed plant residues is to assess whether there is an additional effect gained by charring the original feedstock. All feedstock materials were ground using a hammer mill such that >60% of the material was <2 mm in size; biochars were prepared from the ground feedstocks. Biochars and air-dried feedstocks were stored in sealed plastic bags at room temperature until use in this experiment (<3 years). Amendments were added to soil at a rate of 10% (*w/w*). Despite being an impractical field application rate, this rate was used to elucidate the impact of biochar and the un-charred biomass on sorption behavior.

Table 2. Proximate and ultimate analyses of the soil amendments used.

Amendment	C ^a (%)	H ^a (%)	N ^a (%)	O ^a (%)	S ^a (%)	Ash ^a (%)	VM ^{bc} (%)	Fixed C ^c (%)	Moisture ^c (%)	pH	Molar Ratios		
											H:C	O:C	C:N
<i>Soybean</i>													
Raw feedstock	44.7	6.4	0.8	42.0	0.1	6.0	20.0	68.0	6.0	7.3	1.72	0.70	65
Biochar (500 °C)	48.0	2.1	1.3	11.1	0.0	37.5	17.0	41.7	3.8	8.7	0.53	0.17	43
<i>Sugarcane Bagasse</i>													
Raw feedstock	48.6	5.9	0.2	39.8	0.0	5.5	80.0	8.3	6.2	4.7	1.46	0.61	284
Biochar (350 °C)	75.2	4.6	0.6	15.8	0.1	3.8	46.5	47.0	2.7	5.0	0.73	0.16	146
<i>Wood chips (grape)</i>													
Raw feedstock	41.6	4.9	1.2	43.5	0.2	8.7	63.1	21.2	7.0	5.8	1.42	0.78	41
Biochar (500 °C)	70.4	2.3	0.9	9.6	0.0	16.8	19.3	64.0	4.0	7.4	0.40	0.10	88

^a Percentages are on a moisture free basis (dried at 105°C); ^b Volatile matter; ^c Percentages are on an air-dried basis.

2.4. Sorption–Desorption

2.4.1. Alachlor Sorption on Ridge Till Versus Chisel Plow Soils

Sorption experiments were performed according to Organization for Economic Co-operation and Development (OECD) guidelines [32]. A completely randomized batch experiment with a $2 \times 2 \times 3 \times 4$ factorial design, with factors of tillage (RT, CP), sampling position (ridge/row, furrow/inter-row), and location (MN, PA, IL), by four field-replicated blocks. Each sorption experiment in the experiment was run in duplicate. Soils (0.5 g) were combined with 9.5 mL 0.01 M CaCl_2 in 50 mL polypropylene centrifuge tubes and spiked with 0.5 mL ^{14}C -alachlor to give an initial solution concentration of $0.060 \text{ mg}\cdot\text{L}^{-1}$ ($225 \text{ Bq}\cdot\text{mL}^{-1}$). After shaking for 5 d, samples were centrifuged (15 min at $1280 \times g$) and 1 mL of the supernatant solution was transferred to a scintillation vial containing 5 mL of scintillation cocktail (EcoLite(+)TM; MP Biomedicals, LLC, Solon, OH, USA). Samples were then vortexed and analyzed for ^{14}C by liquid scintillation counting (LSC) (AccuFLEX LSC-8000; Hitachi, Tokyo, Japan).

Sorption coefficients (K_d , $\text{L}\cdot\text{kg}^{-1}$) were calculated as follows:

$$K_d = C_s / C_e, \quad (1)$$

where C_e is the solution alachlor concentration after equilibration ($\text{mg}\cdot\text{L}^{-1}$), and C_s is the amount of alachlor sorbed ($\text{mg}\cdot\text{kg}^{-1}$). The concentration of alachlor sorbed is inferred from the change in solution concentration:

$$C_s = (C_i - C_e) \times (V/M), \quad (2)$$

where C_i is the initial solution concentration, V is the volume of solution added, and M is the mass of the sorbent. The sorption coefficients normalized to the organic carbon content of the soil (%OC) were calculated by the following (K_{oc} , $\text{L}\cdot\text{kg}^{-1}$):

$$K_{oc} = (K_d / (\%OC)) \times 100. \quad (3)$$

2.4.2. Alachlor Sorption/Desorption on Amended Soil

Alachlor sorption on amended soils was evaluated by the batch equilibration method described above. While this method may not be representative of true field conditions, it was selected in an attempt to normalize treatments. A randomized $4 \times 2 \times 3 \times 2$ factorial design was used with factors of feedstock type (four levels: none, SS, SC, W), addition type (two levels: biochar, raw), soil (three levels: MN, PA, IL) and two replicates. Again, 5.0 g of RT (furrow) soils from MN, IL, and PA were weighed into centrifuge tubes and mixed with 0.5 g of amendment (if used) (two replicates). Subsequently, 9.5 mL 0.01 M CaCl_2 and 0.5 mL ^{14}C -alachlor spiking solution were added to each sample tube to give an initial solution concentration of $0.060 \text{ mg}\cdot\text{L}^{-1}$ ($225 \text{ Bq}\cdot\text{mL}^{-1}$); solutions were added immediately after amendments with no incubation period. Samples were shaken for 24 h, centrifuged (15 min at $1280 \times g$), and 1 mL aliquots of supernatant solutions were removed and analyzed by LSC as detailed above to quantify alachlor sorption.

Alachlor desorption from the control and amended soils was evaluated immediately following sorption analysis using the dilution method [33]. An additional 9.5 mL 0.01 M CaCl_2 were added to sample tubes (total volume = 18.5 mL) and samples were again shaken for 24 h, centrifuged, and supernatants were analyzed by LSC. Desorption K_d values were calculated as the ratio of sorbed versus solution alachlor concentrations (Equation (1)).

2.5. Mineralization

Alachlor mineralization experiments were conducted with a single soil (PA, CP-F) using a completely randomized $3 \times 3 \times 2$ factorial design, with feedstock (three levels: SS, SC, W) and amendment type (none, biochar, raw) as the factors analyzed with two replicates. Each experimental

unit consisted of a 250 mL biometer culture flask equipped with a side tube, in which a vial containing 10 mL of 2.5 M NaOH was placed to trap carbon dioxide (CO₂). Prior to the addition of alachlor, soils (5 g) with and without amendments (0.5 g) were placed in flasks, 1 mL of water was added to the soil, and the samples were incubated for 4 d at 25 °C to stimulate microbial activity. Then, ¹⁴C-alachlor solution was added dropwise using a microliter syringe at a rate of 0.13 mg·kg⁻¹ to the soil and vials of NaOH were positioned in the flasks. Soil samples were incubated at 25 °C for a period of 30 days. Vials with NaOH were removed and replaced at each sampling time (7, 14, 21, and 30 days) and flasks were simultaneously aerated. To determine the amount of evolved ¹⁴CO₂, a 1-mL aliquot of NaOH solution was mixed with 5 mL of scintillation cocktail and samples were left in the dark for 24 h prior to counting via LSC. This method of evaluating herbicide mineralization is consistent with ASTM methodology (STP 865) and has been successfully utilized in previous studies (e.g., [7]).

The ¹⁴C-alachlor mineralization (i.e., ¹⁴CO₂ evolution) mean data were fit to a first-order kinetic model:

$$C_t = C_0 (1 - e^{-kt}), \quad (4)$$

where C_0 is ¹⁴CO₂ concentration at time zero; C_t is concentration of ¹⁴CO₂ at time t ; k is a mineralization rate constant (days⁻¹); and t is the incubation time (days). Alachlor degradation rates were not evaluated in this study because LSC analysis alone cannot quantify distinct metabolites; however, mineralization rates nevertheless provide valuable information regarding the persistence of herbicides in the environment.

2.6. Statistical Analysis

Alachlor sorption–desorption coefficients (K_d) and mineralization (total CO₂ production and rate constant) data were subjected to analysis of variance (ANOVA). When treatments were significantly different between the treatments, averages were compared by Tukey's honest significant difference (HSD) test ($p < 0.05$). Statistical analysis was performed in R (version 3.3.2) [34]. Figures were plotted using Sigma Plot® (Version 13.0 for Windows, 2014, Systat Software Inc., Point Richmond, CA, USA).

3. Results and Discussion

3.1. Alachlor Sorption in Tillage Systems

Despite the fact that the tillage management had a 4-year history at these sites [35], there was no significant difference in the sorption of alachlor due to the tillage managements (RT versus CP) (Figure 1). The average (\pm standard error (SE)) sorption coefficients (K_d) were 8.8 (± 0.2), 8.7 (± 0.2), and 5.8 (± 0.1) L·kg⁻¹ for the IL, MN, and PA soils, respectively. The significantly lower sorption in the PA soils can, in part, be attributed to its lower SOC content (Table 1). There were no significant differences in the SOC content of the soils as a consequence of the tillage management (Table 1). Thereby, the lack of significant differences in alachlor sorption as a function of tillage is not surprising. Normalizing K_d values for the SOC of each soil resulted in similar K_{oc} values across the sites: 180 L·kg⁻¹ for PA and IL soils and 200 L·kg⁻¹ for the MN soil. As expected, the K_{oc} values are similar across the sites (≈ 200 L·kg⁻¹).

Ridge tillage can affect the spatial distribution of SOC. Shi et al. [36] found that ridge tillage produced low SOC in the inter-rows, high SOC in the crests, and medium SOC in the shoulders relative to moldboard plow and no-till. However, there was no statistically significant difference for alachlor sorption between the sampling positions (ridge versus furrow (RT); row versus furrow (CP)) from the three sites (MN, IL, and PA) in the present study ($p > 0.05$; Tukey's test) (Figure 1). Furthermore, there was no significant variability noted between sites (MN, IL, and PA) in the K_{oc} values, suggesting similar sorption mechanisms (i.e., SOC dependency) across all locations.

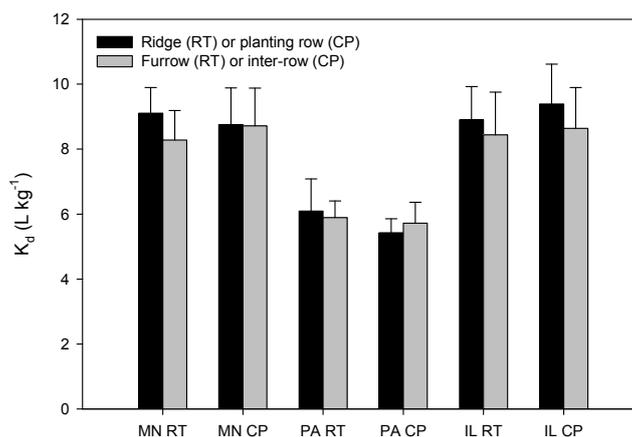


Figure 1. Alachlor sorption on MN, PA, and IL soils under ridge-till (RT) and chisel-plow (CP) tillage management systems. RT data are separated into ridge and furrow sampling positions, while CP data are separated into planting row and inter-row soils. K_d values shown are the replicate means (MN, PA: $n = 8$; IL: $n = 16$); error bars represent standard deviation.

Previous studies comparing alachlor sorption and leaching under varying tillage practices have reported mixed effects. Locke et al. [26] found that alachlor sorption was greater and more rapid on soil from no-till plots than conventionally tilled soil, which the authors attributed to an increase in SOC with no-till. Likewise, Clay et al. [19] reported the greatest alachlor adsorption in the top 5 cm of a no-till soil, where soil SOC was highest. In a study of alachlor runoff from conventional and conservation tillage fields, the total herbicide transport with runoff was reduced, but this was due to a reduction in runoff volume rather than a reduced herbicide concentration [37]. Results from these and other [38] runoff studies suggest no change in herbicide immobilization via sorption with varying tillage systems, which is consistent with our findings. Furthermore, studies reporting positive effects of conservation tillage on alachlor sorption often compare extremes, i.e., conventional tillage versus no-till, which leaves 90–100% of residues on the field. Comparisons of intermediate conservation tillage strategies, such as ridge-till (studied here), are less common. The results from this work suggest alachlor sorption will not be affected within the first 4 years following alteration of tillage practice; however, further studies of indirect effects, such as changing water dynamics, are needed to fully evaluate alachlor dissipation in the field.

3.2. Alachlor Sorption/Desorption in Amended Soils

The effects of raw feedstock and biochar amendments on alachlor sorption are shown in Figure 2 for the MN (a), IL (b), and PA (c) soils. Raw feedstock amendments showed a slight, albeit insignificant, increase in alachlor sorption, but did not vary among the raw soybean stover, sugarcane bagasse, and wood chips. Biochar amendments consistently sorbed more alachlor than their raw feedstock counterparts, and the sorption differed among the biochar materials. The greatest increase in alachlor sorption across the three soils resulted from the wood chips biochar addition, with K_d values increasing on average from $1.4 L \cdot kg^{-1}$ in unamended soil to $32 L \cdot kg^{-1}$. The K_{oc} values of the amended samples were calculated based on the assumption that the amended soil OC value equals the sum of the unamended soil OC and the C content of the amendment. The K_{oc} values of the raw feedstock additions range from 40 to $63 L \cdot kg^{-1}$, with an average value of $55 L \cdot kg^{-1}$, which is very similar to the value for SOC across the three soil types ($34 L \cdot kg^{-1}$). However, the calculated average K_{oc} values of the three biochar-amended soils were greater than the unamended soils: soybean residue ($150 L \cdot kg^{-1}$), sugarcane bagasse ($112 L \cdot kg^{-1}$), and wood chips ($314 L \cdot kg^{-1}$).

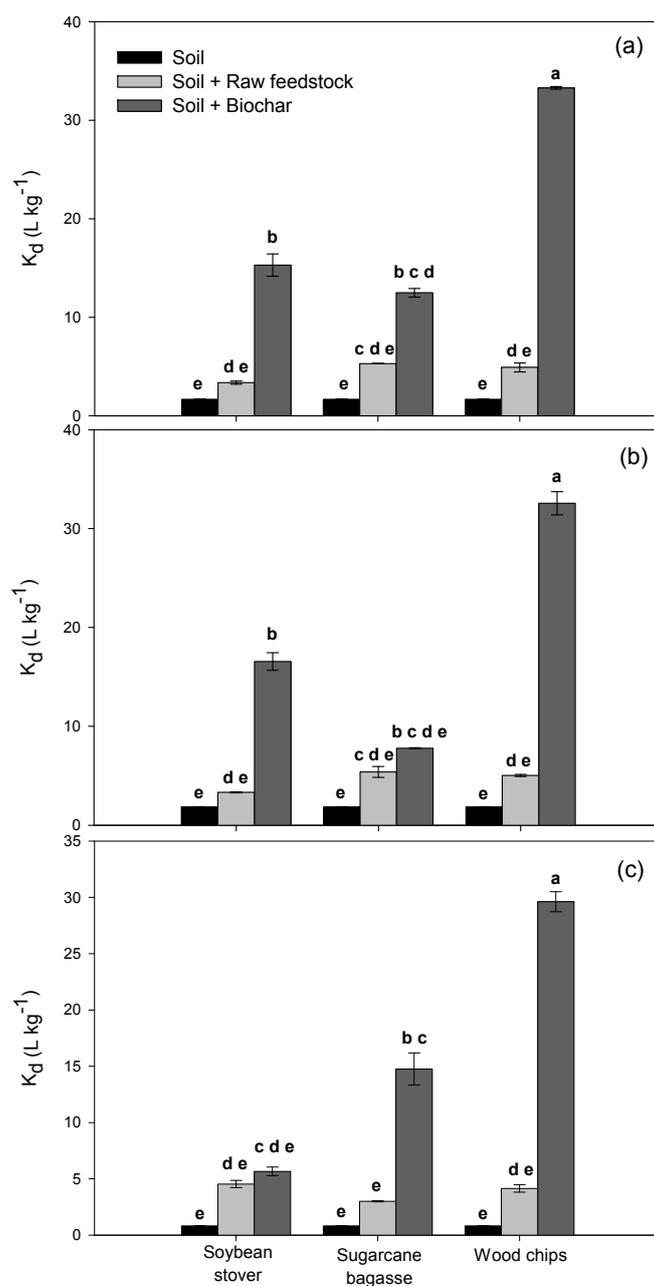


Figure 2. Alachlor sorption on (a) MN, (b) IL, and (c) PA soils with raw feedstock and biochar amendments (10% *w/w*). Different letters indicate significant differences in K_d values based on Tukey HSD comparisons.

The different sorption capacities of the three biochar amendments may be due to multiple differences in their properties. Previous studies have found that the fraction of C influences the sorption capacity of biochar for organic compounds [39]. However, normalizing by C (i.e., K_{oc}) did not reduce the variability among the feedstock materials in the present work. The K_{oc} variability may signify the importance of other biochar components (e.g., ash), physical structure, or chemical properties (e.g., pH) for alachlor sorption. Alternatively, it could indicate differences among the C fractions of the biochars and the accessibility of binding sites as a function of feedstock type. For example, the lower H:C and O:C ratios of the wood biochar suggest a greater fraction of aromatic C, which increases the likelihood of π - π orbital overlap as a binding mechanism [40]. The increased degree

of aromaticity can also explain the greater sorption capacity of the biochars than the raw feedstocks. However, the exact causes of the sorption differences were not fully elucidated in this experiment.

Comparisons of plant residues versus charred materials on alachlor sorption in soils can be inferred from studies of sugarcane straw management. Traditionally, straw residue has been managed through in-field burning; however, in recent years, it has become common practice to leave unburnt residues on the field (green harvest). Alachlor sorption on highly weathered tropical soils under these two systems was studied by Giori et al. [31,41]. In one study, the authors found that sorption was greater in soils collected from sugarcane fields managed without burning, correlating with higher SOC contents [41]. In contrast, when soils under no-burn systems were amended with straw and straw ash, the straw alone had no effect on sorption, while the ash increased alachlor sorption by up to 4 times ($K_{d,app} = 1.2$ versus $5.4 \text{ L}\cdot\text{kg}^{-1}$) [31]. Our results are consistent with the latter study, where the charred material has a larger initial impact on sorption than unprocessed biomass.

Desorption of alachlor was hysteretic for unamended soils; that is, once sorbed, the alachlor did not readily desorb, resulting in a higher K_d for desorption than for sorption (Table 3). Desorption hysteresis for alachlor from raw feedstock-amended soils was similar to that from the unamended soil. This was expected, as alachlor sorption for unamended and raw feedstock-amended soils was not significantly different (Figure 2). Desorption hysteresis for biochar-amended soils was also similar to unamended soils; this result, however, was surprising in view of the significant increase in sorption of biochar-amended soils. The hysteretic behavior of alachlor on biochar-amended soils suggests that while greater quantities of alachlor are retained in amended soils, the herbicide is not more tightly bound to biochar than SOC; this may indicate a similar binding mechanism. Based on the collective desorption data, it appears that, regardless of whether alachlor is applied to unamended or amended soils, the use of sorption K_d values would over predict movement in field soils.

Table 3. Alachlor desorption properties on control and amended soils expressed as a ratio of the K_d of desorption to the K_d of adsorption.

Feedstock	Amendment	$K_d \text{ desorption}/K_d \text{ adsorption}$		
		MN	IL	PA
	Control	1.7 ± 0.0	1.8 ± 0.0	2.5 ± 0.0
Soybean stover	Raw feedstock	1.7 ± 0.1	1.7 ± 0.0	1.2 ± 0.1
	Biochar	2.0 ± 0.1	2.1 ± 0.1	5.8 ± 0.8
Sugarcane bagasse	Raw feedstock	1.5 ± 0.0	1.5 ± 0.2	2.2 ± 0.0
	Biochar	1.3 ± 0.1	2.1 ± 0.0	1.0 ± 0.0
Wood chips	Raw feedstock	1.6 ± 0.1	1.6 ± 0.1	1.6 ± 0.1
	Biochar	1.9 ± 0.1	1.8 ± 0.0	1.7 ± 0.0

It is noteworthy that the addition of biochar to soils had a greater impact on the sorption of alachlor than the alteration in tillage management (RT versus CP) or the addition of raw biomass. Furthermore, the K_{oc} values of the biochar-amended soils demonstrate a difference in the normalized sorption capacities of biochar compared to SOC, which suggests potentially different interactions or variance in the number of binding sites per g of material.

3.3. Alachlor Mineralization in Amended Soils

Table 4 shows cumulative $^{14}\text{CO}_2$ evolution from ^{14}C -alachlor mineralization to equal approximately 10% of the applied alachlor in the control soil over the 30 d incubation period. This amount was similar to those reported in a study by Locke et al. [25], where cumulative mineralization accounted for only 7% (CT) or 13% (NT) of applied alachlor during a 54 day incubation. These amounts were higher than alachlor mineralization rates reported by others: 2% after 32 days [42], and <1.7% [7]. It is important to note that the low alachlor mineralization rates do not reflect

the degradation rates, which are much faster; degradation half-lives in fields under no-tillage and conventional tillage ranged from 7 to 38 days [7–9,25]. Alachlor can be transformed by the loss of side chains from the molecule, which accounts for the faster degradation rates. For instance, biodegradation by *Candida xestobii* decreased the initial alachlor concentration by 70% in 3 days [43], and a mixed microbial consortia decreased the concentration by 63% after 21 days of incubation [44]. However, it is much more difficult to break the ring, and very few micro-organisms have been identified that are able to mineralize the alachlor ring [45,46]. As a result, alachlor metabolites (ethanesulfonic acid (ESA) and oxanilic acid (OXA)) have been detected in water-monitoring studies and can accumulate due to the delayed mineralization step [14]. Although the metabolites of alachlor are considered less biologically reactive than the parent chemical [47], mineralization rates offer a conservative estimate of the fate of applied alachlor.

Table 4. Total $^{14}\text{CO}_2$ released throughout the 30 days incubation period expressed as a % of the initial ^{14}C -alachlor added to soils and first order kinetics of $^{14}\text{CO}_2$ evolution throughout the incubation period (fit using mean values for each time point).

Feedstock	Amendment	Total $^{14}\text{CO}_2$ (%) ¹	k (days ⁻¹) ²	R^2
	Control	10.4 ± 2.4 ^a	0.040 ± 0.017	0.981
Soybean residue	Raw feedstock	7.0 ± 0.5 ^{ab}	0.042 ± 0.014	0.986
	Biochar	4.6 ± 0.4 ^b	0.046 ± 0.013	0.989
Sugarcane bagasse	Raw feedstock	4.0 ± 0.6 ^b	0.045 ± 0.008	0.995
	Biochar	3.4 ± 0.5 ^b	0.042 ± 0.010	0.993
Wood chips	Raw feedstock	4.2 ± 0.3 ^b	0.055 ± 0.007	0.997
	Biochar	3.8 ± 1.6 ^b	0.017 ± 0.021	0.963

¹ mean ± standard deviation ($n = 2$); ² mean ± standard error. Different letters indicate significant differences between means (Tukey HSD).

Biochar amendments significantly decreased alachlor mineralization in soil to less than half of that in unamended soil (Table 4). With the exception of soybean stover, raw feedstock materials also significantly decreased alachlor mineralization. The slower degradation of alachlor in pine-amended (5% w/w) and oak-amended (5% w/w) soils as compared to unamended soil has been attributed to higher sorption of alachlor [48]. The decrease in mineralization observed here can also be attributed to increased sorption, which decreases the availability of alachlor residues to the degrading micro-organisms.

4. Conclusions

This study examined the overall impact of tillage and amendment addition as means to improve alachlor sorption in the soil system across three soil types. The aim was to assess the effects of multiple management strategies on alachlor fate through laboratory batch experiments and incubations. This work highlights the importance of SOC on alachlor mobility and degradation, and concludes that management strategies which alter this property the fastest have the greatest effect on alachlor fate. Our results showed that tillage management (RT versus CP) had no effect on the SOC content in three midwestern U.S. soils after 4 years of implementation, and, in turn, no effect on alachlor sorption; therefore, alachlor availability in these soils would presumably not be affected in this timeframe. In contrast, biochar amendments in soil significantly increased alachlor sorption and decreased mineralization immediately following their incorporation at rates of 10% w/w . The corresponding raw feedstocks had no significant effect on alachlor sorption and only marginally decreased mineralization, which is consistent with their lesser impact on SOC compared to the biochar. These findings demonstrate the relative effect that biochar as a soil amendment has over tillage alterations and raw feedstock applications. Additional work is needed to assess the long-term effects of both tillage

and biochar, particularly in the field where factors such as temperature and water flow dynamics can be evaluated. Furthermore, lower and more economically feasible biochar application rates should also be studied.

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