

Metolachlor Sorption and Degradation in Soil Amended with Fresh and Aged Biochars

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ABSTRACT: Addition of organic amendments such as biochar to soils can influence pesticide sorption–desorption processes and, in turn, the amount of pesticide readily availability for transport and biodegradation. Sorption–desorption processes are affected by both the physical and chemical properties of soils and pesticides, as well as soil–pesticide contact time, or aging. Changes in sorption–desorption of metolachlor with aging in soil amended with three macadamia nut shell biochars aged 0 (BC_{mac-fr}), 1 year (BC_{mac-1yr}), and 2 years (BC_{mac-2yr}) and two wood biochars aged 0 (BC_{wood-fr}) and 5 years (BC_{wood-5yr}) were determined. Apparent sorption coefficient (K_{d-app}) values increased with incubation time to a greater extent in amended soil as compared to unamended soils; K_{d-app} increased by 1.2-fold for the unamended soil, 2.0-fold for BC_{wood-fr}, 1.4-fold for BC_{wood-5yr}, 2.4-fold for BC_{mac-fr}, 2.5-fold for BC_{mac-1yr}, and 1.9-fold for BC_{mac-4yr}. The increase in calculated K_{d-app} value was the result of a 15% decrease in the metolachlor solution concentration extractable with CaCl₂ solution with incubation time in soil as compared to a 50% decrease in amended soil with very little change in the sorbed concentration. Differences could possibly be due to diffusion to less accessible or stronger binding sites with time, a faster rate of degradation (in solution and on labile sites) than desorption, or a combination of the two in the amended soils. These data show that transport models would overpredict the depth of movement of metolachlor in soil if effects of aging or biochar amendments are not considered.

KEYWORDS: *availability, degradation, aging, sorption, biochar, metolachlor*

INTRODUCTION

To protect ground and surface waters from contamination, knowledge of pesticide degradation and sorption–desorption processes is required. Sorption controls the amount of chemical that is available for pest control as well as the amount of chemical available for leaching and runoff. Additionally, sorption governs pesticide bioavailability; for a pesticide to be available for plant uptake and microbial degradation, it must be present in solution (i.e., not sorbed). Therefore, research on the mechanisms affecting pesticide bioavailability in soil and sediments¹ has focused on sorption–desorption processes and bound residue formation.

Sorption–desorption reactions are affected by both the physical and chemical properties of soils and pesticides, as well as soil–pesticide contact time, or aging. Using a variety of methods, sorption of multiple classes of pesticides has been observed to increase with aging in soils.^{2–9} Slow diffusion within small pores of soil aggregates, hydrophobic partitioning into solid humic materials,¹⁰ entrapment in hydrophobic surface nanopores,¹¹ and sorption to nondesorbable sites of soil organic matter¹² have all been proposed as possible mechanisms involved in the aging process. An increase in sorption with aging in soils would decrease the amount of available pesticide, thereby limiting its activity and biodegradation over time.

The addition of organic amendments, such as biochar, can influence the availability and, in turn, biodegradation of pesticides in soils. Biochar, the carbon-rich product of biomass pyrolysis, possesses a high sorption capacity for various

pesticides. For instance, sorption of diuron¹³ and pyrimethanil¹⁴ in soil was observed to increase following the addition of wood biochar. Numerous other combinations of pesticides and biochars have been studied with similar results.^{15,16} Decreases in pesticide degradation in biochar-amended soils have also been reported. This reduced degradation is often attributed to increased pesticide sorption and, in turn, decreased pesticide bioavailability. For instance, Spokas et al.¹⁷ observed an increase in atrazine sorption and decreased dissipation when a sandy loam soil was amended with 5% (w/w) of sawdust biochar. Similarly, atrazine mineralization decreased in soil amended with 1% (w/w) wheat char as a result of increased sorption.¹⁸ Comparable trends were also observed with acetochlor¹⁷ in biochar-amended soils, as well as diuron after a 10 week incubation study.¹⁹

As previously mentioned, biodegradation depends in part on the availability of the pesticide; however, biodegradation is also contingent on the presence and activity of pesticide-degrading microorganisms. In addition to its direct effect on sorption of pesticides, biochar may also affect the numbers and activity of soil microorganisms, although its effects are variable. Biochar amendments to soils have been shown to stimulate soil C mineralization in some studies,^{20,21} whereas others found inhibitory effects.^{17,22–24} The stimulatory effect of biochar on

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carbon mineralization may be a result of the biochar itself acting as a mineralizable C source.^{25,26} Alternatively, biochar may sequester soil organic matter within its pore network, protecting it from degradation and inhibiting mineralization.^{17,27,28} With regard to pesticide degradation, Mukherjee²⁹ observed an increase in atrazine degradation in a sandy loam soil with organic amendments, which could be explained by general microbial stimulation. In contrast, other studies have shown no effect of biochar on pesticide degradation.³⁰

The effects of biochar amendments are most often evaluated using biochars that are freshly applied to soils; however, biochars undergo physical and chemical changes with time in soils. Physically, incorporation into soil can modify the pore structure and particle size of biochar,³¹ influencing its recalcitrance and ability to act as a habitat for microorganisms.³² It has been shown that weathered biochar particles were heterogeneous, covered with a wide variety of mineral and organic matter, and were very different from the surfaces of the fresh biochars.³² With time, dissolution and leaching of soluble salts and organic compounds present in the biochar also occur,³³ which can modify the pH surrounding biochar particles. Biochar aged in soil becomes oxidized as it mainly functions as a reducing agent.³² In addition to its surface redox activity, biochars can initially have acidic or basic properties based on the presence of different surface functional groups.^{34–36} Changes to such surface chemistries over time influence a variety of biochar properties, including wettability, reactivity,¹⁵ and retention of ions through electrostatic interactions.³⁷ Although the physicochemical changes to biochar have been documented, the implications of these changes are not well understood. Further research is required to evaluate the effects on pesticide accumulation and efficacy in biochar-amended soils.

Metolachlor is a chloroacetanilide, its persistence and solubility make it a contaminant of concern in surface and ground waters. Metolachlor is soluble in water (488 mg L⁻¹ at 20 °C) and is moderately sorbed by most soils (sorption range = 99–307 mL mg⁻¹),³⁷ with the greatest sorption occurring on soils with high organic matter and clay contents. Reported half-life values for metolachlor range from 15 to 70 days in different soils.^{38,39} In water, the herbicide is highly persistent over a wide range of pH values, with reported half-life values of >200 and 97 days in highly acid and basic conditions, respectively.³⁹ Metolachlor dissipation in soil mainly occurs via biological degradation, rather than chemical processes.^{40–43} The degradation of metolachlor in soils has been proposed to occur via cometabolic processes that are affected by soil texture, microbial activity, and bioavailability.⁴⁴ In the top few centimeters of soil photodegradation is thought to contribute to dissipation losses; however, metolachlor is relatively stable under natural sunlight, with only ~6.6% degrading in 30 days.³⁹ On the basis of its sorption–desorption and degradation behavior, metolachlor has the potential for offsite transport, particularly in soils with low organic carbon content. Leaching of metolachlor in soil has been reported to occur,⁴⁵ making groundwater contamination a concern. Increased sorption and/or degradation from biochar soil amendments may help to reduce the risk of metolachlor contamination.

The objective of this study was to evaluate the biogeochemical transformation of biochar with field aging using various characterization techniques and subsequently determine the effects of both fresh and aged biochars on the availability of metolachlor residues in soils. This was done by

monitoring metolachlor degradation and sorption over time in unamended and biochar-amended soils. Data from this study aid in understanding how biochar changes in soil over time and the ramifications for pesticide behavior in soil.

MATERIALS AND METHODS

Soil and Chemical. The soil used for the laboratory studies was collected from the University of Minnesota's Research and Outreach Station in Rosemount, MN, USA (44°45' N, 93°04' W). Soil at the site is a Waukegan silt loam (Mollisol-Typic Hapludolls) (USDA classification), containing approximately 22% sand, 55% silt, and 23% clay, pH 6.0, and organic carbon (OC) 2.52%. Surface soil (0–15 cm) was collected, sieved to <2 mm, and homogenized for the study. Average annual temperature at the site is 6.9 °C with 887 mm of annual precipitation (102 cm snowfall).⁴⁶

Metolachlor (99% chemical purity) and uniformly ring-labeled [¹⁴C] metolachlor (specific activity = 54.6 μCi mg⁻¹, 99.2% radiochemical purity) were graciously supplied by Syngenta Crop Protection, Greensboro, NC, USA (Figure 1). Unlabeled metolachlor was mixed with ¹⁴C-metolachlor to give a final solution concentration of 37800 kBq mL⁻¹.

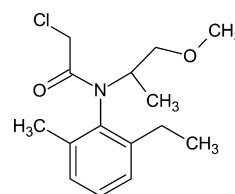


Figure 1. Chemical structure of metolachlor.

Biochar. Biochars used in this study were prepared from macadamia nut shells and hardwood chips at 850 °C (fast pyrolysis) and 550 °C (slow pyrolysis), respectively. In addition to the freshly prepared biochars for each feedstock, macadamia nut biochars aged in soil for 1 and 4 years and wood chip biochar aged for 5 years were studied (Table 1). Both biochars were aged in a Waukegan silt loam containing approximately 22% sand, 55% silt, and 23% clay with a pH (1:1 H₂O) of 6.3–6.6 and 2.6% OC. After each aging period, biochar particles were manually separated from the soil. Brunauer–Emmett–Teller (BET) surface area was measured by quantifying the sorption of nitrogen gas at 77 K (NOVA 4200e, Quantachrome Instruments, Boynton Beach, FL, USA). Before analysis, samples were degassed at 200 °C for 2 h because we wanted to achieve a specific surface area (SSA) representative of actual conditions (versus a “cleaned” surface at 300 °C for 16 h).

Surface morphologies of the various biochars were determined using a JEOL 6500 scanning electron microscope. Surface functional groups of the biochars were determined using a Nicolet Series II Magna-IR System 750 FTIR spectrometer, recording the spectrum region from 4000 to 400 cm⁻¹ with a resolution of 2 cm⁻¹ (University of Minnesota Characterization Facility) with an attenuated total reflection (ATR) interface. This technique permitted the direct examination of the surface without the confounding impacts of grinding particles and pelletizing [because you do not know if what you were viewing in the pellet indeed was the original surface]. Dissolved organic carbon (DOC) was extracted from biochar by shaking 0.5 g of biochar with 10 mL of 0.01 M CaCl₂ for 15 min. The suspensions were centrifuged at 10000 rpm for 20 min and filtered through a 0.45 μm pore nylon filter. Solutions were analyzed using a total carbon analyzer (Shimadzu TOC-V). In addition, total nitrogen and organic carbon of biochars were analyzed. Biochar pH was measured in a 1:5 (w/v) biochar/deionized water mixture.

Metolachlor Sorption in Aged Unamended and Amended Soils. Duplicate 10 g samples of soil were spread in a thin layer and spiked dropwise with 500 μL of methanolic ¹⁴C-metolachlor solution at 20 mg L⁻¹. The final concentration of chemical in soil was 1.0 mg kg⁻¹. After the methanol evaporated, the biochar was added at a rate of

Table 1. Biochar Physicochemical Properties

biochar feedstock	approx particle size (cm)	production temp (°C)	field time (years)	label	pH	SSA (m ² g ⁻¹)	DOC (mg L ⁻¹)	total inorg C (%)	total OC (%)	total N (%)	C/N
macadamia nut shells	5	850	0	BC _{mac} -fr	7.74	0.16	21.5	0.8	76.8	0.7	110.3
	4		1	BC _{mac} -1yr	8.55	0.01	53.5	1.0	83.6	0.3	265.4
	0.5		4	BC _{mac} -4yr	6.77	0.63	6.7	0.2	79.1	0.4	192.0
hardwood	10	550	0	BC _{wood} -fr	7.21	0.42	15.6	0.7	78.1	0.7	113.2
	0.5		5	BC _{wood} -5yr	7.56	2.31	8.3	1.0	77.7	0.2	336.4

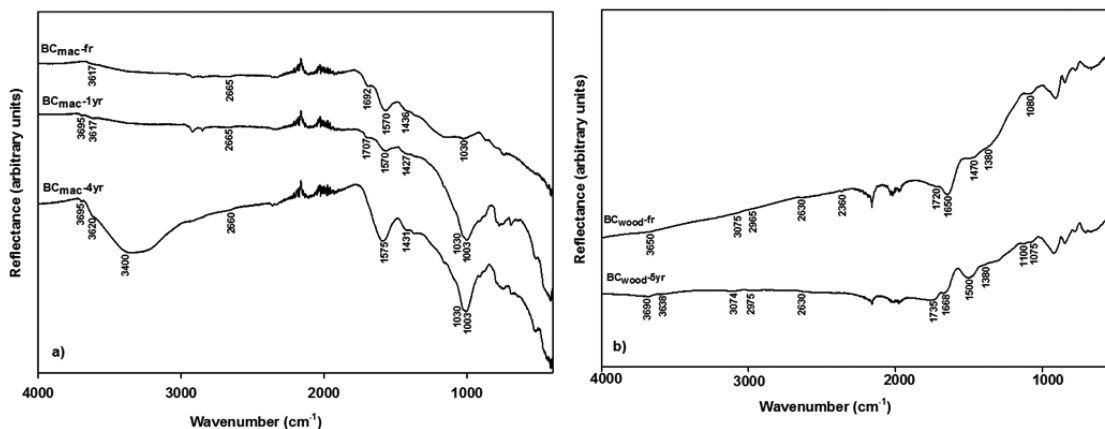


Figure 2. Attenuated total reflectance (ATR) infrared spectra of (a) macadamia nut shell biochars (BC_{mac}-fr, BC_{mac}-1yr, and BC_{mac}-4yr) and (b) hardwood biochars (BC_{wood}-fr and BC_{wood}-5yr).

10% (w/w) to the soil and thoroughly mixed; soil and soil+biochar moisture contents were adjusted to 10% (w/w). Samples were then transferred to 30 mL glass centrifuge tubes, which were incubated at 25 °C within stoppered 250 mL glass Erlenmeyer flasks for 0, 2, 4, 6, and 8 weeks. A glass vial containing 3 mL of 0.5 M NaOH was placed inside the flask by attachment to the inside of stoppers.

To determine the metolachlor mineralization rate, NaOH solutions were replaced and analyzed for ¹⁴CO₂ weekly, thereby also aerating the flask. One milliliter aliquots of NaOH solutions were added to 5 mL of EcoLite(+) cocktail (MP Biomedicals) and ¹⁴C-radioactivity analyzed by liquid scintillation counting (LSC) for 10 min, using a Tri-Carb 1500 Packard instrument (Packard Instrument Co., Downers Grove, IL, USA). Solutions were kept in the dark over 48 h prior to measurement (no chemiluminescence was observed).

At time 0 (immediately after the moisture of the soil and soil +biochar was adjusted) and after each incubation period, duplicate soil and soil+biochar samples were first extracted with 20 mL of 0.005 M CaCl₂ by shaking on a horizontal shaker for 24 h. The soil slurries were then centrifuged at 1500 rpm for 30 min, and 10 mL of supernatant was removed. For ¹⁴C analysis, 1 mL aliquots of the supernatants were added to 5 mL of scintillation cocktail and analyzed by LSC, as previously described. The removed supernatant was replaced with 10 mL of methanol and the extraction conducted as described above. This was repeated for a second and third extraction with 10 mL of methanol.

Extracted soil from random samples during the incubation was air-dried, and 0.3 g subsamples were mixed with an equal volume of cellulose powder and then oxidized in a Packard Tri-Carb model 307 sample oxidizer (Packard Instrument Co., Downers Grove, IL, USA) to determine nonextractable (bound) residues. Released CO₂ was trapped in Carbo-sorb (Packard Instrument Co., Meriden, CT, USA), mixed with toluene-based scintillation cocktail, and the ¹⁴C counted. Instrument oxidation and recovery efficiency was >98% based on recovery of freshly spiked ¹⁴C standards.

The aqueous and methanolic extracts were analyzed for parent metolachlor by high-performance liquid chromatography (HPLC) using a Waters 600E chromatograph coupled to a Waters 2996 diode array detector (Waters Corp., Milford, MA, USA). The following

chromatographic conditions were used: Phenomenex C₈ column (150 mm length × 4.6 mm i.d.), acetonitrile/water (50:50) eluent mixture at a flow of 1 mL min⁻¹, 100 μL injection volume, and UV detector of 214 nm. Metolachlor fractions were collected from 0 to 5 min and then each minute up to 10 min. One milliliter aliquots of each collected fraction were counted via LSC to enable calculation of the percentage of parent metolachlor in the extracted ¹⁴C.

To calculate apparent sorption coefficients, K_{d-app} , after different aging periods, it was assumed that aqueous-extractable metolachlor represented the solution phase concentration (C_e) and that the methanol-extractable metolachlor represented the sorbed phase concentration (C_s). K_{d-app} was calculated as follows: $K_{d-app} = C_s/C_e$.

RESULTS AND DISCUSSION

Biochar Characterization. FTIR spectra of the fresh (unaged) macadamia nut shell (BC_{mac}-fr) and wood biochars (BC_{wood}-fr) and of macadamia nut shell biochars aged for 1 year (BC_{mac}-1yr) and 4 years (BC_{mac}-4yr), and of wood biochar aged for 5 years (BC_{wood}-5yr) are shown in Figure 2. The spectra of BC_{mac}-fr and BC_{mac}-1yr were determined in a previous study.⁴⁷ The appearance of new peaks in the infrared spectra of the aged macadamia nut shell biochars compared to those present in the spectra of the fresh biochar provides evidence for soil mineral incorporation onto the surface of the biochars. Additional bands at 3695 and 1003 cm⁻¹ for BC_{mac}-1yr and BC_{mac}-4yr, corresponding to the O–H stretching and Si–O vibrations of clay minerals, could be due to soil mineral incorporation onto the surface of the biochars^{36,48} being more pronounced for BC_{mac}-4yr. The band at 2660 cm⁻¹ was assigned to O–H stretching vibration of carboxylic groups from the film layer that coats the surface of the fresh biochar. The band close to 1700 cm⁻¹ corresponds to C=O stretching vibration mode, and the group of bands between 1030 and 1090 cm⁻¹ can be assigned to C–O stretching vibrations corresponding to the carboxylic acid group. The decrease of the intensity of the band at 1700

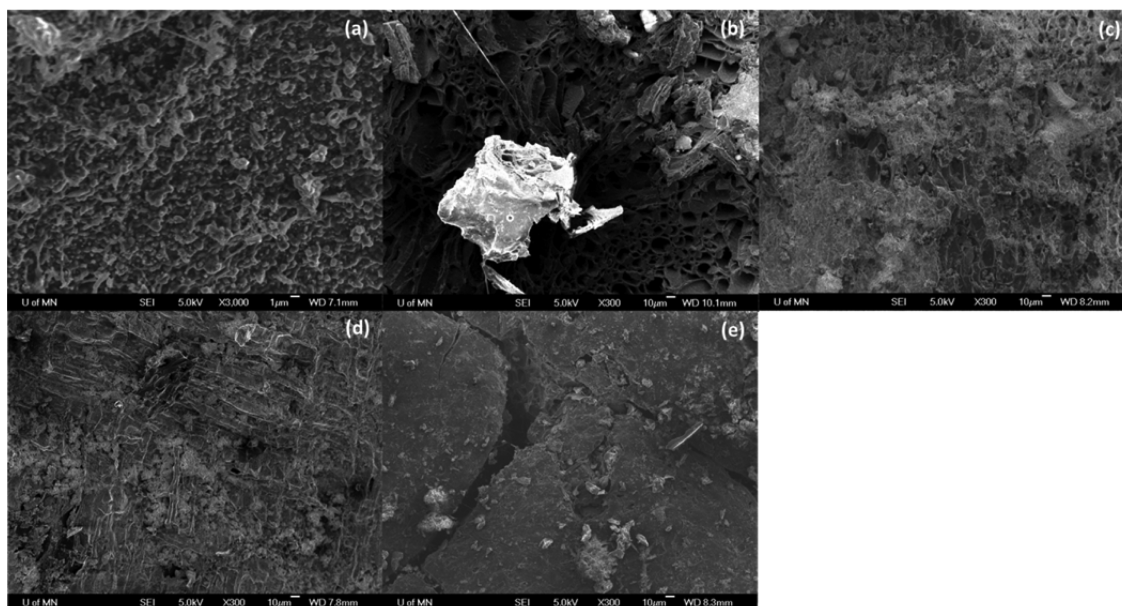


Figure 3. (a, d) SEM image showing the layer of sorbed organics on the surface of the fresh macadamia nut shells and hardwood biochars; (b, e) soil particles on the surface of BC_{mac}-1yr and BC_{wood}-5yr; (c) surface covered with soil particles for biochar aged 4 years (BC_{mac}-4yr).

Table 2. Extractable ¹⁴C and ¹⁴C-Metolachlor as a Function of Incubation Time

sorber	analyte	% of applied ^a				
		0 weeks	2 weeks	4 weeks	6 weeks	8 weeks
soil	total ¹⁴ C	84.5 ± 1.4	85.7 ± 0.5	79.9 ± 0.4	74.5 ± 0.4	68.9 ± 1.2
	¹⁴ C -metolachlor	79.6 ± 2.5	81.2 ± 0.9	74.6 ± 0.9	68.2 ± 0.1	61.8 ± 0.9
soil + BC _{wood} -fr	total ¹⁴ C	84.0 ± 3.2	79.4 ± 0.8	79.9 ± 1.8	74.7 ± 1.8	68.8 ± 1.1
	¹⁴ C -metolachlor	78.5 ± 3.3	75.0 ± 1.1	72.7 ± 2.1	69.6 ± 0.5	57.9 ± 0.2
soil + BC _{wood} -5yr	total ¹⁴ C	81.7 ± 1.5	84.9 ± 0.9	80.8 ± 2.9	74.7 ± 1.6	67.6 ± 1.7
	¹⁴ C -metolachlor	78.1 ± 2.4	80.7 ± 0.1	75.0 ± 2.7	67.0 ± 1.6	57.1 ± 2.3
soil + BC _{mac} -fr	total ¹⁴ C	89.9 ± 1.1	81.0 ± 6.3	74.8 ± 0.4	73.2 ± 0.6	69.7 ± 0.6
	¹⁴ C -metolachlor	85.1 ± 1.2	76.7 ± 7.6	65.5 ± 1.0	61.8 ± 0.4	55.3 ± 0.2
soil + BC _{mac} -1yr	total ¹⁴ C	99.4 ± 7.6	88.5 ± 3.6	75.0 ± 4.1	76.8 ± 5.3	74.9 ± 0.4
	¹⁴ C -metolachlor	94.7 ± 7.6	81.0 ± 5.9	64.3 ± 4.0	64.2 ± 4.9	59.8 ± 1.4
soil + BC _{mac} -4yr	total ¹⁴ C	87.3 ± 6.1	89.5 ± 0.3	87.7 ± 8.1	71.5 ± 0.5	70.5 ± 3.5
	¹⁴ C -metolachlor	82.6 ± 5.0	85.4 ± 0.8	78.1 ± 10.0	55.9 ± 1.3	53.7 ± 0.9

^a ± standard deviation; bold values are statistically different from the time 0 sample within each treatment (unpaired *t* test; *P* < 0.05).

cm⁻¹ and the increase of the band at 1400 cm⁻¹ correspond to the C—H bending and the carboxylate anion stretching⁴⁹ for the aged biochars and, in comparison with the BC_{mac}-fr, reveal a partial elimination of the acidic groups in the film with the aging process and a partial interaction of the carboxylate anion. In addition, BC_{mac}-4yr spectra show bands at 3400 and 1600 cm⁻¹, which correspond to water hydration.

FTIR of BC_{wood}-5yr shows bands at 3690 and 1100 cm⁻¹ assigned to the O—H stretching and Si—O vibrations of clay minerals as was shown for BC_{mac}. The bands at 2630, 1720, and 1075 cm⁻¹ corresponded to the OH, C=O, and C—O stretching vibrations of the carboxylic acid group, respectively. The bands at 3075 and 1660 cm⁻¹ were correlated with the aromatic structure of the biochar. The decrease of the intensity of the band at 1720 cm⁻¹ and the increase of the band at ~1470

cm⁻¹ correspond to the C—H bending and the carboxylate anion stretching⁴⁹ for the aged biochars in comparison with the BC_{wood}-fr, revealing a possible increase of carboxylic groups due to oxidative process during the aging.

Figure 3 shows the SEM images of the fresh and aged macadamia nut shell biochars (Figure 3a–c) and the fresh and aged wood biochars (Figure 3d,e). SEM images of fresh macadamia nut shell biochar show a film covering and blocking the micropores as well as any physical surface features (Figure 3a). In contrast, the surface of the BC_{mac}-1yr shows a highly porous surface, with only some of the pores being blocked by soil particles or a coating (Figure 3b). The SEM image of the macadamia nut shell biochar aged for 4 years shows that most of the pores were filled after the fourth year in the soil (Figure 3c). SEM images of fresh wood biochar show organic oils

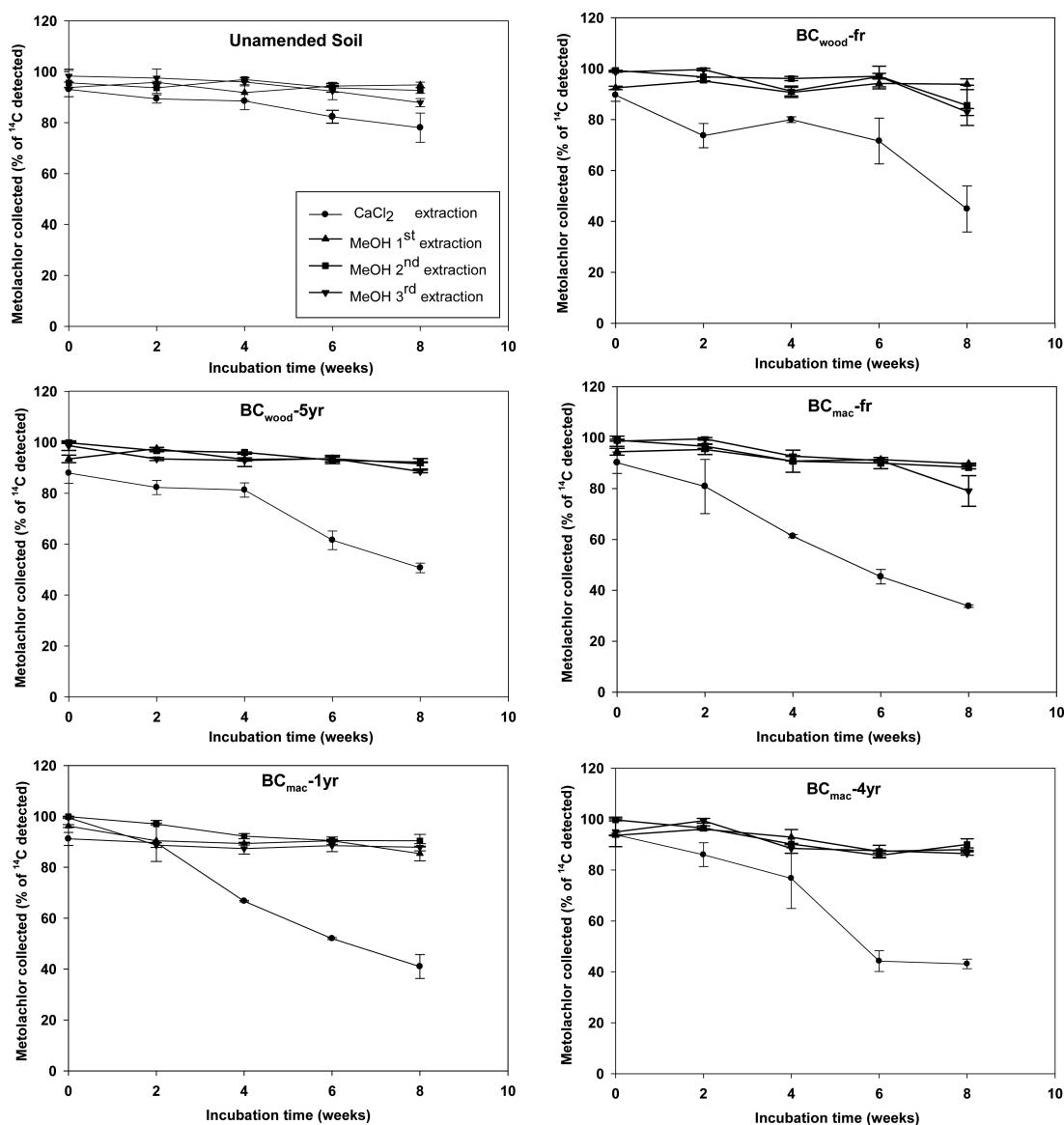


Figure 4. Metolachlor collected by HPLC expressed as a percentage of the total ^{14}C detected by LSC. Error bars indicate standard deviation.

coating the surface, as was observed for fresh macadamia nut shell biochar. The $\text{BC}_{\text{wood-5yr}}$ image has evidence of cracking and fracturing of the biochar surface.⁵⁰

The specific surface area (SSA) of macadamia nut shell biochar increased from $0.16 \text{ m}^2 \text{ g}^{-1}$ for fresh biochar to $0.63 \text{ m}^2 \text{ g}^{-1}$ for biochar aged for 4 years ($\text{BC}_{\text{mac-4yr}}$) (Table 1). SSA for fresh wood biochar ($0.42 \text{ m}^2 \text{ g}^{-1}$) increased with time after soil application by a factor of 5, to $2.31 \text{ m}^2 \text{ g}^{-1}$ for the wood biochar aged for 5 years. The increase of biochar SSA with time after soil application, except for $\text{BC}_{\text{mac-1yr}}$, is assumed to be due to the elimination of the organic film from the BC-fr surface exposing the underlying micropores, as was shown in FTIR studies (Figure 2). However, as the organic film from the fresh biochar surface is eliminated, some pores will be filled with organic and mineral matter, resulting in a small net increase in SSA. DOC was inversely related with the SSA (Table 2) and could be due to the elimination in soil of the organic covering on the fresh biochar (Figure 3).

Metolachlor Residue Distribution in Aged Soil. Total extractable ^{14}C and ^{14}C -metolachlor from soil and biochar-amended soils is shown in Table 2. The average amount of total

extractable ^{14}C (CaCl_2 + methanol) from soil and biochar-amended soil decreased with incubation time from 88 to 70% after 8 weeks. The ^{14}C not accounted for in the extracts was presumed to be due to irreversible binding. Little $^{14}\text{CO}_2$ was detected ($<0.1\%$) during the incubation period in unamended and amended soils, presumably due to a lack of microorganisms capable of mineralizing the ring of metolachlor. After combustion of randomly selected soil samples after extraction throughout the incubation, the mass balance of recovered ^{14}C was on average $>93\%$.

During the 8 week of incubation, the average extractable ^{14}C -metolachlor in soil and the five biochar-amended soils (Table 2) decreased from 83 to 58%, presumably due to microbial degradation and/or irreversible binding. Differences between the percentages of ^{14}C and ^{14}C -metolachlor recovered (% of applied) can be explained by ^{14}C corresponding to unidentified ^{14}C -labeled degradates. In unamended soil, 17.8% was degraded and/or irreversibly bound during the 8 week incubation. In comparison, in soil amended with fresh or aged woodchip biochar, an average of 20.8% of the metolachlor was degraded and/or irreversibly bound during the 8 weeks. The change in

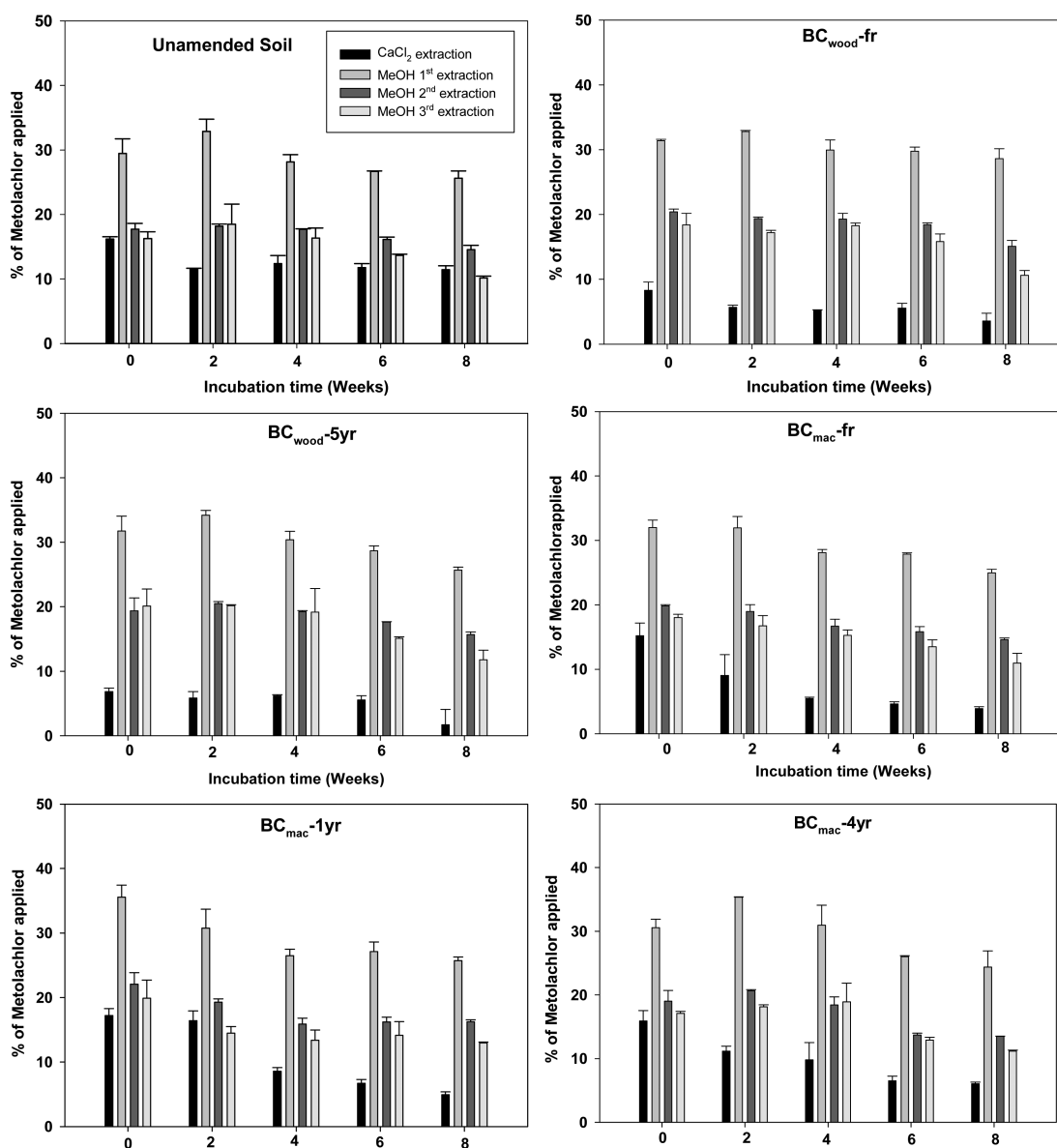


Figure 5. Percentage of recovered ¹⁴C-metolachlor in CaCl₂ and MeOH extracts. Error bars indicate standard deviation.

extractable metolachlor in the fresh and aged macademia nut amended soil, an average of 31.5%, was significantly greater than for soil or woodchip-amended soil. If the increased metolachlor loss is via degradation in biochar-amended soil as opposed to irreversible binding, it could be attributed to increases in numbers and activities of microbial biomass previously reported in soil amended with biochars,^{26,51} although biomass was not quantified in this study.

On the basis of the amounts of extractable ¹⁴C-metolachlor over time, degradation was shown to be taking place by the aqueous extract concentrations. Almost all of the methanol-extracted ¹⁴C during the incubation period was determined to be metolachlor (Figure 4). In contrast, of the total extractable ¹⁴C in the CaCl₂ solution, the percentage of ¹⁴C-metolachlor decreased in all cases at the end of the 8 weeks (from 93 to 78% for the unamended soil; from 90 to 45% for BC_{wood}-fr; from 88 to 51% for BC_{wood}-5yr; from 90 to 34% for BC_{mac}-fr; from 91 to 41% for BC_{mac}-1yr; from 94 to 43% for BC_{mac}-4yr). This reduction was higher for the soils amended with biochar than for the unamended soil (15%) and more pronounced for the

soil amended with BC_{mac} than for BC_{wood}. The reduction in the fraction of ¹⁴C-metolachlor in the total extractable ¹⁴C was less pronounced with the aged biochars.

The amount of ¹⁴C-metolachlor recovered in CaCl₂ extracts (of the amount applied) decreased during the 8 week incubation period for both the unamended and amended soils (Figure 5). The observed decrease was more pronounced in the biochar-amended soils and was greater with BC_{mac} than BC_{wood} (from 16 to 11% in unamended soil, from 8 to 3% in BC_{wood}-fr, from 7 to 2% in BC_{wood}-5yr, from 15 to 4% for in BC_{mac}-fr, from 17 to 5% from BC_{mac}-1yr, and from 16 to 6% in BC_{mac}-4yr). Differences between fresh and aged biochar on CaCl₂-extractable metolachlor over time were not observed. The sum of ¹⁴C-metolachlor in the three methanol extracts also tended to decrease with incubation time (Figure 5), from 63 to 50% in unamended soil, from 70 to 54% in BC_{wood}-fr, from 71 to 53% in BC_{wood}-5yr, from 70 to 50% in BC_{mac}-fr, from 78 to 55% in BC_{mac}-1yr, and from 67 to 49% in BC_{mac}-4yr. These results could indicate that the formation of nonextractable ¹⁴C-bound residues significantly increased with incubation time.

Table 3. Aging Effects on Metolachlor Sorption Coefficients

aging time (weeks)	K_{d-app}^a (L kg ⁻¹)					
	soil	BC _{mac-fr}	BC _{mac-1yr}	BC _{mac-4yr}	BC _{wood-fr}	BC _{wood-5yr}
0	0.71 ± 0.02	0.84 ± 0.12	0.81 ± 0.01	0.75 ± 0.04	1.54 ± 0.22	1.85 ± 0.16
2	1.08 ± 0.02	1.44 ± 0.42	0.73 ± 0.02	1.21 ± 0.08	2.22 ± 0.10	2.30 ± 0.42
4	0.91 ± 0.08	2.00 ± 0.02	1.19 ± 0.02	1.27 ± 0.23	2.31 ± 0.07	1.97 ± 0.06
6	0.88 ± 0.06	2.29 ± 0.20	1.57 ± 0.05	1.37 ± 0.12	2.14 ± 0.25	2.05 ± 0.22
8	0.83 ± 0.08	2.00 ± 0.39	2.06 ± 0.16	1.45 ± 0.04	3.07 ± 1.07	2.55 ± 0.53

^a ± standard deviation; bold values are statistically different from the time 0 sample within each treatment (unpaired *t* test; *P* < 0.05).

Differences between macadamia nut and hardwood biochar properties may in part explain the observed differences in metolachlor extractable fractions (Figure 5; Table 1). Macadamia nut biochar has lower SSA than hardwood biochar and higher DOC. Both SSA and DOC affect sorption, which influences the extractable fractions of metolachlor. The higher DOC content may block biochar sorption sites, as suggested by the organic film in the SEM images, thereby reducing metolachlor sorption and leaving it more readily available to degrade.⁵²

Metolachlor Sorption in Aged Unamended and Amended Soils. Metolachlor sorption in unamended and amended soils was determined from the distribution ¹⁴C-metolachlor between methanol-extractable fractions (sorbed phase concentrations) and CaCl₂-extractable fractions (solution phase concentrations). Metolachlor apparent sorption coefficients were calculated at time 0 and again after 2, 4, 6, and 8 weeks of incubation (Table 3). At time 0, metolachlor sorption was greater in biochar-amended soil as compared to unamended soil, consistent with observations for other pesticides.^{13–16} Apparent sorption values were greater in soil amended with wood biochar as compared to soil amended with macadamia nut shell biochar, possibly as the result of the higher SSA of the wood biochar (Table 1). Differences in organic compositions of the biochars (carbonized organic matter or noncarbonized organic matter) may affect the sorption metolachlor.^{53,54}

Calculated metolachlor apparent sorption coefficients increased after aging to a greater extent in biochar-amended soils as compared to unamended soil. K_{d-app} values increased with incubation time by a factor of 1.2-fold for the unamended soil, as compared to factors of 2.4-fold for BC_{mac-fr}, 2.5-fold for BC_{mac-1yr}, 1.9-fold for BC_{mac-4yr}, 2.0-fold for BC_{wood-fr}, and 1.4-fold for BC_{wood-5yr}. Similar trends were seen by Cox et al.,⁵⁵ who found imidacloprid K_{d-app} values increased with aging in soil by an average of 2.8-fold during the incubation period. Likewise, Regitano et al.⁵⁶ and Regitano and Koskinen⁵⁷ reported that simazine sorption to soil increased by a factor of 2–3-fold after 7 days and that nicosulfuron K_{d-app} values in soil increased after 27 days. The amended soil results are in agreement with previous research that showed greater increases in aged K_{d-app} values in soils with low sorption capacity.

Our results suggest an increased sorption capacity following soil exposure, which is in direct conflict with prior hypotheses of a soil particle pore-clogging model leading to decreased biochar sorption.⁵⁸ Both of these observations could be correct as it depends on the initial state of the biochar (pore sizes and if soil minerals fit) and what postproduction treatments have occurred. For the biochars used here, the original biochar was coated with a film that could have prevented metolachlor from entering the interior biochar pores. In addition, even storage of

biochar at ambient conditions can result in significant alterations of biochar's surface chemistry.⁵⁹

In summary, data from this study show that biochar has the potential to decrease metolachlor availability and transport through increased sorption and/or degradation. Sorption in amended soils was affected by the physical and chemical properties of the biochar, differing among feedstock materials and aging times. Metolachlor sorption, as characterized by K_{d-app} values, increased with time in unamended and biochar-amended soils; however, the magnitude of the increase was greater in the biochar-amended soils. The exact mechanism that caused the increased sorption is not clear. The increasing sorption coefficients can be attributed to degradation in solution, which leaves sorbed metolachlor, which may have diffused into less accessible or stronger sorption sites. The addition of biochar to soil may have also increased metolachlor biodegradation as a result of the microbial stimulation by the amendments or a physical entrapment due to the exposure of the coated pore structure in the fresh biochar. Regardless of the mechanism, these results indicate that transport models would likely overpredict the depth of metolachlor movement in soil if the effects of aging and biochar amendments are not considered.

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Notes

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ABBREVIATIONS USED

USDA, United States Department of Agriculture; DOC, dissolved organic carbon; LSC, liquid scintillation counting; HPLC, high-performance liquid chromatography; FTIR, Fourier transform infrared; SEM, scanning electron microscope; SSA, specific surface area; ATR, attenuated total reflectance

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