Influence of Soil Biochar Aging on Sorption of the Herbicides MCPA, Nicosulfuron, Terbuthylazine, Indaziflam, and Fluoroethyldiaminotriazine

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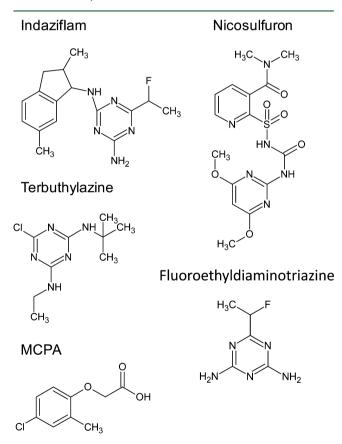[‡]USDA-Agricultural Research Service, 1991 Upper Buford Circle, Room 439, St. Paul, Minnesota 55108, United States
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ABSTRACT: Sorption of four herbicides and a metabolite of indaziflam on a fresh macadamia nut biochar and biochars aged one or two years in soil was characterized. On fresh biochar, the sorption was terbuthylazine (K_d = 595) > indaziflam (K_d = 162) > MCPA (K_d = 7.5) > fluoroethyldiaminotriazine (K_d = 0.26) and nicosulfuron (K_d = 0). Biochar surface area increased with aging attributed to the loss of a surface film. This was also manifested in a decline in water extractable organic carbon with aging. Correspondingly, an increase in the aromaticity was observed. The higher surface area and porosity in aged biochar increased sorption of indaziflam ($K_{dBC-2yr}$ = 237) and fluoroethyldiaminotriazine ($K_{dBC-1yr}$ = 1.2 and $K_{dBC-2yr}$ = 3.0), but interestingly decreased sorption of terbuthylazine ($K_{dBC-1yr}$ = 312 and $K_{dBC-2yr}$ = 221) and MCPA ($K_{dBC-1yr}$ = 2 and $K_{dBC-2yr}$ = 2). These results will facilitate development of biochars for specific remediation purposes.

KEYWORDS: MCPA, terbuthylazine, nicosulfuron, indaziflam, biochar, aging

■ INTRODUCTION

Biochar is a carbon-rich solid material produced by heating biomass in an oxygen limited environment and consists of both mineral and organic phases, where the organic phase typically exhibits a high concentration of either aromatic regions or more reactive aliphatic regions.[1] Due to the predicted long microbial mineralization half-lives, biochar is an important stable C pool in soils and sediments.[2] The stability of a particular biochar is dependent on several factors including the nature of the reactions that take place between the biochar and soil constituents such as dissolved organic and inorganic matter, micro-organisms, and plant roots.[1] However, the extent, rates, and implications of the interactions between biochar and soil components are not well understood. Little research has been undertaken to determine biochar weathering and reactions that occur after application of biochar to soil.[3,4]

Interactions between biochar and clay mineral surfaces are similar to those between organic matter and clay mineral surfaces in soil, especially for those biochars that have high mineral content (i.e., ash content). Interactions will depend on the type of clay (2:1, 1:1), the distribution of different functional groups on the clay (siloxane, OH) and the organic matter (COOH, C=O, C–O, CN), the polarity of these compounds, and the composition and concentration of cations and anions in the soil solution.[5] The adsorption of soil materials onto black carbon protects this phase from oxidation and decomposition.[6] This implies that the mineral attachment to biochar is important in the stabilization process.

Addition of biochar to agricultural soils has been shown to increase sorption and to decrease the dissipation of pesticide in soils,[7−9] but the understanding of organo−mineral interactions of biochar in soils, and the consequences of aged biochars for pesticide interactions, is not clear. Kookana[10] proposed that

with time it is possible that mineral particles may cover the reactive surfaces of biochars thereby masking the sorption capacity of biochars for organic compounds such as pesticides. This in turn would lessen their capacity to reduce the efficacy of pesticide. Yang and Sheng[11] found that adsorption of dissolved soil organic matter (DOM) during aging of ash surfaces reduced diuron adsorptivity by 50−60%, but there is no information on other classes of herbicides.

MCPA and nicosulfuron are weak acid herbicides and considered relatively mobile compounds in soil with runoff and leaching risks for surface water and groundwater.[12,13] The herbicide terbuthylazine is a weak base herbicide widely used in olive production in Spain, but restricted in certain areas because of its mobility and potential ground and surface water contamination.[14] Indaziflam is also a weak base, and potentially mobile in soil.[15] Fluoroethyldiaminotriazine is a triazine metabolite of indaziflam of which little is known. Biochar additions to soil could be useful to increase sorption and decrease the dissipation of mobile herbicides in soils[7−9] or to remove them from contaminated water.[16]

The objectives of this study were to characterize the interactions between biochar and soil following field application as a means to determine the mechanisms of soil components incorporation into biochar and the effect of soil/biochar aging on herbicide sorption. Biochar from macadamia nut shell feedstock was used as a soil amendment (1% w/w) in an agronomic field trial in Rosemount, MN. After one and two years, the biochar particles were manually separated from the

soil and the surface chemistry of fresh and aged biochar was characterized. Knowledge gained on the mechanisms of mineral incorporation with biochar would be useful to reveal the interactions and aggregation of biochar and soil materials and how this affects the fate and behavior of herbicides.

■ MATERIALS AND METHODS

Chemicals. Pure analytical (>99%) standards and radiochemicals of indaziflam (N-[(1R,2S)-2,3-dihydro-2,6-dimethyl-1H-inden-1-yl]-6-[[(1R)-1-fluoroethyl]-1,3,5-triazine-2,4-diamine) (3.96 MBq mg^{-1}, 97.9% radiochemical purity) and fluoroethyldiaminotriazine (6-[[(1R)-1-fluoroethyl]-1,3,5-triazine-2,4-diamine) (3.79 MBq mg^{-1}, 90% radiochemical purity) were graciously supplied by Bayer Crop Science (Wuppertal, Germany). Nicosulfuron (2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide) (2.33 MBq mg^{-1}, >98% radiochemical purity) was provided by DuPont Crop Protection. Unlabeled MCPA (4-chloro-2-methylphenoxyacetic acid) (purity = 98.9%) and terbuthylazine (6-chloro-N-ethyl-N′-(2-methyl-2-propanyl)-1,3,5-triazine-2,4-diamine) (purity = 99.6%) were purchased by Dr. Ehrenstorfer Lab. Chemical structures of the pesticides are shown in Figure 1 and physicochemical characteristics in Table 1 (data from www.eu-footprint.org[17] and www.chemaxon.com[18]).

Figure 1. Chemical structures of indaziflam, nicosulfuron, terbuthylazine, fluoroethyldiaminotriazine, and MCPA.

Biochar. Three macadamia nut shell biochars, ranging in soil equilibration time (zero, one, and two years), were used as pesticide sorbents (Table 2). The biochar was aged in a Waukegan silt loam containing approximately 22% sand, 55% silt, and 23% clay with a pH (1:1 H$_2$O) of 6.3−6.6, and 2.6% organic carbon (OC). Average annual temperature is 6.85 °C with 887 mm of annual precipitation (102 cm snowfall).[19]

The specific surface area of the biochars was measured by nitrogen surface sorption, using a Micromeritics ASAP 2420 and the Brunauer,

Table 1. Physicochemical Characteristics of the Pesticides Used

pesticide	mol wt (g mol^{-1})	solubility in water (pH 7, 20 °C) (mg L^{-1})	K_{ow} (log P) (pH 7, 20 °C)	pK_a
terbuthylazine	229.71	6.6	3.4	1.9
indaziflam	301.36	2.8	2.8	3.5
MCPA	200.62	29390	−0.81	3.7
fluoroethyldiaminotriazine	157.00			4.10
nicosulfuron	410.41	7500	0.61	4.78

Table 2. Physicochemical Properties of the Biochars

biochar	pH	SSA (m^2 g^{-1})	DOC (mg L^{-1})	abs^a (254 nm^{-1})	SUVA$_{254}$ (L mg^{-1} m^{-1})
BC-fr	6.5	0.09	80.4	1.29	3.70
BC-1yr	6.6	69.77	31.6	0.84	6.12
BC-2yr	6.7	5.79			

^{a}Absorbance.

Emmett, and Teller (BET) method on a previously degassed 0.2 g sample at 8 °C during a 24 h period. The pH was determined in a 1:5 biochar:deionized water slurry. Dissolved organic carbon (DOC) was extracted from biochar by shaking 5 g of the sorbent with 20 mL of 0.01 M CaCl$_2$ for 15 min. The suspension was centrifuged at 8000 rpm for 15 min and filtered through a 0.45 μm pore nylon filter. The solution was diluted (1:5) in 0.01 M CaCl$_2$ and analyzed using a total carbon analyzer (Shimadzu TOC-V). The absorbance of the extracted DOC was measured with a VWR UV-3100 PC at 254 nm. The estimated aromaticity, SUVA$_{254}$ (L mg^{-1} m^{-1}), was calculated using the equation

$$SUVA_{254} = a_{254}/DOC$$

where a_{254} is the absorbance coefficient measured at 254 nm (m^{-1}) and was defined as $a_\lambda = 2.303 A_\lambda/l_L$; A_λ is the absorbance, and l_L is the path length of the optical cell in meters (here l_L = 0.01 m). DOC is the dissolved organic carbon expressed in (mg L^{-1}). SUVA$_{254}$ has previously been found to be a useful parameter for estimating the dissolved aromatic carbon content.[20]

The surface morphology of the sample was studied using a JEOL 6500 scanning electron microscope. The functional groups of the biochars were determined using a Nicolet Series II Magna-IR System 750 FTIR spectrometer, recording the spectral region from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} (University of Minnesota CharFac facility).

Sorption Experiments. Sorption experiments were conducted using the batch equilibrium technique according to OECD guideline 106.[21] Duplicate 0.1 g biochar samples were equilibrated with 8 mL of 0.01 M CaCl$_2$ solution containing initial concentrations of 1 mg L^{-1} terbuthylazine and MCPA, 0.3 mg L^{-1} fluoroethyldiaminotriazine and indaziflam, and 0.2 mg L^{-1} nicosulfuron. Radiolabeled chemicals were added to nonradioactive solutions to give a final solution concentration of ∼174 Bq mL^{-1} for fluoroethyldiaminotriazine, indaziflam, and nicosulfuron. The 0.01 M CaCl$_2$ solution was used as the background electrolyte to maintain constant ionic strength of sorption and desorption equilibration solutions and to facilitate flocculation of the soil. Suspensions were shaken mechanically at 21 ± 2 °C for 24 h and centrifuged at 370g for 30 min, and the supernatant was removed for analysis of the equilibrium concentration.

For fluoroethyldiaminotriazine, indaziflam, and nicosulfuron, 1 mL aliquots of the clear supernatant were mixed with 5 mL of scintillation cocktail (Ecolite, ICN Biomedicals, Costa Mesa, CA) and the amount of radioactivity was determined by liquid scintillation counting for 1 min in a liquid scintillation analyzer (1500 TRI-CARB, Packard Instruments, Downers Grove, IL). The amount of the chemicals in solution was calculated by considering the specific activity of each chemical. The equilibrium concentrations (C_e) of terbuthylazine and

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MCPA were determined by HPLC with a Waters 600E chromatograph coupled to a Waters 996 diode array detector, under the following conditions: Nova-Pak C18 column (150 mm length × 3.9 mm i.d.); flow rate, 1 mL min^{-1}, 25 μL injection; eluent system for terbuthylazine 50:50 (v/v) water/acetonitrile mixture and UV detection at 220 nm; eluent system for MCPA 60:40 (v/v) methanol/diluted H$_3$PO$_4$ (pH 2) mixture and UV detection at 230 nm. Differences between the initial (C_i) and equilibrium (C_e) solution concentration were assumed to be sorbed (C_s). The sorption coefficient (K_d) was calculated as C_s/C_e.

RESULTS AND DISCUSSION

Biochar. Fourier transform infrared spectra (FTIR) of the fresh biochar (BC-fr) and biochars aged 1 (BC-1yr) or 2 (BC-2yr) years are disp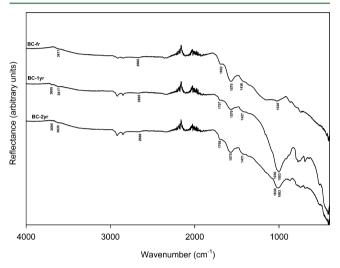layed in Figure 2. The appearance of new peaks in the infrared spectra of the aged biochars compared to those present in the spectra of the fresh biochar provides evidence for chemical alteration of the surface moieties due to the interactions between the soil and biochar. Additional bands at 3695 and 1003 cm^{-1} for BC-1yr and BC-2yr, 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 (see Figure 3c−e). The band at ∼2660 cm^{-1} can be assigned to O−H stretching vibration of carboxylic groups from fatty acids that coat 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 about 1700 cm^{-1} and the increase of the band at 1400 cm^{-1} correspond to the C−H bending and the carboxylate anion stretching[22] for the aged biochars and, in comparison with the BC-fr, reveal a partial elimination of the unsaturated fatty acid with the aging process and a partial interaction of the carboxylate anion.

Figure 3 shows the SEM images of the fresh biochar (BC-fr) (Figure 3a,b), the biochar aged 1 year and a biochar aged 4 years in soil (Figure 3c−f). SEMs of fresh biochar show a macropore (Figure 3a) with an organic layer coating the micropores and remaining surface structures (Figure 3b). In contrast, the surface of the BC-1yr shows a highly porous surface, with only some of the pores having a range of organic and mineral matter (Figure 3c,d). The SEM image of the biochar aged 2 years show that most of the pores were filled after longer exposure in the soil (Figure 3e,f). Lin et al.[23] observed that clay and mineral particles were adhered to the biochar surface, the mineral attachment occurred preferentially around the biochar external surface, and most of the pores inside the biochar were free of mineral phases. This agrees with our observations.
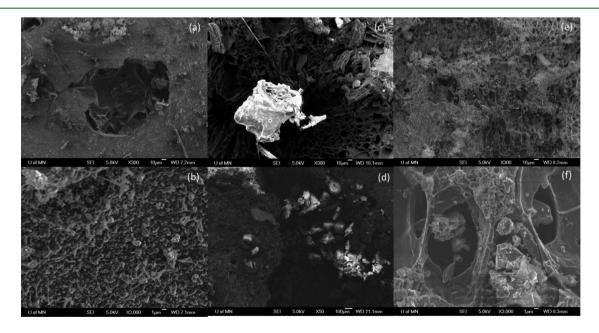

Figure 2. Attenuated total reflectance (ATR) infrared spectra of fresh biochar (BC-fr) and biochars aged 1 (BC-1yr) and 2 years (BC-2yr).

Figure 3. (a) SEM image showing a macropore on the fresh biochar (×300 magnification). (b) Fatty lipid surface (organic layer) on the fresh biochar (×3000). (c) Soil particles on the porous surface of BC-1yr (×300). (d) Soil particles on the porous surface of BC-1yr (×50). (e) Surface and pores covered with soil particles for biochar aged 4 years (×300). (f) Surface and pores covered with soil particles on the porous surface of BC-4yr (×3000). Note the significant difference in the appearance of the BC surface in panels b and f, which are at the same magnification (×3000).

Table 3. Sorption Coefficients (K_d) for the Pesticides in the Biochars

	K_d (L kg^{-1})				
biochar	terbuthylazine	indaziflam	MCPA	fluoroethyldiaminotriazine	nicosulfuron
BC-fr	595 ± 9	162 ± 20	7.49 ± 2.00	0.26 ± 0.15	0.00 ± 0.00
BC-1yr	312 ± 27	156 ± 18	2.23 ± 0.00	1.18 ± 0.75	0.00 ± 0.00
BC-2yr	221 ± 4	237 ± 25	2.48 ± 0.00	2.95 ± 0.92	0.03 ± 0.02

The specific surface area (SSA) of the biochars (Table 1) increased with time after soil application, from 0.095 m^2 g^{-1} for the fresh biochar (BC-fr) to 69.774 m^2 g^{-1} for biochar aged 1 year. The increase in SSA is assumed to be due to the elimination of the organic film from the BC-fr surface exposing the underlying micropores. The SSA was still higher than the initial biochar after 2 years (5.786 m^2 g^{-1}), even though some pores were filled with organic and mineral matter (Figure 3e,f).

Complex reactions take place on biochar surfaces, especially for those biochars that have high mineral content. Due to the high-temperature pyrolysis (850 °C) of the biochar, a high mineral-ash biochar with characteristics of a highly aromatic composition and recalcitrant microbial decomposition are expected.[3] Several mechanisms for interactions between biochar and minerals or biochar and organic matter have been hypothesized:

(i) The interactions at mineral surfaces could be cation−π interactions between mineral surface cations and with the negative electrostatic surface of the aromatic ring,[24] hydrogen−π interactions between the face of electron-rich π-system of the aromatic ring of the biochar and the H silanol groups of the minerals, or n−π electron donor−acceptor interactions (n = nonbonding electrons at siloxane surface) between a nitroaromatic compound (π-acceptor) and a basal siloxane surface.

(ii) π−π interactions could happen between the π-donor or π-acceptor system of the biochar with the natural organic matter (NOM) or polar−π interactions between aromatic systems with positively polarized or charged organic moieties. It has been shown that NOM can suppress sorption of organic contaminants on environmental black carbon by blocking micropores.[25]

The decline in DOC of BC-1yr (31.6 mg L^{-1}) in comparison to BC-fr (80.4 mg L^{-1}) (Table 2) could be a result of the natural elimination in soil of the organic covering on the fresh biochars and also for the degradation of the more labile fraction of DOC, which would enhance the proportion of recalcitrant aromatics,[26] increasing the aromaticity (SUVA$_{254}$) (6.12 L mg^{-1} m^{-1} for BC-1yr and 3.70 L mg^{-1} m^{-1} for BC-fr). Cox et al.[27] found that the humification index (HIX) of DOC from a solid organic amended with a high amount of aromatic molecules after two months of soil incubation shows just a small increase with residence time. This can be attributed to the sorption of organic matter that must be more humified and have higher adsorption capacities. Lin et al.[23] noticed that the hydrophobic DOC fraction decreased in a biochar mineral complex indicating that hydrophobic DOC could be immobilized in the complex because of a strong affinity toward clays.[28]

Sorption Experiments. The greatest sorption for the fresh and two aged biochars was for indaziflam and terbuthylazine, both weak bases (Table 3). At the pH of the solutions (6.5−6.7) while >99% of both chemicals would be molecular species, cationic species may significantly contribute to the net sorption through (1) an interaction of a positively charged ion with the negative electrostatic potential surface of the aromatic ring of the biochars,[23] (2) carboxylic groups of the organic surface covering of the fresh biochar, and (3) partially being sorbed in the pores of the aged biochar. As the cation is sorbed, a portion of the molecular species is protonated to reestablish the solution equilibrium. The greatest sorption of terbuthylazine is due to a high number of cationic species at the same pH as compare to indaziflam. In addition, dispersive and hydrophobic forces are thought to act in support of this type of association.[29] For pesticides with low water solubility, organic matter provides important sorbent surfaces in soil because phase partitioning is driven by hydrophobic interactions.[30] Cox et al.[31] found a high sorption of simazine in a soil amended with humified organic matter. Sorption values (K_d) of indaziflam and terbuthylazine found in different soil were 27.44−4.86 (Alonso et al., 2011)[32] and 3.7−0.4 (Alister et al., 2011),[33] respectively. These values are around 10 and 300 times higher than the adsorption observed for biochars for indaziflam and terbuthylazine.

The K_d values for the aged biochars (BC-1yr and BC-2yr) decreased for terbuthylazine ∼52% for BC-1yr and ∼63% for BC-2yr with respect to BC-fr because of a decrease of the number of the cationic molecules with the increase of the pH and due to a decrease of the carboxylic groups of the surface of the aged biochars for a natural elimination or a sorption of the unsaturated acid in soil. Conversely, for indaziflam the BC-2yr K_d value increased ∼43% in comparison with BC-fr and BC-1yr. Indaziflam sorption could be more affected for the hydrophobic interactions than terbuthylazine due to its lower solubility, so the increase of the number of available pores from removal of the organic layer aids sorption. As we mentioned above, aging may have altered the qualitative DOC character affecting its chemical affinity.

Nicosulfuron and MCPA are weak acids and at the pH of the solutions (6.7−6.5) >98% of the molecules are anionic. This negatively charged species could create a repulsion to negative groups on the biochar surface, and only the molecular species are sorbed. Cabrera et al.[34] evaluated several biochars made from different feedstocks under different pyrolysis conditions and observed a correlation between MCPA sorption and the biochar surface area, where BC2 biochar with the same characteristic of BC-fr had the smaller SSA value (3.3 m^2/g) and showed the lower K_d value. No sorption of nicosulfuron was observed on the biochars, which may be due to higher repulsion of anionic molecules (>99%). Unlike other sulfonylureas for which adsorption is usually controlled by organic C content, different results show that clay mineralogy plays an important role in nicosulfuron adsorption.[35−37] For MCPA, an increase of anionic molecules is expected at more alkaline conditions, which decreases the sorption of the molecular species and enhances the charge repulsion interaction for BC-1yr and BC-2yr. Oliveira et al. (2001)[38] found K_d values for nicosulfuron of 0.14−1.38 in six Brazilian soils, and Reginato and Koskinen (2008)[39] determined in three American soils and two Brazilian soils values in the range of 0.14−1.81. Lopez Piñeiro (2013)[40] established K_d values of

MCPA in different soils of 0.29−0.43. The increase on MCPA sorption in biochar was 18 times even for this herbicide where biochar surface repulsion happened and only the molecular species are sorbed. Nicosulfuron K_d values are higher in soils than in biochars.

According to the K_d values of biochar in the four herbicides mentioned above, it appears that the sorption depends on the pK_a and hydrophobicity of the chemical. This indicates that the metabolite of indaziflam (fluoroethyldiaminotriazine) would be more polar than the parent compound, which explains the lower values of K_d (0.26−2.95) than the parent and its dependency on the biochar pH explaining the sorption increase in BC-1yr and BC-2yr. Using a theoretical pK_a value for fluoroethyldiaminotriazine of 4.10 (www.chemaxon.com),[18] a higher percentage of cationic molecules and sorption than indaziflam is predicted, so the difference in the observed sorption could be due to the differences in the hydrophobic biochar interactions.

These results indicate that, for a biochar made under high pyrolysis conditions, the sorption of pesticides depends highly on the hydrophobicity of the chemicals. The aging process of the biochars modified the pH of the solution and correspondingly affected the sorption behavior of the herbicides. Even so, the aged biochars are highly effective in adsorbing terbuthylazine and indaziflam, due to its high initial adsorptivity.

Our results indicate that biochar and soil components interaction happened in the surface of the aged biochars and the specific surface area (SSA) increased with this process. For this biochar the major facet of the aging process was loss of the sorbed organic films present on the fresh biochar particle. The adsorption of pesticides is highly dependent not only on biochar characteristics but also on the physicochemical characteristics of the pesticides. For the biochar examined here, aged biochars in soils still remain highly effective at adsorbing pesticides, due to the high initial adsorptivity. Due to the variable nature of biochars, individual characterization of the biochar used as soil amendment is recommended prior to field applications. However, these results do indicate the potential for increased sorption behavior to exist 2 years after the initial biochar application, despite the observed clogging of biochar pore space with soil particles. In addition, it is important to match the target chemical characteristics with the correct biochar properties to optimize the sorption potential of biochar in a particular application.

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Notes
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