

Reduction of Diuron Efficacy with Biochar Amendments

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Abstract—Amending soil with biochar (BC) can change the sorption properties of soil. However, much of this concern is based on studies from BC produced from wood and crop residues. Since BC can be made from a wide range of feedstock, it is important to cover all the aspects of feedstock applied as the soil amendments. Six types of feedstock were examined in this study, including a compost, a papermill waste, a leguminous biomass, two bioenergy crop biomass (switchgrass pellet and 3-years-old shrub willow wood chip), and an oak wood biomass. The raw feedstock was pyrolyzed at 300°C and 500°C, respectively. We investigated how feedstock and pyrolytic temperature affect diuron sorption and used a bioassay of the BC amendments in a loamy soil to test the change of herbicide efficacy. With the pyrolytic temperature increasing, the diuron sorption rate increased. The 300°C BCs developed a slightly higher diuron sorption rate than the raw materials, and a considerable enhancement in diuron sorption rate was observed for all 500°C BCs. Similar to the sorption capacity of the herbicide, the sequence in reducing herbicide efficacy was 500°C BC > 300°C BC > raw material. Hence, our results suggest that the effect of herbicide effectiveness from BC amendments can be reduced when raw material is converted into BC, especially the BC produced at the high temperature (>500°C).

Index Terms—Bioassay, herbicide, NMR, pyrolysis, sorption.

I. INTRODUCTION

Biochar (BC) is the byproduct of the pyrolysis of biomass material. Because of its chemically and biologically stable form, BC can persist in nature for long periods of time. Many researchers have proposed pyrolyzing biomass into BC as a way to divert carbon (C) from a rapid biological C cycle into a slow geological C cycle, and BC soil amendments can thus effectively sequester atmospheric carbon dioxide in soils [1]. Biochar amendments in soils also provide the agronomical benefits of enhancing soil fertility and increasing crop yield [1], [2], and have recently been implemented in many experiments worldwide [3]–[6].

Comparing to other types of organic matter or soils, BC is known to be a strong sorbent for organic compounds. The sorption of hydrophobic organic compounds by BC can be 10-1000 times greater than sorption by other types of organic

matter [7] or even up to 400-2500 times more effective than that of soil [8]. Therefore, amending BC in soil may have potential to cause significant changes in the sorption properties of soils. BC amendments may enhance herbicide sorption and affect the efficacy, movement, and degradation of herbicides in soils [9]–[14]. The alteration of herbicide efficacy could be an important topic for weed control in agricultural management practices because farmers would apply more herbicide to BC-amended soils to compensate for its decreased herbicide efficiency. This activity subsequently increases commercial expenses and environmental risk.

Much concern with the alteration of herbicide efficacy by BC amendment arises from the studies using few type of BC that produced from wood biomass [10], [14] or crop residues [8], [15]. Since BC can be made over a wide range of feedstock, such as the agricultural, municipal, and forestry biomass/wastes [1], [2], it is important to cover all the aspects of feedstock applied as the soil amendments. In addition to the type of feedstock material, the sorptive properties of BC can differ with the pyrolytic process, especially the temperature experienced during combustion because the high pyrolytic temperature (> 500°C) produces BC with more carbonization [16]. Such highly carbonized structure of BC is proposed to be the major sorptive sites for organic compounds [10]. As little information is available to understand the sorption properties for BC over a range of feedstock along with their pyrolytic temperature, it is required to investigate the sorptive properties of BC from different feedstock and pyrolytic temperature.

In this study, six types of feedstock including a compost, a papermill waste, a leguminous biomass, two bioenergy crop biomass (switchgrass pellet and 3-years-old shrub willow wood chip), and an oak wood biomass were examined. The raw feedstock was pyrolyzed at 300 °C and 500 °C, respectively. Our objectives were to investigate how feedstock and pyrolytic temperature affect diuron sorption and to test the change of herbicide efficacy using a bioassay of the BC amendments in a loamy soil.

II. MATERIALS AND METHODS

A. Feedstock

Six types of feedstock including a compost, a papermill waste, a leguminous biomass, two bioenergy crop biomass (switchgrass pellet and three-year-old shrub willow wood chip), and an oak wood biomass were included in this study.

The compost raw material was the commercial compost made by the spent mushroom compost and swine manure mixtures and composted under the indoor windrow turner for six months. Organic matter content was labelled at 60% along

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with 2.5% N, 4.5% P₂O₅, and 0.8% K₂O. Papermill waste was collected from Chunghua Paper Co., Ltd, located in Hualien County, Taiwan, which produce 150,000 tons paper per years. The feedstock was the mixtures of waste wood bark chip and waste sludge.

Leguminous plant material (*Sesbania roxburghii*) was collected from the Taoyuan District Agricultural Research and Extension Station in Northern Taiwan. The *Sesbania* is one of the most common types of leguminous green manure in Taiwan, and is also popular in other tropical and subtropical regions (Palm and Sanchez, 1991). The *Sesbania* was harvested 50 d after planting. The plant was at the stage of early blooming, and the mean height was 120 cm.

Bioenergy crop biomass included a switchgrass pellet and a shrub willow wood chip. Switchgrass (*Panicum virgatum*) and shrub willow (*Salix spp.*) were planted in the Fingers Lakes regions, New York, USA. Both crops were planted intended for the renewable bioenergy. Mature switchgrass biomass was harvested in fall and pelletized into a 0.7 cm wide pellet. Shrub willow was harvested at three-year-old, and cut into a 3 cm long and 1 cm wide wood chip.

Oak wood was purchased from the commercial red oak (*Quercus rubra*) firewood. Original wood log was split into a 30 cm long and 10 cm wide wood chunk. We further cut the wood chunk into 1 cm cube before pyrolysis.

B. Pyrolytic Process

Except of papermill waste that was pyrolyzed at 350 °C and 500 °C, the feedstock was pyrolyzed at 300 °C and 500 °C, respectively. Approximately 30 g of dry raw material was packed into a 300 mL stainless steel container, loosely sealed with a lid, and pyrolyzed inside a muffle furnace under anoxic condition. The temperature was increased to the desired temperature for 30 min and held at the desired temperature for 2 h. The produced BC were ground to pass through a 1 mm sieve for the following analyses. The unconverted raw material was ground as well and used as an unconverted control for comparison with the converted BC samples.

C. Properties of Raw Material and BC

To determine the content of C, N and H contents of the raw material and converted BC, the samples were further ground using a ball grinder (Oscillating Mill MM400 by Retsch, PA, USA) and measured using an elemental analyzer (Perkin Elmer 2200, MA, USA) after removing the inorganic C with 0.1N HCl. The ash content was determined using the loss on ignition method, in which the samples were put in a crucible and ignited at 550 °C for 2 h. The C, N, H, and ash contents of the raw material and BC were presented on a dry basis. The pH values of the raw material and BC were measured in 1:20 w/v raw material- or biochar-water mixtures after shaking for 1 h. The specific surface area of BCs was determined from N₂ adsorption isotherms at 77 K using an ASAP 2200 system (Micromeritics, Norcross, GA, USA). Prior to adsorption experiments, the BC and soil samples were degassed at 378 K under a pressure of < 10⁻⁴ Pa for at least 15 h. Applying the BET model to the N₂ adsorption isotherms afforded the specific surface area (S_{BET}).

The chemical structures of the raw material and converted BC were examined using a solid-state ¹³C NMR spectrometer.

The solid-state ¹³C NMR spectra were measured on a Bruker Avance III 400 NMR spectrometer operating at a ¹³C frequency of 100 MHz with standard ramp cross-polarization magic angle spinning (CPMAS) spectroscopy. The powder sample was packed in a 4 mm diameter zirconia rotor and spun at a speed of 10 kHz. A contact time of 3 ms and a pulse delay of 1 s were used for all spectra, and 10,000 scans were accumulated. The chemical shift regions assigned to the major types of C were 0-45 ppm for alky C, 45-110 ppm for O-alkyl C, 110-145 ppm for aryl C, 145-165 ppm for O-aryl C, and 165-190 ppm for carboxyl C [17], [18].

D. Diuron Sorption Measurements

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, >98% purity), a commonly used non-selective herbicide for pre-emergent and post-emergent weed control, was used as the sorbate to evaluate the herbicide sorption properties on BCs. Two sets of measurements were made. The first set employed a single solution concentration at 20 mg L⁻¹ for determining sorption rate of each raw material and BC. The second set used 5 solution concentrations (2.5, 5, 10, 15, 20 mg L⁻¹) to determine sorption isotherms, but were only conducted in the switchgrass pellet, willow wood chip, and oak wood raw material and their BCs. In both sets, the sorption experiments were conducted using the batch equilibrium technique in duplicate. A BC sample weighing 0.01 g was suspended in 10 mL aliquots of aqueous sorbent solution containing an initial diuron concentration at 20 mg L⁻¹ or ranging from 2.5 to 20 mg L⁻¹. The aqueous phases received 200 mg L⁻¹ NaN₃ to inhibit aerobic microbial degradation. The suspensions were shaken on a rotary shaker at 120 rpm shaker at 27 °C in the dark for 24 h. Preliminary kinetic experiments had shown that the sorption of diuron reached equilibrium within 24 h. The solution was then filtered using a 0.45-μm membrane (PALL, Millipore Millex-GS; Millipore, Billerica, MA). An aliquot of the filtrate was transferred to an amber vial and analyzed for the remaining amount of each sorbate. Diuron was quantified using high-performance liquid chromatography (HPLC) with a Waters X-Bridge RP-18 TM column and a Water Alliance 2695 series. The mobile phase was 70:30 MeOH: H₂O (v:v) at a flow of 1 mL min⁻¹, and the sample injection volume was 50 μL. The UV wavelength used to detect diuron and atrazine was 254 nm.

Because of the minimal sorption of the vials and the apparent lack of biodegradation, the amount of sorbed diuron (Q_e , mg g⁻¹) was calculated based on the difference between the equilibrium concentration and the initial concentration, as Eq. (1) shows:

$$Q_e = (C_o - C_e)[V/m] \quad (1)$$

The terms Q_e is the amount of sorbed diuron; C_o and C_e represent the initial and equilibrium concentrations of diuron in the aqueous solution; V is the solution volume; and m is the weight of the raw material or BC samples. All measurements were conducted in duplicate with a variation generally < 5%, and the average data were reported. The sorption isotherm was fitted with the commonly used Freundlich equations, given as Eqs. (2).

$$Q_e = K_f C_e^n \quad (2)$$

The term Q_e is the amount of sorbed diuron. C_e is the equilibrium concentration. K_f ($[(\text{mg}/\text{g}) (\text{mg}/\text{L})^n]$) and n (dimensionless) are the Freundlich parameters of the corresponding system.

E. Biological Assays

Two diuron levels of 1.5 and 6 mg kg⁻¹ soil were used to assess the effects of herbicide on the growth of ryegrass in soil with and without raw material or BC amendments. The 1.5 mg kg⁻¹ soil was at the low end of the recommended use range, and the 6 mg kg⁻¹ soil was at the high end of the recommended use range. Amendments of raw material, 300°C BCs, and 500°C BCs were added to the soil at rates of 1%, respectively. A cultivated soil collected from Taoyung County, Taiwan, at a depth of 0 to 15 cm served as the control soil [19]. This cultivated soil is developed in an alluvial fan terrace that was derived from Quarternary-aged materials and classified as a Typic Plinthaquic Paleudalf with loam texture and 1.4 % soil organic carbon content.

The diuron was prepared at 60 and 240 mg L⁻¹ solutions in acetone. Five milliliters of diuron solution were added to 200 g soil with and without BC amendments to achieve diuron levels of 0 (acetone with no diuron), 1.5 and 6 mg kg⁻¹ soil. The soil was thoroughly mixed and placed into a round plastic pot measuring 10 cm in width and 8 cm in height. For each pot, ten pregerminated ryegrass seeds with extended radicles and hypocotyls measuring 5 - 15 mm in length were placed evenly on the surface of the soil. The pots were then placed in a completely randomized block design in a greenhouse. The growth of the ryegrass seeds was daily monitored and maintained with adequate water throughout the experiment. The mortality of the ryegrass seeds that influenced by diuron was visually observed starting after 7 days, and the survival rate (no injury) was evaluated after 21 days. A 100% survival rate indicated no effect of the herbicides, and a 0% survival rate indicated complete effect of herbicides. Except of papermill waste that was pyrolyzed at 350 °C and 500 °C, the feedstock was pyrolyzed at 300 °C and 500 °C, respectively.

III. RESULTS

A. Composition and Structure of Raw Material and BCs

The physical/chemical characteristics of raw material and BCs are tabulated in Table I. Among the selected raw materials, the compost and papermill waste showed the highest ash but least C contents. The values were much higher/or less than other biomass-based raw materials. High N content was found in the papermill waste and the *sesbania* biomass. A higher pH value was found in the compost and papermill waste that showed the pH values at 6.9 and 7.0, respectively, compared to other raw materials that had pH values less than 5.5.

During the pyrolytical process, the C content rose as the pyrolytical temperature increased. By contrast, N and H contents declined as the pyrolytical temperature increased. These changes in elemental composition were reflected in changes in elemental ratios. The C/N ratio rose with the

pyrolytical temperature, whereas the H/C ratios decreased with the pyrolytical temperature. The ash content and pH value increased with the pyrolytical temperature (Table I).

The specific surface area showed a significantly low values < 3.0 m² g⁻¹ for all raw material and 300°C BCs. Higher specific surface area were found in the 500°C BCs, especially for the willow wood chip and oak wood 500°C BC that had specific surface area at 101.8 and 227.7 m² g⁻¹, respectively.

The NMR spectra indicated the substantial alteration of chemical structure through pyrolysis (Fig. 1). The raw materials were mainly dominated with o-alkyl C, representing the cellulose and hemicellulose structure. With the pyrolytic process, peaks at 50-110 ppm (carbohydrates) and 160-190 ppm (carboxyl) were declined and peaks at 0-50 ppm (alkyl-C, only for 300°C BC) and 110-160 ppm (aryl-C or aromatic C) were developed. A dominant peak at 130 ppm was observed for all BC pyrolyzed at 500°C, indicating chemical structure in the 500°C BCs was primarily aromatic-C.

B. Sorption to Diuron

The sorption of diuron at a single concentration solution by raw materials and BCs is shown in Table I. Except the compost raw material that had diuron sorption rate at 1.4 mg g⁻¹, other raw materials displayed the diuron sorption rate below 0.9 mg g⁻¹. The negative value in the papermill waste raw material could be due the release of native organic chemicals during sorption experiment.

With the pyrolytic process, the diuron sorption rate increased. The 300°C BCs developed a higher diuron sorption rate than the raw materials, and a considerable enhancement in diuron sorption rate was further observed for all 500°C BCs. Particularly, the 500°C BCs from willow wood chip and oak wood displayed the highest diuron sorption rate at 10.9 and 11.6 mg g⁻¹, respectively.

Sorption isotherms on switchgrass, willow wood chip and oak wood raw materials and their 300°C and 500°C BCs further corroborated previous results (Fig. 2). Over the range of equilibrium solution concentration, the diuron sorption rate on the 500°C BCs was approximately one order of magnitude greater than raw feedback materials and 300°C BCs. The curves of sorption isotherms were well fit to the Freundlich model (Table II), and the model indicated that the diuron sorption isotherm on the 500°C BCs was extremely non-linear, with exponent n value between 0.17 and 0.20, compared with exponent n values of between 0.39 and 0.55 and between 0.83 and 0.92 for the 300°C BCs and raw materials, respectively, which indicated a more linear-like sorption isotherm.

C. Bioassays

Compared to the soil without amendment that showed non ryegrass seeds survival under diuron application, the amendments of raw organic matter, 300°C BCs, and 500°C BCs to soils enhanced the survival rate of ryegrass, a sign of the reduction of diuron efficacy (Table III). At the low end of diuron application (1.5 mg kg⁻¹), the average survival rate for raw material amendment was 50% and increased to 80% and 93% for 300°C BC and 500°C BCs, respectively. At the high end of diuron does (6 mg kg⁻¹), much less survival rate was observed. The amendments of raw material showed <10% ryegrass seed survival rates; however, the reduction of diuron

efficacy was still apparent for 500°C BCs. Particularly, the amendments of compost, willow, and oak wood 500°C displayed >65% survival rates.

TABLE I: CHARACTERISTICS FOR RAW MATERIAL, 300°C BIOCHAR, AND 500°C BIOCHAR OF COMPOST, PAPERMILL WASTE, *SESBANIA* BIOMASS, SWITCHGRASS PELLET, WILLOW WOOD CHIPS, AND OAK WOOD

	Yield %	pH	C N H			Ash	Surf. area m ² g ⁻¹	Diu. ^a mg g ⁻¹
			mg g ⁻¹ (dry mass basis)					
Compost								
Raw	-	6.9	172	24	38	452	0.3	1.4
300°C	ND	7.7	207	20	28	488	7.7	2.4
500°C	ND	8.8	228	13	13	604	12.9	2.9
Papermill waste								
Raw	-	7.0	295	52	26	319	0.3	-2.1
350°C	ND	7.2	323	47	40	352	1.5	2.3
500°C	ND	7.6	359	44	32	503	7.3	2.5
Sesbania biomass								
Raw	-	5.2	487	48	53	100	1.2	0.2
300°C	60	7.1	587	41	28	150	2.7	4.7
500°C	35	10.7	595	24	8	250	17.5	2.8
Switchgrass pellet								
Raw	-	5.5	434	13	87	65	1.1	0.9
300°C	47	7.0	679	8	59	79	1.1	1.3
500°C	27	10.0	834	10	41	116	85.5	5.9
Willow wood chips								
Raw	-	5.1	449	5	91	24	0.7	0.4
300°C	62	6.2	571	2	62	31	1.2	2.9
500°C	26	8.7	817	3	41	65	101	10.9
Oak wood								
Raw	-	4.5	462	1	85	18	0.3	0.9
300°C	58	4.7	601	1	58	20	1.0	2.3
500°C	25	8.2	827	2	40	20	227	11.6

^aDiuron sorption at initial concentration at 20 mg L⁻¹

TABLE II: FREUNDLICH PARAMETERS FOR SORPTION ISOTHERM OF DIURON ON RAW MATERIAL, 300°C BIOCHAR, AND 500°C BIOCHAR OF SWITCHGRASS PELLET, WILLOW WOOD CHIPS, AND OAK WOOD

	K _f	n	R ²
Switchgrass pellet			
Raw	0.08	0.83	0.99
300°C	0.48	0.55	0.95
500°C	3.43	0.20	0.99
Willow wood chips			
Raw	0.09	0.89	0.99
300°C	0.84	0.45	0.97
500°C	7.03	0.16	0.99
Oak wood			
Raw	0.09	0.92	0.95
300°C	0.80	0.39	0.94
500°C	8.92	0.17	0.99

IV. DISCUSSION AND CONCLUSION

A. Characterization of Raw Material and Biochar

Among the selected raw materials, the compost and papermill waste showed the highest ash content and pH values, which may reflect the additions of alkaline minerals in the spent mushroom wastes and papermill processes or the loss of labile organic matter during compost or management [20]. After pyrolysis, higher C content and lower H contents were observed on all BC samples which were consistent with previous studies [16], [17], [21]. The results reflect the thermal dehydration (loss of H₂O), demethylation (loss of CH₃), and decarboxylation (loss of CO₂) during the pyrolytic process. The increasing ash content with pyrolytic temperature suggests that mineral ash is selectively preserved toward gaseous and liquid products. Because the ash contains

mostly bases such as Ca, Mg, and K, high ash content in the 300°C BC and 500°C BCs is responsible for their high pH values (Table I) [22].

TABLE III: SURVIVAL RATE (%) OF RYEGRASS SEEDS IN SOIL UNDER DIURON DOSES (0, 1.5 AND 6 MG/KG) AND BCs AMENDMENTS 3 WEEKS AFTER PLANTING

	Rate of diuron (mg/kg)			Rate of diuron (mg/kg)			
	0	1.5	6	0	1.5	6	
Control^a	100	0	0				
Compost							
Raw	100	90	10	Switchgrass pellet			
300°C	100	95	30	Raw	100	62	5
500°C	100	100	65	300°C	100	62	33
				500°C	100	84	53
Papermill waste							
Raw	100	40	5	Willow wood chips			
350°C	100	80	25	Raw	100	50	10
500°C	100	100	30	300°C	100	85	40
				500°C	100	95	80
Sesbania							
Raw	100	23	3	Oak wood			
300°C	100	60	27	Raw	100	40	5
500°C	87	88	53	300°C	100	95	55
				500°C	100	95	65

^aControl soil without amendment

The decreases in O-alkyl C and carboxylic C and the increase in aromatic C with increasing pyrolytic temperature was consistent with previous studies [16], [17], [21]. The alkyl C structure of the 300°C BCs samples resulted from the alkyl C condensation during thermal degradation of the biomass, which was also detected in other biochars produced at lower pyrolytic temperatures [16], [17]. At higher pyrolytic temperatures, the alkyl C structure is destroyed and a condensed aromatic C structure is formed.

B. Sorption of Diuron

The higher sorption capacity of diuron found on 500°C BC is in agreement with studies using the carbonaceous materials [7], [8]. Such high sorption capabilities of diuron on BCs corresponded well with their high aromaticity, in which the aromatic structures grant BC surface to be hydrophobic and therefore enhance diuron sorption through hydrophobic interaction on BC surface. The formation of aromatic C also helps delocalize electrons of the basal plane of the BC surface and enhances the π - π interaction between the aromatic ring of diuron molecule and the basal planes of the BC surface [23], [24]. In addition, the increase in surface area may be another reason for the higher sorption capacity of diuron on BCs, where the surface area was significantly increased from raw material to 500°C BCs (Table I) [10]. Among the raw materials, the compost sample had the highest diuron sorption capacity, which may be due to the formation of humus during composting process that has higher sorption capacity than that of the fresh biomass material [25].

The 500°C BCs also exhibit a high nonlinearity. It is because high sorption capacity exists at the lower equilibrium concentration and bend the sorption isotherm toward a nonlinear shape [26], [27]. By contrast, the sorption to the raw material tended to be linear, showing a partition model rather than the sorption [7]. The 300°C BC displayed an intermediate sorptive properties between nonlinear and linear, which the sorption could be contributed by both partition and sorption.

Overall, the results are in agreement with many studies demonstrating that the BC fraction of soils/sediments with a higher BC fraction possesses stronger sorption capacity and

sorption nonlinearity than the non-BC fraction [7], [8], [28], [29]. The high sorption capability of BC is generally due to its relatively rigid, planar and aromatic surface, whereas the non-BC material is less condensed and consists of more polyanionic macromolecules [7]. Under low temperature (300°C) pyrolysis, the sorption capacity and sorption nonlinearity of pyrolysis can be greatly altered.

soils effectively reduce herbicide efficiency [9]-[14], [30]. Similar to the sorption capacity of the herbicide, the sequence in reducing herbicide efficiency was 500°C BC > 300°C BC > raw material. Hence, the effect of herbicide effectiveness from BC amendments can be reduced when raw material is converted into BC, especially the BC produced at high temperature (>500°C).

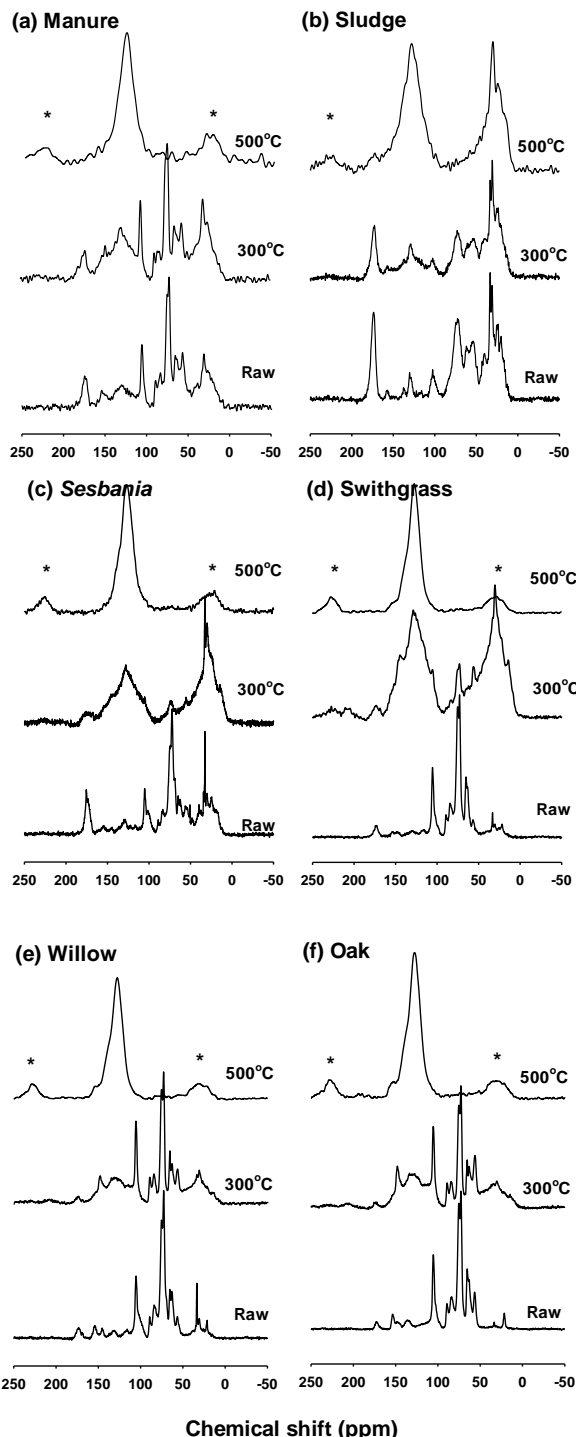


Fig. 1. Solid state ^{13}C NMR spectra for raw material, 300°C biochar, and 500°C biochar of (a) compost, (b) papermill waste, (c) *sesbania* biomass, (d) swithgrass pellet, (e) willow wood chips, and (f) oak wood. The asterisk refers to spinning side bands at ca. 100 ppm from the dominant aromatic C resonance at 129 ppm.

C. Reduction of Diuron Efficacy

The results of the bioassay in herbicide experiments and the results of previous studies suggest that BC amendments in

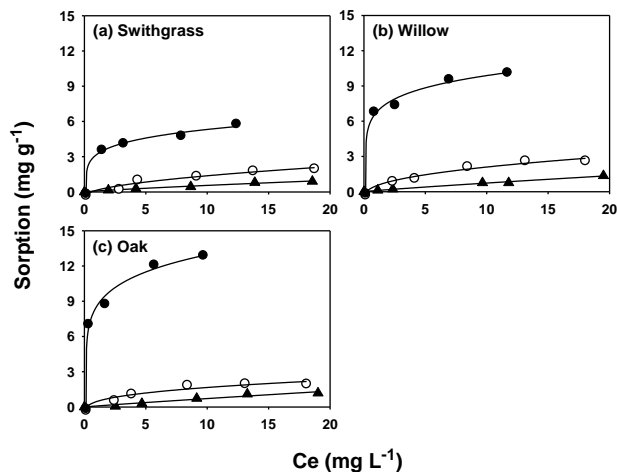


Fig. 2. Sorption isotherm for diuron on raw material, 300°C biochar, and 500°C biochar of (a) swithgrass pellet, (b) willow wood chips, and (c) oak wood.

Along with its recalcitrance in environments, the BC amendment may have a long term effect on herbicide efficacy. Although Cheng *et al.* (2014) [19] proposed that the effectiveness of herbicide efficacy from BC may decrease with time, the old BC samples still exist a higher sorption rate than non-BC organic matter [13], [14], [30]-[32]. However, because BC may be amended periodically in agricultural applications, the aging process of BC in reducing herbicide inefficacy would become less important.

Although BC amendments inactivate herbicide efficiency, they may have the positive outcome in reducing the risk of environmental contamination and human exposure to contaminants. For example, the amendment of contaminated sediments with BC has been proposed as a management method to immobilize organic contaminants and biological accumulation in benthic organisms [33].

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