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Effects of biochars on the fate of acetochlor in soil and on its uptake in maize seedling[☆]

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ABSTRACT

Biochar (BC) can alter the fate and bioavailability of pesticides in soil. In this study, the effects of three types of BCs (made of crofton weed, wood chips and rice hull) on the sorption of acetochlor, a common herbicide, were investigated. The acetochlor sorption constants (K_f value) were 309.96 $\mu g^{1-n}L^{n}/kg$ (biochars made of ricehull, BCR), 3.54 $\mu g^{1-n}L^{n}/kg$ (biochars made of crofton weed, BCH) and 2.27 $\mu g^{1-n}L^{n}/kg$ (biochars made of wood chips, BCW). The persistence of acetochlor was 8 times greater when 1% BCR was added to the soil. Moreover, the half-life of acetochlor increased with increasing amounts of BC in the soil. The soil was amended with BCH (made of crofton weed) for two different aging period (10 d and 20 d) to evaluate the effects of aged BC on acetochlor accumulation in maize seedlings (*Zea mays L*). Amendment with 10 d-aged BCH in soil decreased the bioaccumulation of acetochlor. However, the concentrations and bioconcentration factors in maize cultivated in 20 d-aged BCH-amended soils were significantly higher than those in soil with no BCH amendments and with 10 d-aged BCH amendments. These results imply that BC aged in soil for a long period can increase the bioaccumulation of acetochlor in plants and the influences of BC on environmental risks of pesticides must be further clarified.

1. Introduction

Overuse of pesticides in agriculture, especially herbicides, has led to contamination in environmental media (Coquillé et al., 2015; Saha et al., 2012). Acetochlor is a member of the class of chloroacetanilide herbicides, and it is a common pre-emergent herbicide for a variety of crops such as corn, peanut, soybean and cotton. It is one of the most widely used herbicides in China with an annual use of over 10,000 tons (Li et al., 2015). Because of its widespread application, acetochlor is frequently detected in both water and soil. In aquatic environments, some studies reported that relatively high concentrations (10–100 ng/L) of acetochlor were detected in drinking water sources and streams in the midwestern United States (Hladik et al., 2008; Scribner et al., 2000). In addition, in soil environments, 0.03–709.37 μg/kg of acetochlor was detected in the riparian soils of northeastern China, and residue concentrations in soils are 54.76 μg/kg for maize land (Sun et al., 2011; Sun et al., 2013). . Furthermore, acetochlor has potential reproductive, neurological and endocrine toxicity to environmental animals (Helbing et al., 2006; Liu et al., 2006; Veldhoen, 2002). Considering the potential genetic toxicity and adverse effects to human and environmental organisms, the U.S. Environmental Protection Agency has classified acetochlor as a B-2 carcinogen (U.S. EPA). Most toxicity tests have focused on aquatic organisms, and little research has been conducted to investigate the uptake of acetochlor by plants. In fact, the bioaccumulation of acetochlor in plants, especially crops, can cause potential risks in the food chain (López-Piñeiro et al., 2013). Therefore, it is important to develop countermeasures against the pesticide-contaminated soils to provide safe

Abbreviations: BCH, biochar produced from crofton weed (herb); BCR, biochar produced from rice hull; BCW, biochar produced from wood; UPLC-MS/MS, ultra-high-performance liquid chromatography-tandem mass spectrometry; QuEChERS, quick, easy, cheap, effective, rugged and safe; BSAF, biota-to-soil accumulation factors; BC, biochar, combustion products of biomass under limited oxygen conditions; SSA, Specific surface area.

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agricultural products.

Biochars (BCs) are combustion products of biomass under limited oxygen conditions (Ahmad et al., 2014; Lundberg and Sundqvist, 2011). Because of their porous structure and huge specific surface area, BC have been reported to increase the sequestration of pollutants in soil. And this increased sequestration can result in the reduction of bioavailable fractions of persistent organic pollutants and pesticides (Gong et al., 2016; Jie et al., 2016; Oleszczuk et al., 2012; Wang et al., 2013). For plants, Yu et al. reported that red gum wood BC amendment in soil significantly decrease the residues of chlorpyrifos and carbofuran in spring onion (Yu et al., 2009); Yang et al. showed that cotton straw BC amendment reduced the total residue levels of chlorpyrifos and fipronil in Chinese chives (Yang et al., 2010). However, the above studies have been conducted on soils amended with fresh BC and the BC may become ineffective in the sorption of herbicides with time in soil (Martin et al., 2012). It's not clear how aged BC impact on the bioavailability of herbicides in plants. Mutual impacts can exist between plants and BC over time; plant roots could grow into and break the pore structure of the biochars, and the mineralization of biochars in soils can be accelerated by root exudates (Hamer et al., 2004; Joseph et al., 2010). Therefore, it is vital to understand the effects of BC on the bioavailability of acetochlor in plants.

Given this background, the aims of this study were (1) to evaluate the effects of different kinds of BC on the sorption of acetochlor in soil; (2) to evaluate the effects of different kinds and quantities of BC on the acetochlor degradation in soils; and (3) to investigate the effects of BC with different aging times on the bioavailability and bioaccumulation of acetochlor in plants.

2. Materials and methods

2.1. Reagents and chemicals

Analytical-grade acetochlor (95.2% chemical purity) was obtained from Green Agricultural Science and Technology Group Co. Ltd. (Beijing, China). The stock solution of acetochlor (10000 mg/L) was prepared by dissolving the weighed herbicide in high-performance liquid chromatography- (HPLC-) grade acetonitrile (>98.0% purity). Analytical-grade sodium azide, calcium chloride and all solvents of HPLC-grade were obtained from Beihua Finechemicals Co. (Beijing, China). The maize seeds *(Zea mays L.)* were bought from the Chinese Academy of Agricultural Sciences (Beijing, China).

2.2. Biochar and soils

2.2.1. Soil

An agricultural soil sample without detectable acetochlor was collected from a planting base of the Chinese Academy of Agricultural Sciences in Langfang, Hebei province of China. The soil was sampled from the upper 10 cm and passed through a 2 mm sieve for the degradation and bioaccumulation experiment. The soil was air-dried and stored at 4 °C for approximately two months before use. The soil physico-chemical properties were analyzed by conventional standard procedures (Lu, 2000), and the data are shown in Table S1 (Supplementary Material).

2.2.2. Biochars

Three kinds of BC (BCR, BCH and BCW) were used in this study. BCR was produced from rice hull; we obtained the BCR from Zhejiang Biochar Engineering Technology Research Center. BCH and BCW were produced in our laboratory. BCH was produced from an invasive weed, crofton weed (*Eupatorium adenophorum Spreng*). BCW was produced from mixed hardwoods included pine (*Pinus*) and poplar (*Populus L*).

Briefly, air-dried raw materials (crofton weed or wood chips) were rinsed and then pyrolyzed at 500 °C under limited oxygen in a muffle furnace. The furnace was first purged with nitrogen for 10 min, heated to 500 °C at a heating rate of 15 °C/min and held for 4 h under a nitrogen atmosphere. The obtained samples were rinsed with deionized water to remove excessive water-soluble inorganics and dried at 80 °C for 24 h (Chen and Huang, 2011; Gong et al., 2016). Then, the prepared BC was ground to a fine powder using a grinder and passed through a 2 mm sieve. In our study, the BC made from crofton weed was denoted BCH, the BC made from wood chips was denoted BCW and the BC made from rice hull was denoted BCR. The physico-chemical properties of the three BCs are listed in Table 1. The specific surface area (SSA) of the biochars was determined using the V-Sorb 2800 P surface area and pore distribution analyzer (Gold APP Instruments Corporation, China). The elemental composition was measured using a CHN element analyzer (vario PYRO cube, Elementar Analysensysteme GmbH, Germany).

2.3. Sorption experiments

To compare the sorption capacity of the three types of BC, the acetochlor sorption experiments were conducted using the batch equilibration technique described in many other studies (Zheng et al., 2010). The detailed sorption experiments are introduced in Supplementary Material Section 1.

2.4. Acetochlor degradation

2.4.1. Acetochlor degradation in soils with different types of BC

Before the degradation experiment, the soil was equilibrated at 25 °C without light for a week with its water content increased to 30% of the maximum water-holding capacity. Taking 1% BCH soil as an example, we weighed 1980 g soil into a white plate, 20 g BCH was spiked with the control soil (1% application rate), and then, the soil was mixed thoroughly. After the amendment, four BC treatments were used in degradation experiments: (i) control soil without BC; (ii) the soil containing 1% BCH; (iii) soil containing 1% BCW; and (iv) soil containing 1% BCR; Each soil used in this experiment was spiked with acetochlor dissolved in acetone to achieve a concentration of 10 mg/kg. Briefly, a small portion (100 g) of each type of soil described above was spiked with 1 mL stock solution of acetochlor (10000 mg/L dissolved in acetone). After solvent evaporation, another portion (400 g) was added to the spiked soil. Then, the whole 500 g of soil was mixed thoroughly, which resulted in an initial concentration of 10 mg/kg. A relatively

Table 1
The physical and chemical properties of three kinds of biochars.

BC	feedstock	SSA (m^2/g)	Pore volume (cm^3/g)	C (%)	H (%)	N (%)	Ca (%)	K (%)	pH
BCH	Crofton weed (herb)	11.40	0.02	68.5	2.53	1.04	2.03	2.93	9.83
BCW	Hardwood	14.14	0.02	41.67	1.42	1.37	6.1	2.04	9.93
BCR	Rice hull	54.95	0.04	23.4	4.03	0.4	0.16	0.6	7.34