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Influence of Biochars on Plant Uptake and Dissipation of Two Pesticides in an Agricultural Soil

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This study investigated the influence of two types of biochars on the bioavailability of two soil-applied insecticides (chlorpyrifos and fipronil) to Chinese chives (*Allium tuberosum*) and dissipation of the pesticides in the biochar-amended soils. The biochars (BC450 and BC850) prepared from the burning of cotton (*Gossypium* spp.) straw chips at two different temperatures (450 and 850 °C) were thoroughly mixed into a soil to achieve 0, 0.1, 0.5, and 1% by soil dry weight. Chinese chives were grown for 5 weeks in the biochar-amended soils spiked with 50 mg kg^{-1} of each pesticide. The loss of both pesticides in soils decreased significantly with increasing amounts of the biochars in the soil. After 35 days of incubation, 58−68% of the pesticides was lost from the control soil, whereas in the soil amended with 1.0% BC850 only 34% of chlorpyrifos and 32% of fipronil were dissipated. More losses of the pesticides were found in the soils with plants due to plant uptake and enhanced microbial degradation. Despite greater persistence of the two pesticide residues in the biochar-amended soils, plant uptake of the two pesticides from the amended soils decreased markedly with increasing biochar content in the soil. With the amendment of 1% of BC850 in the soil, the total chlorpyrifos and fipronil residues in plant biomass decreased to 19 and 48% of those in the control treatment, respectively. Thus, biochar BC850 was found to be effective in reducing the bioavailability of both pesticides from the soil. Biochar could be applied to sequester pesticide residues in contaminated soils and to reduce plant uptake.

KEYWORDS: Pesticide; black carbon; bioavailability; plant uptake; degradation

INTRODUCTION

Soil contamination has become an increasing environmental problem as a result of anthropogenic activities (*1*−*4*). Pesticide residues are one group of contaminants in soils that have received great attention in the past decades (*5*, *6*). With heavy use of pesticides in modern agricultural production, pesticides have been frequently detected in agricultural soils (*1*, *2*, *5*−*7*). Pesticide residues in soils may enter vegetables cultivated on the contaminated soils and cause a great threat to the produce quality and human health (*8*). Plant uptake of organic compounds is an important process in the consideration of the risks associated with land contamination, the role of vegetation in the global cycling of persistent organic pollutants, and the potential for industrial discharges to contaminate the human food chain (*9*−*12*). Remedial actions are needed to reduce the translocation and accumulation of pesticides in plants to obtain safe agricultural products from contaminated soils.

Black carbon (BC) is a product of the weathering of graphitic carbon in rocks and of incomplete combustion of fossil fuels and vegetation, which has various types such as soot, char, charcoal, and biochar (*13*, *14*). Biochar refers to those carbonized residues that are produced from incomplete combustion of biomass and have nano- to mesoporous structures with high specific surface areas (SSA) (*14*). Biochar has been known to act as a super-sorbent for organic contaminants in soil/sediment (*15*−*17*). Aging of the biochar in the soil for up to 12 months did not substantially reduce its adsorptivity for diuron, indicating its refractory surface properties (*18*). Yu et al. (*19*) have found that the sorption and desorption behaviors of diuron are strongly influenced by the presence of biochars in soil, and they also noted an increase in sorption−desorption hysteresis, suggesting that sorption by biochar can facilitate sequestrations due to its nanoporosity.

Adsorption to BC can render hazardous organic contaminants in soils and sediments less available to organisms and hinder their off-site transport into receiving environments (*20*). There are a number of studies that have reported decreased bioavailability to benthic invertebrates of organic contaminants in sediments due to the presence of BC (*21*−*25*) and decreased plant uptake of pesticides from soils amended with activated carbon or biochar (*26*, *27*).

Biochars are widely generated in situ by field burning of vegetation, a common postharvest agricultural practice for disposal of crop residues, weed control, and immediate land clearing and land-use change (*28*). It has been reported that more than 600

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million tons of straws are produced per year in China, more than 50% of which are burned for the purposes of quick waste disposal and immediate land clearing (*29*−*31*). Such agricultural practices have contributed to the high level of biochar found in some soils (*13*, *32*−*34*), which may strongly influence the environmental fate and behavior of organic contaminants in soils. Although enhanced sorption of organic contaminants (including pesticides) and increased sorptive nonlinearity for soils containing BC have recently become research topics of interest, the review of the available literature shows that there is insufficient information on the influence of crop residue derived biochars on plant uptake of organic contaminants such as pesticides in soil.

The objectives of the present study were (i) to investigate the potential of soil amendments with cotton straw derived biochar at different concentrations to reduce the uptake of the pesticides chlorpyrifos and fipronil by Chinese chive plants (*Allium tuberosum*) from soil and (ii) to compare the effects of the two types of biochars on their relative potential for sequestration and effect on dissipation (degradation and/or sequestration) of the pesticides in soil. The two pesticides are commonly applied to the soil to treat root rotting of Chinese chives in China.

EXPERIMENTAL PRODUCEDURES

Biochars. The biochars were produced from cotton (*Gossypium* spp.) straws at two different temperatures (450 and 850 °C) as described previously (*19*). Briefly, air-dried cotton straw chips were pyrolyzed at 450 and 850 °C under limited oxygen in a muffle furnace to make two types of biochars (referred to as BC450 and BC850). The straw was cut into pieces of about 2 cm in length and placed into porcelain crucibles with lids. The straw materials were burned in a muffle furnace (SX-4-10, Jiangsu, China). The specific temperature programs were maintained as follows: 2 h at 450 °C for BC450 and 1 h at 850 °C for BC850, respectively. Subsequently, the muffle furnace cooled naturally. Finally, the prepared biochar materials were ground into powder on a disk-rotating mill and passed through a 280 mesh sieve. All prepared biochar materials were stored in a dryer until use. The specific surface area (SSA) and pore size distribution of the two biochars were evaluated using the Brunauer, Emmett, and Teller (BET) nitrogen adsorption technique (*35*) at 77 K, using an automated manometric gas adsorption apparatus (*36*) and ultrahigh-purity gaseous nitrogen (99.999%). Briefly, nitrogen adsorption−desorption isotherms were measured on a Micromeritics ASAP 2020 analyzer (Micromeritics Co., Norcross, GA) at liquid nitrogen temperature. The samples were outgassed at 250 °C for 12 h at the degas port and then transferred to the analysis port for the measurement. The SSA of each biochar was calculated by using the BET method, and the total pore volume was evaluated from nitrogen uptake at a relative pressure of about 0.99. Micropore and mesopore volumes were estimated by the *t*-plot methods and the Barrett−Johner−Halendar (BJH) methods, respectively.

The SSAs of BC850 and BC450 were 158.8 and 3.9 $m^2 g^{-1}$, respectively. BC850 was a microporous material, with the volume of specific microspore, volume of total specific pore, and microporosity being 0.036 $cm^3 g^{-1}$, 0.095 $cm^3 g^{-1}$, and 37.9%, respectively. BC450 was a mesoporous material with the volume of total specific pore of about 0.008 $cm^3 g^{-1}$.

Soil and Pesticides. The fresh soil used in the experiment was collected from the surface soil layer (0−20 cm) in a vegetable-growing area of Guangzhou, China. The soil belonged to clay loam texture, which contained 1.35% organic materials, 27.9% sand, 38.5% silt, and 33.6% clay. The soil had a pH of 4.01 (in 0.01 M $CaCl_2$/water/soil = 5:1, v/w), a maximum water-holding capacity (MWHC) of 48% (v/v), and a cation exchange capacity of 7.00 cmol(+) kg^{-1}. After air-drying, the soil was passed through a 2 mm sieve. Biochar-amended soils were prepared by thoroughly mixing the soil with accurately weighed biochar on a rotary shaker for 7 days. The percentages of the two biochar materials in the amended soils were 0, 0.1, 0.5, and 1% (w/w), respectively.

Chlorpyrifos (> 98.2%) and fipronil (> 97.5%) were obtained from Shanghai Pesticide Research Institute (Shanghai, China) and Dr. Ehrenstorfer GmbH (Augsburg, Germany), respectively. Chlorpyrifos is an organophosphate pesticide with a low water solubility (1.4 mg L^{-1} at 25 °C) and high hydrophobicity (log K_{ow} = 4.70) (*37*). Fipronil is a member of the phenyl pyrazole class of pesticides. It is a new soil and foliar broad-spectrum insecticide discovered and developed by Rhone-Poulenc between 1985 and 1987 and placed on the market in 1993 (*38*). Fipronil has a low water solubility (1.9 mg L^{-1} at 25 °C) and log K_{ow} = 4.01, but a high solubility in organic solvents such as acetone (solubility > 50%) (*37*).The average K_{oc} value for fipronil in eight South Australian soils was measured to be 825 (*39*).

Plant Growth Experiment. Chinese chives (*A. tuberosum*) were used as the test plant in this experiment. Seedlings of about 20 cm in height were selected to conduct plant experiments using a plastic container (10 cm in diameter and 10 cm in height) as a closed system allowing no leaching loss of water or the applied pesticides. Each container was filled with 500 g (dry weight) of the biochar-free soil or biochar-amended soils, and then 2.5 mL of 10 mg mL^{-1} pesticide solution in acetone was added into each container, resulting in a spiked concentration of 50 mg kg^{-1} for each pesticide. A relatively high insecticide concentration was chosen in this experiment as these two insecticides are often used by direct soil application to control soil insect pests at high rates. The seven biochar amendments used in this experiment were control (0% biochar), three amendments with BC450 (0.1, 0.5, 1%), and another three with BC850 (0.1, 0.5, 1%). The combination of seven biochar treatments and two pesticides, together with a pesticide blank (biochar-free soil), resulted in a total of 15 treatments. Each treatment was carried out in seven replicates. The treated soils were thoroughly mixed and shaken for 24 h in a rotary shaker, which was followed by evaporation of acetone for 2 days.

After the solvent acetone was evaporated, 120 mL of deionized water was added into each container to adjust the content of water in the soils to about 50% of MWHC. An aliquot of 5 g of soil was taken from each container to determine the pesticide concentrations. The seven replicates were then divided into two subgroups: three were used for uptake experiment with plants, and the other four were used as dissipation experiments without plants. Half of the four containers were sterilized by autoclaving at 120 °C under 300 kPa chamber pressure for 30 min three times within 3 days before the addition of chlorpyrifos or fipronil and used as sterilized controls. Chinese chive seedlings were carefully washed with water, and four seedlings were planted in each plastic container. The growth chamber was maintained at 28/20 °C day/night temperatures with a 12 h lighting cycle. The plants were watered every second day to maintain the soil moisture.

At the end of the experiment (5 weeks after planting), the plants were cut at the soil level and weighed to obtain the fresh weights of the aboveground biomass. The underground parts of the plants were removed from the soil substrate and carefully and thoroughly washed with tap water to remove the substrate on the surface of the roots and then air-dried at room temperature (25 °C) for 24 h. Particular care was exercised to remove soil particles from the root mass to avoid contamination. The underground parts were also weighed to obtain the fresh biomass weights. After all of the plants had been removed, a small quantity (5 g) of the soil samples was collected for analysis after thorough mixing.

Residue Extraction and Cleanup. To evaluate the influence of the biochar on the dissipation of chlorpyrifos and fipronil in unplanted soils, 5 g of soils was taken from the containers on the 7th, 14th, 21st, and 35th days after treatment to determine the amounts of the pesticides remaining. Soil samples were dried at 40 °C for 12 h.

Soil and plant samples were extracted using a QuEChERS method, which has been reported earlier (*7*). Briefly, each sample (5 g) was weighed into a 37 mL centrifuge tube, and 2 mL of water was added to the tube. The contents of the tube were mixed and left for 30 min, and then 10 mL of acetonitrile was added to the tube. The tube was capped and shaken vigorously by hand for 1 min. To induce phase separation and pesticide partitioning, a buffer−salt mixture (consisting of 4 g of magnesium sulfate anhydrous grit, 1 g of sodium chloride, 0.5 g of disodium hydrogen citrate sesquihydrate, and 1 g of trisodium citrate dehydrate) was added to the suspension derived from the first extraction. The tube was closed, shaken vigorously by hand for 1 min, and centrifuged for 3 min at 2500 rpm. Then 5 mL of the acetonitrile phase was transferred into a centrifugation tube already containing 0.75 g of $MgSO_4$ and 150 mg of primary secondary amine (PSA) sorbent. The tube was closed, shaken vigorously by hand for 30 s, and centrifuged for 3 min at 1500 rpm. The extracts were dried under a gentle nitrogen stream. The dry residue was redissolved with 1 mL of

hexane or HPLC mobile phase. Each final extract was then filtered through a 0.45 μm membrane filter into a 2 mL amber glass vial. The vials were kept at −18 °C until analysis. The concentrations of chlorpyrifos in the soils and plants were measured by high-performance liquid chromatography (HPLC) and gas chromatography−mass spectrometry (GC-MS), respectively. The concentrations of fipronil in the soils and plants were measured by GC-MS. The recovery tests were performed by spiking the two pesticides into fresh soil and plant samples. The spiked samples were stored in a refrigerator overnight before extraction. The recoveries were 78−95 and 85−93% for chlorpyrifos and fipronil in the soil and biochar-amended soils, with the fortified concentrations of 1−50 mg kg^{-1}. The recoveries were 72−93 and 67−86% for chlorpyrifos and fipronil in fresh plant materials, with the fortified concentrations of 0.1−10 mg kg^{-1}.

Residue Analysis. Analysis of chlorpyrifos residue in soil samples was carried out on an Agilent 1200 series HPLC equipped with a diode array detector (Santa Clara, CA) and an SGE C18 RS column (250 × 4.6 mm, 5 μm) (Melbourne, Australia). The column temperature was set at 40 °C. Acetonitrile/water (7:3, v/v) was used as the mobile phase at a flow rate of 1 mL min^{-1}. The UV wavelength for detection of chlorpyrifos was 270 nm. The injection volume was 50 μL. Standard curves were generated freshly with each analytical batch using solutions within the measured concentration range (from 0.1 to 20.0 mg L^{-1}).

An Agilent 6890N gas chromatograph (Santa Clara, CA) connected to an Agilent 5975B MSD mass spectrometer with a J&W Scientific DB-5 column (30 m × 0.25 μm i.d., 0.25 μm film thickness) (Folsom, CA) was used to analyze chlorpyrifos residue in plant samples and fipronil residues in soil and plant samples. For determination of chlorpyrifos, the instrumental conditions were as follows: inlet temperature, 250 °C; splitless injection mode with split vent, 30 mL min^{-1} at 1 min and gas saver, 20 mL min^{-1} at 2 min; flow rate of the carrier gas helium, 1 mL min^{-1}. Oven temperature program was raised from 70 °C (held for 2 min) to 150 °C at 25 °C min^{-1} and then to 280 °C at 10 °C min^{-1} and held for 10 min. The MS interface temperature was 280 °C; MS source, 230 °C; and MS Quad, 150 °C. Selected ion mode was used in the detection and quantification for chlorpyrifos (at a retention time of 13 min) with a target ion of m/z 314. For determination of fipronil, the instrumental conditions were as follows: inlet temperature, 280 °C; splitless injection mode with split vent, 30 mL min^{-1} at 1 min and gas saver, 20 mL min^{-1} at 2 min; helium flow rate, 1 mL min^{-1}. The oven was programmed from 150 °C (held for 1 min) to 260 °C (held for 6 min) at 6 °C min^{-1}. The MS interface temperature was 280 °C; MS source, 230 °C; and MS Quad, 150 °C. Selected ion mode was used in the detection and quantification for fipronil (at a retention time of 9.5 min) with a target ion of m/z 367.

The limit of quantification (LOQ) of a pesticide was calculated as 10 times the standard derivations (SD) of seven replicates of the spiked samples at the concentration of 10 μg/kg. The LOQs for chlorpyrifos were 0.17 mg kg^{-1} dw in soil by HPLC and 0.004 mg kg^{-1} dw in plant by GC-MS, whereas the LOQs for fipronil were 0.012 mg kg^{-1} dw in soil and plant by GC-MS.

Data Analysis. To assess the statistical differences among the plant uptake of pesticides from biochar-amended soils, pesticide residues in biochar-amended soils, and the plant biomass, Duncan's multiple -range test was conducted with SPSS Statistics 17.0. The differences between the dissipation rates of pesticides from soils amended with biochars and the control were analyzed using a t test.

Dissipation data for the two pesticides in the soil were analyzed using the first-order reaction kinetic model. The data were fitted into the kinetic equation

$$C_t = C_0 \, e^{-kt}$$

where C_0 is the initial concentration of the added pesticide, C_t is the concentration of the pesticide at time t (days), e is the base of the natural logarithm, t is the time in days, and k is the reaction rate constant determined as the slope value from test substance dissipation curves. Linear regression analysis was performed for the experimental data after logarithm transformation according to the above kinetic equation. The half-life (DT_{50}) was calculated from the reaction constant ($DT_{50} = 0.693/k$). The dissipation fraction of each pesticide was expressed by the following formula: % = $(C_0 - C_t)/C_0$.

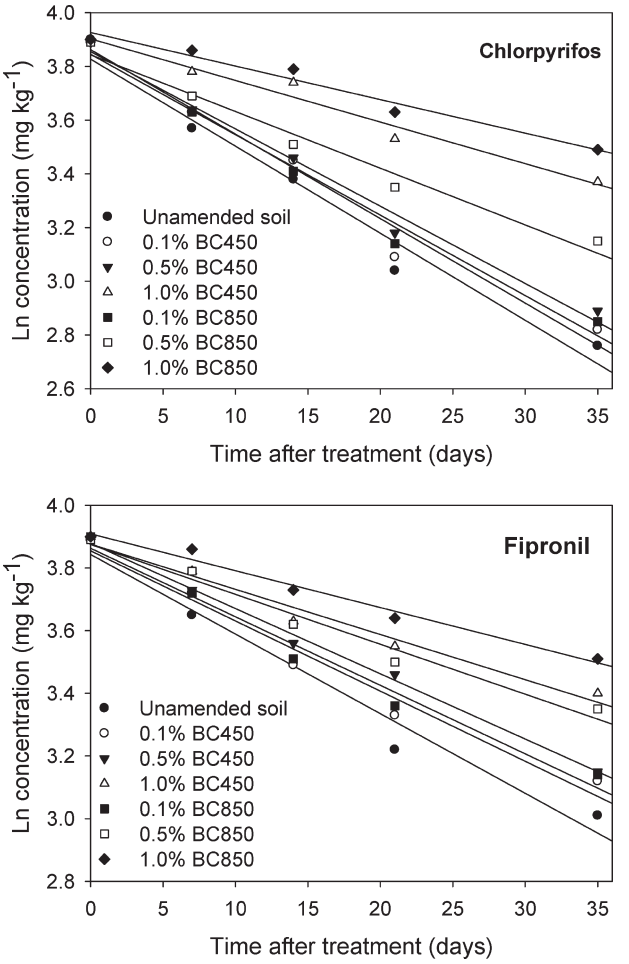

Figure 1. Dissipation of chlorpyrifos and fipronil over time in the nonsterile original soil and the nonsterile soils amended with two biochars. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively.

RESULTS AND DISCUSSION

Dissipation of Pesticides in the Biochar-Amended Soils. The losses of chlorpyrifos and fipronil residues with time in the original soil and those amended with biochars are shown in **Figures 1** (in nonsterilized soil) and **2** (in sterilized soil). The biochar amendment caused a marked decrease in the dissipation of the two pesticides in the soils. The pesticide dissipation decreased with increasing contents of both biochars; however, biochar BC850 was more effective in reducing the loss of both pesticides. At the end of 35 days of incubation, a total of 68 ± 0.7% of applied chlorpyrifos and 58 ± 2.2% of fipronil residue were lost from the unamended soil under nonsterilized conditions and 28 ± 1.0% of chlorpyrifos and 24 ± 2.4% of fipronil under sterilized conditions. In contrast, only 34 ± 0.1% chlorpyrifos and 32 ± 0.4% of fipronil degraded/sequestered from the soil amended with 1.0% BC850 under nonsterilized conditions and 14 ± 1.2% of chlorpyrifos and 12 ± 0.1% of fipronil under sterilized conditions. Biochar BC450 inhibited the dissipation of the pesticides to a much lesser degree under both sterilized and nonsterilized conditions.

The half-lives of the two pesticides under different treatments were estimated by fitting the concentration data to the first-order kinetic equation (**Table 1**). For chlorpyrifos the half-life increased from 21.3 days in the unamended soil to 55.5 days in the soil amended with 1.0% BC850 ($p < 0.01$) under nonsterilized conditions. Correspondingly, the half-life for fipronil was increased from 27.3

to 60.3 days ($p < 0.01$) under nonsterilized conditions. Similar trends were found for both pesticides in the soils under sterilized conditions. The half-lives for chlorpyrifos and fipronil under sterilized conditions were 2.2−3.3 times higher than those under nonsterilized conditions. This suggests that microorganisms were a key factor in the dissipation of the two pesticides in the soils. The key mechanism for the decreased dissipation in the biochar-amended soils was most likely due to lower bioavailability of both pesticides to microbial organisms because of their strong sorption onto the biochars and reduced desorption from the biochars (*19*, *27*). Similar results have been reported on the reduced biodegradation of diuron and benzonitrile by selected microorganisms in the presence of wheat char (*28*, *40*).

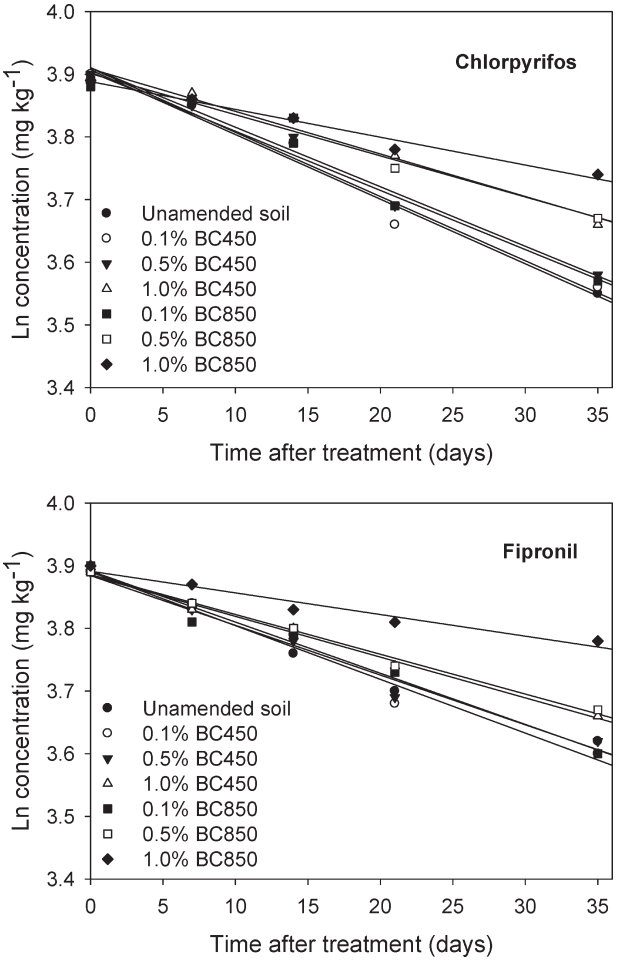

Figure 2. Dissipation of chlorpyrifos and fipronil over time in the sterile original soil and the sterile soil amended with two biochars. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively.

The pesticide dissipation (through degradation and/or sequestration) in the soils was also compared between the treatments with and without the plants (**Figure 3**). As shown in **Figure 3**, similar results were found for the two pesticides. The loss of the pesticide residues was faster in the presence of plants than in the absence of plants in most treatments (including unamended soil) and especially in the case of the soils amended with biochar BC850 ($p < 0.05$). The final residue concentrations of both chlorpyrifos and fipronil in the planted soils with or without biochar amendment were all lower than those of the corresponding treatments without plants. The increased loss of pesticides from the soils with plants was at least due to the combined effect of uptake and increased degradation of the pesticides. Plants could stimulate both microbial and biochemical activity in the surrounding soil and mineralization of contaminants in the rhizosphere through release of exudates and enzymes (*8*, *41*).

Plant Uptake of Pesticides from Soils with/without Amendment of Biochars. Chinese chives cultivated in the soils amended with biochars produced higher biomass than those cultivated in the control soils (**Figure 4**). Biochars produced from incomplete combustion of vegetation generally comprise a range of compounds and could indirectly enhance plant growth through nutrients and trace elements and improving soil physical and biological properties (*13*). The biomass fresh weights of Chinese chives from BC850-amended soils were all higher than those from BC450-amended soils ($p < 0.05$). Chinese chives cultivated in the soils containing chlorpyrifos produced greater biomass than those in the soils spiked with fipronil. This was true for each level of biochar amendment (**Figure 4**). The fresh weight (mean ± standard deviation) of Chinese chives (including aboveground and

Table 1. Half-Lives (DT_{50}) of Chlorpyrifos and Fipronil in the Soils with and without the Presence of Biochars[a]

	chlorpyrifos		fipronil	
biochar treatment	DT_{50} (days)	correlation coefficient (r)	DT_{50} (days)	correlation coefficient (r)
		Nonsterilized Soil		
unamended soil	21.3 ± 0.64	0.97	27.3 ± 1.06	0.97
0.1% BC450	22.0 ± 0.14	0.98	30.8 ± 1.56	0.97
0.5% BC450	24.1 ± 0.99	0.99	33.3 ± 0.96	0.99
1.0% BC450	44.4 ± 1.77**	0.97	47.5 ± 2.27*	0.98
0.1% BC850	23.1 ± 2.76	0.98	31.8 ± 1.48	0.98
0.5% BC850	32.7 ± 0.28**	0.98	43.6 ± 3.89*	0.97
1.0% BC850	55.5 ± 0.64**	0.97	60.3 ± 0.71**	0.98
		Sterilized Soil		
unamended soil	67.3 ± 1.91	0.97	78.8 ± 1.74	0.99
0.1% BC450	69.3 ± 9.66	0.97	81.5 ± 2.37	0.97
0.5% BC450	74.5 ± 7.47	0.98	86.6 ± 6.23	0.98
1.0% BC450	101 ± 6.69	0.97	104 ± 5.41	0.99
0.1% BC850	73.7 ± 8.14	0.98	84.2 ± 4.85	0.99
0.5% BC850	107 ± 1.13**	0.98	108 ± 3.68	0.99
1.0% BC850	158 ± 10.1**	0.98	198 ± 9.52*	0.97

[a] Mean ± STD ($n = 2$). Statistical differences of DT_{50} values between unamended soils and biochar amended soils are designated by *, $p < 0.05$, and **, $p < 0.01$.

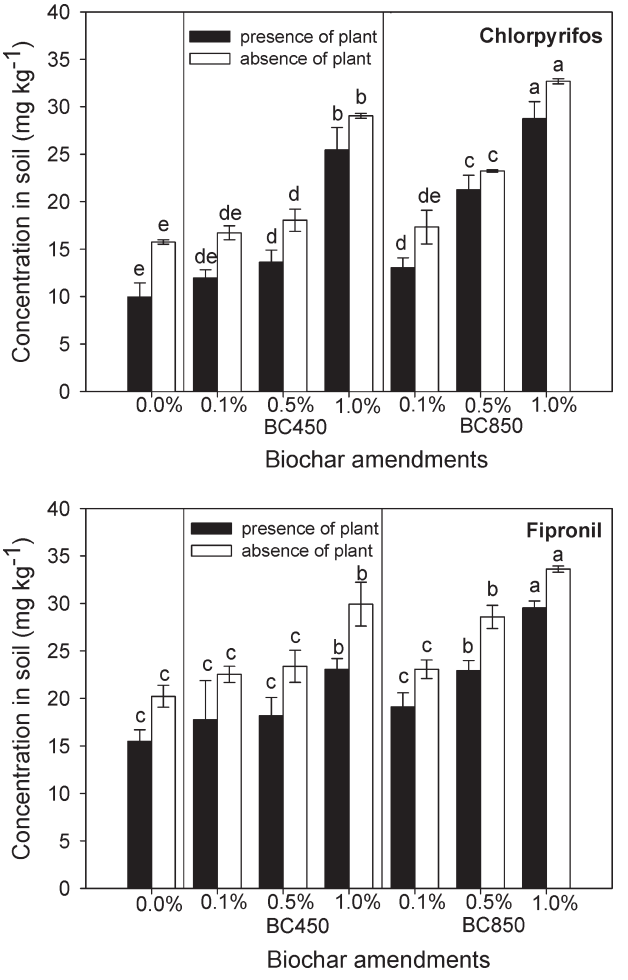

Figure 3. Comparison of the pesticide residue concentrations in the soils amended with/without biochars in the presence and absence of plant. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. Error bars indicate standard deviations of the measured values (n = 3). Different letters above the same bar type indicate significant difference (Duncan, $p < 0.05$).

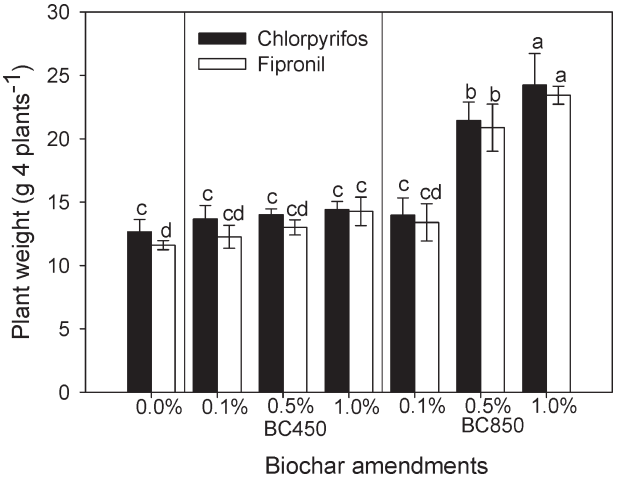

Figure 4. Fresh weights of Chinese chives plants cultivated in the biochar-free soils and biochar-amended soils fortified with chlorpyrifos and fipronil at the initial concentration of 50 mg kg^{-1}. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. Error bars indicate standard deviations of the measured values (n = 3). Different letters above the same bar type indicate significant difference (Duncan, $p < 0.05$).

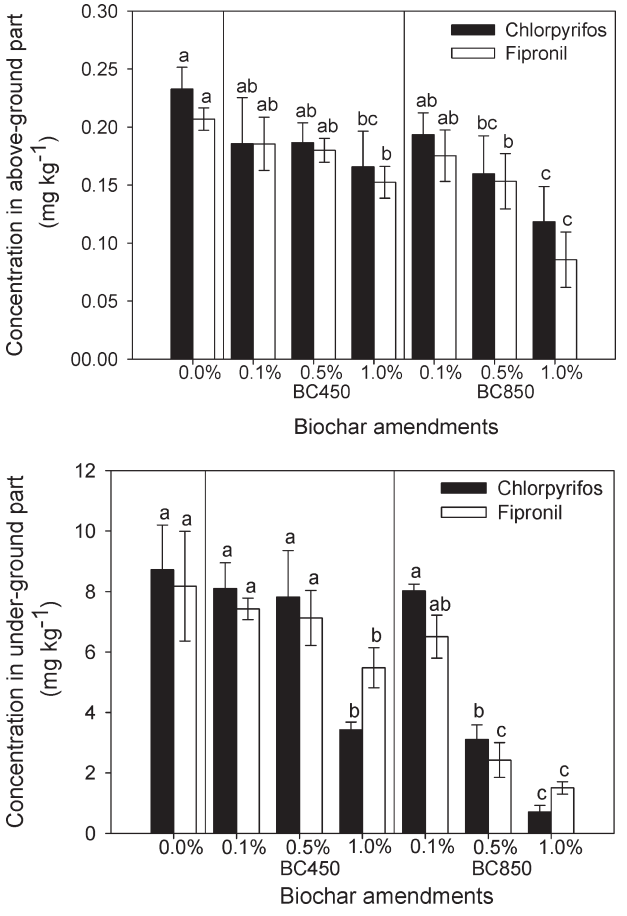

Figure 5. Concentrations of chlorpyrifos and fipronil residues in underground and aboveground parts of Chinese chives. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. Error bars indicate standard deviations of the measured values (n = 3). Different letters above the same bar type indicate significant difference (Duncan, $p < 0.05$).

underground parts) harvested from the soils with chlorpyrifos and different levels of biochar treatment was 16 ± 4.5 g (four plants)$^{-1}$, in comparison with 15 ± 4.6 g (four plants)$^{-1}$ for those from fipronil treatments, but they had no statistically significant difference ($p > 0.05$).

After 5 weeks of growth in the treated soils, the residues of chlorpyrifos and fipronil were determined in the aboveground and underground parts separately. **Figure 5** shows that the concentrations for both pesticide residues in both aboveground parts and underground parts were lower in the Chinese chive plants grown in the soils amended with 1% BC850 biochars ($p <$ 0.05). For example, the concentration of chlorpyrifos in the underground plant parts decreased from 8.7 ± 1.5 mg kg^{-1} in the control soil to only 0.7 ± 0.2 mg kg^{-1} in the soil amended with 1.0% BC850. Similarly, the concentration of fipronil in underground plant parts was decreased from 8.2 ± 1.8 in the control soil to 1.5 ± 0.2 mg kg^{-1} in the soil amended with 1.0% BC850. The pesticide residues in the aboveground plant parts were found to be 6−45 times lower than those in the underground parts for both pesticides (**Figure 5**).

Root concentration factor (RCF) was calculated by dividing the pesticide concentration in underground plant parts by the concentration remaining in soils at the end of the experiment (*42*). The RCFs of chlorpyrifos and fipronil in the soils amended with different rates of the two kinds of biochars declined as the content of biochars in the soils increased. For the plants cultivated in the

Table 2. Uptake of Pesticide Residues (Micrograms) in Different Parts of the Plants Measured at the End of the 35 Day Experiment[a]

		chlorpyrifos			fipronil		
	charcoal in soil (%)	M_T	M_P	M_R	M_T	M_P	M_R
original soil	0	61.8 ± 6.5 a	1.3 ± 0.1 a	60.5 ± 6.5 a	51.3 ± 7.0 a	1.1 ± 0.03 a	50.1 ± 7.0 a
BC450	0.1	59.5 ± 6.5 a	1.2 ± 0.3 a	58.3 ± 6.3 a	51.0 ± 4.3 a	1.0 ± 0.08 a	50.0 ± 4.2 a
	0.5	54.8 ± 4.4 a	1.3 ± 0.1 a	53.4 ± 4.5 a	50.0 ± 6.1 a	1.1 ± 0.04 a	48.9 ± 6.1 a
	1.0	27.4 ± 3.3 c	1.1 ± 0.3 a	26.3 ± 3.2 c	41.0 ± 3.9 ab	1.1 ± 0.1 a	40.0 ± 3.9 b
BC850	0.1	57.2 ± 3.1 a	1.4 ± 0.2 a	55.9 ± 3.0 a	47.1 ± 9.1 ab	1.1 ± 0.2 a	46.0 ± 9.2 b
	0.5	42.2 ± 2.7 b	1.3 ± 0.3 a	40.9 ± 2.9 b	34.8 ± 8.2 bc	1.1 ± 0.2 a	33.8 ± 8.3 bc
	1.0	12.0 ± 2.8 c	1.1 ± 0.2 a	10.9 ± 2.8 c	24.6 ± 2.7 c	0.7 ± 0.2 b	23.9 ± 2.5 c

[a] M_T represents the total uptake amount (μg) (mean ± STD, $n = 3$) of each pesticide in the whole plants of each pot; M_P and M_R represent the uptake amount (μg) (mean ± STD, $n = 3$) of each pesticide in the aboveground and underground parts of Chinese chives, respectively. Different letters after the values of the same column represent statistically significant differences ($p < 0.05$).

untreated soil, the RCFs of chlorpyrifos and fipronil were 0.88 and 0.53, respectively. For the plants grown in the soils amended with BC450 at 0.1, 0.5, and 1%, the RCF values were 0.68, 0.57, and 0.13 for chlorpyrifos and 0.42, 0.39, and 0.24 for fipronil, respectively. With biochar BC850 in the soils at 0.1, 0.5, and 1.0%, the corresponding RCF values for chlorpyrifos were 0.62, 0.15, and 0.02, and for fipronil these values were 0.34, 0.11, and 0.05, respectively.

Cotton straw derived biochars, especially BC850, were particularly effective in reducing the uptake of both pesticides by plants, and this treatment also showed higher biomass production ($p < 0.05$). To assess the effect of dilution due to greater biomass, the total amounts of pesticide residues taken up by plants were calculated by multiplying the residue concentration with the plant biomass (**Table 2**). The total amounts of plant uptake of the pesticides in the whole plant or in the plant parts (underground or aboveground parts) all decreased with increasing biochar content in the soils. After the biomass variations were taken into consideration, the 1.0% BC850 treatment was still most effective, and it reduced the total plant uptake of chlorpyrifos by 81 ± 2.3% and that of fipronil by 52 ± 3.8% in the control treatment. Even for the treatments with 1% BC450, plant uptake reductions of up to 56 ± 3.1% for chlorpyrifos and 20 ± 4.6% for fipronil were achieved. The woody chars have been considered to be more highly condensed and more aromatic with higher surface area as shown in our previous study (*19*, *27*), yet the cotton straw derived biochars used in the present study were still effective in reducing the plant uptake of pesticides. The results from our previous study (*19*, *27*) and the present study demonstrate that compared to parent material the temperature of formation is more important and that at the same temperature (e.g., 850 °C) biochars produced from both types of parent materials would be effective in remedial treatment of contaminated soils. Pesticide poison accidents of eating Chinese chives are quite frequent in China due to application of high rates of pesticides such as chlorpyrifos to treat root rotting problems. The experiments from the present study clearly showed that amendment of biochars (especially 1% BC850) reduced pesticide contamination of Chinese chives.

The decrease in bioavailability of the two pesticides in the biochar-amended soils is attributed to the following two processes: (i) reduced degradation and increased sequestration of pesticides due to reduced bioavailability to soil microorganisms and (ii) reduced uptake of pesticide residues in plant parts due to reduced bioavailability to plants. The results from the present study demonstrate that biochar amendment could reduce the bioavailability of pesticide residues in a soil and thus significantly reduce their uptake by plants from the contaminated soil.

Conclusions. This study showed that biochar amendment in a soil could markedly reduce the bioavailability of pesticides to soil microorganisms and plants grown in the contaminated soil, thus resulting in decreased dissipation and plant uptake of the pesticides in the soil. With the presence of plants, more losses of the pesticides were observed in the soils because of plant uptake and enhanced microbial degradation. Biochar produced from cotton residues at a relatively high temperature (850 °C) is likely to be more effective than that those produced at lower temperatures, mainly due to its higher surface area and microporosity and greater ability to sequester pesticides in soils. Soil amendment with biochars for sequestration purposes may be applied as an in situ remediation technique to minimize pesticide residues in agricultural produce from contaminated soils.

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