



Impact of woodchip biochar amendment on the sorption and dissipation of pesticide acetamiprid in agricultural soils

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ABSTRACT

Pyrolysis of vegetative biomass into biochar and application of the more stable form of carbon to soil have been shown to be effective in reducing the emission of greenhouse gases, improving soil fertility, and sequestering soil contaminants. However, there is still lack of information about the impact of biochar amendment in agricultural soils on the sorption and environmental fate of pesticides. In this study, we investigated the sorption and dissipation of a neonicotinoid insecticide acetamiprid in three typical Chinese agricultural soils, which were amended by a red gum wood (*Eucalyptus* spp.) derived biochar. Our results showed that the amendment of biochar (0.5% (w/w)) to the soils could significantly increase the sorption of acetamiprid, but the magnitudes of enhancement were varied. Contributions of 0.5% newly-added biochar to the overall sorption of acetamiprid were 52.3%, 27.4% and 11.6% for red soil, paddy soil and black soil, respectively. The dissipation of acetamiprid in soils amended with biochar was retarded compared to that in soils without biochar amendment. Similar to the sorption experiment, in soil with higher content of organic matter, the retardation of biochar on the dissipation of acetamiprid was lower than that with lower content of organic matter. The different effects of biochar in agricultural soils may attribute to the interaction of soil components with biochar, which would block the pore or compete for binding site of biochar. Aging effect of biochar application in agricultural soils and field experiments need to be further investigated.

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1. Introduction

Biochar is produced by thermal decomposition of biomass under limited or absence of oxygen supply at relatively low temperatures (<700 °C). Biochar is usually produced with the intent to be applied in soil, or as a byproduct of thermal pyrolysis of carbon-rich biomass to make biofuel (Laird et al., 2009; Lehmann and Joseph, 2009; Yao et al., 2010). Studies have shown that the incorporation of biochar in soils could be an effective practice in sequestering carbon and reducing greenhouse gas emissions (Lehmann et al., 2006; Glaser et al., 2009; Spokas et al., 2009; McHenry, 2010), altering the soil nutrient availability and increasing crop production (Graber et al., 2010; Major et al., 2010), and also improving soil microbial activity (Steiner et al., 2008). In addition, biochar in soil has also been shown to be particularly effective in sorption and sequestration of organic contaminants (Chun et al., 2004; Lehmann et al., 2006; Yu et al., 2006; Bornemann et al., 2007). Amendments of small amount of charred materials in soil would dominate the overall sorption of organic contaminants. For example, ashes containing char produced from burning of

wheat and rice residues were reported to be up to 400–2500 times more effective than soil in sorbing herbicide diuron in the concentration range of 0–6 mg L⁻¹ (Yang and Sheng, 2003). Our previous research also found that soil amended with biochar derived from pyrolyzation of red gum (*Eucalyptus* spp.) chips greatly enhanced the sorption of diuron, and increased the non-linearity of the sorption isotherm and the extent of sorption–desorption hysteresis (Yu et al., 2006). The enhanced sorption by amending soil with biochar strongly influenced the fate and behavior of organic contaminants in the environment. Incorporation of small amount of char in soils has shown adsorptive inhibition of biodegradation of benzonitrile (Zhang et al., 2005), reduction of herbicidal efficacy of diuron to barnyard grass (Yang et al., 2006), and suppression of plant uptake of pesticides from soil (Yu et al., 2009; Yang et al., 2010). As a result, biochar as a soil amendment is increasingly attracting the attention of policy makers and great interests of scientific communities in recent years. However, the extent of impact of biochar amendment in real agricultural soils on the sorption and environmental fate of pesticides has so far received limited attention.

In countries such as China and India, partially combusted residues from firewood are commonly added to soil by mixing these residues with livestock dung as organic manure fertilizer. Other

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sources of biochar in soil are from direct burning of plant residues (e.g. wheat and rice stalks) for land clearing and immediate land re-use, as well as natural combustion such as wildfires. Such practices have contributed to the high level of biochar like materials (commonly termed as black carbon) found in the soils (Skjemstad et al., 1996; Young et al., 2005; Lehmann et al., 2006). In addition, the potential environmental and agricultural advantages of biochar have led to the recommendation of intended application of biochar in agricultural soils in recent years.

It has been observed that sorption ability of black carbon (BC) in contaminated sediment matrices was not as strong as that of the “clean” BC isolated from sediments through low-temperature combustion (Cornelissen and Gustafsson, 2004). In some soils/sediments, the sorption of contaminants did not correlate well with the BC contents, even though BC have been reported to be the dominant sorption phase for organic contaminants (Singh and Kookana, 2009). The interaction of soil organic substances (Jonker et al., 2004; Kwon and Pignatello, 2005; Endo et al., 2009; Koelmans et al., 2009; Wen et al., 2009) and/or soil mineral fraction (Celis et al., 2006; Singh and Kookana, 2009) with BC was proposed to account for the discrepancy. This interaction may lead to the sorption site competition and/or pore blockage of BC, thus attenuating its sorption capacity. To better understand the impact of biochar amendment on the fate of the pesticides in the environment, it is necessary to characterize the effect of biochar application on the sorption and dissipation of pesticides in agricultural soils with different physicochemical properties, which will be most helpful for assessing the risk and/or modeling the fate of the pesticides in the environment.

Acetamiprid ((E)-N¹-[(6-chloro-3-pyridyl) methyl]-N²-cyano-N¹-methyl-acetamide) belongs to neonicotinoid group of insecticides. It has been widely used in the control of sucking insect pests, such as aphids, leafhoppers and whiteflies. In the present study, biochar produced by incomplete combustion of red gum chips (*Eucalyptus* spp.) was incorporated into three Chinese agricultural soil samples. The sorption/desorption behavior and the dissipation of acetamiprid in the soils with and without amending of biochar were determined. The objectives of this research were: (i) to investigate the influence of biochar on the sorption and desorption behavior of pesticide acetamiprid in agricultural soils with different physicochemical properties; and (ii) to characterize the influence of biochar on the dissipation of acetamiprid in different agricultural soils.

2. Materials and methods

2.1. Chemicals

Analytical standard of acetamiprid (99.9% chemical purity by GC) was purchased from Sigma–Aldrich. It has an aqueous solubility of $2.95 \times 10^3 \text{ mg L}^{-1}$ at 25 °C and pH = 7 and a Log K_{ow} of 0.8 at 20 °C (US EPA, 2002). The stock solution of acetamiprid (1000 mg L^{-1}) was prepared by dissolving the accurately weighed insecticide in HPLC grade acetonitrile. Sodium azide and calcium chloride of analytical grade and all solvents of high-performance liquid chromatography (HPLC) grade were obtained from Merck Pty Limited (Victoria, Australia).

2.2. Biochar and soils

The biochar was produced from red gum wood (*Eucalyptus* spp.) at 450 °C as described in the previous study (Yu et al., 2006). Briefly, air dried red gum woodchips were pyrolyzed at 450 °C under limited oxygen in a muffle furnace. The prepared biochar was hand-ground to a fine powder by mortar and pestle and passed through a 200 µm sieve. The specific surface area (SSA) and pore size distribution of the biochar were evaluated using BET nitrogen adsorption technique at 77 K and have been reported earlier (Yu et al., 2006). The SSA of the biochar was $27.3 \pm 0.04 \text{ m}^2 \text{ g}^{-1}$, analysis of the pore size distribution indicated that its maximum peak occurring at pore width of 1.1 nm (Yu et al., 2006).

Three surface agricultural soil samples (0–0.15 m) used in this experiment were: a red soil collected from a vegetable field near the Nanchang city of Jiangxi Province, southeast China (RS), a black soil collected from a wheat field near Haerbin city of Heilongjiang Province, northeast China (BS), and a paddy soil collected from a paddy field near Wuxi city of Jiangsu Province, east China (PS), respectively. The three soils are typical agricultural soils in China. The collected soils were air dried at 40 °C, ground and passed through a 2-mm sieve. The selected physicochemical properties of the soils are given in Table 1.

Biochar amended soils used in the experiment were set at 5 g biochar kg^{-1} soil. The biochar amended soils were thoroughly mixed on a rotary shaker for 2 d before their use as sorbents for sorption/desorption, and soil dissipation experiments.

2.3. Sorption and desorption

Sorption of acetamiprid was carried out by the batch equilibration technique as described in many other studies (Yang and Sheng, 2003; Yu et al., 2006; Zhang et al., 2010a). The soils were suspended in 10 mL of 0.01 M CaCl_2 solutions (containing 0.5% NaN_3 to inhibit microbial activity) spiked at concentrations of 0.5–25 mg L^{-1} of acetamiprid. The amounts of soils and biochar amended soils used in the experiment were adjusted to allow for 30–80% of the added chemical to be sorbed at equilibrium. Based on our preliminary experiments, an aliquot of 1.0 g soil sample was used. The suspensions were shaken on a rotary shaker in dark at room temperature ($22 \pm 2 \text{ }^\circ\text{C}$) at 120 rpm for 24 h. Our preliminary kinetic experiments showed sorption of acetamiprid on biochar amended soils reached an apparent equilibrium within 24 h. After shaking, the suspensions were centrifuged at 6000 rpm for 60 min, an aliquot of the supernatant in each tube was taken out and analyzed by HPLC.

Desorption experiments were conducted by conventional single-step decant-refill technique (Zhang et al., 2010b). After sorption reached equilibrium, the tubes were centrifuged and 5 mL of the supernatant in each tube was taken out for analysis. Another 5 mL of 0.01 M CaCl_2 (including 0.5% NaN_3) was added into each tube. After shaken for another 24 h and then centrifuged at 6000 rpm for 60 min, the acetamiprid desorbed from soils and biochar amended soils was analyzed by HPLC.

All tests were performed in triplicate. Losses during the test were monitored by including two blank controls in each test: one tube that only had a chemical solution without any sorbent

Table 1
Physical and chemical properties of the soil samples.

Soil	Clay (%)	Silt (%)	Sand (%)	Organic matter (%)	pH	CEC (cmol kg^{-1})
RS	56	27	16	1.5	4.4	10.3
PS	16	54	30	1.7	6.6	16.4
BS	22	38	40	4.6	7.5	27.6

and the other control tube that only had the sorbent and CaCl_2 solution without chemical. Tests showed losses due to adsorption to glassware and degradation were negligible and no interferences were found during the analysis.

2.4. Soil dissipation

An aliquot of 20 g soil or biochar amended soil samples were weighed into 250 mL glass bottles. Each sample was treated with 0.20 mL of acetamiprid stock solution (1000 mg L^{-1} in acetonitrile), resulting in an initial concentration of 10 mg kg^{-1} . The soil samples were then thoroughly mixed by shaking in a rotary shaker in dark for 24 h, followed by evaporation of organic solvent in dark for another 24 h. Deionized water was added into each bottle to adjust the content of water in the soils to about 60% of maximum water-holding capacity. The bottles were closed with cotton plugs and then incubated in dark at $25 \pm 2^\circ \text{C}$ until the residue of acetamiprid in soil was analyzed at 0, 1, 3, 5, 7, 14, 28 d. Soil moisture was maintained by adding the required amount of water at 2 d intervals.

2.5. Soil extraction

At each sampling time, three bottles were taken out and 50 mL of acetonitrile was added to each bottle. The acetamiprid residue in soils with and without biochar was extracted by vortex mixed for 1 min, then ultrasonically extracted for 30 min, and shaken in a rotary shaker for 2 h. Following phase separation by centrifuging at 6000 rpm for 15 min, 10 mL of the supernatant was withdrawn and dried under gentle N_2 gas at 40°C and then redissolved in 1 mL of HPLC mobile phase. The pesticide concentration was measured by HPLC. The recoveries were 84.2 ± 1.7 – $94.3 \pm 1.3\%$ for acetamiprid in the soils and biochar-amended soils, with the fortified concentrations of 0.5 – 10 mg kg^{-1} .

2.6. HPLC analysis

The samples were analyzed using an Agilent 1200 series HPLC equipped with a variable wavelength detector (VWD) and a ZORBAX SB-C₁₈ RS column ($250 \times 4.6 \text{ mm}$, $5 \mu\text{m}$). The mobile phase consisted of 70% acetonitrile and 30% water at a flow rate of 1 mL min^{-1} . The detection wavelength for VWD detector was set at 210 nm. The injection volume was $20 \mu\text{L}$. The detection limit for acetamiprid was 0.05 mg L^{-1} .

2.7. Data analysis

All the sorption and desorption isotherms were fitted using the Freundlich equation. The dissipation data for acetamiprid in the soils were analyzed using the pseudo first-order reaction kinetic model. The dissipation fraction of each pesticide was expressed by the following formula: $\% = (C_0 - C_t)/C_0 \times 100\%$.

A statistical analysis system (SAS) mixed model was used to analyze the differences between the dissipation rates of pesticide from soils amended with/without biochar and the controls using a *t*-test.

3. Results and discussion

3.1. Sorption and desorption

The sorption and desorption of acetamiprid in the three soils with and without amendment of biochar were illustrated in Fig. 1. Apparently, the sorption data over the entire range of ace-

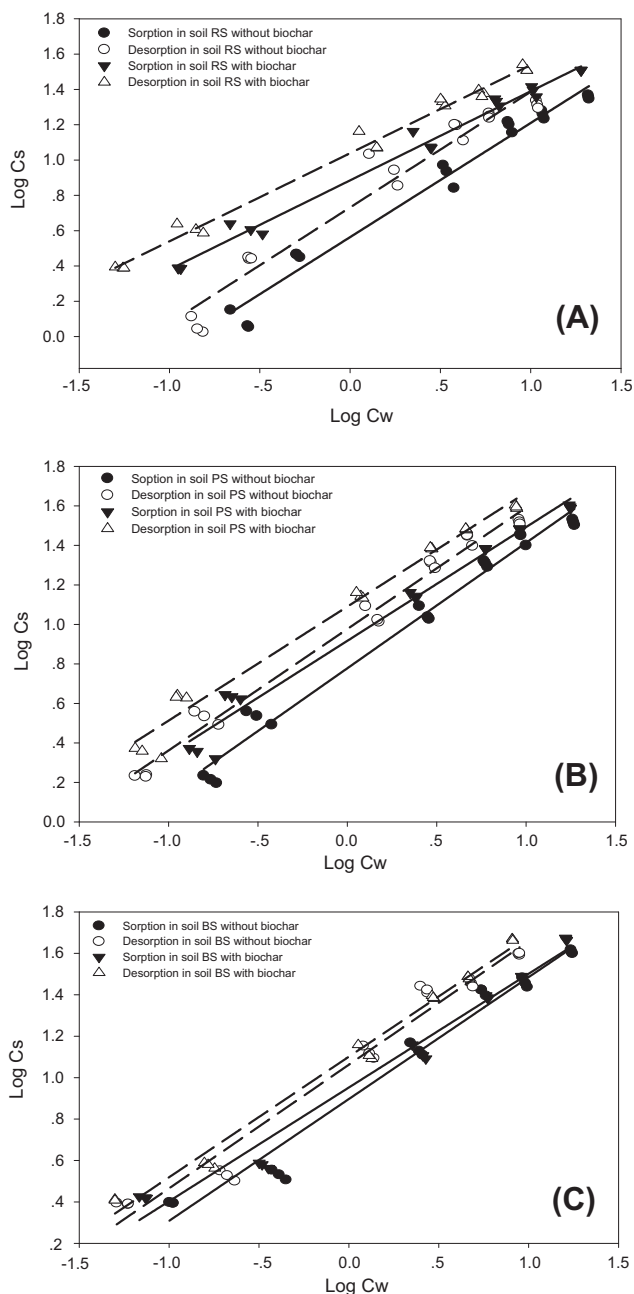


Fig. 1. Sorption and desorption of acetamiprid in soils with or without biochar amendment. (Lines and dash lines are the sorption and desorption isotherms fitted to Freundlich equation, respectively; A. Soil RS, B. Soil PS, and C. Soil BS).

tamiprid concentrations were well described by the Freundlich equation with $R^2 \geq 0.97$ (Table 2). For the three unamended soils, the resulted Freundlich K_f values followed the order of $\text{BS} > \text{PS} > \text{RS}$, whereas the Freundlich exponent N_f of $\text{BS} < \text{PS} \approx \text{RS}$. The results revealed that sorption of acetamiprid in the three natural soils followed the order of $\text{BS} > \text{PS} > \text{RS}$, which coincided with the trend of soil organic matter (OM) contents. The relatively low K_f values (3.7–7.9, Table 2) found in the three agricultural soils showed that acetamiprid is hard to be sorbed by soils and has the mobile potential for surface and groundwater pollution, which was also reported in the literature (Carbo et al., 2007).

As expected, biochar amendment enhanced the sorption of acetamiprid and changed the sorption isotherms to be more non-linear; however, the magnitudes were different among the three

Table 2

Freundlich constants for the sorption and desorption of acetamiprid in soils with and without the amendment of biochar.

Treatment	Sorption			Desorption				
	K_f	N_f	R^2	K_d^a	K_f	N_f	R^2	K_d^a
Soil RS	3.7	0.7	0.97	3.7	5.4	0.7	0.96	5.4
Soil PS	6.0	0.6	0.98	6.0	9.5	1.0	0.99	9.5
Soil BS	7.9	0.6	0.97	7.9	10.6	0.7	0.97	10.6
RS + 0.5% biochar	7.7	0.5	0.99	7.7	11.1	0.5	0.98	11.1
PS + 0.5% biochar	8.3	0.6	0.98	8.3	12.6	0.6	0.99	12.6
BS + 0.5% biochar	9.0	0.5	0.98	9.0	12.3	0.6	0.94	12.3

^a K_d is the sorption coefficient estimated from the Freundlich sorption isotherms at $C_e = 1.0 \text{ mg L}^{-1}$.

agricultural soils (Table 2). Due to the nonlinear nature of the isotherms, a direct comparison of sorption affinities among the soils with and without biochar is only valid for a single solution concentration (e.g., C_w of 1 mg L^{-1}), where $K_f = K_d (C_s/C_w)$ at $C_w = 1 \text{ mg L}^{-1}$. As shown in Table 2, the resulted K_d values of biochar amended soils were all higher than those of the original soils. Assuming that the inherent sorption capability of the soils would not change in the presence of biochar, the calculated net increase of K_d values for soil RS, PS and BS were 4.0, 2.3 and 1.1 L kg^{-1} , respectively, due to the amendment of 0.5% biochar. The relative contributions from biochar to the overall sorption were 52.3%, 27.4% and 11.6% for RS, PS and BS, respectively. The effectiveness of biochar amendment in enhancing the sorption capacity of acetamiprid followed the decreasing order of $RS > PS > BS$, which was adversely related to the OM content for the three soils. Similar results reported by Zhang et al. (2010b) showed that the magnitude of sorption enhancement for phenanthrene by biochar amendment in soil with low indigenous organic carbon content was greater than that with high organic carbon content.

The deviation of sorption enhancement by amending the same amount of biochar in different soils suggested that the sorption of acetamiprid on biochar might be suppressed in some soils. It has been proved that soil water soluble organic matters could be sorbed by BC, leading to competition with the added organic substances for limited sorption site and/or pore block of BC, thus decreasing its sorption capacity (Kwon and Pignatello, 2005; Koelmans et al., 2009). The lowest magnitude of sorption enhancement for biochar amendment in soil BS was easily to be understood due to its relatively high content of organic matter (4.6%, Table 1) and high sorption affinity for acetamiprid compared to the other two kinds of soil. For soil RS and PS, which have relatively the same content of OM, the big differences of biochar amendment in sorption enhancement (Table 2) might be attributing to the different properties of soil OM (solubility, molecular size, etc.) (Cornelissen and Gustafsson, 2006; Koelmans et al., 2009). The impact of different soil soluble OM on the sorption properties of biochar need to be further investigated.

Results of single-step desorption of sorbed acetamiprid revealed that there is a clear discrepancy between desorption and sorption isotherms for soils with or without biochar, which is indicative of hysteresis (Fig. 1). As indicated in Fig. 1 and Table 2, higher deviation between sorption and desorption branch for soils amended with 0.5% biochar was observed (for example, the deviation between the solid phase acetamiprid concentration in desorption and sorption branches were higher in biochar amended soils than that of original soils, at the equilibrium concentration of 1 mg L^{-1}), suggesting that incorporation of biochar in the three agricultural soils slightly increased the sorption–desorption hysteresis of acetamiprid. These may due to the entrapment of acetamiprid molecules in meso- and microporous structure of biochar, which was difficult to be washed out (Yu et al., 2006).

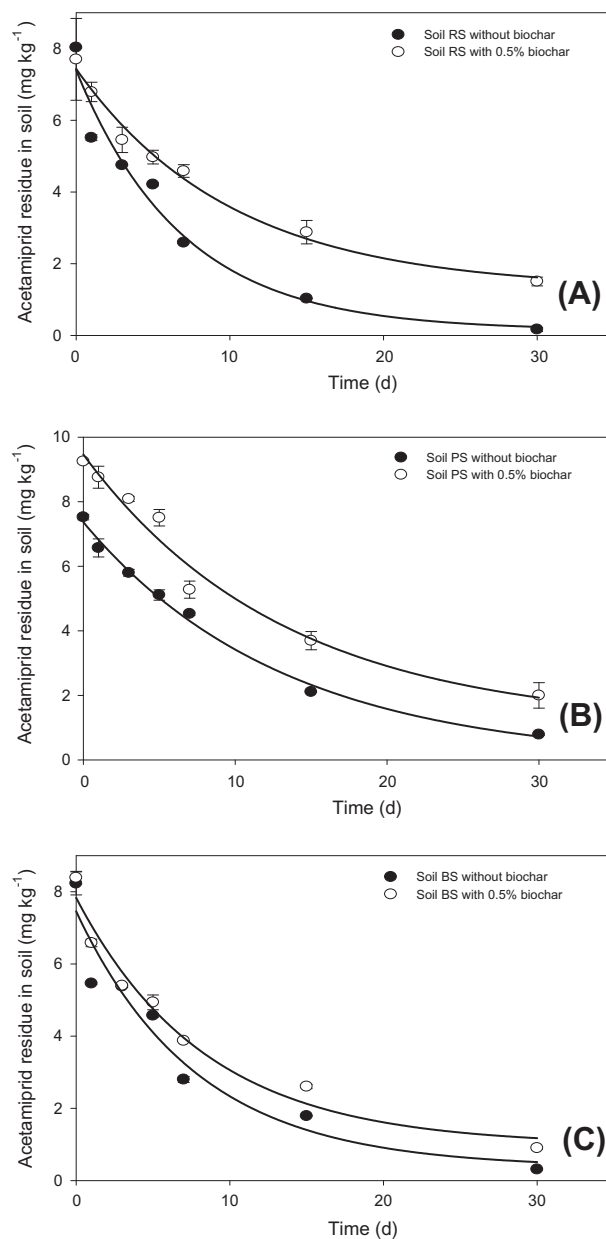


Fig. 2. Concentrations of acetamiprid remaining over time in the soils with and without amendment of biochar. (A. Soil RS, B. Soil PS, and C. Soil BS).

3.2. dissipation of pesticide in soils

The dynamic residue of acetamiprid with time from original soils and soils amended with biochar are shown in Fig. 2. As expected, the amendment with biochar leads to a decrease in the dissipation rate of pesticide residue from all the three agricultural soils, but the extent of impact is different.

At the end of 30 d of incubation, a total of $97.9 \pm 0.7\%$, $89.5 \pm 0.3\%$, and $95.5 \pm 0.1\%$ of applied acetamiprid was lost from the soil RS, PS and BS, respectively. In contrast, the corresponding acetamiprid degraded/sequestered from the biochar amended soils was only $67.0 \pm 6.5\%$, $78.4 \pm 4.4\%$ and $86.9 \pm 0.1\%$. Soil RS amended with 0.5% biochar resulted in over 30% in the decrease of acetamiprid loss from soil, which was the most effective one for reducing the loss of acetamiprid compared to the other two agricultural soils. We conducted soil dissipation experiment in cotton plug closed glass bottles, loss of acetamiprid through leaching was not

Table 3
Half-lives of acetamiprid in soils with and without amendment of biochar.

Treatment	First-order equation	R ²	DT ₅₀ ± SD (d)
Soil RS	$y = 7.0e^{-0.13x}$	0.99	5.5 ± 0.2
Soil PS	$y = 7.3e^{-0.08x}$	0.99	9.2 ± 0.3
Soil BS	$y = 7.1e^{-0.10x}$	0.98	6.7 ± 0.4
RS + 0.5% biochar	$y = 6.8e^{-0.05x}$	0.95	13.2 ± 0.8
PS + 0.5% biochar	$y = 9.0e^{-0.05x}$	0.97	13.3 ± 1.0
BS + 0.5% biochar	$y = 7.1e^{-0.07x}$	0.99	10.0 ± 0.5

allowed and evaporation was also thought to be very low. The decreased loss of acetamiprid found in biochar amended soils is ascribed to mainly slow degradation and/or sequestration of pesticide.

The data were all fitted to a first-order equation to estimate half-lives of acetamiprid in different treatments (Table 3). In all the three agricultural soils, acetamiprid have relatively short half lives, with DT₅₀ ranging from 5.5 to 9.2 d. Acetamiprid dissipated faster in soil RS and BS than in soil PS. A control experiment showed that the DT₅₀ increased to 24.5 d in sterilized soil BS, which suggested that soil microbial degradation is the main factor that leads to the loss of acetamiprid from soils. Sorption of pesticide by soils will reduce its concentration in soil water, therefore, reduce pesticide bioavailability and degradation (Gevao et al., 2000). The sorbed pesticides are available for biodegradation only after their desorption, followed by diffusion into soil solution. The fastest dissipation of acetamiprid found in soil RS among the three soils may attribute to its lowest sorption affinity (Table 2) with low content of organic carbon, which resulted in more free acetamiprid available for soil organisms. While for soil BS, its high content of organic carbon (Table 1) could supply more nutrients and incentive the activity of soil microorganisms (Schnürer et al., 1985; Zhang et al., 2005) to break down pesticide in soil water more quickly, leading to more sorbed pesticide to be released (desorbed). These might be the main reason for the relatively fast dissipation of acetamiprid in soil BS than that in soil PS, although soil BS has the highest sorption capacity among the three soils.

Amending soil RS with 0.5% biochar led to the increase of half-life of acetamiprid from 5.5 d in unamended soil to 13.2 d (a statistically significant increase at $p < 0.05$). The corresponding increase of DT₅₀ in soil BS was from 6.7 d to 10.0 d, and in soil PS was from 9.2 d to 13.2 d (Table 3). The key mechanism for decreasing dissipation of acetamiprid in biochar amended soils was most likely due to the increase of sorption and reduced desorption from biochar surface (Yu et al., 2006), which lowers the bioavailability for soil organisms. Similar results about the reduced biodegradation of other pesticides in soils by selected microorganisms in the presence of char have been reported by other researchers (Zhang et al., 2005; Yang et al., 2006; Loganathan et al., 2009). In accordance with the effect of sorption enhancement, effect of biochar amendment in soils in retardation of acetamiprid dissipation follows the order of RS > PS > BS (Table 2). Our finding suggested that to accurately assess the environmental fate of pesticides in agricultural soils containing biochar, the interaction of soil components with biochar need to be considered, otherwise the impact of biochar could be misestimated.

4. Conclusions

The results from this study confirmed that biochar application in agricultural soils could enhance the sorption of the pesticide and reduce its dissipation rate. The magnitude of sorption enhancement and degree of reduction of the dissipation rate were more prominent in soils with low content of organic matter. Our

results implied that soil organic matter may associate with biochar, which would block its pore and/or compete for sorption sites. Therefore, when assessing the risk of pesticide in soils containing biochar, the interaction of biochar with other soil component needs to be considered. Furthermore, as our works were conducted at laboratory conditions, all the results are the initial effects, further experiments of long-term effects, especially under field conditions need to be investigated. In addition, as soil application of biochar for carbon sequestration and altering soil fertility is becoming more and more popular, this practice would reduce the bioavailability of pesticide in soil, which may lead to the compromise of the efficacy of soil applied pesticides, prolonging the residue time of pesticides, and decreasing the plant uptake of pesticide from soil. The extent of such effects of different biochars in various soils is needed for further studies.

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