

## Enhanced and irreversible sorption of pesticide pyrimethanil by soil amended with biochars

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### Abstract

Biochar derived from partial combustion of vegetation is ubiquitous and potentially effective in sequestration of environmental contaminants. Biochars were prepared by burning of red gum (*Eucalyptus* spp.) woodchips at 450 and 850°C (labeled as BC450 and BC850). These two biochars were found to possess markedly different properties in terms of surface area and porosity. Short-term equilibration tests (24 hr) were conducted to assess the sorption-desorption behavior of pyrimethanil in the soil amended with various amounts of biochar of each type, with a special focus on the desorption behavior of the sorbed pesticide through four times successive desorption by dilution. Sorption coefficient and isotherm nonlinearity of the amended soils progressively increased with the content of biochar in the soil. Biochar BC850 with higher surface area and microporosity showed a stronger effect on the reversibility of sorption pesticide. The soils amended with 5% BC450 and 1% BC850 had nearly the same sorption capacity for pyrimethanil; however, their desorption processes were very different with 13.65% and 1.49% of the sorbed pesticide being released, respectively. This study suggested that biochar in soil could be an important factor for immobilization of a pesticide and thus affecting its environment fate in soil.

**Key words:** biochar; pyrimethanil; sorption; desorption

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### Introduction

Biochar, which is produced from incomplete combustion of fossil fuel and biomass, plays an important role in the global carbon cycles and environmental processes of contaminants (Bird and Cali, 1998; Chiou et al., 2000; Crutzen and Angreae, 1990; Kuhlbusch, 1998). Biochar can significantly contribute to the sorption and sequestration of organic contaminants such as pesticides in soil due to its special physiochemical properties (Accardi-Dey and Gschwend, 2003; Allen-King et al., 2002; Ahamad et al., 2001; Chiou et al., 2000; Lohmann et al., 2005). Biochar amendment of soils can affect the fate of organic contaminants in the soil environment and their potential risks to human and ecosystem health. In countries such as China and India, partially combusted residues are commonly added to soil through agricultural practices, such as adding the burnt-residues from firewood and livestock dung as fertilizer. Direct burning of plant residues for land clearing and immediate land re-use as well as application of charcoal as soil amendment (Lehmann et al., 2006) are

also important sources of biochar in soils. Such agricultural practices together with natural combustion processes (such as forest fires) may contribute to the high levels of biochar found in some soils (Guo and Lin, 2001; Schmidt et al., 1996; Skjemstad et al., 1996; Young et al., 2005; Lehmann et al., 2006). Since pesticide contamination is a significant issue in some agricultural soils, studying the interaction between biochar and pesticide in soil can help understand the fate of pesticides in soil.

Enhanced sorption of pesticides due to the presence of biochar in soil or sediment has already been reported since 1960s. Hilton and Yuen (1963) found that some Hawaiian soils could maintain high sorptivity for herbicides after removal of organic matter by severe oxidation, which may attribute to the presence of biochar in soils received from regular burning of cane trash. Yamane and Green (1972) reported that the presence of biochar in soil could not only enhance the sorption of pesticides, but also change the sorption isotherm from Freundlich type of soil to Langmuir type. Biochars produced from burning of wheat and rice residues were reported to be up to 2500 times more effective than soil in sorbing diuron over the concentrations of 0–6 mg/L (Yang and Sheng, 2003a). The wheat ash aged

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in soil up to 12 months could remain > 50% contribution to the total diuron sorption (Yang and Sheng, 2003b). Biochar produced under different combustion conditions (temperature and oxygen supply), and different precursors (hardwood vs. herbaceous) may possess different physiochemical properties such as chemical composition, surface area and adsorptive characteristics (Cao et al., 2009; Chen et al., 2008; Patterson et al., 1987; Shafizadeh, 1984; Yuan et al., 2004; Yu et al., 2006).

High sorption of a contaminant plus its low rate of desorption from geosorbents like biochar may lead to the sequestration and protection of the contaminant from soil organism, thus influencing its fate and toxicity as well as associated risk to human and ecological health (Alexander, 1995; Huang et al., 1998; Kan et al., 1998; Nam and Alexander, 1998). Test with model hydrophobic sorbent made of polystyrene beads showed that more than 98% of phenanthrene could be sorbed from solution by sorbents that contained 5–400 nm or 300–400 nm pores within 1 hr. Sorbed phenanthrene was very difficult to be desorbed (only < 1.0% and < 3.4% desorption from the two types of polystyrene beads, respectively), thus lead to a very low rate of biodegradation. In contrast, the nonporous polystyrene bead could remove most of the compound from solution, but the sorbed compound was easily desorbed and readily available to microorganisms (Nam and Alexander, 1998). Therefore, the microporosity of the sorbents such as polystyrene or biochar can have a strong influence on the release behaviour of sorbed compounds.

Braida et al. (2003) reported the pronounced hysteresis in the sorption/desorption of benzene in water to pure-form maple-wood biochar prepared by oxygen-limited pyrolysis. They postulated that the hysteresis was due to the pore deformation of biochar by the solute, which resulted in the pathway of desorption being different from that of sorption. Our previous study (Yu et al., 2006) showed that the sorption coefficient of diuron, its isotherm non-linearity and the extent of sorption-desorption hysteresis, all markedly increased with increasing contents of wood-derived biochars in soil.

Pyrimethanil is an aniline-pyrimidine fungicide commonly used for the control of grey mould and leaf scab on grape, strawberry, tomato, fruit, vegetables and ornamentals in both greenhouse and open field situations (Tomlin, 2000). It is moderately mobile in soil ( $K_{oc}$ : 265–751 mL/g) (Tomlin, 2000). Field trials showed that pyrimethanil is a moderate persistent substance in soil with a half life of 23–54 days (EFSA, 2006; Vanni et al., 2003). Verdisson et al. (2001) reported that pyrimethanil was the most toxic (+) a non-target aquatic plant (*Lemna minor*) among the three fungicides widely used in Champagne's vineyards. The aim of the present study was to investigate the sorption and desorption behavior of pyrimethanil on soil amended with different amounts of two types of biochars. The biochars used in the study were produced from combustion of red gum (*Eucalyptus* spp.) woodchips. This study specially focused on the release behavior of the sorbed pesticide from biochar amended soils. The results could help further

understand the fate and bioavailability of pyrimethanil in soil environment.

## 1 Materials and methods

### 1.1 Chemicals

Analytical standard of pyrimethanil (chemical purity by GC 99.9%) was purchased from Sigma-Aldrich (Sydney, Australia). Pyrimethanil is an anylopyrimidine fungicide with a vapor pressure of  $2.2 \times 10^{-3}$  Pa, and water solubility of 121 mg/L at 25°C (Tomlin, 2000). Sodium azide was obtained from Fluka (Sydney, Australia), while calcium chloride of analytical grade and all solvents of HPLC grade were from Merck Pty Limited (Victoria, Australia).

### 1.2 Biochars, soil and sorbents

The synthesis of biochar has been described by Yu et al. (2006). Briefly, the woodchips of red gum were air-dried at 40°C and pieces less than 5 mm were hand picked for the carbonization process. The woodchips were loosely placed in porcelain crucibles with lids in a temperature programmable muffle furnace (S.E.M., Australia). The furnace was ramped from room temperature to the final temperature (450 and 850°C) within one hour. The final temperature was held for 2 hr for the biochar burned at 450°C, and one hour for the biochar at 850°C due to the higher combustion temperature. The prepared biochar materials were grounded to a fine powder on a disk-rotating mill for 3 min. In the following, abbreviations BC450 and BC850 are used for biochar prepared at 450 and 850°C, respectively. The specific surface area (SSA) and pore size distribution of the two biochars were evaluated using BET nitrogen adsorption techniques at 77 K. The SSA of BC850 and BC450 were 566 and 27 m<sup>2</sup>/g, respectively. BC850 was a microporous material which has pore width essentially less than 1 nm, with the maximum peak occurring at a pore width of about 0.49 nm. BC450 has a very low level of microporosity with the maximum peak at a pore width of about 1.1 nm (Yu et al., 2006).

The soil used in this experiment was collected from the Roseworthy Campus, University of Adelaide. After air drying at 40°C, the soil was passed through a 2-mm sieve. This soil is sandy loam soil which contained 87.8% sand, 1.3% silt, 8.3% clay, and 1.4% organic matter. The soil had a pH value of 6.8 in a 1:5 (soil:water, W/W) soil suspension, a maximum water holding capacity of 34.2% (W/W) and a cation exchange capacity of 9.3 cmol (+)/kg.

Biochar amended soils used in the experiment were prepared by mixing the above soil and the biochar materials (BC450 and BC850) at different ratios. The percentages of each biochar material in the soil were: 0, 0.1%, 0.2%, 0.5%, 0.8%, and 1.0% (W/W) for BC850, and 0, 0.1%, 0.5%, 1.0%, 2.0%, and 5.0% (W/W) for BC450. The biochar amended soils were thoroughly mixed on a rotary shaker for 7 days before they were used as sorbents for sorption and desorption experiments.

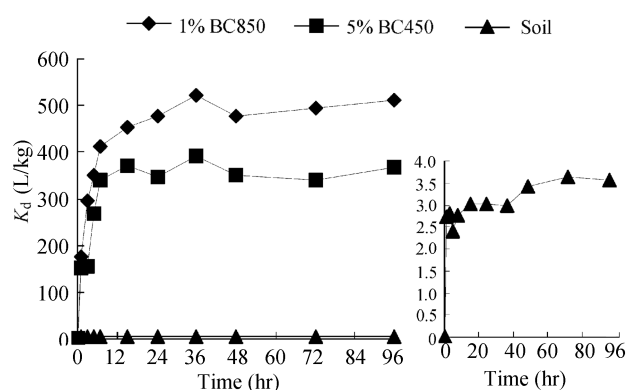
### 1.3 Batch sorption

Pyrimethanil sorption by the sorbents was conducted by the batch equilibration technique as described in previous studies (Yang and Sheng, 2003a; Yuan et al., 2004; Kan et al., 1998). The sorbents were suspended in 10 mL of 0.01 mol/L CaCl<sub>2</sub> solutions (containing 0.5% NaN<sub>3</sub> to inhibit microbial activity) spiked at concentrations of 1 to 21 mg/L of pyrimethanil. The amounts of biochar amended soil used in the experiments were adjusted to allow for 30%–80% of the added chemical to be sorbed at equilibrium. Based on our preliminary experiments, for BC450 amended soil an aliquot of 1.0 g soil was used for 0, 0.1%, 0.5%, 1.0% and 2.0% and only 0.2 g soil for 5.0%. For BC850 amended soils, an aliquot of 0.5 g soil was used for 0.1% and 0.2% and only 0.2 g for 0.5%, 0.8%, and 1.0% amendment. The suspensions were shaken on a rotary shaker at room temperature (22 ± 2°C) and 120 r/min for 24 hr (preliminary experiment showed that the time duration was sufficient to reach apparent equilibrium, the sorption kinetic data of pyrimethanil on soil amended with highest content of both biochars (1.0%, BC850, 5.0% BC450) and soil are shown in Fig. 1), and then centrifuged at 4000 r/min for 60 min. After centrifugation, an aliquot of the supernatant in each tube was taken out and analyzed directly by high performance liquid chromatography (HPLC).

Each sorption test was done in triplicates. 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 and the other control tube that only had the sorbent and CaCl<sub>2</sub> solution without chemical solution. Tests showed losses due to adsorption and degradation were negligible (consistent with the persistent and non-volatile nature of the pesticide) and no interference was found during the analysis of solutions.

### 1.4 Desorption

Desorption experiments were conducted on soil samples initially treated with 21 mg/L pyrimethanil solution. After equilibrating sorption for 24 hr, the tubes were centrifuged and 5 mL of the supernatant in each tube was taken out for analysis. Another 5 mL of 0.01 mol/L CaCl<sub>2</sub> (including 0.5% NaN<sub>3</sub>) was added again into each tube, and then shaken for another 24 hr, the pyrimethanil desorped from



**Fig. 1** Kinetic sorption of pyrimethanil on soil and biochar amended soils.

soil and biochar amended soil was analyzed. We repeated the desorption process more than three times for each tube. All tests were performed in triplicates. The cumulative values for desorption were calculated as below.

### 1.5 Instrument analysis

Analysis of pyrimethanil in the supernatant fraction from sorption and desorption experiments was carried out on an Agilent 1100 series HPLC fitted with a diode array detector and a SGE C18 RS column (250 mm × 4.6 mm, 5 μm). Acetonitrile (ACN) and water were used as the mobile phase, which was programmed from 50% ACN at 0 min to 80% ACN at 5 min. The flow rate of mobile phase was kept at a constant rate of 1 mL/min. The UV wavelength for detection of pyrimethanil was 259 nm. The detection limit for pyrimethanil was 0.05 mg/L.

### 1.6 Data analysis

All the sorption isotherms were fit to the linear form of the Freundlich equation (Eq. (1)).

$$\log C_w = \log K_f + N_f \log C_s \quad (1)$$

where,  $C_w$  (mg/L) is the concentration of a chemical in solution,  $C_s$  (mg/kg) is the concentration of the chemical in the sorbents,  $K_f$  ((mg/kg)/(mg/L) <sup>$N_f$</sup> ) is the Freundlich sorption coefficient, and  $N_f$  is the unitless Freundlich exponent indicative of sorption mechanism.

We also fit the sorption isotherms to linear form of Langmuir equation (Eq. (2)).

$$\frac{C_w}{C_s} = \frac{1}{S_{\max}} \times K_L + \frac{C_w}{S_{\max}} \quad (2)$$

where,  $C_w$  (mg/L) stands for the final sorbate concentration,  $S_{\max}$  (mg/kg) denotes the maximum uptake of sorbate,  $K_L$  (mg/L) is the Langmuir coefficient, and  $C_s$  (mg/kg) is the sorbed amount at equilibrium.

To assess the goodness of model fit of the sorption data, ANOVA was performed using the REG (regression) procedure of Statistical Analysis System (Version 8.01, SAS Institute Inc., USA).

We calculated the desorption rate (R) according to Eq. (3).

$$R = \frac{C_{S_0} - C_{S_t}}{C_{S_0}} \times 100\% \quad (3)$$

where  $C_{S_0}$  (mg/kg) and  $C_{S_t}$  (mg/kg) are the amount of a compound sorbed by sorbents before and after desorption process, respectively.

## 2 Results and discussion

### 2.1 Sorption of pyrimethanil

Biochar amendment into the soil not only enhanced the sorption of pyrimethanil but also changed the sorptive characteristic of the soil. The sorption data of pyrimethanil on the soil and biochar amended soils over the entire range of equilibration concentrations were fitted to Freundlich

equation. The increasing values of Freundlich sorption coefficient  $K_f$  combined with the decreasing values of exponent  $N_f$  with biochar content indicated that the sorption of pyrimethanil by the amended soils progressively increased with increasing content of biochars in the soil (Table 1). The  $N_f$  values of Freundlich model decreased from 0.81 to 0.20 and 0.19 (Table 1), as the amount of biochar in soil increased from 0.1% to 5.0% for BC450 and from 0.1% to 1.0% for BC850, respectively, indicating a progressive increasing of the nonlinearity degree of the sorption isotherms with increased biochar amendment. While the mechanisms of sorption are not clear, the increasing non-linearity of the isotherm together with the microporous nature of the biochar produced at higher temperature suggests that the sorption was most probably due to both surface adsorption as well as absorption into micropores of biochar. Most of the sorption data could fit well to the Freundlich model ( $R^2 > 0.9$ ,  $P < 0.001$ ), but at the high levels of biochar amendment, the fit was found to be poorer for both types of biochars (the values of  $R_f^2$  were 0.89 and 0.93 for 5.0% BC450 and 1.0% BC850 amended soil, respectively). Instead, the data were found to be better fitted to the Langmuir model in these cases (Table 2). Fitting of the sorption data with Langmuir model also revealed that the  $S_{max}$  value of biochar amended soils increased with increasing content of biochar in the soil, especially in case of biochar BC850.

## 2.2 Desorption of pyrimethanil from sorbents

The desorption of pyrimethanil were assessed on the soil samples initially treated with 21 mg/L pyrimethanil

solution. Before the desorption process was initiated, the amount of pyrimethanil sorbed by the original soil was calculated to be 43.25 mg/kg, and were 51.05, 75.40, 112.84, 175.37, 420.01 mg/kg for the soils amended with 0.1% BC450, 0.5% BC450, 1.0% BC450, 2.0% BC450, and 5.0% BC450, respectively. The corresponding sorbed pesticide amounts were 67.28, 127.67, 245.37, 385.90, 428.13 mg/kg, respectively for the soils amended with 0.1% BC850, 0.2% BC850, 0.5% BC850, 0.8% BC850, and 1.0% BC850. For the high biochar-amended soils, their sorbed pesticide amounts were nearly equal to the maximum sorption capacities.

Figure 2 shows the desorption of pyrimethanil from the soils amended with different amounts of biochars (BC450 and BC850) during the four successive (96 hr) desorption steps, expressed as percentages of the initial amount adsorbed (desorption rate). More than half of the pyrimethanil sorbed by the original soil was desorbed after washing for four times. For the biochar amended soils, the amount of pyrimethanil desorbed at each of the four desorption stages decreased when the content of biochar in the soil increased (Fig. 2). For the soil amended with 5.0% BC450 and 1.0% BC850, there were only 13.65% and 1.49% of the pyrimethanil could be desorbed after four times washing, respectively. The results revealed that due to the strong sorption capacity, biochars could lead to slow desorption or sequestration of a compound. The irreversibility of the pesticide sorption may result in the low bioavailability of the pesticide in biochar amended soils (Yang et al., 2006; Zhang et al., 2005; Yu et al., 2009).

Desorption behavior of the sorbed pesticide depends on

**Table 1** Freundlich model of pyrimethanil sorption isotherms

Biochar	Content of biochar in soil (%)	$K_f$ ((mg/kg)/(mg/L) <sup><math>n</math></sup> )	$N_f$	$R_f^2$	$F$ value	$P$ value
BC450	0.0	4.36 ± 0.68	0.81 ± 0.04	1.00	745.65	<0.0001
	0.1	5.89 ± 1.03	0.80 ± 0.02	0.99	368.14	<0.0001
	0.5	13.76 ± 0.79	0.66 ± 0.03	0.99	293.15	<0.0001
	1.0	46.94 ± 3.42	0.30 ± 0.04	0.98	260.93	<0.0001
	2.0	96.91 ± 6.87	0.24 ± 0.03	0.99	198.90	<0.0001
BC850	5.0	263.76 ± 5.73	0.20 ± 0.01	0.89	41.30	0.0014
	0.1	18.91 ± 1.34	0.44 ± 0.03	0.99	374.72	<0.0001
	0.2	49.49 ± 1.49	0.29 ± 0.08	0.98	214.91	<0.0001
	0.5	123.55 ± 6.34	0.24 ± 0.06	0.98	173.79	<0.0001
	0.8	227.94 ± 2.34	0.20 ± 0.01	0.97	161.07	<0.0001
1.0	273.25 ± 3.69	0.19 ± 0.01	0.93	76.33	0.0001	

$K_f$ : Freundlich affinity coefficient;  $N_f$ : Freundlich exponent;  $R_f^2$ : Freundlich determination coefficient.

**Table 2** Langmuir model of pyrimethanil sorption isotherms

Biochar	Content of biochar in soil (%)	$S_{max}$ (mg/kg)	$K_L$ (mg/L)	$R_L^2$	$F$ value	$P$ value
BC450	0.0	–	–	–	–	–
	0.1	101.01 ± 8.98	16.74 ± 0.82	0.87	34.18	0.0021
	0.5	104.17 ± 10.06	6.39 ± 1.06	0.95	54.17	0.0007
	1.0	120.48 ± 6.52	1.94 ± 0.02	0.96	116.96	0.0001
	2.0	175.44 ± 12.34	0.60 ± 0.04	0.99	431.59	<0.0001
BC850	5.0	416.67 ± 4.38	0.42 ± 0.01	0.99	453.62	<0.0001
	0.1	81.30 ± 2.52	4.54 ± 0.13	0.94	84.70	0.0003
	0.2	111.11 ± 5.86	1.82 ± 0.12	0.93	82.20	0.0005
	0.5	238.10 ± 12.79	1.05 ± 0.09	0.97	193.25	<0.0001
	0.8	384.62 ± 8.63	0.65 ± 0.03	0.99	357.22	<0.0001
1.0	416.67 ± 15.48	0.29 ± 0.02	1.00	635.78	<0.0001	

$S_{max}$ : maximum sorbate uptake;  $K_L$ : Langmuir affinity coefficient;  $R_L^2$ : Langmuir determination coefficient.

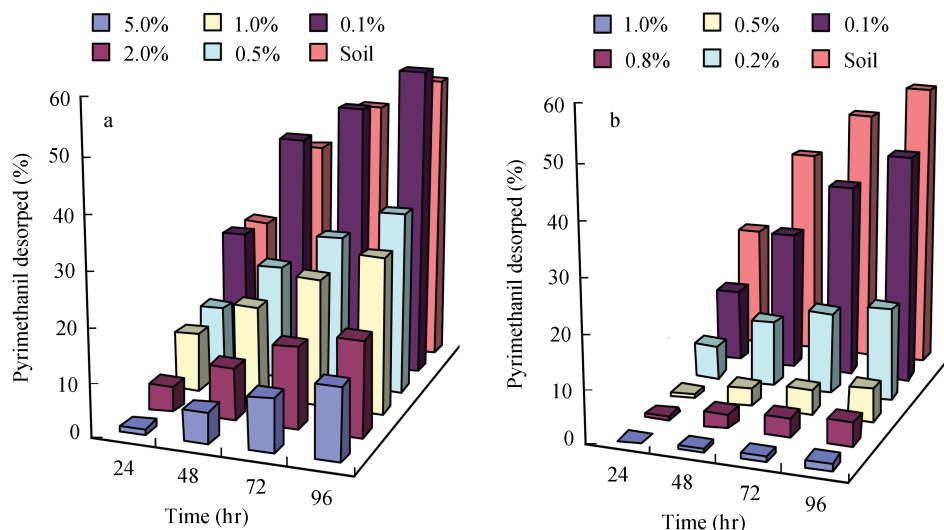


Fig. 2 Desorption of pyrimethanil from soil amended with different contents of BC450 (a) and BC850 (b).

the source of biochars. Biochar produced from red gum woodchips at 850°C had a higher surface area and microporosity in comparison with that produced at 450°C (Yu et al., 2006). In the present study, comparable sorption capacities could be achieved with different biochar amendments (e.g., 0.2% BC850 versus 1.0% BC450, and 1.0% BC850 versus 5.0% BC450, as shown in Tables 1 and 2), but the percentage of pyrimethanil desorbed from the soil amended with BC850 was much lower than the soil amended with BC450 (Fig. 2). It has been recognized that surface specific adsorption, entrapment into micropores and partitioning into condensed structures of soil organic matter are the main causes of chemical sequestration (Ghosh et al., 2000). With comparable levels of sorption, irreversibility of the sorbed pesticide was much more prominent in the case of BC850. This is probably due to the higher surface area and microporosity of BC850. When the molecules of a pesticide partition into the micropores of biochar, it could become tightly entrapped and difficult to be desorbed, which is consistent with the results of previous studies (Nam and Alexander, 1998; Braida et al., 2003).

According to the pore deformation hypothesis for desorption hysteresis (Lu and Pignatello, 2002; Braida et al., 2003), holes (micropores) in sorbents may be forced to expand by the thermal motion of incoming sorbate molecules, creating new internal surface area in solid during the sorption process. Molecules may even force their way into holes which were initially too small to accommodate them. During the desorption process, a lag phase can exist between sorbate molecules leaving their holes and relaxation of the surrounding matrix to its original state. This cycle results in irreversible sorption because sorption and desorption are occurring to/from different physical environments. This hypothesis gives a good explanation for the highly irreversible sorption of biochar with a high microporosity. As the pore structure and pore size of biochar depends greatly on the formation conditions (Shafizadeh, 1984; Patterson et al., 1987; Yuan et al., 2004), the degree of sorbate induced pore deformation occurred on different biochar samples might be

different. In the present study, BC450 has less micropores (maximum peak occurred for pore widths of about 1.1 nm) (Yu et al., 2006). Most pores in BC450 are “too large”, pyrimethanil molecules could enter the pore easily, and the pyrimethanil molecules captured in the hole also escape easily. On the other hand, owing to its large surface area and high microporosity, biochar BC850 possesses more micropores, which could trap more sorbate molecules, thus result in its highly irreversible sorption. Therefore, biochar properties are responsible for the differences in sorption capacity and desorption hysteresis of the two biochars.

### 3 Conclusions

Biochar produced from incomplete combustion of red gum woodchip could enhance the sorption of pesticide pyrimethanil when incorporated into soil, and also increase the sorption isotherm nonlinearity. The desorption irreversibility progressively increased with the increasing ratio of biochar in the soil. The marked effects of biochar on the sorption capacity and desorption irreversibility is expected to have strong influences on the bioavailability of organic contaminants in terrestrial and aquatic ecosystems.

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