Chemosphere 76 (2009) 665–671

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Reduced plant uptake of pesticides with biochar additions to soil

Xiang-Yang Yu [a,b], Guang-Guo Ying [a,c], Rai S. Kookana [a,*]

[a] CSIRO Land and Water, PMB No. 2, Glen Osmond 5064, Australia
[b] Pesticide Biological and Ecological Research Center, Jiangsu Academy of Agricultural Sciences, Nanjing 210014, China
[c] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 16 January 2009
Received in revised form 1 April 2009
Accepted 1 April 2009
Available online 5 May 2009

Keywords:
Pesticide
Charcoal
Black carbon
Bioavailability
Plant uptake
Produce contamination

ABSTRACT

We investigated the effectiveness of two types of biochars in reducing the bioavailability of two soil-applied insecticides (chlorpyrifos and carbofuran) to Spring onion (*Allium cepa*). The biochars prepared from the pyrolysis of *Eucalyptus* spp. wood chips at 450 and 850 °C (BC850) were thoroughly mixed into the soil to achieve 0%, 0.1%, 0.5% and 1% by soil weight. A spring onion crop was grown for 5 wk in the biochar-amended soils spiked with 50 mg kg^{-1} of each pesticide. The loss of both pesticides due to degradation and or sequestration in soils decreased significantly with increasing amounts of biochars in soil. Over 35 d, 86–88% of the pesticides were lost from the control soil, whereas it was only 51% of carbofuran and 44% of chlorpyrifos from the soil amended with 1.0% BC850. Despite greater persistence of the pesticide residues in biochar-amended soils, the plant uptake of pesticides decreased markedly with increasing biochar content of the soil. With 1% of BC850 soil amendment, the total plant residues for chlorpyrifos and carbofuran decreased to 10% and 25% of that in the control treatment, respectively. The BC850 was particularly effective in reducing phytoavailability of both pesticides from soil, due to its high affinity for and ability to sequester pesticide residues.

1. Introduction

Biochar is formed by incomplete combustion of biomass and has been shown to be particularly effective in sorption and sequestration of organic contaminants in soil due to its greater surface area, high microporosity and other physiochemical properties (Chiou et al., 2000; Allen-King et al., 2002; Accardi-Dey and Gschwend, 2003; Chun et al., 2004; Lohmann et al., 2005; Yu et al., 2006). Biochars produced from burning of wheat and rice residues were reported to be up to 2500 times more effective than soil in sorbing diuron herbicide (Yang and Sheng, 2003). James et al. (2005) evaluated sorption of phenanthrene on various wood chars produced at varying heating temperature and concluded that in addition to surface area, heterogeneous surface properties contribute to sorptive ability of biochars. Incorporation of a small amount of biochar in a soil has also been shown to inhibit the microbial degradation of benzonitrile (Zhang et al., 2005), and reduce herbicidal efficacy of diuron to barnyard grass (Yang et al., 2006). Hydrophobic sorbents with nanoporosity have been reported to sequester organic compounds and reduce their bioavailability. For example, tests with model sorbents by Nam and Alexander (1998) showed that with glass and polystyrene beads (with no porosity) phenanthrene was rapidly mineralized whereas with porous polystyrene beads, containing 5- or 300–400 nm pores, little of the compound was desorbed and only <7% of sorbed phenanthrene was mineralized. We have also previously found (Yu et al., 2006) that the sorption and desorption behaviour of diuron is strongly influenced by the presence of biochars in soil. We noted an increase in sorption–desorption hysteresis, which suggested that sorption by biochar can facilitate sequestration of organic contaminants due to its nanoporosity.

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. Other practices such as direct burning of plant residues (e.g. sugarcane trash) and natural combustion such as forest fires have contributed to the high level of biochar found in some soils (Schmidt et al., 1996; Skjemstad et al., 1996; Young et al., 2005; Lehmann et al., 2006), which may strongly influence the environmental fate and behavior of organic contaminants in soils. Despite increasing interest in biochar application into soil for carbon sequestration to abate climate change (Lehmann et al., 2006), currently little information exists in literature if biochar amendment to soil can reduce the plant uptake of pesticide residues. Such a practice, if found effective, can assist in management of contaminated agricultural and urban soils from past use of pesticides.

The objectives of this study were therefore to investigate (i) the effectiveness of biochars in reducing the bioavailability and plant

* Corresponding author. Tel.: +61 8 83038450; fax: +61 8 83038565.
E-mail address: Rai.Kookana@csiro.au (R.S. Kookana).

0045-6535/$ - see front matter
doi:10.1016/j.chemosphere.2009.04.001

uptake of pesticides with different water solubility from soil, and (ii) to compare the effects of the two types of biochars on their relative potential for sequestration of pesticides in soil. We assessed this for two commonly used pesticides with contrasting properties (carbofuran and chlorpyrifos) in soil amended with two kinds of biochars by investigating (i) dissipation (degradation and/or sequestration) of the two pesticides from soil and (ii) by assessing the plant uptake of pesticide residues by spring onion (*Allium cepa*).

2. Materials and methods

2.1. Biochars

The biochars were produced from Red gum wood (*Eucalyptus* spp.) at two different temperatures (450 and 850 °C) as described previously (Yu et al., 2006). Briefly, air dried red gum woodchips 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 prepared biochar materials were hand-ground to a fine powder in a grinder and roller and passed through a 200 μm sieve. The specific surface area (SSA) and pore size distribution of the two biochars were evaluated using BET nitrogen adsorption techniques at 77 K and have been reported earlier (Yu et al., 2006). The SSA of BC850 and BC450 were 566 $m^2 g^{-1}$ and 27 $m^2 g^{-1}$, respectively. BC850 was a microporous material with all pores being essentially less than 1 nm in pore width and the maximum peak occurring at pore widths of about 0.49 nm, whereas BC450 had a lower level of microporosity with the peak maxima occurring at a pore width of about 1.1 nm (Yu et al., 2006).

2.2. Soil and pesticides

A sandy loam soil locally known as red-brown earth (a Xeralf) was collected from the Roseworthy Campus of the University of Adelaide. The soil consisted of 87.8% sand, 1.3% silt, 8.3% clay and 1.4% organic matter. The soil had a pH of 6.8 (1:5, soil:water), a maximum water holding capacity (MWHC) of 35% (v/v) and a cation exchange capacity of 9.3 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 d. The percentages of two biochar materials in the amended soils were: 0%, 0.1%, 0.5%, and 1.0% (w/w), respectively.

Carbofuran (>99%) and chlorpyrifos (>99%) were obtained from Sigma–Aldrich (Sydney, Australia). Carbofuran and chlorpyrifos were selected in this study because the two pesticides are widely used to control soil insect pests and their residues have been found in some vegetables in China (Chen et al., 2006). Carbofuran is a nonvolatile carbamate compound with a vapor pressure of 0.031 mPa at 20 °C, a water solubility of 320 mg L^{-1} at 20 °C, and a log K_{ow} of 1.52 (Tomlin, 2000). Chlorpyrifos is an organophosphate pesticide with a low water solubility (1.4 mg L^{-1} at 25 °C) and high hydrophobicity (log K_{ow} of 4.70) (Tomlin, 2000). Solvents of HPLC grade (acetonitrile, acetone, dichloromethane, and hexane) used in the extraction and instrumental analysis were all obtained from Merck Pty Limited (Victoria, Australia). Sodium sulphate dehydrates and florisil used in the extraction and clean-up processes were obtained from Sigma–Aldrich (Sydney, Australia).

2.3. Plant growth experiment

Spring onion (*A. cepa*) planted in vermiculite (procured from a local nursery in Adelaide) was used as the test plant in this study. Seedlings of about 20 cm in height were selected to conduct plant experiments using plastic containers (10 cm in diameter and 10 cm in height) as a closed system allowing no leaching loss of water or pesticides. Each container was filled with 500 g of the biochar-free soil or biochar-amended soils, and then 2.5 mL of 10 mg mL^{-1} pesticides solution in acetone was added into each container, resulting in a spiked concentration of 50 mg kg^{-1} for each pesticide. We chose a relatively high insecticide concentration in this research as these two insecticides are used as direct soil application to control soil insect pest, and may produce temporary elevated concentrations in the rhizosphere. The seven biochar amendments used in this experiment were control (0% biochar), three amendments with BC450 (0.1%, 0.5% and 1.0% BC450) and other three with BC850 (0.1%, 0.5% and 1.0% BC850). 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 five replicates. The soils were thoroughly mixed and shaken for 24 h in a rotary shaker, which was followed by evaporation in acetone for another 2 d.

After the solvent acetone was evaporated, 90 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 soil were taken out from each container to determine the pesticide concentrations. The five replicates were then divided into two subgroups, three were used for uptake experiment with plants, and the other two were used as degradation experiments without plants. Spring onion seedlings were removed from the vermiculite and carefully washed with water and 30 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 2 d to maintain the soil moisture.

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

2.4. Residue extraction and clean up

To evaluate the influence of biochars on the degradation of carbofuran and chlorpyrifos in unplanted soils, 5 g of soils were taken out from the containers on the 7th, 14th, 21st and 35th day after treatment to determine the amounts of the pesticides remaining. Soil samples were dried at 40 °C for 12 h and 1 g of soil was extracted with 10 mL acetone/hexane (1:1, v/v) mixture for chlorpyrifos, and acetonitrile for carbofuran, by the procedure as follows: Vortex mixed for 1 min, ultrasonically extracted for 2 h, and shook in a rotary shaker for 12 h. Following phase separation by centrifuging at 1300*g* for 15 min, 1 mL of supernatant was dried under N_2 gas and redissolved in 1 mL of HPLC mobile phase. The pesticide concentration was measured by HPLC. The recoveries were 89–98% and 86–94% for carbofuran and chlorpyrifos in the soil and biochar-amended soils, respectively, with the fortified concentrations of 1–50 mg kg^{-1}.

An aliquot of 5 g plant sample was mixed with 20 g of sodium sulphate dehydrates and ground in mortar and pestle. The mixtures were then extracted with 30 mL of solvents (acetone/hexane (1:1, v/v) for chlorpyrifos, and acetone for carbofuran). The extraction procedures were the same as that for the soil samples. After centrifugation at 1300*g* for 15 min, 25 mL supernatant were collected and dried under N_2 gas, then redissolved in 1 mL of hexane. The extracts were subjected to florisil clean-up with the procedure as follows.

A mass of 1 g florisil was placed in a 0.5 cm diameter glass pipettes with acid washed glass wool at the bottom. The column was washed with 2 mL hexane, and then the sample extraction solution was put on the top of the column. For chlorpyrifos, the clean up procedure was as follows: 5 mL of hexane passed through the column and discarded, and then another 5 mL of hexane/dichloromethane (1:1, v/v) was used to wash out chlorpyrifos sorbed by the florisil, collected and dried under N_2, and then dissolved in 1 mL hexane for determination of chlorpyrifos by GC–MS. For carbofuran, after the column was washed with 5 mL of hexane and 5 mL of hexane/dichloromethane (1:1, v/v), the pesticide was eluted with another 5 mL of dichloromethane. The extract was collected and dried under N_2 gas, and then dissolved in 1 mL of mobile phase for determination of carbofuran by HPLC. The recoveries were 65–80% for carbofuran and 73–90% for chlorpyrifos in plant materials, respectively, with the fortified concentrations of 0.01–10 mg kg^{-1}.

2.5. Residue analysis

For both pesticides, the amounts of residues in soils were analyzed by HPLC. However, the residues of chlorpyrifos in plant samples were analyzed by GC–MS and of carbofuran by HPLC. Analysis of chlorpyrifos residue in soil samples and carbofuran residue in soil and plant samples was carried out on an Agilent 1100 series HPLC equipped with a diode array detector and a SGE C18 RS column (250 × 4.6 mm, 5 μm). Acetonitrile/water (3:7, v/v) was used as the mobile phase at a flow rate of 1 mL min^{-1} for carbofuran. The UV wavelength for detection of carbofuran was 210 nm. The injection volume was 50 μL. Analysis of chlorpyrifos by HPLC was the same as carbofuran, except for the mobile phase, which was acetonitrile/water (7:3, v/v), and the UV wavelength for detection of chlorpyrifos was 270 nm. The detection limit for carbofuran and chlorpyrifos was set to 0.01 mg L^{-1}. Standard curves were generated freshly with each analytical batch using solutions within the measured concentration range (from 0.1 to 5.0 mg L^{-1}) and was found to be stable during the analytical period.

GC–MS was used to analyze chlorpyrifos in plant samples. 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 and helium flow rate at 1 mL min^{-1}. Oven temperature program was: 70 °C (2 min) to 150 °C at 25 °C min^{-1}, to 280 °C at 10 °C and then hold for 10 min. The MS interface temperature was 280 °C, MS source

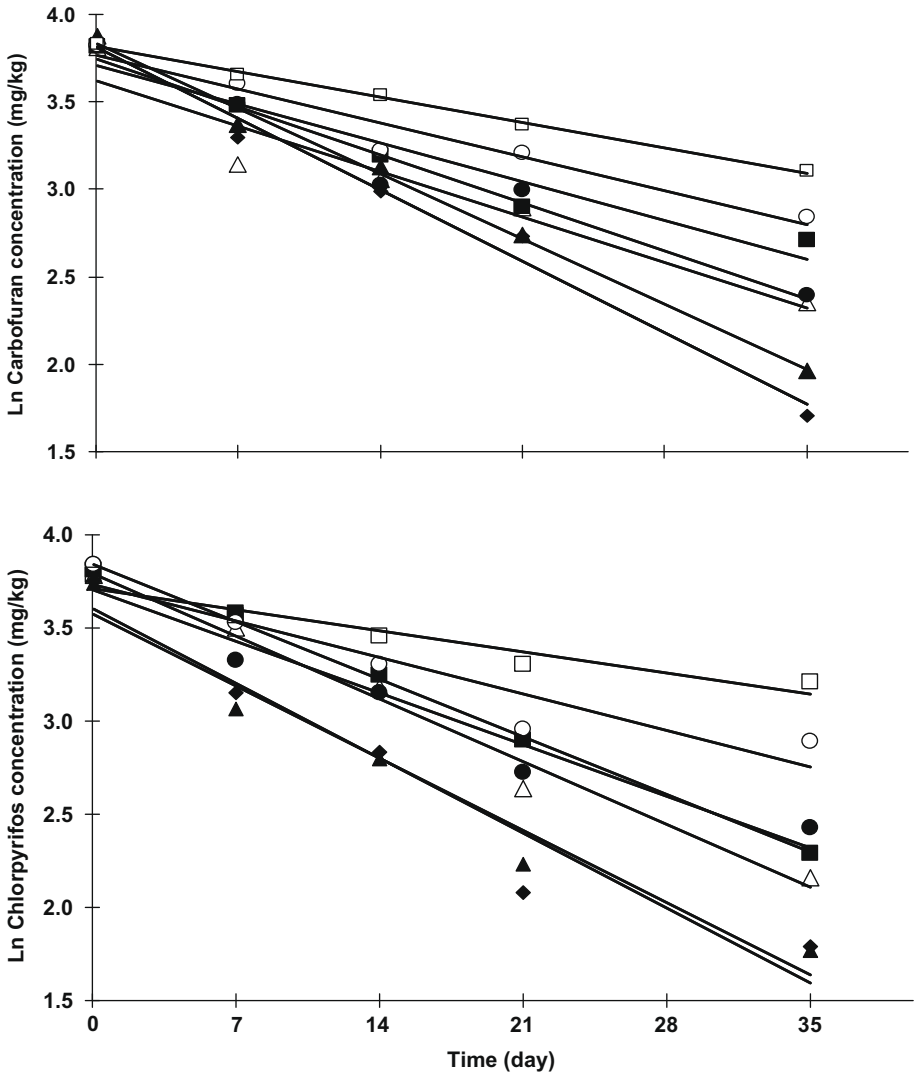

Fig. 1. Natural log of concentrations of chlorpyrifos and carbofuran remaining over time in the original soil and the soil amended with two biochars. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. —◆— Unamended soil; —▲—0.1% BC450; —●—0.5% BC450; —■—1.0% BC450; —△—0.1% BC850; —○—0.5% BC850; —□—1.0% BC850.

Table 1
Half-lives of carbofuran and chlorpyrifos in soil as affected by the presence of biochar.

Content of biochar	Carbofuran		Chlorpyrifos	
	DT_{50} (d)	Correlation coefficient (r)	DT_{50} (d)	Correlation coefficient (r)
Unamended soil	11.9	0.992	12.1	0.966
0.1% BC450	13	0.997	12.5	0.977
0.5% BC450	17.5	0.982	17.5	0.972
1.0% BC450	21.7	0.968	15.6	0.999
0.1% BC850	18.6	0.957	14.3	0.992
0.5% BC850	25.1*	0.973	24.8**	0.944
1.0% BC850	33.3**	0.998	42.8**	0.961

* ($p < 0.05$) represent statistical difference between DT_{50} in soil amended with biochar and in unamended soil.
** ($p < 0.01$) represent significant difference between DT_{50} in soil amended with biochar and in unamended soil.

230 °C, and MS Quad 150 °C. Selected ion mode was used in detection and quantification for chlorpyrifos (12.8 min) with a target ion of m/z 314.

2.6. Data analysis

To assess the statistical differences among the plant uptake of pesticides from biochar-amended soils, pesticides residue in biochar-amended soils, and the plant biomass, a Duncan's multiple range test was conducted with Statistical Analysis System Version 6.12. The differences between the dissipations rates of pesticides from soils amended with biochars and the control were analyzed using a t-test.

3. Results and discussion

3.1. Dissipation of pesticides from soils in the presence of biochar

The losses of chlorpyrifos and carbofuran residues with time from unamended soils and those amended with biochars are shown in Fig. 1. The amendment with biochars caused a marked decrease in the dissipation of pesticide residues from soil. Since the leaching was not allowed from soil, this loss has been ascribed to mainly degradation and/or sequestration of pesticides. The residue dissipation decreased with increasing content of both biochars, however the BC850 was most effective in reducing the loss of pesticide. At the end of 35 d of incubation, a total of 86% of applied chlorpyrifos and 88% of carbofuran residue was lost from the unamended soil. In contrast, only 44% chlorpyrifos and 51% of carbofuran degraded/sequestered from the soil amended with 1.0% BC850. BC450 inhibited the rate of decay to a much lesser degree.

The data were fitted to a first-order equation to estimate half-lives of the two compounds in different treatments (Table 1). In all but two cases the data fitted well ($r > 0.96/p < 0.009$) to the first-order decay. The data for 0.5% BC850 for chlorpyrifos and 0.1% BC850 treatment for carbofuran showed poorer but still statistically significant fit at 5% level ($r > 0.94/p < 0.015$). For chlorpyrifos the half-life increased from 12.1 d in unamended soil to 42.8 d for soil amended with 1.0% BC850 (a statistically significant increase at $p < 0.05$). The corresponding increase for carbofuran was from 11.9 d to 33.3 d (significant at $p < 0.05$). The key mechanism for this effect was most likely due to strong sorption of pesticides and reduced desorption from biochars surface (Yu et al., 2006) leading to poorer bioavailability of pesticides. Similar results about the reduced biodegradation of diuron and benzonitrile by selected microorganisms in the presence of wheat char have been reported by other workers (Zhang et al., 2005; Yang et al., 2006).

We also compared the pesticide dissipation (through degradation and/or sequestration) from the various treatments in the presence and absence of plants. The data for both pesticides essentially showed similar effects and therefore only carbofuran data are shown here (Fig. 2). The loss of the pesticide residues was faster in the presence of plants in most treatments (including unamended soil) and especially in the case of biochar BC850. The final residue concentrations of both carbofuran and chlorpyrifos remaining in all plant/soil treatments with or without biochar amendment were all lower than that of the corresponding treatment without plants. The increased loss of pesticides from the soils in the presence of plants was due to the combined effect of uptake and increased degradation of the pesticides. Plants could stimulate both microbial and biochemical activity in surrounding soil and mineralization of pollutants in the rhizosphere through release of exudates and enzymes (Fang et al., 2001; Sun et al., 2004). We only measured the final concentration of carbofuran and chlorpyrifos in the biochar-amended soils and control soils with and without plants. Therefore, we cannot offer any mechanistic explanation on the pesticides transformation reactions under the different treatments. The effect of biochar amendments on plant uptake of these pesticides is described below.

3.2. Plant uptake of pesticides from soil in the presence and absence of biochars

Spring onion cultivated in the soils amended with biochars produced higher biomass than those cultivated in the control soils (Fig. 3). The biomass fresh weights of spring onion from BC850 amended soils were all higher than those from BC450 amended soils. Spring onion cultivated in the soils containing carbofuran produced greater biomass than those in the soils spiked with chlorpyrifos. This was true for each level of biochar amendment (Fig. 3). The average fresh weight of spring onion (including above-ground and below-ground parts) harvested from the soils with carbofuran and different levels of biochar treatment was 28 ± 5 g 30 plants^{-1}, in comparison with only 21 ± 6 g 30 plants^{-1} for those from chlorpyrifos treatments. Biochars produced from incomplete combustion of vegetation generally comprise of a range of compounds and could indirectly enhance plant growth through nutrients and trace elements and improving soil physical and biological properties (Lehmann et al., 2003; Lehmann et al., 2006).

After 5 wk of growth in the treated soils, the residues of carbofuran and chlorpyrifos were determined in the above-ground and underground parts (onion bulb and roots) separately. The data in Fig. 4 show that the pesticide residues in both above-ground parts as well as below-ground parts for both pesticides were lower in the plants that were grown in soils amended with biochars. For example, the concentration of carbofuran in the under-ground plant parts decreased from 14.4 ± 0.8 in control soil to only 1.8 ± 0.4 mg kg^{-1} in the soil amended with 1.0% BC850. Similarly the corresponding decrease of chlorpyrifos uptake was from 14.1 ± 1.7 to 0.8 ± 0.1 mg kg^{-1} in the presence of 1.0% BC850. The residues in the above-ground parts were found to be 20–250 times

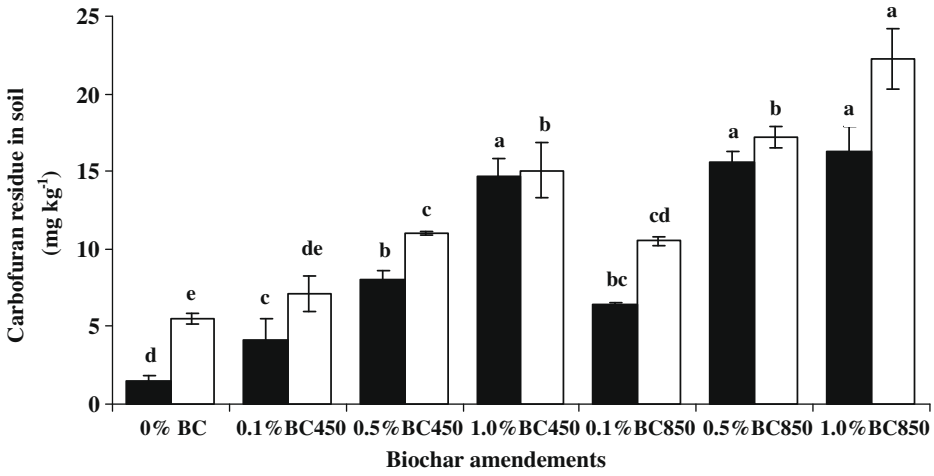

Fig. 2. Carbofuran residues in soil amended with biochars in the presence (■) and absence of plant (□). BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. Error bars indicate standard deviation. Different letters above the same bar type indicate significant difference (Duncan, $p < 0.05$).

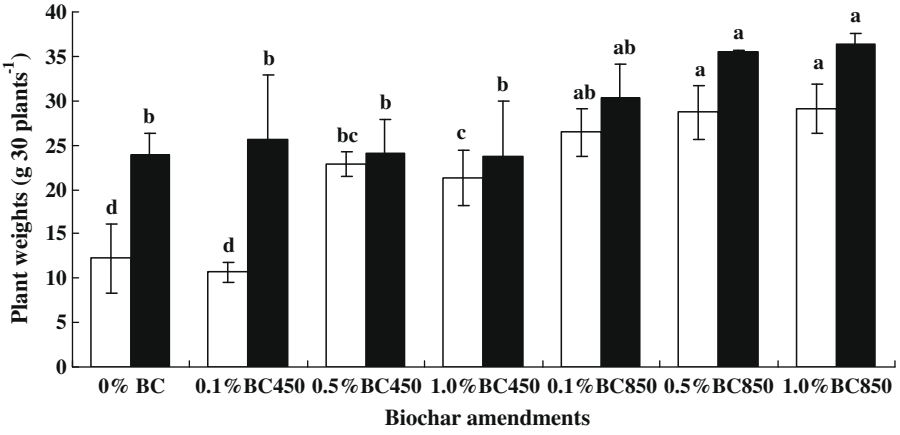

Fig. 3. Fresh weights of spring onion plants cultivated in the biochar-free soils and biochar-amended soils fortified with carbofuran (■) and chlorpyrifos (□) at the initial concentration of 50 mg kg^{-1}. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. Error bars indicate standard deviation. Different letters above the same bar type indicate significant difference (Duncan, $p < 0.05$).

lower than those in the underground parts for both pesticides (Fig. 4). The residues of carbofuran were higher than those for chlropyrifos for any treatment, presumably due to the differences in their hydrophobicities.

Root concentration factor (RCF) is generally expressed as the concentration of a pesticide in underground parts divided by the concentrations in soil (Calamari et al., 1987). In this study, the RCF were calculated by dividing the pesticide concentration in under-ground plant parts by the concentration remaining in soils at the end of experiment. The RCF of carbofuran and chlorpyrifos in the soils amended with different rates of the two kinds of biochar progressively declined as the content of biochar in the soils increased. For the plants cultivated in the untreated soil, the RCF of carbofuran and chlorpyrifos were 9.4 and 3.4, respectively. With the biochar BC850 in the soils at 0.1%, 0.5% and 1.0%, the corresponding RCF values for carbofuran were 1.8, 0.3 and 0.1, and for chlorpyrifos these were 1.2, 0.2 and 0.04, respectively.

Clearly the BC850 biochar was particularly effective in reducing the uptake of both pesticides by plants, and this treatment also showed higher biomass production. To assess the effect of dilution due to greater biomass, the total amounts of pesticides residues taken up by plants were calculated by residue concentration multiplied 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 the above-ground part) all decreased with the increasing char content of soil. After taking the biomass variations in consideration, 1.0% BC850 treatment was still most effective and it reduced the total plant uptake of carbofuran by 75% and of chlorpyrifos by 90% of that in the control treatment.

The lack of bioavailability of two pesticides in char amended soils is supported by (i) the reduced degradation and increased sequestration of pesticides (reflecting reduced bioavailability to microorganisms) and (ii) the reduced uptake of pesticide residue in plant parts (reflecting reduced phytoavailability). In previous studies (e.g. Yang and Sheng, 2003; Yu et al., 2006) sequestration of pesticides in the presence of biochar in soil due to nanoporous nature of the biochars have also been observed. The nature and properties of biochar is strongly affected by the temperature experienced during combustion (Yuan et al., 2004; Sheng et al., 2005; Yu et al., 2006). Under relatively high pyrolysis temperatures (500–700 °C), the biochar derived from wheat was found to be well carbonized and had a relatively high surface area and low oxygen content (Yuan et al., 2004). Such biochars have been reported to show high affinity for organic compounds (Yuan et al., 2004; Sheng et al., 2005), especially for polar solutes (Yuan et al., 2004; Zhu et al., 2005). Biochar derived from Eucalyptus tree wood under relative higher temperatures had higher microporosity and showed higher sequestration of organic compounds (Yu et al., 2006; Borne-

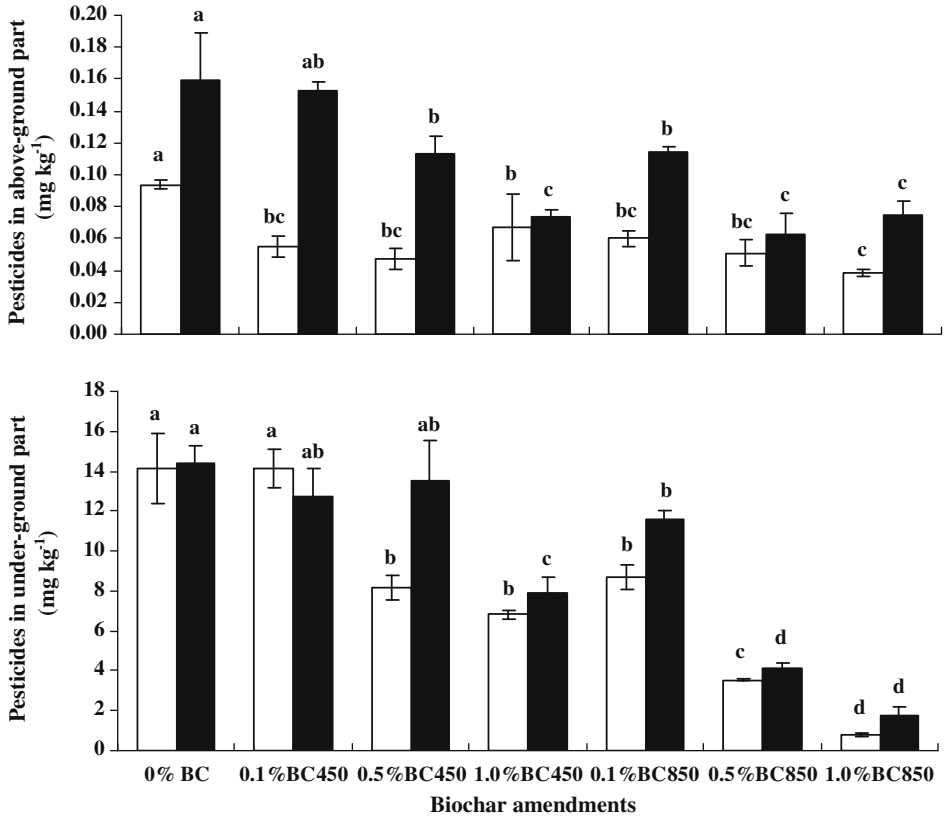

Fig. 4. Concentration of carbofuran (■) and chlorpyrifos (□) residue in underground and above-ground parts of spring onion. BC450 and BC850 represent biochars that were produced at 450 and 850 °C, respectively. Error bars indicate standard deviation. Different letters above the same bar type indicate significant difference (Duncan, $p < 0.05$).

Table 2
Total amount of plant uptake of pesticide residue in different parts (μg) measured at the end of 35-d experiment.

Charcoal	Content in soil (%)	Carbofuran			Chlorpyrifos		
		M_T	M_P	M_R	M_T	M_P	M_R
Original soil		98 a	2.9 a	95 a	64 a	0.7 bc	63 a
BC450	0.1	97 a	3.0 a	94 a	58 ab	0.4 d	57 ab
	0.5	87 a	1.8 c	85 a	63 a	0.7 bc	63 a
	1.0	66 b	1.3 d	65 b	45 bc	1.0 ab	44 bc
BC850	0.1	99 a	2.5 b	97 a	65 a	1.1 a	64 a
	0.5	53 c	1.5 cd	51 c	32 c	1.0 ab	31 c
	1.0	25 d	1.5 cd	24 d	7.1d	0.6 cd	6.4 d

M_T represents the total amount of pesticides uptake in the whole plants. M_R and M_P represent the amount of pesticide, which were calculated by plant concentration multiplied with plant biomass taken up by the underground parts and above-ground parts of spring onion, respectively. The different letters after the values of the same column represent statistical difference ($p < 0.05$).

mann et al., 2007). The current study shows that incorporation of biochars in soil could directly reduce the bioavailability of pesticides in soils, and thus can significantly reduce their plant uptake from a contaminated soil.

4. Conclusions

This study showed that incorporation of biochar in soil could markedly reduce the bioavailability of pesticides and, in particular, this phenomenon can potentially be harnessed to reduce the plant uptake of pesticides from contaminated soils. Biochar produced 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, nanoporosity and greater ability to sequester organic compounds. The increasing interest in soil amendment with biochars for carbon sequestration purposes may be further enhanced due to the potential role that biochar can play in minimizing the pesticide residue in agricultural produce. The application of the findings from this study should be explored under field conditions.

Acknowledgements

We thank ASTE Crawford Fund for the training award to Dr. XY Yu. Thanks also to our CSIRO colleagues, Evelyn Krull, Danni Oliver, Lester Smith and Tasha Waller for their guidance and help during the experiments.

References

Accardi-Dey, A., Gschwend, P.M., 2003. Reinterpreting literature sorption data considering both absorption into organic carbon and adsorption onto black carbon. Environ. Sci. Technol. 37, 99–106.

Allen-King, R.M., Grathwohl, P., Ball, W.P., 2002. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments and rocks. Adv. Water Resour. 25, 985–1016.

Bornemann, L.C., Kookana, R.S., Welp, G., 2007. Differential sorption behaviour of aromatic hydrocarbons on charcoals prepared at different temperatures from grass and wood. Chemosphere 67, 1033–1042.

Calamari, D., Vighi, M., Bacci, E., 1987. The use of terrestrial plant biomass as a parameter in the fugacity model. Chemosphere, 2359–2364.

Chen, Z.D., Yuan, Y.W., Chen, X.H., 2006. Residue dynamics of chlorpyrifos in *Allium tuberosum*. J. Safety Environ. 6, 41–43.

Chiou, C.T., Kile, D.E., Rutherford, D.W., Sheng, G.Y., Boyd, S.A., 2000. Sorption of selected organic compounds from water to a peat soil and its humic-acid and humin fractions: potential sources of the sorption nonlinearity. Environ. Sci. Technol. 34, 1254–1258.

Chun, Y., Sheng, G.Y., Chiou, C.T., Xing, B.S., 2004. Compositions and sorptive properties of crop residue-derived chars. Environ. Sci. Technol. 38, 4649–4655.

Fang, C.W., Radosevich, M., Fuhrmann, J.J., 2001. Characterization of rhizosphere microbial community structure in five similar grass species using FAME and BIOLOG analyses. Soil Biol. Biochem. 33, 679–682.

James, G., Sabatini, D.A., Chiou, C.T., Rutherford, D., Scott, A.C., Karapanagioti, H.K., 2005. Evaluating phenanthrene sorption on various wood chars. Water Res. 39, 549–558.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. Mitig. Adapt. Strategy Global Change 11, 403–427.

Lehmann, J., da Silva Jr., J.P., Steiner, C., Nehls, T., Zech, W., Glaser, B., 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferrosol of the central Amazon basin: fertilizer, manure and charcoal amendments. Plant Soil 249, 343–357.

Lohmann, R., MacFarlane, J.K., Gschwend, P.M., 2005. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbor sediments. Environ. Sci. Technol. 39, 141–148.

Nam, K., Alexander, M., 1998. Role of nanoporosity and hydrophobicity in sequestration and bioavailability: tests with model solids. Environ. Sci. Technol. 32, 71–74.

Schmidt, M.W.I., Knicker, H., Hatcher, P.G., KÖgel-knabner, I., 1996. Impact of brown coal dust on the organic matter in particle-size fractions of a Mollisol. Org. Geochem. 25, 29–39.

Sheng, G.Y., Yang, Y.N., Huang, M.S., Yang, K., 2005. Influence of pH on pesticide sorption by soil containing wheat residue-derived char. Environ. Pollut. 134, 457–463.

Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., Mcclure, S.G., 1996. The chemistry and nature of protected carbon in soil. Aust. J. Soil Res. 34, 251–271.

Sun, H.W., Xu, J., Yang, S.H., Liu, G.L., Dai, S.G., 2004. Plant uptake of aldicarb from contaminated soil and its enhanced degradation in the rhizosphere. Chemosphere 54, 569–574.

Tomlin, C.D.S., 2000. The Pesticide Manual. 12th Ed., British Crop Protection Council. Farnham, Surrey, UK.

Yang, Y.N., Sheng, G.Y., 2003. Enhanced pesticide sorption by soils containing particulate matter from crop residue burns. Environ. Sci. Technol. 37, 3635–3639.

Yang, Y.N., Sheng, G.Y., Huang, M.S., 2006. Bioavailability of diuron in soil containing wheat-straw- derived char. Sci. Total Environ. 354, 170–178.

Young, R., Wilson, B.R., Mcleod, M., Alston, C., 2005. Carbon storage in the soils and vegetation of contrasting land uses in northern New South Wales, Australia. Aust. J. Soil Res. 43, 21–31.

Yu, X.Y., Ying, G.G., Kookana, R.S., 2006. Sorption and desorption behavior of diuron in soil amended with charcoal. J. Agr. Food Chem. 54, 8545–8550.

Yuan, C., Sheng, G.Y., Chiou, C.T., Xing, B.S., 2004. Composition and sorptive properties of crop residue-derived chars. Environ. Sci. Technol. 38, 4649–4655.

Zhang, P., Sheng, G.Y., Feng, Y.C., Miller, D.M., 2005. Role of wheat-residue-derived char in the biodegradation of benzonitrile in soil: nutritional stimulation versus adsorptive inhibition. Environ. Sci. Technol. 39, 5442–5448.

Zhu, D.Q., Kwon, S., Pignatello, J.J., 2005. Adsorption of single-ring organic compounds to wood charcoals prepared under different thermochemical conditions. Environ. Sci. Technol. 39, 3990–3998.