"Black is the new green": the blue shades of biochar

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Abstract
In recognition of the potential role that "Biochar or Black Carbon" can play in sequestration of carbon, reducing the emission of greenhouse gases and improving the soil fertility, phrases such as "Black is the New Green" have been coined (Marris 2006) and the International Biochar Initiative (www.biochar-international.org) has been started. While the benefits of biochar applications to soil fertility have been well recognised, the potential negative implications of biochar amendment to soils, especially the impact on contaminant fate, dispersal and build-up is thus far not fully appreciated. This paper presents research that shows that biochar addition to soil can potentially lead to accumulation of contaminants residues in soil. The highly reactive biochar can render applied pesticide ineffective and consequently much higher application rates may be needed for the desired pest and disease control. Biochar itself can potentially serve as a source of combustion related toxicants such as polynuclear aromatic hydrocarbons (PAHs) and dioxins. The implication of biochar amendment to soil and potential implications for the environmental accumulation, distribution and food safety of pesticides needs to be fully understood before recommending widespread application of biochar to soils as a climate change mitigation initiative.

Key Words
Biochar, carbon sequestration, climate change, contaminants, pesticides, efficacy.

Introduction

The importance of biochar in sequestration of carbon, reducing the emission of greenhouse gases and improving the soil fertility has led to the International Biochar Initiative (www.biochar-international.org) promoting biochar as a soil amendment which is increasingly attracting the attention of policy makers in USA (Bracmort 2009), Australia and elsewhere. "Black is the new green" as one of the articles in Nature (Marris 2006) put it. Benefits of biochar applications to soil have been well recognised and articulated. However, there are some potential negative implications of biochar application to soils especially the impact on contaminant dynamics in soil environment. The long term impact of biochar amendments on environment to soils is yet to be fully understood.

Biochar 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 (e.g. Accardi-Dey and Gschwend 2003; Chun *et al.* 2004; Yu *et al.* 2006). Biochars produced from burning of wheat and rice residues were reported to be up to 2500 times more effective in sorbing organic contaminants than soil (Yang and Sheng 2003, James *et al.* 2005). In a previous study, Yu *et al.* (2006) reported that the sorption and desorption behaviour of diuron herbicide is strongly influenced by the presence of biochars in soil. While this may be a desirable outcome in managing a contaminated soil, the strong affinity of biochar for organic contaminants may also have a downside in agricultural soil. The presence of small amounts of biochar in soils can rapidly inactivate the applied amount of pesticide to soil thus rendering it ineffective and potentially requiring much higher rates of applications of pesticides inputs. Besides, the biochar could itself serve as a source of dispersal of toxic organic contaminants such as PAHs and dioxins, which are produced during the combustion process itself. The objective of this study was therefore to assess the impact of biochar amendment to soil on degradation of applied pesticide as well as its effect on plant uptake of pesticides and potential implication for the efficacy of pesticides in soil.

Methods

Biochars

The biochars were produced from Red gum wood (*Eucalyptus* spp.) at two different temperatures (450 and 850 ^{o}C) as described previously (Yu *et al.* 2006). The woodchips were pyrolyzed at 450 and 850 ^{o}C under limited oxygen in a muffle furnace to make two types of biochars (referred to as BC450 and BC850). The specific surface area (SSA) of BC850 and BC450 were 566 m^2/g and 27 m^2/g, 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).

Soil and pesticides
A 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 $cmol_c$ /kg. 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.

Two insecticides (carbofuran and chlorpyrifos) were selected in this study because these are widely used to control soil insect pests and their residues have been found in some vegetables in China (Yu *et al.* 2006). Carbofuran is a nonvolatile carbamate compound with a vapour pressure of 0.031 mPa at 20 ^{o}C, a water solubility of 320 mg/L at 20 ^{o}C, and a log K_{ow} of 1.52. Chlorpyrifos is an organophosphate pesticide with a low water solubility (1.4 mg/L at 25 ^{o}C) and high hydrophobicity (log K_{ow} of 4.70).

Plant experiment.
Spring onion (*Allium cepa*) planted in vermiculite was used as the test plant in this study. Seedlings of about 20 cm in height were planted in plastic containers (10 cm in diameter and 10 cm in height) as a closed system allowing no leaching loss of water or pesticides. The soil (500 g) in each container was spiked at concentration of 50 mg/kg for each of the two pesticides. 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 the other three with BC850 (0.1, 0.5 and 1.0% BC850). Each treatment was carried out in five replicates. The amended soils were thoroughly mixed and shaken for 24 h in a rotary shaker, which was followed by evaporation in acetone for another 2 d. Sufficient water was added into each container to adjust the content of water in the soils to about 50% of maximum water holding capacity. An aliquot of 5 g soil was taken out from each container to determine the initial pesticide concentrations. The growth chamber was maintained at 28/20^{o}C day/night temperatures with a 12 h lighting cycle. The plants were watered every 2 d to maintain the soil moisture.

Residue analysis
Five weeks 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 thoroughly washed with tap water to remove the substrate on the surface of the roots, then air-dried at the room temperature for 24 h. The underground parts were also weighed to obtain the fresh biomass weights. After all the plants were removed, a small quantity (5 g) of the soil samples was collected for analysis after thorough mixing. An aliquot of 5 g plant sample was mixed with 20 g of sodium sulphate dehydrate and ground in mortar and pestle. The mixtures were then extracted with 30 mL of solvent (acetone/hexane (1:1, v/v) for chlorpyrifos, and acetone for carbofuran). 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. Further details on analytical method have been published elsewhere (Yu *et al.* 2009).

Results and Discussion

Decreased bioavailability to microbes and increased persistence with increasing biochar content in soil
Persistence of both carbofuran and chlorpyrifos insecticides increased with increased biochar content in soil indicating reduced bioavailability to soil microorganisms, as shown in Figure 1 for carbofuran as an example. At the end of 35 d of incubation, a total of 86% of applied chlorpyrifos and 88% of carbofuran residues were lost from the control treatment, whereas only 44% chlorpyrifos and 51% of carbofuran degraded from the soil amended with 1.0% BC850. BC450 inhibited the rate of decay to a much lesser degree. Similar results showing increased persistence 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).

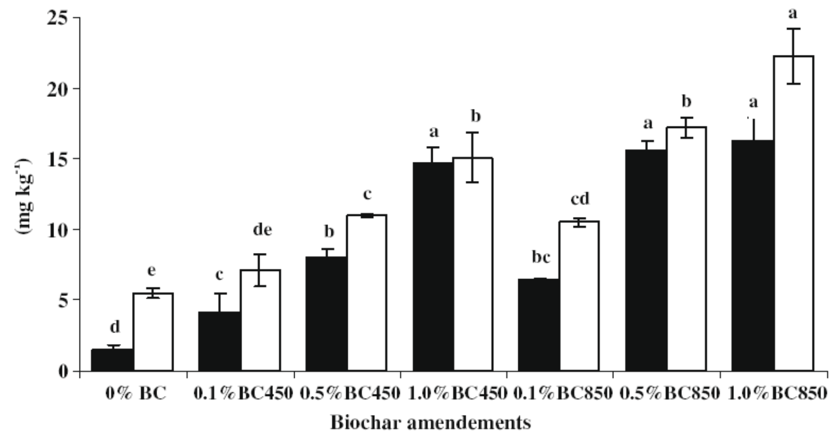

Figure 1. Demonstration of increased persistence of carbofuran insecticide in soil with increasing contents of two types of biochar in soil (BC450 and BC850 are two wood biochars produced at 450° C and 850°C, respectively). Different letters above the same bar type indicate significant difference (Duncan, p < 0.05). Source: Yu *et al.* 2009.

Decreased phyto-availability and plant uptake in the presence of biochar in soil
The data in Figure 2 show that the residues in both above-ground parts as well as below-ground parts of spring onions for both pesticides progressively decreased in the plants that were grown in soils amended with increasing amounts of biochars, especially that produced at higher temperature (BC 850). For example, the concentration of carbofuran in the underground plant parts decreased from 14.4±0.8 in control soil to only 1.8±0.4 mg/kg in the soils 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 in the presence of 1% BC850. The residues in the above-ground parts were found to be 20-250 times lower than those in the underground parts for both pesticides (Figure 2). The residues of carbofuran were generally higher than those for chlropyrifos for any treatment, presumably due to the lower hydrophobicity of the former.

Clearly the bioavailability of pesticides to microbes for degradation (Figure 1) as well as to plants for uptake decreased as the content of the biochars in soil increased (Figure 2). This shows that the efficacy of applied pesticides could be markedly reduced in the presence of highly reactive biochars, such as BC850 used in this study. Incorporation of small amounts of biochar in a soil has also been noted to inhibit the microbial degradation of pesticides and reduce herbicidal efficacy by other workers also (e.g. Yang *et al.* 2006).

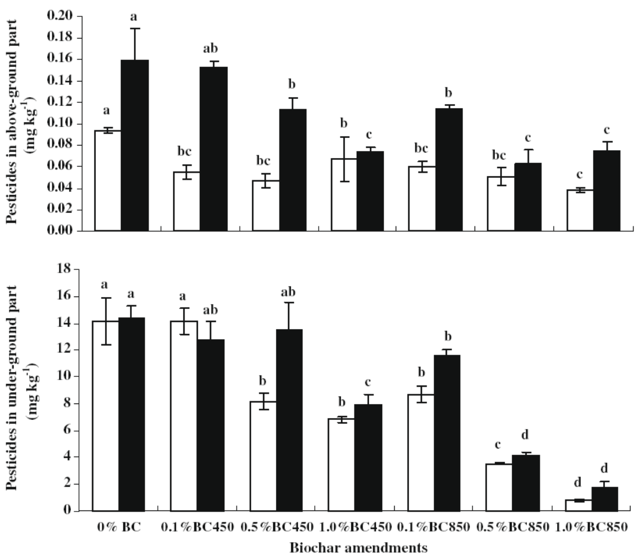

Figure 2. Demonstration of decreased plant uptake of two insecticides (carbofuran – solid bars and chlorpyrifos – empty bars) in above- and under-ground plant parts of spring onion with increasing contents of two types of biochars in soil (BC450 and BC850 are two wood biochars produced at 450° C and 850°C, respectively). Different letters above the same bar type indicate significant difference (Duncan, p < 0.05). Source: Yu *et al.* 2009.

Conclusion and Implications

The data presented above show that biochar amendment to soil can potentially lead to accumulation of contaminants residues in soil. Incorporation of a small amount of biochar in a soil has also been shown to inhibit the microbial degradation of pesticides and reduce herbicidal efficacy by other workers. The highly reactive biochar can render the applied pesticides ineffective and much higher pesticide application rates may be needed for the desired control of pests and diseases. Biochar itself can potential serve as a source of combustion related contaminants such as polynuclear aromatic hydrocarbons (PAHs) and dioxins. The implications for long term fate of contaminants and efficacy of applied pesticides in controlling pest and diseases need to be established before adopting the practice of widespread application of biochar as a climate change mitigation initiative.

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