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The use of biochar to reduce soil PCB bioavailability to *Cucurbita pepo* and *Eisenia fetida*

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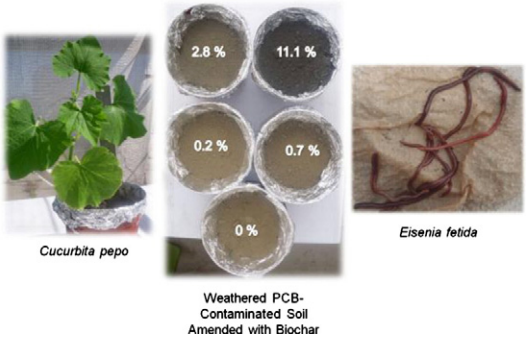
HIGHLIGHTS

- Two concentrations of weathered PCB-contaminated soil were amended with (0, 0.2, 0.7, 2.8, and 11.1% w/w) of biochar.
- Biochar additions decreased the uptake of PCBs into plant tissue by 89% after 50 days.
- Biochar amendment significantly decreased the bioavailability of PCBs to earthworms by 88% after 50 days of exposure.
- Biochar has potential to serve as a mitigation technology at Brownfield sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar is a carbon rich by-product produced from the thermal decomposition of organic matter under low oxygen concentrations. Currently many researchers are studying the ability of biochar to improve soil quality and function in agricultural soils while sustainably sequestering carbon. This paper focuses on a novel but complimentary application of biochar – the reduced bioavailability and phytoavailability of organic contaminants in soil, specifically polychlorinated biphenyls (PCBs). In this greenhouse experiment, the addition of 2.8% (by weight) biochar to soil contaminated with 136 and 3.1 μg/g PCBs, reduced PCB root concentration in the known phytoextractor *Cucurbita pepo* ssp. *pepo* by 77% and 58%, respectively. At 11.1% biochar, even greater reductions of 89% and 83% were recorded, while shoot reductions of 22% and 54% were observed. PCB concentrations in *Eisenia fetida* tissue were reduced by 52% and 88% at 2.8% and 11.1% biochar, respectively. In addition, biochar amended to industrial PCB-contaminated soil increased both aboveground plant biomass, and worm survival rates. Thus, biochar has significant potential to serve as a mechanism to decrease the bioavailability of organic contaminants (e.g. PCBs) in soil, reducing the risk these chemicals pose to environmental and human health, and at the same time improve soil quality and decrease CO_2 emissions.

1. Introduction

In recent years, the popularity of biochar as a soil amendment has substantially increased, mostly in response to increased global carbon emissions and deterioration of agricultural soil quality. Biochar is a carbon rich by-product produced from the pyrolysis of organic matter under zero oxygen concentrations at relatively low temperatures (<700 °C) (Verheijen et al., 2010). Due to its high porosity (Downie

Abbreviations: PCBs, polychlorinated biphenyls; POPs, persistent organic pollutants; AC, activated carbon; PAH, polyaromatic hydrocarbon; RMC, Royal Military College of Canada; MAE, microwave assisted extraction; CEC, cation exchange capacity; BAF, bioaccumulation factor.

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et al., 2009), specific surface area (Liang et al., 2006; Yin Chan and Xu., 2009) and carbon content (Winsley., 2007), biochar decreases nutrient and water leaching loss (Atkinson et al., 2010), increases soil cation exchange (Chan et al., 2007; Cheng et al., 2008; Novak et al., 2009a), sustainably sequesters carbon and improves the overall sorption capacity of soil (Cheng et al., 2008).

Persistent organic pollutants (POPs) are organic compounds with low water solubility and, resistant to environmental degradation by biological, photoylic and chemical processes (White and Zeeb., 2007). Research has suggested that carbon rich, charcoal-like materials such as biochar and activated carbon (AC) have the ability to sorb POPs and thus limit their bioavailability in sediments and soil. However, little data exists on the potential of using biochar, which as a consequence of its production, is a greener and more cost effective material than activated carbon. The production process of biochar is different from that of AC, in that AC is further 'activated' through physical or chemical treatments to maximize the porosity (Marsh and Rodríguez Reinoso., 2006). Commercial production of activated carbon requires expensive equipment, and as a result AC has much higher associated costs than biochar. Biochar production is also more sustainable than the production of AC as it does not require chemical reagents and biochar can be made from waste materials including those from municipalities, the forestry and agriculture industries (crop and animal) (Bridgwater., 2003).

Sorption studies utilizing activated carbon predate those of biochar, and currently there is substantially more information available on ability of AC (Amstaetter et al., 2012; Beckingham and Ghosh., 2011; Cho et al., 2007, 2009; Ghosh et al., 2011; Hale et al., 2012; Langlois et al., 2011; Lunney et al., 2010; Millward et al., 2005; Oen et al., 2011, 2012; Sun and Ghosh., 2008) to sorb contaminants. A few studies have suggested that biochar amended to soil may function in the remediation of organic pollutants such as polyaromatic hydrocarbons (PAHs) (Chen and Yuan., 2011; Hale et al., 2011) and pesticides (Cao et al., 2009, 2011; Saito et al., 2011; Xu et al., 2012; Yu et al., 2011, 2010; Zheng et al., 2010), and to sediments for polychlorinated biphenyls (PCBs) (Cornelissen et al., 2005a, 2005b). A recent study, found that biochar produced from pine needles under a high pyrolytic temperature (700 °C) increased the sorption of PAHs in agricultural soils (Chen and Yuan., 2011). Another 2011 study reported a 91% suppression of dieldrin uptake into cucumber plants with biochar produced from wood chips (Saito et al., 2011). Zheng et al. (2010) reported that biochar (produced from greenwaste at 450 °C) exhibited a high sorption affinity to atrazine and simazine, and was effective at removing these pesticides from aqueous solution (Zheng et al., 2010). Xu et al. (2012) proposed that biochar made from bamboo added to soil at 5% (ww) could be used as possible *in situ* sorbent for pentachlorophenyl and thus minimize the contaminants' bioavailability to earthworms (Xu et al., 2012). Thus the addition of biochar to soil or sediment has potential to function as a mitigation technology for a variety of POPs.

The sorption of organic contaminants by biochar is a result of two separate processes – i) relatively weak and linear *ab*sorption into amorphous organic matter, and ii) relatively strong and non-linear *ad*sorption onto the biochar surface (Chen et al., 2008; Cornelissen et al., 2005a, 2005b; Huang and Chen., 2010; Koelmans et al., 2006; Smernik., 2009). The sorption and subsequent immobilization of POPs to carbon materials would control their toxicity and fate, and decrease the potential adverse health effects associated with their bioaccumulation through the food web (Cho et al., 2009; Cornelissen et al., 2011; Ghosh et al., 2011; Langlois et al., 2011; Xu et al., 2012).

Soil and sediment contamination of PCBs in particular, is widespread as a result of extensive use, improper storage facilities and accidental releases (Safe, 1994). Traditionally, the remediation of PCBs involved soil excavation and transport, prior to off-site treatment by solvent extraction, thermal desorption, incineration, or landfilling (Campanella et al., 2002). However, these techniques themselves can be detrimental to the environment, extremely costly and in some cases infeasible, due to the extent of contamination (Gerhardt et al., 2009). The use of phytoextraction, a volume reduction technology in which plants (e.g. *Cucurbita pepo* spp. *pepo*) are used to mobilize and accumulate significant amounts of the contaminant from the soil, has been a successful *in situ* green remediation strategy for POPs (Ficko et al., 2010; Huelster et al., 1994; Low et al., 2011; White., 2009; Whitfield Åslund et al., 2007, 2008; Zeeb et al., 2006). However phytoextraction has been shown to have limited effectiveness as contaminant concentration increases (Chaudhry et al., 2005; Vila et al., 2007; Zeeb et al., 2006) and the high cost of traditional remediation technologies usually dictates that low concentrations of PCBs are left on site. Despite many successes in both high cost traditional and low cost green remediation technologies, there are still concerns that significant PCB contamination remains in the soils at Brownfield sites, and consequently PCBs continue to enter the food chain and pose environmental and human health risks (Smith., 2012).

The current greenhouse study provides an evaluation of the ability of biochar to minimize the uptake of PCBs by the known PCB phytoextractor *C. pepo* ssp. *pepo* cv. Howden (pumpkin) and a common invertebrate species, *Eisenia fetida* (redworm). The reduced uptake of organic contaminants due to biochar soil additions would provide significant social benefits by reducing or eliminating the potential adverse effects of these substances entering the food chain. In addition, minimizing the bioavailability of organic contaminants in soil may alleviate some of the financial burden associated with the remediation of contaminated sites while reducing greenhouse gas emissions and improving soil quality.

2. Materials and methods

2.1. Greenhouse soil preparation

Weathered soils contaminated with commercial Aroclors 1254 and 1260 were collected from a contaminated site in Etobicoke, Ontario (Canada). The site is a former manufacturing facility for electrical transformers. Soils were collected from two areas on site, and were determined to have PCB concentrations of 136 ± 15.3 and 3.1 ± 0.75 μg/g, respectively. Using the sodium acetate method for cation exchange capacity (CEC) described by Laird and Fleming (2008), the PCB-contaminated soil had an average CEC of 10.22 cmol/kg ($n = 3$) and the pH of the soil was 7.72. Previously this soil was characterized (Whitfield Åslund et al., 2007, 2008) as being coarse-grained and sandy with a total organic carbon content of 3.5%. The soils were dried, sieved to 16 mm, and then homogenized separately using the Japanese pie-slab mixing method (Pitard., 1993).

2.2. Experimental design and sample collection for C. pepo tissue

The two soils (136 and 3.1 μg/g) were amended in triplicate (A, B, and C) with 0, 0.2, 0.7, 2.8 or 11.1% (w/w) biochar obtained from Burt's Greenhouses in Odessa, ON. The biomass feedstock of this biochar consisted of wood waste, mostly from used shipping pallets and construction. The temperature within the pyrolysis equipment reached 700 °C, and occurred over ~30 min. Each treatment ($n = 10$) was tumbled at 30 rpm for 24 h in a leachate soil tumbler at the Analytical Services Unit located at Queen's University. Vermiculite (density = 0.11 g mL^{-1} Schultz™, Bratford, ON,) was added to all treatments in a 2:1 v/v soil:vermiculite ratio to increase soil aeration. The soil/biochar/vermiculite mixture (total weight per planter of 2.25 kg) was placed in bottom perforated 8-inch diameter planting pots ($n = 30$) lined with aluminum foil.

Each planter received three pumpkin (*C. pepo* ssp. *pepo* cv. Howden) seeds purchased from the 'Ontario Seed Company' (Waterloo, ON), however extra seedlings were removed such that each planter

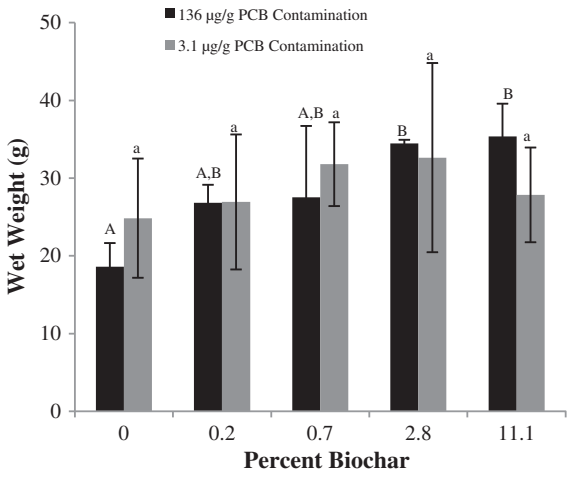

Fig. 1. Harvested wet weight of *Cucurbita pepo* shoots in unamended PCB-contaminated industrial soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper-case (136 µg/g PCB-contaminated soil) and lower-case letters (3.1 µg/g PCB-contaminated soil) indicate statistically significant differences between treatments ($p<0.05$).

contained only one growing plant. Pumpkin plants were grown in the greenhouse located at the Royal Military College of Canada (RMC), measured on a weekly basis and harvested in 50 days. Greenhouse temperature was maintained at 27 °C (±6 °C) and the pumpkins were grown under a 14:10 h (day:night) fluorescent photoperiod. Planters were top and bottom watered to maintain ~35% soil moisture.

A 30 g composite soil sample was collected from replicates for all treatments both immediately after soil tumbling with and without (i.e. control) biochar and after 50 days. All soils remained frozen until analysis. Particle size distribution by sieving performed on oven-dried samples (95 to 125 °C, 16 h) and pH of freshly tumbled treatments were analyzed by the Analytical Sciences Group at the Royal Military College of Canada (SI Fig. 1, Table 1). Cation exchange capacity of Burt's biochar, PCB-contaminated soil, and PCB-contaminated soil with biochar additions, all aged 50 days was calculated via the sodium acetate method outlined by Laird and Fleming (2008).

After 50 days, plants were harvested by cutting the shoot of the pumpkin with acetone rinsed scissors as close to the soil surface as possible. The soil in the planter was then emptied onto a tray (cleaned and rinsed with acetone between samples) and the root tissues collected. Air-monitoring of the greenhouse indicated that PCB concentrations were below detectable limits (<0.01), therefore aerial deposition on the plant tissues was considered insignificant. Plant tissues (root and shoot) were washed using running water, patted dry, and weighed to the nearest hundredth of a gram. They were then placed in individually labeled Whirlpak® bags and frozen until analysis.

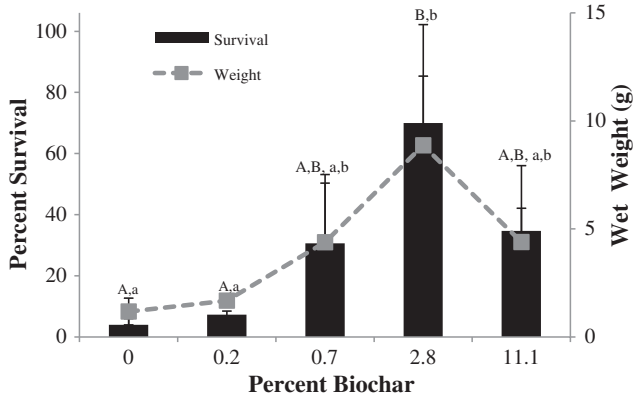

Fig. 2. Percent survival and wet weight of *Eisenia fetida* after 50 days of exposure to 136 µg/g unamended PCB-contaminated soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper case letters indicate statistically significant differences in worm survival between treatments and lower case letters indicate significant difference in worm weights between treatments ($p<0.05$).

2.3. Experimental design and sample collection for E. fetida tissue

Following plant harvest, redworms (*E. fetida*) (n = 50 worms, average weight = 20 ± 1.0 g) purchased from 'The Worm Factory' (Westport, ON), were added to the biochar treatments (i.e. 0, 0.2, 0.7, 2.8, 11.1%) in the 136 µg/g PCB-contaminated soil. The planters were covered with perforated aluminum foil and the worms were removed from the soil after 50 days. Soil moisture was maintained at ~35% moisture. Deceased earthworms were not included for PCB analysis as they could not be depurated.

Surviving worms were collected by emptying the soil from each planter onto a tray (cleaned and rinsed with acetone between samples). Collected worms were then counted, washed using a container of clean water, weighed, depurated for 72 h at 4 °C, dried for 24 h at 25 °C and stored in individually labeled Whirlpak® bags and frozen until analysis.

2.4. Analytical procedures

2.4.1. PCB Aroclors in soil, plant, and worm samples

Plant root and shoot samples were analyzed by microwave-assisted extraction (MAE) at the RMC. Microwave-assisted extraction was performed at a temperature of 120 °C for 35 min in 30 mL of 1:1 hexane:acetone mixture using a Milestone Ethos SEL microwave extraction system. Following extraction, sample extracts were concentrated using a Syncore, the solvent exchanged for hexane, and then extracts were applied to a Florisil column for cleanup.

PCB concentrations in soil and worm tissues were analyzed via Soxhlet extraction, based on the methods described by (Whitfield Åslund et al., 2007) and performed at the Analytical Services Unit located at Queen's University. Briefly, worm samples were finely chopped using metal scissors (rinsed with acetone between samples) and homogenized. Soil and chopped worm samples were dried overnight in a vented oven at 25 °C for approximately 12–18 h, and then ground with sodium sulfate and Ottawa sand. Decachlorobiphenyl (DCBP) was used as an internal surrogate standard. All soil and worm samples were extracted in a Soxhlet apparatus for 4 h at 4–6 cycles per hour in 250 mL of dichloromethane. The use of both extraction methods was validated by (Whitfield Åslund et al., 2008).

Plant, worm and soil extracts were analyzed for total Aroclors, using an Agilent 6890 Plus gas chromatograph equipped with a micro-^{63}Ni electron capture detector (GC/µECD), an SPB™-1 fused silica capillary column (30 m, 0.25 mm ID × 0.25 µm film thickness) and HPChem station software. The carrier gas was helium, at a flow rate of 1.6 mL/min. Nitrogen was used as the makeup gas for the electron capture detector (ECD). Detection limits were 0.1 µg/g. All values were reported as µg/g dry weight.

2.4.2. Quality assurance/quality control (QA/QC)

One analytical blank, one control and one analytical duplicate sample were prepared and analyzed for every nine samples analyzed by Soxhlet or MAE. The control sample was spiked with a known amount of either Aroclor 1254 or 1260. Decachlorobiphenyl (DCBP) was added to each sample as a surrogate standard prior to extraction. None of the analytical blanks contained any PCB congeners at concentrations above detection limits (0.1 µg/g for total Aroclors) and all control samples were between 80 and 110% of the expected value. Relative standard deviations between the samples and their

analytical duplicate were below 24% for all results and the average surrogate recovery for samples analyzed for total Aroclor was 98%.

2.5. Statistical analyses

PCB concentrations (soil and tissue) are reported on a dry-weight basis. The tissue concentration data were analyzed by one-way analysis of variance (ANOVA) (dependant variable: shoot, root or worm PCB concentration; independent variable: percent biochar) followed by a post hoc Tukey comparison (levels of: percent biochar). Shoot and worm wet weights were compared between soil types (i.e. high or low level of PCB contamination) using a two-way ANOVA. Percent reductions in shoot, root and worm tissue among biochar percentages were also compared between types of biochar using a two-way ANOVA. All residuals of the data were determined to be normally distributed as determined by a Kolmogorov Smirnov test for normality. When data failed to meet the assumptions, data were $\log_{10}$-transformed. A significance level of $\alpha = 0.05$ was used for all tests, and results were recorded with the standard error of the mean. All statistical analyses were performed using SPLUS 8.0.

3. Results and discussion

3.1. Plant shoot and worm harvestable biomass

PCB concentrations in both control soils did not vary from the beginning (136 ± 15.3 and 3.1 ± 0.75 μg/g) to the end (153 ± 3.4 and 3.4 ± 0.29 μg/g) of the experiment. Traditionally, biochar amendments have been used as a method to increase plant productivity in agriculture (Chan et al., 2007; Lehmann et al., 2003). Pumpkin shoot weights significantly increased in size by 85 and 90% in the 136 μg/g PCB-contaminated soil, with biochar additions of 2.8 and 11.1%, respectively ($p<0.05$) (Fig. 1). Pumpkin shoot wet weights did not differ among the two levels (136 μg/g and 3.1 μg/g) of soil contamination at any biochar application rate (Fig. 1). Whitfield Åslund et al. (2007, 2008) documented that *C. pepo* accumulated significant concentration of PCBs in plant shoots without jeopardizing plant health. Increase in shoot biomass could be due to biochar's ability to maintain soil moisture (Busscher et al., 2010; Novak et al., 2009a; Novak et al., 2009b) and provide macronutrients (potassium, phosphorous) and micronutrients (copper) (Lehmann et al., 2003; Novak et al., 2009a). Also oxidation of the biochar surface creates carboxyl groups which contribute to a higher cation exchange capacity (CEC) than in unamended control soil (Chan et al., 2007; Cheng et al., 2008; Liang et al., 2006). CEC is a measure of the negatively charged sites on a biochar or soil particle and is important as soil with a high CEC is better able to retain nutrients (e.g. Ca^{2+}, K^{+}, and Mg^{2+}) to replenish those removed from the soil water by plant uptake (Liang et al., 2006). The Burt's biochar used in this study had a CEC (NaOAc) of 24.2 cmol/kg, whereas, the PCB-contaminated soil (136 μg/g) had a CEC of 10.4 cmol/kg. Upon addition of 2.8 and 11.1% Burt's biochar to the 136 μg/g PCB-contaminated soil the CECs were only slightly higher at 12.8 and 10.8 cmol/kg, respectively after 50 days. The small difference could be due to the short duration of our experimental design (i.e. 50 days) as well as the soil and biochar heterogeneity. Future studies should analyze the CEC of the soil after several months or many years of biochar amendment to determine the long term benefits to soil CEC and seek further statistical significance.

Another soil improvement ability of biochar is that it can reduce the overall tensile strength of the soil (Lehmann et al., 2011). Reductions in tensile strength may be especially important for revegetation of contaminated sites where the soil quality is often intensely degraded (Lunney et al., 2010). Biochar addition to soils at contaminated sites to lower tensile strength may alleviate root elongation and proliferation problems, allow seeds to germinate more easily, and allow invertebrates to move more readily through the soil. After 50 days of pumpkin growth, the 136 μg/g PCB-contaminated soil in the control treatment had become hard and thus it was more difficult to harvest the root tissue. Roots were easily harvested with gentle force from the soil treated with 2.8% and 11.1% biochar. Biochar additions to the 3.1 μg/g PCB-contaminated soil did not significantly increase plant growth. This area of the PCB-contaminated site has been revegetated for many years and subsequently is not as degraded as the soil collected in the area of higher contamination. It is not uncommon to observe greater yield improvements as a result of biochar soil amendments in degraded soils, as was the case in this study (Kimetu et al., 2008; Major et al., 2010; Novak et al., 2009b).

The presence of earthworms is considered a useful indicator of soil health (Snapp and Morrone., 2008). When collecting the 136 μg/g PCB-contaminated soil it was observed that earthworms of any species were absent from the site, however there were some occupying the area contaminated with 3.1 μg/g PCBs. Thus, the soil contaminated with the higher amount of PCB contamination was selected for the earthworm study. If biochar is to improve soil functions at Brownfield sites it must allow for re-habitation of the earthworm population and not have an adverse effect on the earthworms that occupy the soil. *E. fetida* were specifically chosen for this study because Langlois et al. (2011) reported no significant differences in worm weights between those

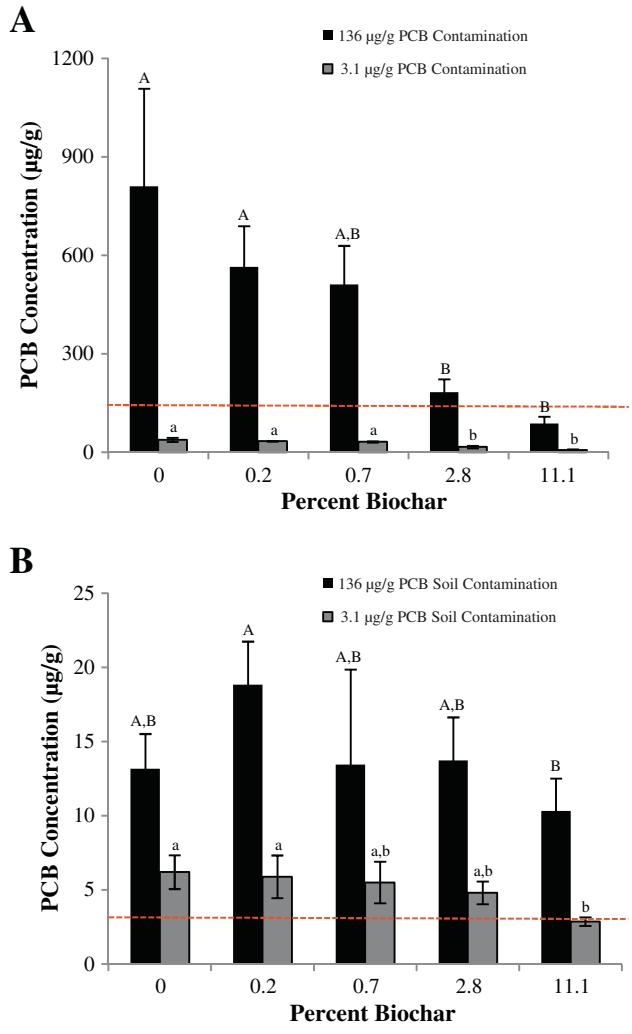

Fig. 3. Polychlorinated biphenyl (PCB) concentrations in root (a) and shoot (b) tissue of *Curcurbita pepo* grown in unamended PCB-contaminated industrial soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper-case (136 μg/g PCB-contaminated soil) and lower-case letters (3.1 μg/g PCB-contaminated soil) indicate statistically significant differences between treatments ($p<0.05$). The line represents (a) the high PCB-contaminated soil concentration of 136 μg/g and (b) the low PCB-contaminated soil concentration of 3.1 μg/g.

exposed to PCB-contaminated soil (>50 μg/g), or PCB-contaminated soil amended with GAC after 2 months. The PCB concentration used in this study (136 μg/g) is not acutely toxic to *E. fetida*, which has an Aroclor 1254 LD_{50} of 4500 μg/g (Fitzpatric et al., 1992). However, soil at Brownfield sites are typically intensely degraded (i.e. lack essential nutrients, substrate quality, and/or vegetative cover) which may not allow for earthworm habitation. *E. fetida* in this study exposed to the control treatment had only a 4 ± 2% survival rate (n = 3). In this greenhouse experiment, the addition of 2.8% biochar to industrial PCB-contaminated soil (136 μg/g) was optimal, significantly increasing the rate of worm survivorship by 17.5 times the control (Fig. 2) ($p<0.5$). It is noteworthy to also mention that addition of 0.7 and 11.1% biochar to the PCB-contaminated soil also increased worm survivorship by 7.7 and 8.8 times the control, respectively. Increases in worm survivorship resulted in up to 2.1 times greater worm weights (at 2.8% biochar addition) at harvest time (50 days) compared to the controls (Fig. 2).

Thus biochar additions can improve the health of soil invertebrates even in Brownfield soil highly contaminated with PCBs. This result, along with the significant increases in plant growth provide optimism for contaminated sites – in that with biochar additions, revegetation and the return of mesofauna are probable and thus the overall soil health and functionality may also be restored.

3.2. PCB concentrations in C. pepo

C. pepo was chosen to study the effects of biochar on the phytoavailability of PCBs because it has been widely documented as an efficient species at phytoextracting PCBs and other organic pollutants (Huelster et al., 1994; Low et al., 2011; White., 2009; Whitfield Åslund et al., 2007, 2008; Zeeb et al., 2006). The translocation and deposition of PCB congeners through the shoot tissue of *C. pepo* occur via transport in the xylem sap (Greenwood et al., 2011). Whitfield Åslund et al. (2008) reported that contaminant transfer pathways such as direct soil contamination, atmospheric deposition and volatilization from soil and subsequent redeposition on shoot tissue were negligible. Thus, if the addition of biochar to the soil reduced PCB uptake by *C. pepo*, it is likely to also reduce uptake by other plant species. As expected, root and shoot tissue of *C. pepo* accumulated substantial amounts of PCBs in the two control treatments (Fig. 3a and b). The extent of PCB bioaccumulation, as determined by a bioaccumulation factor ($BAF = [PCB]_{tissue}/[PCB]_{soil}$) in this study (0.11) was comparable to

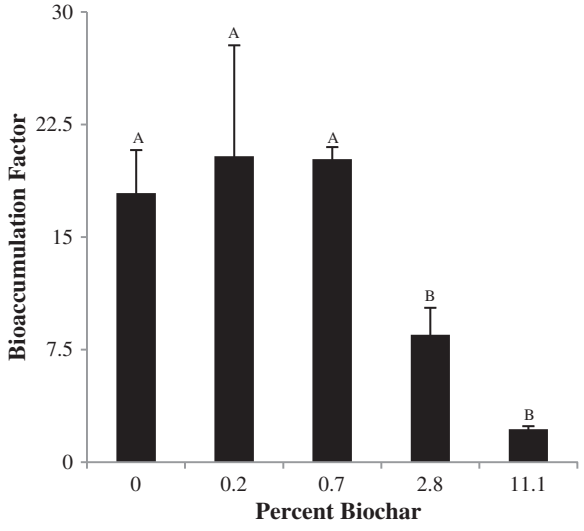

Fig. 4. Bioaccumulation factor of polychlorinated biphenyls (PCBs) into *Eisenia fetida* exposed to an unamended (control) 136 μg/g PCB-contaminated industrial soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper-case letters indicate statistically significant ($p<0.05$) differences between treatments.

that of Whitfield Åslund et al. (2007) (0.15) who determined that there was potential for *in situ* phytoextraction of PCBs (Whitfield Åslund et al., 2007). Generally shoot BAFs decrease as the soil concentration increases (Zeeb et al., 2006). The soil concentration in the current study was roughly three times higher than that of Whitfield Åslund et al. (2007).

In both soils, the addition of biochar significantly reduced PCB levels in the plant roots. In soil with 136 μg/g PCB-contamination, the PCB concentration in root tissue decreased by 77% and 89% ($p<0.05$) with 2.8% and 11.1% biochar amendment, respectively (Fig. 3a). In soil with 3.1 μg/g PCB-contamination, biochar amendment at 2.8% and 11.1% reduced the concentration of PCBs in *C. pepo* root tissue 58% and 83%, respectively; $p<0.05$) (Fig. 3a).

The addition of biochar had less of an effect on PCB uptake into the plant shoots. At an 11.1% rate of biochar amendment in 3.1 μg/g PCB-contaminated soil, a significant 54% reduction in shoot tissue was observed ($p<0.05$) (Fig. 3b). Although not significant ($p = 0.058$), biochar amendment at a rate of 11.1%, to 136 μg/g PCB-contaminated soil, reduced the shoot concentration of *C. pepo* by 22%. Significant reductions were not seen for plant shoots in soil amended with lower concentrations of biochar. These results are consistent with a study by Langlois et al. (2011) which determined that 12.5% AC amendment reduced the PCB concentration (Aroclor 1254) in root tissue of *C. pepo* by 97%, but only by 63% in shoot tissue (Langlois et al., 2011). Lunney et al. (2010) demonstrated that uptake of DDT into shoots and roots was eliminated with the addition of high levels of AC to soils contaminated with 1100 ppb DDT (Lunney et al., 2010).

The significant reductions in PCB concentrations into *C. pepo* root and shoot tissue observed, are consistent with Graber et al. (2011), Mesa and Spokas (2011), Nag et al. (2011) and Yu et al. (2009), which have stated that biochar soil amendment may also lead to decreased efficacy of soil-applied herbicides. Thus, although biochar amendment to minimize the phytoavailability of organic compounds such as PCBs has a profound positive effect from a remediation point of view; it may have a negative effect from an agricultural standpoint. Hence, careful consideration of site specific characteristics is necessary before applying biochar amendment, on a large scale.

3.3. PCB concentrations in E. fetida

The greatest reductions in PCB uptake by *C. pepo* were observed in the 136 μg/g PCB-contaminated soil, thus biochar treatments at this concentration were chosen for worm exposure. Worms exposed to 136 μg/g PCB-contaminated soil had PCB concentrations of 2440 μg/g. This 18-fold (Fig. 4) increase in tissue concentration illustrates the ability of PCBs to bioaccumulate within an organism (BAF = 18.0 ± 2.9), and the potential for them to biomagnify through the food chain (Beckingham and Ghosh., 2011; Ghosh et al., 2011; Millward et al., 2005). Treatment of 136 μg/g PCB-contaminated soil with 2.8% and 11.1% biochar, significantly ($p<0.05$) reduced the bioaccumulation of PCBs into the worm tissue by 53% and 88%, respectively. Worms in the 0.2% and 0.7% amendments had PCB concentrations that were not significantly different from the control. Biochar is a porous material consisting mostly of micropores (<2 nm) that provide surface area for contaminant binding (Cornelissen et al., 2005a, 2005b; Kasozi et al., 2010; Spokas et al., 2009; Yu et al., 2010; Zheng et al., 2010). It is possible that biochar adsorbed the PCB molecules so strongly that the contaminant-biochar complex cannot be broken down by digestive enzymes and microbial flora as it passes through the gut of *E. fetida* (Langlois et al., 2011), resulting in reduced worm PCB concentrations.

These large reductions of the bioavailability of PCBs to the earthworm *E. fetida* are consistent with Xu et al. (2012) who used a chemical extraction method using methanol to represent bioavailability of pentachlorophenyl to earthworms. In this study the authors found that compared to the control, the concentration of pentachlrophenyl extracted by methanol decreased by 56% in the soil amended with 5%

(w/w) bamboo biochar. The high efficacy of biochar to reduce PCB bioaccumulation in invertebrates can be compared to the efficiency of activated carbon. Langlois et al. (2011) determined that an addition of 12.5% AC to soil significantly reduced PCB bioaccumulation in *E. fetida* by 99% (Langlois et al., 2011). It will be useful in future studies to include activated carbon as a positive control to directly compare the efficiency of biochar and activated carbon to minimize the bioavailability of organic contaminants.

Sorption of contaminants is a key process that controls the toxicity, transport and fate of non-polar organic compounds such as PCBs (Cornelissen et al., 2005a, 2005b; Ghosh et al., 2011; Koelmans et al., 2006). In the past few years much work has been published as a result of laboratory kinetic testing, that organic contaminants are adsorbed onto the surfaces and absorbed into the organic matter of biochar (Cornelissen et al., 2005a, 2005b; Kasozi et al., 2010; Spokas et al., 2009; Yu et al., 2010; Zheng et al., 2010). In comparison, this study demonstrates sorption and hence immobilization of PCBs by biochar in a complex scenario with biological components such as weathered PCB-contaminated soil, earthworms and plants. This study provides evidence that biochar has significant potential to serve as a mechanism to sequester PCBs in the soil, thereby, minimizing their bioavailability and potential to enter the food chain. This technology, possibly in combination with bioaccessibility assays to determine appropriate cleanup levels, based on environmental and human health risks (e.g. Dean and Ma, 2007), could be used during Brownfield site closure, where traditional remediation approaches or phytoextraction have been exhausted, yet levels of residual contamination remain.

Biochar is produced by the pyrolysis of organic matter; however, many types of organic matter can be used, varying from sawdust to corn stalks to chicken manure to construction wastes, under different pyrolysis conditions. These differences are expected to alter the biochar's physiochemical properties and its sorption capabilities (Yao et al., 2011). Care must be taken to ensure that the biomass itself does not contain any contaminants (e.g. heavy metals, PAHs, PCBs). Thus, before this technology can be implemented *in situ*, careful characterization of the biochar including, contaminants, sorption capacity, specific surface area, cation exchange and those suggested by the International Biochar Initiative (IBI) should be conducted.

In this greenhouse experiment biochar produced the greatest percent reductions in *C. pepo* shoot and root material as well as *E. fetida* tissue when added at 11.1% (w/w). However, statically significant reductions in PCB concentration in root and worm tissues were achieved at 2.8% (w/w), which is a much more realistic application rate for large-scale experiments such as at a PCB-contaminated Brownfield sites, and this concentration is currently recommended by some researchers for activated carbon amendment (Langlois et al., 2011, McLeod et al., 2007, Zimmerman et al., 2005). Thus, future work should focus on field-relevant application rates and direct comparisons between the efficiency of different biochars with activated carbon at ca. 3%. Many groups have investigated the potential of activated carbon to sorb PCBs in aquatic sediments and terrestrial soils; this study is the first to present reductions in PCB phytoavailability and bioavailability in weathered PCB-contaminated soil. Given that biochar costs are typically 50–75% less than the cost of the activated carbon, and the additional agricultural and environmental benefits, this is a promising new application of biochar.

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